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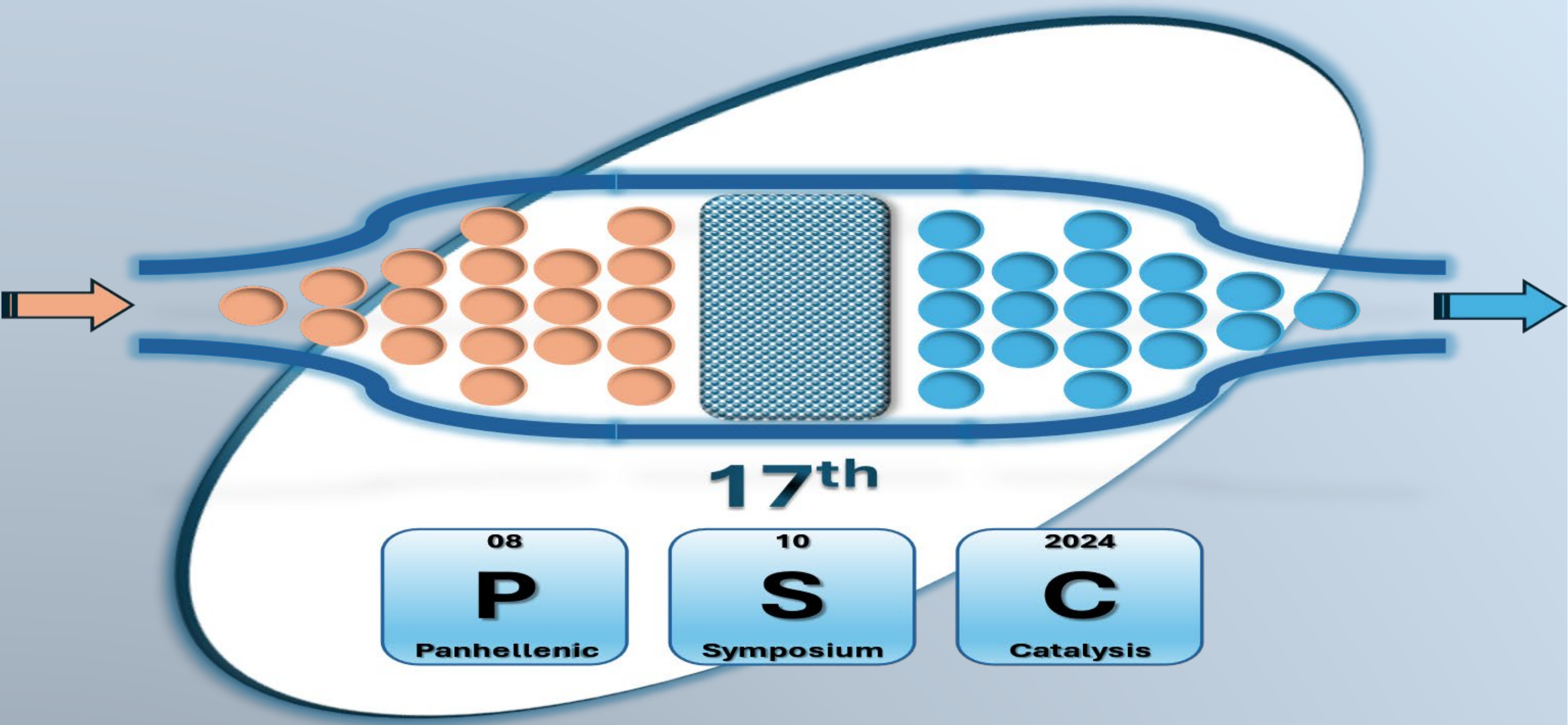
Shaping a Sustainable Future Through Catalysis



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"From Metal to Metal-free Heterogeneous Catalysts: A Journey into more Sustainable Chemical Processes"

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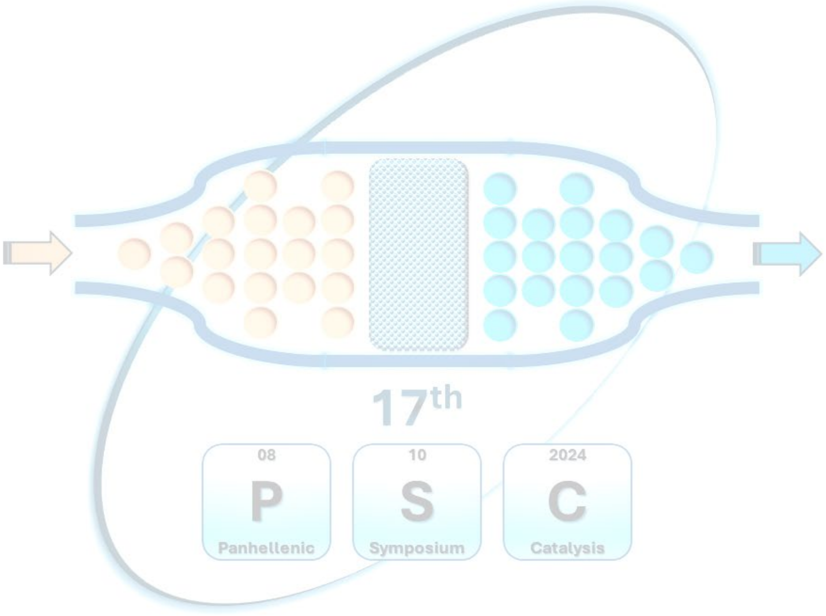

Oxidation of methanol and CO over $Fe_xCo_{3-x}O_4$ catalysts: is there a common trend?

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Keywords: (Carbon monoxide, methanol, oxidation, mixed oxides)

Introduction

Co_3O_4 is one of the most active TMOs in CO oxidation, although its activity decreases noticeably in the presence of water vapor in the feed, a common occurrence in practice. Cation doping of Co_3O_4 could enhance its catalytic activity and stability in CO and VOC oxidation. Iron is a favorable candidate as a dopant due to its capacity to switch between Fe^{2+} and Fe^{3+} oxidation states. Additionally, its insertion into the Co_3O_4 spinel structure leads to changes in the chemical bonding of the surface, creating lattice imperfections and oxygen vacancies. In the present work, $Fe_xCo_{3-x}O_4$ mixed oxide catalysts have been evaluated in the oxidation of CO in the absence and presence of methanol and H_2O. Temperature-programmed desorption and reaction (TPD and TPSR) techniques were combined with in situ-DRIFTS experiments to investigate the interaction of CO and CH_3OH with the catalyst surface.

Materials and Methods

$Fe_xCo_{3-x}O_4$ mixed oxide catalysts have been synthesized with various Fe/(Fe+Co) atomic ratios, spanning the whole composition range and were characterized by XRD, XPS, H_2-TPR and N_2 physisorption. The interaction of CO and methanol with the catalysts was investigated with CO-TPD, CH_3OH-TPD/TPSR, $CO/CH_3OH/O_2$ and DRIFTS experiments. The catalysts were evaluated in CO, methanol and CO-methanol oxidation reactions in the absence and presence of H_2O.

Results and Discussion

The samples with Fe/(Fe+Co) ratio up to 0.50 retain the initial spinel structure of Co_3O_4 with an accompanying increase in lattice constant. $Fe_xCo_{3-x}O_4$ oxides are highly active in the oxidation of CO even at ambient temperature under ''wet'' conditions. At the same time, addition of iron leads to decrease of activity in CH_3OH oxidation. According to the CO-TPD results, the progressive replacement of Co^{3+} by Fe^{3+} ions results in a systematic decrease in the number density of CO adsorption sites but also to a significant improvement in the intrinsic activity of the catalysts. The addition of CH_3OH in the reactant feed resulted in a dramatic inhibition of CO oxidation, shifting the temperature required for complete conversion of CO to a higher temperature by 100°C. CO-CH_3OH co-adsorption/TPSR experiments combined with in situ-DRIFTS measurements demonstrated that at high CH_3OH surface coverage, CH_3OH does not inhibit CO adsorption leading to accumulation of CO as a "spectator" species on the catalyst surface which cannot get oxidized in the presence of adsorbed methanol species.

Significance

The objectives of the study are twofold: (i) to provide convincing answers on the origin of the inhibiting effect encountered in the oxidation of CO-CH_3OH mixtures, (ii) to understand why addition of iron to Co_3O_4 promotes CO oxidation but diminishes CH_3OH oxidation, which implies that design of a highly active, universal total oxidation catalyst is more challenging than it seems.

Plasmon-Assisted Molecular Catalysis (PAMC): an emerging field

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Keywords: plasmonic, $Ag^0@SiO_2$, hot electrons, oxidation catalysis, Mn^{IV}=O, formic acid, FADH, H_2

Introduction

Plasmonic nanoparticles (PNPs) offer a novel route for exploitation of light-photons i.e. via localized surface plasmon resonance (LSPR). So far PNPs, have been used in catalytic processes where the plasmonic nanoparticles themselves were the active centres. Herein we discuss a new concept, where a [molecular catalyst] is operating *in tandem* with [photoexcited PNP]. This constitutes a Plasmon-Assisted Molecular Catalysis (PAMC), approach [1]. Herein the PAMC concept is exemplified for two catalytic systems (a) a {Mn^{II}-complex} catalyst, used for alkene epoxidation in the presence of H_2O_2 and (b) a {Fe^{II}-complex} catalyst used for H_2 production from HCOOH. In both cases the PNPs were of $Ag^0@SiO_2$ where the plasmonic Ag-core is coated with a 3nm-ultrathin SiO_2 nanolayer.

Results and discussion

(a) In the case of {Mn^{II}-complex}/H_2O_2/alkene epoxidation, photoexcitation of $Ag^0@SiO_2$ results in reversible switch-off of the catalytic process. Thus, the oxidation catalytic process can reversibly switch on/off upon switching off/on the illumination. This novel phenomenon we show that is due to a reversible inhibition of the formation of the catalytic transient LMn^{IV}=O state, by [hot electrons] generated by the photoexcited $Ag^0@SiO_2$ PNPs.[2] (b) In the case of {Fe^{II}-complex}/HCOOH, photoexcitation of the $Ag^0@SiO_2$ results in dramatic boosting of H_2 production. That is, an optimised catalytic system [Fe^{II}/polyphospine /FA/ $Ag^0@SiO_2/hv$] achieves ~ 1000% increase in H_2-production. As we show, this novel phenomenon can be attributed to [hot electrons generation] by photoexcited $Ag^0@SiO_2$ [3]. These two examples provide novel perspectives in catalytic technologies, via harnessing of plasmonicaly -generated hot-electrons in Plasmon-Assisted Molecular Catalysis.

Acknowledgments

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Strategies to overcome challenges in the catalytic hydrogenation of CO_2

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Global warming, caused primarily by anthropogenic emissions of CO_2 from the combustion of fossil fuels in industry, transport and energy production, is one of the most serious challenges of the 21st century. Despite the implementation of several climate change mitigation policies, CO_2 emissions continued to grow at an annual rate of 1.7 % during the period 2010 - 2020. The urgent need to reduce human-induced CO_2 emissions has led to intense research for developing efficient technologies for the capture of CO_2 and its re-utilization as carbon feedstock to value-added chemicals and alternative fuels in the context of circular economy.

Among CO_2 valorization technologies, the catalytic hydrogenation of CO_2 to oxygenates and hydrocarbons has turned out to be a promising route. Notwithstanding the great appeal of this strategy, the direct conversion of CO_2 via catalytic hydrogenation comes with a set of challenges that have so far limited its large-scale deployment and commercialization. A major challenge lies in the thermodynamic stability and inertness of the fully oxidized CO_2 molecule that restricts its conversion to low levels. On top of that, catalyst deactivation from metal sintering, poisoning from typical off-gases contaminants and low water resistance decreases further the CO_2 conversion and the yield to the desired products.

In the lecture, we will discuss examples from our work showcasing efficient strategies to overcome some of these hurdles. Water separation combined with catalytic conversion in a single step can alleviate thermodynamic limitations and significantly boost conversion. We will show the experimental proof-of-concept of the sorption enhanced CO_2 hydrogenation to methanol over classical Cu-based catalysts, considering important aspects for the efficient implementation of the process, such as type of sorbent, reaction and regeneration conditions, stability in cyclic operation etc. The systematic investigation of the deactivation and stability of the Cu-based catalyst in the presence of off-gas impurities will also be discussed, with focus on the fundamental understanding of how the poisons affect the active sites. Finally, the preparation of novel CO_2 conversion catalysts via advanced preparation methods, such as 3D printing technology, will be addressed.

PROMETHEUS catalyst: the first ever Copper-based automotive catalyst homologated for Euro6 application

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Keywords: Copper catalyst; platinum group metals; catalytic converter; PGMs.

Introduction

MONOLITHOS Catalysts & Recycling Ltd, has succeeded in developing a disruptive technology called "PROMETHEUS catalyst", that allows the partial substitution of PGMs by Cu without compromising catalytic activity compared to the state-of-the-art PGM-based autocatalysts. Recently, PROMETHEUS catalyst became the first ever Cu-based autocatalyst being homologated for Euro6 application. The homologation has been granted by the National Standards Authority of Ireland (NSAI) and is applicable for the whole European Union, for up to 1.2lt engines, while homologation procedure for vehicles with higher engine displacements is currently under way.

Experimental

Prometheus TWC that incorporates Cu/Pd/Rh nanoparticles supported on a CeO_2-ZrO_2 mixed oxide (high OSC material), is produced following a patented protocol [1]. Catalytic activity has been validated both in lab scale experiments as well as in real world tests after installation on vehicles.

Results and discussion

PROMETHEUS catalyst type approval emission tests have been performed by TÜV SÜD Auto Service GmbH (Figure 1). For all pollutants, the reduction in emissions using the full-scale PROMETHEUS catalyst varied between 25-55% compared to the legislative Euro6 limits, even though it incorporates 50-85% less PGMs compared to the PGM-based commercial catalysts (partial substitution by Cu).

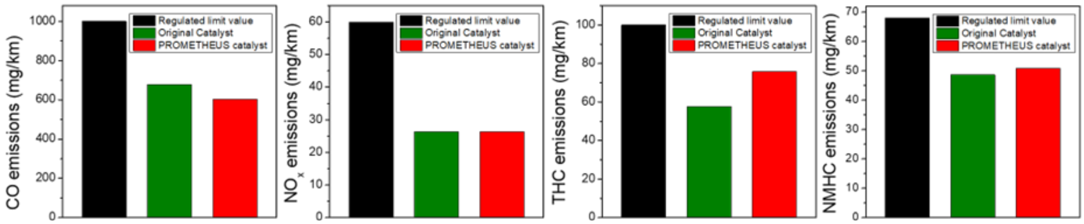

Figure 1: Results of emission tests performed by TÜV SÜD Auto Service GmbH.

In addition, the use of impure/recycled PGMs for the production of new autocatalysts (TWC and DOC), has already been confirmed, with catalysts prepared using recycled PGMs outperforming the corresponding benchmark catalysts prepared using commercially available PGMs, both as fresh and hydrothermally aged catalysts.

Significance of work

The combined use of recycled PGMs and the incorporation of Cu reduces the production cost of new catalytic converters while reducing the supply risk of EU for PGMs. PROMETHEUS technology has also been expanded to applications besides automotive catalysts, such as nanocatalysts for maritime applications, photocatalysts to be used in coatings, vulcanization catalysts for tire industry and the catalytic conversion of CO_2 to value-added products.

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Size and Shape Effects in Catalysis Exemplified by Ceria-based metal oxides

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Catalysis constitutes a field of diverse applications, including, among others, the production of high-commodity chemicals and fuels and the abatement of hazardous substances, all playing a key role towards sustainability. In this context, the rational design and development of cost-efficient catalyst formulations with tailored properties constitutes the main research pillar in the field of catalysis. Towards this direction, the fine-tuning of local surface chemistry by means of advanced synthetic and promotional routes has recently gained particular attention. In specific, the adjustment of size, shape and electronic state of multi-component metal oxide systems at the nanoscale though appropriate synthesis methods and nano-engineering strategies can exert a profound influence not only to the reactivity of metal sites, but to the interfacial activity as well, resulting in the development of highly active and stable materials for real-life energy and environmental applications [1-3].

In the present talk, the pivotal role of size and shape engineering in catalysis is elaborated and exemplified on the basis of transition metal catalysts based on CeO_2. The underlying mechanism of the size- and shape-effects in catalysis is initially discussed. A thorough characterization of ceria-based composites of distinct nano-morphology (rods, cubes, polyhedra) is presented next, so as to gain insight into the impact of different exposed facets into key physico-chemical properties. It is clearly disclosed that size and shape functionalization can notably affect key activity descriptors with direct catalytic implications. Most importantly, the combination of ceria particles of specific nano-arcitecture with late 3-d transition metals may very well induce synergistic metal-ceria interactions, thus offering extremely active and stable catalytic composites for various heterogeneous processes. Besides, from a practical standpoint, novel catalyst formulations with similar or even superior reactivity to that of noble metal-based catalyst may be obtained, such as Ni/CeO_2-nanorods for CO_2 hydrogenation processes [4-8]. Last but not least, an overall rationale and design guidelines towards the fabrication of earth-abundant metal oxide catalysts for application in various chemical reactions of energy and environmental significance are provided.

Acknowledgments
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Novel operation modes and architectures of electrocatalytic systems for renewable energy driven chemistry

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Keywords: Electrochemical membrane reactors, Plasma, Nitrogen fixation, Carbon dioxide fixation

Introduction

In view of energy transition, coupling of electrical, chemical, and thermal energy needs of the different industrial sectors is required. Electrochemical membrane reactors (EMRs) have the potential to be a large part of the solution. EMRs are based on solid electrolytes that can be directly controlled by an external electric current and employ current collecting electrodes which catalytically support electrochemical and other coupled reactions. In this contribution, we will discuss (i) a novel operation mode based on plasma for nitrogen fixation and (ii) an innovative cell architecture for synergistically integrating thermal with electrocatalysis for converting carbon dioxide to methane [1,2].

Experimental

Material development and characterization can be found elsewhere [1,2].

Results and discussion

Plasma activated EMR with either oxygen ion or proton conductors were developed and implemented for the conversion of nitrogen and water to valuable industrial precursors i.e. nitric oxide and ammonia respectively. Pure electrochemical approaches suffers from low yield. Plasma activation was successfully utilized for increasing the reactivity of nitrogen and thus achieving product concentration at 3-4 orders of magnitude higher than equilibrium (in the absence of plasma), while >80% selectivity to nitrogen fixation is observed.

Proton conducting EMRs operating temperature window is ideally suited for the valorization of carbon dioxide to methane, however the state-of-the-art is suffering with low yields. By integrating proton conducting EMRs with catalytic bed reactors in a novel cell architecture, we were able to go beyond the state-of-the-art and achieve selectivity > 95% and conversion > 90%.

Significance of work

With increasing global interest in renewable energy technology in the backdrop of climate change, storage of electrical energy has become particularly relevant. Most sustainable technologies (e.g. wind, solar) produce electricity intermittently. Thus, converting electrical energy and elementary molecular building blocks (i.e. H_2O, CO_2, N_2) into energy rich ones (e.g. H_2, CO, CH_4, NH_3) or chemical feedstock (e.g. NO, syngas) is of paramount importance.

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The Art of Designing Multifunctional Catalysts for Added-Valued Products: fundamentals and market perspectives

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Keywords: catalyst design; activity descriptors; spectroscopy tools; microscopy

Introduction

Catalysis is in the heart and forefront of any fuel-related deployment technology. In particular, the use of catalysis in the transformation of wastes into energy and fuels is a sector with a revenue forecast in 2027 of USD 54.8 billion and a Growth Rate CAGR of 7.4% from 2020 to 2027. This research is of strategic priority for the United Arab Emirates as it has been stated in the UAE Energy Vision 2050. Wastes can be in the gas, liquid or solid state. Exploiting catalysis technologies to turn wastes into valuable products gains ground.

Experimental

All the catalysts were synthesized via simple wet-impregnation and their microstructure, surface coordination environment, redox behaviour and acid/base properties were analyzed. Attempt to link the structure with the catalytic performance and/or any post synthesis process is discussed.

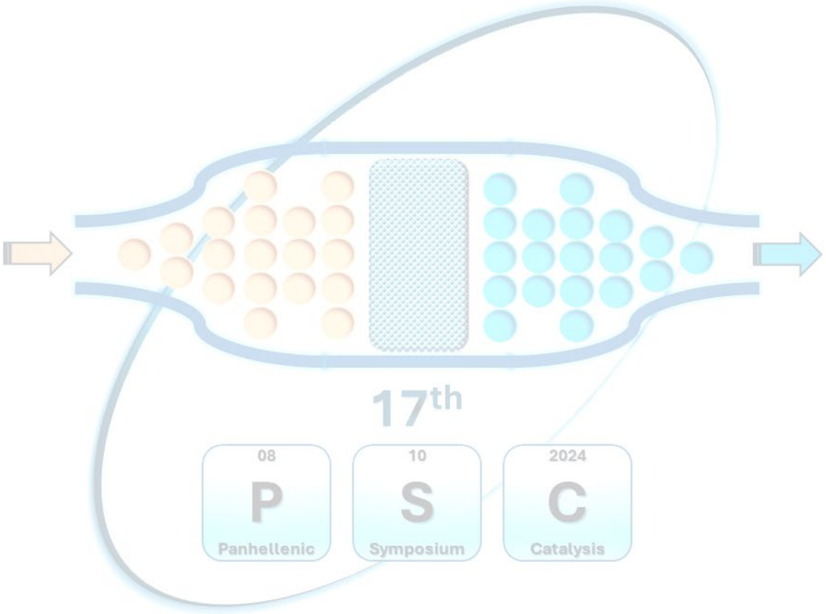
Results and discussion

In this talk some case studies of how catalysis and surface science principles are applied onto transforming certain waste feeds (CO2, bio-oil) into added-value products are discussed. The design criteria of catalysts for CO2 methanation, dry reforming of methane and bio-oil hydrodeoxygenation are discussed from the perspective of how to achieve a paradigm shift. A suite of analytical tools, such as in situ XRD, Synchrotron XAS, X-ray photoelectron Spectroscopy along with transient techniques (temperature programmed reduction/reaction/desorption are discussed in conjunction to the catalytic activity. Some discussion on market analysis and perspectives of TRL advancement are also included.

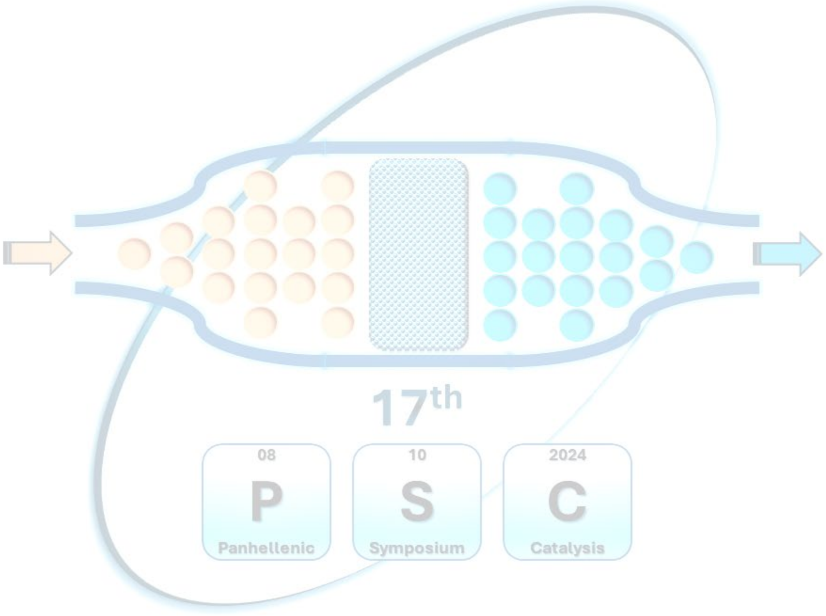
Significance of work

This work focuses on some challenges of the waste to added value chemicals transformations; highlighting the journey of catalyst design to catalyst evaluation and how advancement of TRL (technology readiness level) can be championed.

Oral Presentations



Session 1: Environmental Catalysis



SO_2 disproportionation studied at 395 K and 12 atm in an *in situ* Raman batch reactor

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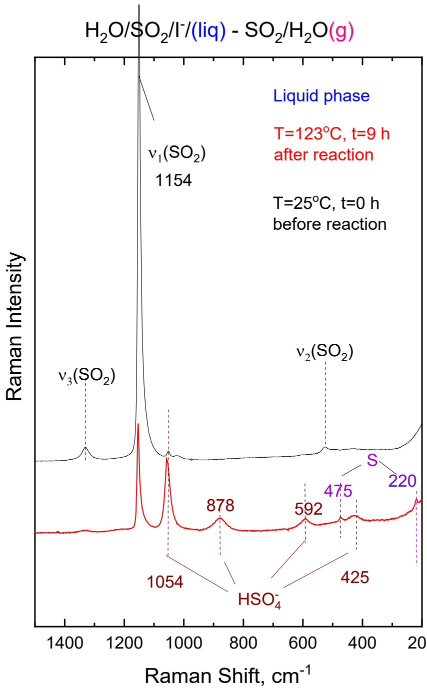
Keywords: in situ Raman spectroscopy, SO_2 disproportionation, Raman batch reactor, solar energy

Sulfur dioxide disproportionation is one of the three steps constituting a sulfur-based thermochemical cycle for thermal energy storage of concentrated solar energy [1]. The pertinent three steps are: a) sulfuric acid splitting; b) SO_2 disproportionation; and c) sulfur combustion. Whereas the first and third steps are in near-to-final stages of development, SO_2 disproportionation has only been studied in laboratory scale [2]. The reaction rate and extent of disproportionation are greatly enhanced by a homogeneous iodide catalyst and high SO_2 pressure (~40 atm).

Raman spectroscopy is used to study the vapors as well as the liquid phase of the $H_2O(l)$-$SO_2(l)$-$I^-(aq)$/$SO_2(g)$-$H_2O(g)$ system at 123 °C and total pressure of 12 atm. The reaction is found to proceed via the scheme:

$$3\mathrm{SO_2}(g,l) + 4\mathrm{H_2O}(l) \xrightarrow{123^o\mathrm{C}} 2\mathrm{HSO_4^-}\ (aq) + \mathrm{S}(s,l) + 2\mathrm{H_3O^+}(aq) \qquad (1)$$

and on cooling : $2\mathrm{HSO_4^-}\ (aq) + 2\mathrm{H_2O}(l) \leftrightarrow\ 2\mathrm{SO_4^{2-}}\ (aq) + 2\mathrm{H_3O^+}(aq)$ (2)



The figure shows the spectrum of the liquid $H_2O(l)$-$SO_2(l)$ phase at 25°C before reaction (black trace) exhibiting the ν_1 - ν_3 modes of $SO_2(l)$ plus traces of $\mathrm{HSO_4^-}$ and the spectrum of the liquid system at 123 °C under a 12 atm pressure after 9 h of reaction (red trace). The SO_2 bands have been diminished, mainly due to evaporation, hence increasing the total pressure in the cell to ~12 atm ($p_{SO_2} = 9.63\ atm$ plus the vapor pressure of water) whilst the $\mathrm{HSO_4^-}$(aq) and S(s,l) bands have emerged. Recording of the vapor Raman spectra and following the intensity of the 1154 cm^{-1} band as a function of time was adequate for inferring rates for reaction (1). Upon cooling, equilibrium (2) shifts partly to the right, as evidenced by the emergence of the $\nu_1(SO_4^{2-})$ mode (spectrum not shown).

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Novel nanostructured Pd/Co-alumina materials for the catalytic oxidation of methanol

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Keywords: Methanol oxidation, Core-shell, Spray-impregnation, Palladium-Cobalt catalysts

Introduction

Methanol (CH_3OH) is gaining more and more interest as an environmentally friendly, clean-burning, biodegradable fuel, is thus considered as promising alternative to conventional transportation fuels: used in gasoline blends, as a diesel substitute for use in heavy-duty vehicles (HDVs) and as a marine bunker fuel. Moreover, CH_3OH combustion/utilization in may decrease emission of undesired pollutants, including CO, unburned hydrocarbons, particulate matters and nitrogen oxides, emitting however other harmful, partial oxidation products, such as formaldehyde and unburned methanol vapor [1]. The activity of several Co/γ-Al_2O_3 and 0.5wt.% Pd-promoted Co/γ-Al_2O_3 catalysts for CH_3OH oxidation was investigated applying different Co loadings and synthesis methods for their preparation.

Experimental

Cobalt-doped alumina catalysts were prepared applying either the conventional wet impregnation (WI) or the advanced spray impregnation (SI) approach, and evaluated as novel oxidation catalysts for CH_3OH oxidation. Selected samples were further promoted with low Pd content (0.5 wt.%) applying either the incipient wetness impregnation (DI) or the SI method. The catalytic materials were fully characterized and evaluated for the methanol oxidation reaction (in a quartz fixed-bed reactor, feed composition: 0.1 vol.% CH_3OH and 0.1 vol.% O_2, temperature range: 30 - 300°C).

Results and discussion

Deposition of Co oxide on the outer surface of the alumina particle via SI method (as evidenced by SEM images) resulted in the enhancement of Co/γ-Al_2O_3 catalysts oxidation activity. Pd incorporation increased catalysts' reducibility (TPR-H_2) and improved catalytic activity. However, Pd incorporation method affected the catalytic performance; when applying the SI method the active phase of Co_3O_4 was probably covered from PdO and was thus not available for the oxidation reaction. On the contrary, the incorporation of Pd with the DI method resulted in better dispersion of PdO all over the Co/Al catalyst surface, maintaining available Co active sites and better Pd-Co interaction. CH_3OH desorption studies revealed the methanol oxidation mechanism; Co/Al catalysts promote partial oxidation of MeOH to formaldehyde (HCHO) and dehydration to dimethyl ether (DME), while Pd-based Co/Al catalysts enhance the desired complete oxidation of CH_3OH to CO_2 and H_2O [2].

Significance of work

The advanced spray impregnation technique resulted in the synthesis of core-shell catalytic nanostructures that secure chemical/thermal stability of the active sites on the catalyst carrier. The optimum 0.5wt.% Pd(DI)-5wt.% Co(SI)/γ-Al_2O_3 achieved a light-off temperature at 48 °C (T_{50}) and complete conversion temperature at 64 °C (T_{90}).

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Unraveling the effect of H_2O on the NH_3-SCR over LDH-derived $Mn_2Cu_1Al_1O_x$ by transient kinetics and *in situ* DRIFTS

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Keywords: Water effect, NH_3-SCR mechanism, transient kinetics, metal-oxides catalysts.

Introduction

The selective catalytic reduction of NO_x by NH_3 (NH_3-SCR) has been widely investigated in terms of catalyst composition, microkinetic modelling and mechanism(s) given its successful commercialization (NO_x control) in both stationary and mobile applications [1]. In this work, the effect of water vapour, an inevitable factor in flue gas, on NH_3-SCR reaction over LDH-derived $Mn_2Cu_1Al_1O_x$ catalyst were comprehensively examined through a set of steady-state experiments, transient kinetic analysis and *in situ* DRIFTS techniques.

Experimental

The $Mn_2Cu_1Al_1O_x$-LDO catalyst was synthesized by the co-precipitation method, as previously described [2].

Results and discussion

Steady-state experiments (Fig. 1a) revealed that H_2O exhibited both inhibitive and promotive effects on NH_3-SCR reaction, which was temperature-dependent. The N_2-selectivity was enhanced during the whole temperature range primarily due to the suppressed NH_3 oxidation and decomposition of NH_4NO_3 intermediate in the presence of H_2O. The decline trend in SCR performance at lower temperatures could be attributed to the weakened reactivity of adsorbed NO_x-s or NH_x-s species under the strong disturbance of co-adsorbed H_2O (Fig. 1b) [3]. On the contrary, at higher temperatures, moderate presence of H_2O facilitated the preservation of NO_x-s/NH_x-s species on the catalysts surface, which further lead to higher N_2 production via the NH_3-SCR process (Fig. 1c).

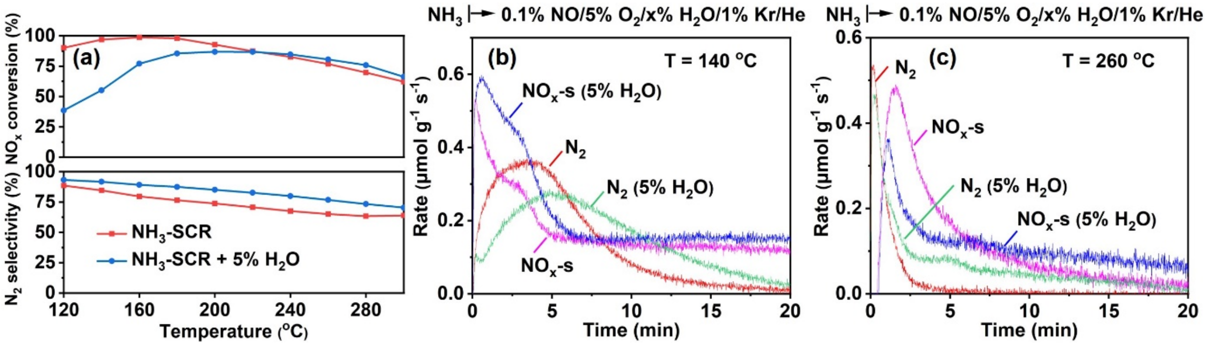

Figure 1. The effect of 5% H_2O on: (a) NO_x conversion and N_2 selectivity; Rates of N_2 formation and NO_x-s adsorbed at (b) 140 °C, (c) 260 °C during the switch: $NH_3 \rightarrow 0.1\%\ NO/5\%\ O_2/x\%\ H_2O$ (t).

Significance of work

This work demonstrated that the unexpected increase in N_2 and N_2O formation in the presence of H_2O, observed through transient kinetic experiments, is due to the enhanced surface concentration of active NO_x-s and NH_x-s adsorbed species, which were able to follow the L-H mechanism.

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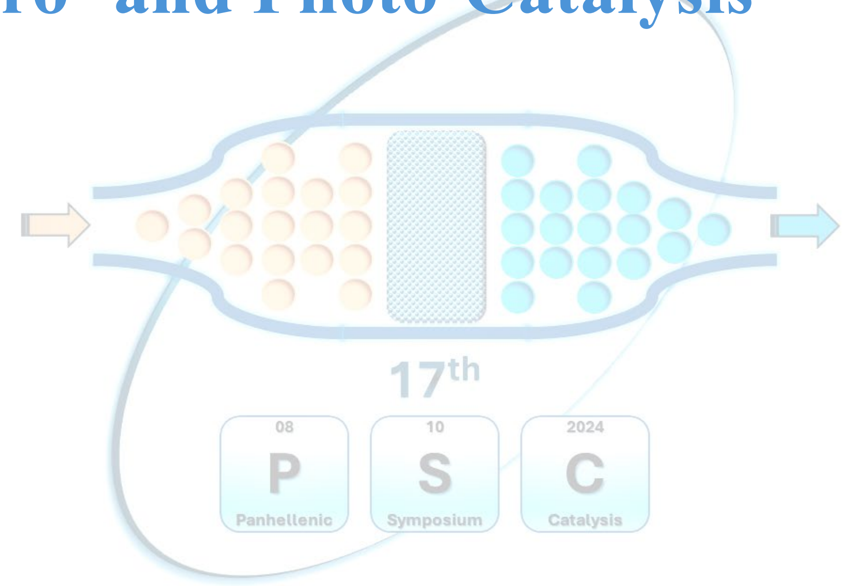
Session 2: Environmental Catalysis / Electro- and Photo-Catalysis



Catalytic VOC oxidation over Mn_2O_3 oxides

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Keywords: (Mn_2O_3, oxidation, VOC, TPD)

Introduction

Catalytic oxidation is one of the most important technologies among those developed to control volatile organic compound (VOC) emissions from static sources. Transition metal oxides, like Mn_2O_3, are active catalysts but the mechanistic aspect of VOC oxidation reactions over these catalysts has not been thoroughly studied. This particular study focuses on the interactions of two different VOCs (propene, butane) with the catalytic surface of Mn_2O_3 oxides. Furthermore, the possible existence of structure sensitivity for the oxidation of propene and butane was investigated by variation of the specific surface area of the catalysts.

Experimental

Mn_2O_3 catalysts were prepared by the citric acid complexation method or bought commercially aiming to obtain different specific surface area. The catalysts were characterized by N_2 physisorption, SEM, p-XRD, XPS, H_2-TPR, Raman spectroscopy and O_2-TPD. The catalysts were evaluated in both propene and butane oxidation under steady state conditions. The interaction between the catalytic surface and the VOCs was investigated with temperature programmed desorption (TPD) and surface reaction (TPSR) experiments.

Results and discussion

All catalysts contain pure Mn_2O_3 crystalline phase with varying specific surface area in the range of 3-30 $m^2 g^{-1}$. XPS data indicate that manganese is present only in the Mn^{3+} oxidation state in the surface of the samples and surface O_{ads}/O_{latt} surface ratios were calculated for each sample. The surface concentration of active sites for each catalyst and reaction were calculated from the TPSR experiments, and samples of higher specific surface area had more active sites per unit surface area. Significant heterogeneity in the catalytic surface is observed from the carbon dioxide desorption profiles following VOC adsorption. The specific reaction rate (mol $s^{-1} m^2$) was higher for samples of higher specific surface area while the turnover frequency (TOF, s^{-1}) was calculated and found to be positively correlated with the O_{ads}/O_{latt} ratios of the samples.

Significance of work

The current work aids in the understanding of the mechanism of VOC oxidation over Mn_2O_3 catalysts and ultimately at the synthesis of fine-tuned catalysts with the desired properties for more efficient propene and butane oxidation.

Acknowledgments

The research project was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the "1st Call for HFRI Research Projects to support faculty members and researchers and the procurement of high-cost research equipment" (Project Number: HFRI-FM17-1876).

Substitution of Cr in $La_{0.75}Sr_{0.25}CrO_{3-\delta}$ by Fe or Ni: effect on conductivity and electrochemical performance

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Keywords: Perovskite oxides, electrolysis, solid oxide cells (SOC).

Introduction

Perovskite-type fuel electrodes are essential for SOC technology improvement, as they are resistant to carbon deposition and present redox stability. Furthermore, their mixed ionic-electronic conductivity is a key characteristic, while different dopants and/or concentrations result in different performance. The present study aims to investigate the effect of B site doping in lanthanum strontium chromite oxide, $La_{0.75}Sr_{0.25}CrO_{3-\delta}$ (LSC), used as fuel electrode in Solid Oxide Cells (SOCs), on its conductivity and electrochemical performance under both oxidating and reducing conditions. The substitution of Cr by the transition metals Fe or Ni, by 10 or 50% mol (LSCF0.1/LSCF0.5, LSCNi0.1/LSCNi0.5), decreases the electronic conductivity while improving the oxides' electrocatalytic activity.

Experimental

The perovskite structure materials were synthesized using the modified sol-gel method with citric acid as described in [1]. The materials were pressed into pellets which were thermally treated to perform conductivity measurements, applying the 4-point/Van der Pauw method. Button cells were prepared using the synthesized materials as fuel electrodes and state-of-the-art electrolytes and oxygen electrodes, and were tested under fuel cell and electrolysis conditions. All electrodes were fabricated using screen printing with a geometric electrode area of ~0.8 cm^2.

Results and discussion

Results showed that LSC has the highest electronic conductivity, which is attributed to the absence of a B-site dopant, thus facilitating electron transfer [2]. LSCNi0.5 and LSCF0.5 exhibited the lowest electronic conductivities, since the concentration of Cr and thus of the redox couple Cr^{3+}/Cr^{4+}, which is responsible along with oxygen vacancies for the electroneutrality of the crystal, are reduced. LSCF0.1 demonstrated the second-highest electronic conductivity, followed by LSCNi0.1. This is attributed to the fact that $r_{Fe^{3+}}$ is closer to $r_{Cr^{3+}}$ than $r_{Ni^{2+}}$, which leads to a less distorted crystal [3]. Among the materials studied, LSCF0.1 exhibited the highest current density in both fuel cell and electrolysis operation modes, while LSC exhibited the lowest performance. Despite the high electronic conductivity of LSCNi0.1/LSCNi0.5, their electrochemical performance was low, indicating that multiple macroscopic and microscopic factors are responsible for electrodes performance.

Acknowledgments

This project is carried out within the framework of the National Recovery and Resilience Plan Greece 2.0, funded by the European Union – NextGenerationEU (Implementation body: HFRI).

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Dynamic simulation of H_2 oxidation on NiFeAu/GDC for SOFCs

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Keywords: SOFC, HOR, EIS, IV

Introduction

This study [1], proposes a microkinetic, thermodynamically consistent hydrogen oxidation reaction model (HOR) pathway/model on a NiFeAu/GDC anodic solid oxide fuel cell (SOFC) electrocatalyst, that can accurately capture, the steady-state HOR electrokinetic polarization (IV) and the Electrochemical Impedance Spectra (EIS) response, in the activation kinetic region (ideal kinetic control).

Experimental

Steady state and Electrochemical Impedance Spectroscopy (EIS) measurements were conducted in a two-electrode setup at 900°C, feeding the cell with 150 [ccm] $H_{2(g)}/O_{2(g)}$ for the fuel/oxygen electrode (LSCoF) respectively. The employed button cell (both electrodes had 20 [µm] thickness and active area of 1.76 [cm^2]), incorporated a novel, in-house developed, electrolyte (8YSZ, 25 [mm] diameter and 150 [µm] thick) supported Ni/GDC fuel electrode, doped with 0.5wt.% Fe and 1wt.% Au [2]. A simulation algorithm has been developed to simulate the spectra and calculate the kinetic constants of the HOR.

Results and discussion

Fig.1 compares the experimentally recorded electrocatalytic data (symbols) with our simulation results (red lines): **a)** IV polarization curve with the proposed 2-step electrocatalytic HOR pathway, **b)** Nyquist Impedance spectrum at I_{SOFC}=60[mA].

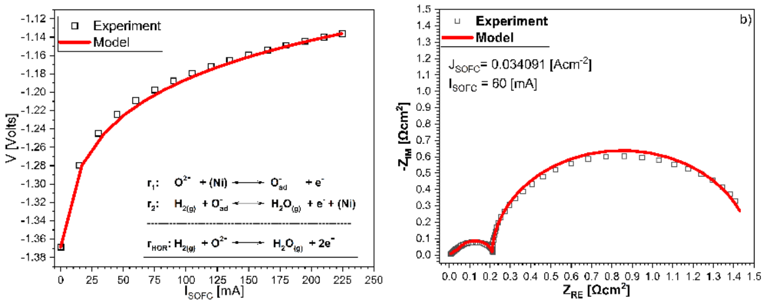

Fig.1 Simulation results: a) IV curve and b) EIS at I=60[mA]

Significance of work

This work sheds light on the elusive HOR kinetics for SOFCs, its steady state and dynamic EIS response as well as the kinetics and energetics of the reaction and the operating state of the catalyst.

Acknowledgments

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Precision Nanoengineering of Metal-Oxide Catalysts at Industrial Scale: Examples and Lessons learned from H_2/CO2 Photocatalysts

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Keywords: Flame Spray Pyrolysis, SMSI, SMOI, subnanoclusters, vacancies, atomic dispersion, Quantum-size , H2 photocatalysis, CO2 photocatalysis.

Introduction

Achieving high-performance catalysis *in tandem* with selectivity is a long sought aim in catalytic technologies. When nanocatalysts are used, diligent control at the nanolevel allows high-gain strategies to be elaborated. To this front, transfer of a successful catalyst design and synthesis from lab-scale to industrial scale is mandatory for full-scale exploitation of the catalytic technology. Photocatalytic H_2-production from H_2O, CO_2 reduction are highly pursued as stat-of-the art green catalyst technologies. Flame Spray Pyrolysis offers a state-of the-art industrial scale technology (TRL >6) for precision engineering of noncatalytic metal oxides [1].

Results and discussion

Herein, we have developed a novel-type of FSP-process based on a now reactor-design that allows *in-situ* fine-dispersion of metal-atoms or sub-nanoclusters on selected Metal-Oxide nanoparticles with high photocatalytic efficiency. We discuss case-studies of nano-$NaTaO_3$ or TiO_2-Quantum-dots, or ZrO_2-quantum-dots produced via FSP-technology [1,2]. These have been decorated with single bismuth (Bi^{3+}) atoms or clusters, or single copper (Cu^{2+}) atoms or clusters via FSP in one-step. Control of the FSP-process parameters allows control of lattice-vacancies (Vo) in the same materials. We discuss the role of Strong-Metal-Support-Interactions (SMSI) in photocatalytic performance. Another direction of precision nanoengineering is discussed based on the case of TiO_2 tightly interfaced with RuO_2, with emphasis on selective interfacing of Rutile(RuO2)-Rutile(TiO2) [3]. We discuss the role of Strong-Metal-Oxide-Interactions (SMOI) in photocatalytic H2/O2-produciton performance. Finally we highlight the possibility of TRL-ladder advancement in precision-engineered catalysts using industrial scale FSP beyond the current-state-of the art [1].

Acknowledgments

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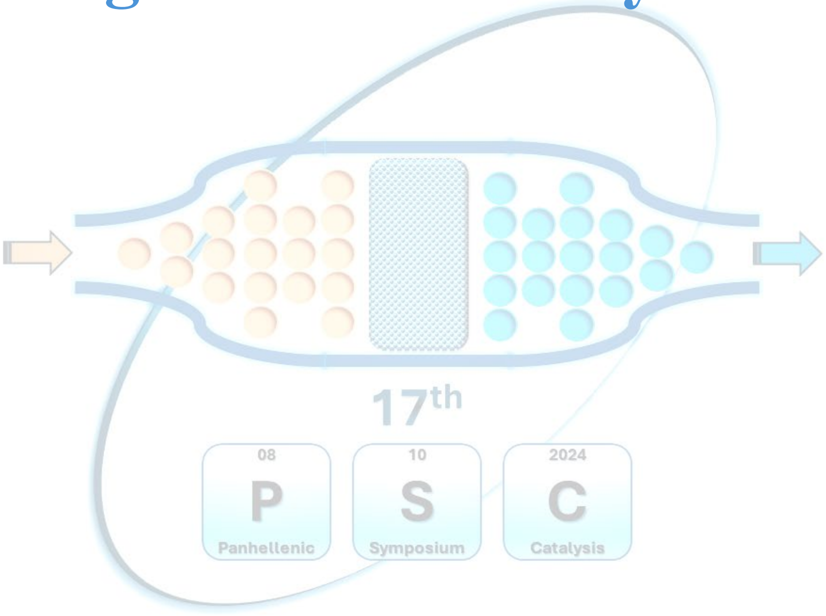
Session 3: Hydrogen Production Technologies / Photocatalysis



Scaling up $BiVO_4$ Photoanodes on Porous Ti Transport Layers for Solar Hydrogen Production

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Keywords: $BiVO_4$ photoanode · Hydrogen ·Photoelectrochemical · Water-splitting.

Introduction

Reducing CO_2 emissions through green energy is critical to combat climate change. Despite advances in renewable electricity, 80% of global energy consumption is from chemical fuels, which are currently fossil fuel-based, necessitating a shift to renewable fuels like hydrogen. Solar energy is abundant, and hydrogen can be produced using photovoltaic cells and electrolysers (PV-E) or integrated photoelectrochemical (PEC) water splitting. PEC has shown promise for cost-effective hydrogen production with efficiencies of up to 19% using optimized materials[1]. Research focuses on affordable photoelectrode materials targeting 10% efficiency, but scaling up for commercial use is challenging due to resistive losses and material inhomogeneity. This work aims to develop scalable, high-performance photoelectrodes.

Experimental

Material development and characterization can be found elsewhere [2a].

Results and discussion

The study focuses on the scalable production and enhancement of $BiVO_4$ photoanodes for PEC water splitting. $BiVO_4$ films were successfully deposited on Ti porous substrates using the s-SILAR method, achieving high activity with 3% W doping[2b]. The scaled-up photoanodes (100 cm^2) maintain ~90% of the photocurrent of 1 cm^2 photoanodes, outperforming literature findings in which scaling-up causes up to a 65% drop in performance. Performance uniformity across large areas was confirmed, indicating the potential for commercial application. EIS analysis showed minimal resistance changes with scaling. Integrating the photoanode with a Si PV cell achieved bias-free water splitting with 2.2% solar-to-hydrogen (STH) efficiency, demonstrating significant advancement in large-area PEC devices.

Significance of work

This work demonstrates a significant advancement in scalable PEC technology for STH generation. By using porous gas diffusion electrode substrates and scalable fabrication processes, we achieved the highest reported photocurrent density for scaled-up photoanodes. The integration of these photoanodes with Si PV cells for bias-free water splitting highlights the potential for commercial PEC devices. Our findings emphasize the importance of innovative photoelectrode design and scalable fabrication techniques in advancing green hydrogen production technologies.

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SO_3 catalytic splitting for sulfur based thermochemical storage of solar thermal energy

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Keywords: SO_3 splitting, catalyst screening, solar energy

Sulfur trioxide splitting ($SO_3 \leftrightarrow SO_2 + \frac{1}{2}O_2$) is an important step in various thermochemical processes. The reaction is endothermic and requires high temperatures, typically between 600°C and 950°C. Recent interest in coupling this reaction with renewable heat sources, such as solar thermal collectors, has spurred research into efficient catalysts that can operate effectively at the lower end of this temperature range. Herein we investigate the catalytic activity of V_2O_5-based supported or mixed oxide catalysts for SO_3 splitting, focusing on performance at temperatures between 640°C and 680°C.

V_2O_5 was either synthesized or obtained commercially. The mixing with the substrate (kaolinite, Al_2O_3) was done either in dry conditions or via standard dissolution-precipitation of substrate and active phase precursor. Finally, selected samples underwent calcination at up to 700°C (4h in air flow) while the rest of them did not. A fixed-bed flow reactor was used for the catalytic activity studies. Catalysts loaded weighed 54 mg, had a particle diameter between $250\ \mu m$ and $125\ \mu m$ and formed a bed height of $4.5\ mm$. The feed consisted of a mixture of 10% SO_2 7.5% O_2 and 82.5% N_2. The flow rate ranged between 80 and 100 $\frac{cm^3}{min}$ to ensure differential operation for the reactor (GHSV: $86000 - 107000\ h^{-1}$, WHSV:133-166h^{-1}). Initially, SO_2 was converted to SO_3 over Pt/SiO_2 in a 390°C–operated pre-converter (operating at 98.40 % SO_2 conversion to SO_3) and the resulting feed was driven to the test reactor. SO_2 produced by SO_3 splitting was quantified using online UV-spectrophotometry. Catalysts were tested over a T-range of 640 - 680°C and activation energies were determined.

The SO_3 consumption rates were in the $60.55 - 14.51\ \frac{ml\ SO_3}{g_{cat} \cdot min}$ range and the respective activation energies ranged between $92 - 160\frac{kJ}{mol}$. Similar activation energies are also reported in literature [1]. In terms of catalyst preparation techniques, it became evident that standard dissolution precipitation with subsequent calcination yielded catalysts with higher activity and lower activation energy. The catalyst with the lower activation energy and activity was the one that had Al_2O_3 as a substrate and did not undergo calcination.

Significance of work

SO_3 splitting catalysts have a major role in solar thermochemical processes. As a result, catalysts that operate in medium temperatures (600°C-700°C) and are cost-effective have a great research interest.

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Iridium-based OER electrocatalysts supported on Titanium suboxides for PEM Water Electrolysis Systems

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Keywords: Hydrogen production, PEM Water Electrolysis, Iridium electrocatalysts, Oxygen Evolution Reaction (OER)

Proton Exchange Membrane (PEM) water electrolysis is considered to be a suitable large-scale hydrogen production method, incorporating important features, such as low operating temperatures and high efficiency, without carbon gas emissions. The Membrane Electrode Assembly (MEA) plays a key role, consisting of a proton conductive membrane (Nafion®) as the electrolyte between anode and cathode electrodes. Noble metals (Pt, Ir, Ru) present remarkable performance during both anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER). As OER demands a significant amount of energy (1.23V vs RHE), iridium is mostly used as the optimum anodic electrocatalyst due to its remarkable activity and stability in highly oxidizing environment [1]; however, the cost of these materials is prohibitive. Reducing the iridium loading is essential for PEM Water Electrolysis to be established as a commercially viable hydrogen production method.

This study focuses on the development of iridium based electrocatalysts supported on modified titanium oxides substrates (Ti_nO_{2n-1}), aiming to a 70% Ir loading reduction. These substrates, known as Magneli phase oxides, are characterized by excellent electrical conductivity and high stability in acidic environment [2], making them a promising solution as supporting materials in order to develop low-cost electrocatalysts. Titanium substrates were synthesized via a non-aqueous sol-gel method [3], followed by a conventional sodium borohydride reduction method [4] for electrocatalysts' development. Materials were subjected to physicochemical (XRD, SEM-EDS, BET) and electrochemical (RDE) characterization in terms of intrinsic activity for the OER performance. The most promising electrocatalysts were applied in 3-layer MEAs for evaluation in a PEM water electrolysis test cell, employing sintered Ti PTLs, by measuring the electrocatalytic activity and long-term stability under practical operating conditions.

Physicochemical characterization confirmed the formation of Ti_nO_{2n-1} substrates and supported Ir/Ti_nO_{2n-1} electrocatalysts; however, low specific area and noticeable inhomogeneity were observed for both, substrates and catalysts. Regarding the electrochemical characterization, RDE measurements were performed to gain information about the intrinsic electrochemical activity of the synthesized electrocatalysts. Comparable and encouraging findings were derived from the evaluation of electrocatalysts in MEAs under practical conditions, performed on a standard PEM water electrolysis cell. The results revealed an electrocatalytic system of significantly reduced noble metal loading, with high catalyst utilization and enhanced anodic stability presenting no loss of the electrocatalytic activity during tests. The electrocatalytic activity of the prepared electrocatalysts was compared with that of commercially available unsupported IrO_2.

Acknowledgments

This project is carried out within the framework of the National Recovery and Resilience Plan Greece 2.0, funded by the European Union –NextGenerationEU (Implementation body: HFRI).

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Engineering of Photocatalytic ZrO_2 Nanocatalysts by Flame Spray Pyrolysis (FSP) technology.

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Keywords: Flame Spray Pyrolysis, ZrO_2 nanocatalysts, Hydrogen production, Electrocatalysis

Introduction

Zirconium based nanocatalysts (ZrBNCs) with controlled monoclinic to tetragonal phase are promising photocatalysts due to their thermal and chemical stability. Also, ZrBNCs are ideal for solid oxide electrolytes and for many other applications. So far, fundamental studies on tetragonal/monoclinic ZrO_2 as photocatalysts without dopants have rarely been reported. Herein we have used Flame Spray Pyrolysis to control the size and photophysical properties of ZrO_2 nanocatalysts.

Experimental

The lack of research on a controlled tetragonal:monoclinic ratio ZrO_2 is attributed to difficulties in the manufacturing process and the mechanical instability of ZrO2 to temperature variations. Through Flame Spray Pyrolysis (FSP) technology we have achieved zirconium nanoparticles with reduced size, controlled composition and oxygen vacancies.

Results and discussion

Herein we present FSP-made ultrasmall (<6nm) ZrO_2 which show formation of mid-gap states based on DRS-UV-Vis analysis. Electron Paramagnetic Resonance (EPR) data reveal formation of lattice-vacancies formed during the FSP process. Furthermore, XRD analysis reveals that the FSP-made ZrO_2 bear variable amounts of monoclinic and tetragonal phases. The ultrasmall (<6nm) ZrO_2 show significant photocatalytic H_2 production efficiency from H_2O. This is due to the formation of mid-gap states that allow absorption of visible light photons as well as $UV_{B,C}$. We underline that pristine monoclinic ZrO_2 with E_{CB} =-900mV vs NHE and a high band gap of E_g=5.8eV is typically classified as non-photoactive semiconductor under sunlight (hv<4eV). Our group demonstrated using, control of oxygen vacancies in ZrO_{2-x} promotes the photocatalytic activity allowing production of green Hydrogen from H_2O[1,2]. Herein, we further explore the size-effect on the photoactivation of ZrO2.

Significance of work

Through this work ZrBNCs are good candidates for HER and CO_2RR for with controlled phase composition can achieve high electrical conductivity, mid gap states in visible light spectrum and Hydrogen production. The results of this work will impact the understanding of ZrBNCs.

Acknowledgments

H.F.R.I. Hellenic Foundation for Research & Innovation

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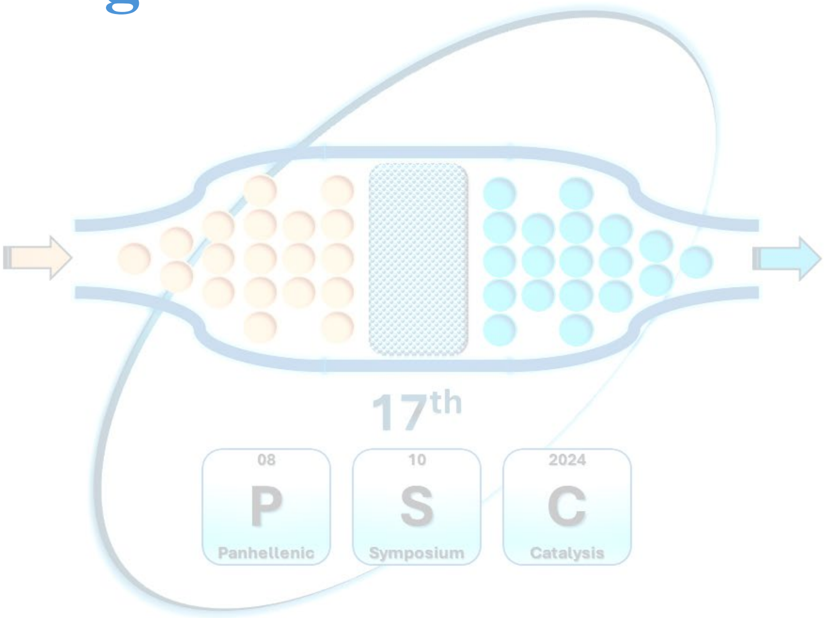
Session 4: Hydrogen Production Technologies



Plasmon-Assisted Dehydrogenation of Formic Acid by a Heterogeneous Molecular Fe-catalyst for H_2 Production.

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Keywords: FADH, H_2, plasmonics, heterogeneous catalysis

Introduction

Catalytic dehydrogenation of formic acid (FADH catalysis) utilizing Fe complexes is one of the most efficient routes for H_2 production[1]. Recently, nanoplasmonics have been incorporated as rate-controlling agents[2], due to their photo-responsive ability initiated by localized surface plasmon resonance (LSPR) phenomena [3] in a homogeneous [$Fe(BF_4)_2 \cdot 6H_2O$/ $P(CH_2CH_2PPh_2)_3$, PP_3] system. Introducing hot electrons into the catalytic system that act as reducing agents, decreases the potential of solution Eh, *in tandem* with increasing its activity. In this study, plasmonic enhancement has been evaluated in terms of yield and scalability in a progressively expanded system, incorporating Fe^{2+} with a low-cost SiO_2@imidazole hybrid material [5] and PP_3.

Experimental

Herein, SiO_2 thin-coated[4] plasmonic silver nanoparticles (Ag@SiO_2) were used as rate-controlling agents for FADH in conjunction with a heterogeneous [SiO_2@imidazole-Fe] catalytic system[5]. Performance has been evaluated versus narrow-band (LED) irradiation intensity at 405 nm, namely at the peak of the photoplasmonic response of the Ag^0@SiO_2 NPs [2].

Results and discussion

Catalytic data indicated a significant enhancement in the H_2-production rate by photoexcited core−shell Ag^0@SiO_2 PNPs. The optimized scaled-up [(SiO_2@imidazole-Fe-PP_3)/HCOOH/Ag^0@SiO_2-hv] catalytic system achieves an almost **~320 %** increase of the H_2-production rate, providing 63 mL H_2 min^{-1} in 100 % illumination intensity and **~210 %** increase (47 mL H_2 min^{-1} in 60 % intensity) *vs* 15 mL H_2 min^{-1} in the absence of Ag^0@SiO_2. The impact of plasmon-assisted molecular catalysis (PAMC) is studied for the first time in a *heterogeneous* molecular catalyst and applied to FADH for H_2 production.

Acknowledgments

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Methane pyrolysis for COx-free Hydrogen Production

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Keywords: hydrogen production, methane pyrolysis, Fe- Co-based catalysts, carbon nanofibers

Introduction

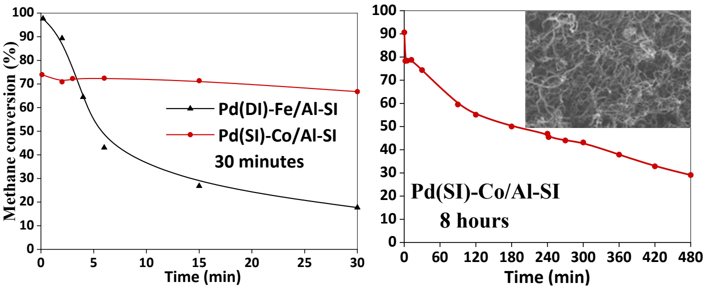
Hydrogen is considered to be one of the cleanest power sources, since its combustion implies zero carbon emissions. Methane Pyrolysis poses a sustainable solution for COx-free hydrogen production, as the products include only hydrogen gas and solid carbon. However, the reaction mechanism requires temperatures as high as 1300° C and the solid co-products are usually low-value carbon allotropies [1]. Hence, catalyst development is urgent, in order to overcome these challenges. The aim of the present study was to prepare inexpensive Fe- and Co- based solid catalysts, via two different syntheses approaches in order to investigate the effect of synthesis method. Selected catalysts were further promoted with small amount of a noble metal, such as Pd.

Experimental

5wt.% Fe or 5wt.% Co on alumina support catalysts were synthesized by Wetness Impregnation (WI) or Spray Impregnation (SI) method. 0.5wt.% Pd was also introduced to both catalysts via Dry Impregnation (DI) or SI methods. All catalysts were characterized by ICP, XRD, BET and SEM methods, while their catalytic behavior was evaluated in a fluidized bed reactor, under 10vol.% CH_4/He stream, at 850° C or 700° C for Fe and Co respectively. The stability of the superior catalyst was also tested for 8 hours time on stream (TOS). Last but not least, the produced carbon co-product (C nanofibers) was characterized by LECO, TPO and TEM techniques.

Results and discussion

Catalyst characterization shows that WI offers a uniform distribution of the metal phase on the support, while the SI creates core-shell structures. In all cases SI method benefits the catalytic activity, while the Fe samples initially outperformed the Co catalysts. Although Pd incorporation had a minor positive effect on Fe-catalysts' performance, it significantly enhanced the catalytic activity of Co-samples. Pd incorporation also promoted the production of carbon nanofiber. Stability evaluation of the SI Pd-Co/alumina catalyst initially showed relatively high rates (~80%) of methane decomposition (during the first 30 min), which diminished however to 29%, after 8 hours TOS experiment.



Left: Positive effect of Pd incorporation on catalytic activity. Right: Stability test and nanofiber production

Significance of work

All tested catalysts exhibited important selectivity towards hydrogen production, while the optimum Pd-based material presented promising stability and commercialization potential due to rather low amount of Pd. Finally, the co-produced nanofibers may have several high added value applications.

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Methanol Steam Reforming over Cu-based catalysts: Mechanistic insights via transient isotopic and operando spectroscopic studies

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Keywords: Operando DRIFTS-MS, Reaction Intermediates, Hydrogen, Methanol Steam Reforming

Introduction

Renewable energy sources and hydrogen technologies are the main pillars driving the energy transition strategies towards climate neutrality in 2050. Green hydrogen derived from water electrolysis supports the pathways of energy sustainability, though elevated cost and absence of infrastructure for storage and distribution are currently the main obstacles. Alternatively, methanol offers an attractive option as hydrogen carrier, being easily produced via steam reforming process over Cu/ZnO catalysts. Latest advances in catalyst engineering regarding high Cu dispersion and ZnO nanostructuring, can promote low-temperature (<200°C) steam reforming, thus matching the operation level of high temperature fuel cell systems.

Experimental

$CuZnO_x$ catalysts were synthesized via hydrothermal method (HTM) and characterized with various techniques. A promising catalyst (HTM#1) was prepared using Na_2CO_3 at 120°C for 24h, followed by calcination at 300°C. HTM#1 and a reference commercial catalyst (HiFuel R120) were initially pretreated under 50% H_2/He at 280°C and then subjected to operando DRIFTS-MS, monitoring key species (H_2, H_2O, CO, CO_2, CH_3OH) and their deuterated isotopes during methanol steam reforming.

Results and discussion

Regarding the Cu-based catalysts, three possible pathways have been considered in the literature in order to interpret the MSR mechanism, involving carbon monoxide (CO*), methyl formate ($HCOOCH_3$*) and formate (HCOO*) species as the surface intermediates. In this work, surface species and various intermediates formed during methanol steam reforming process were analyzed via DRIFTS-MS setup. Methanol was dissociatively adsorbed on the active sites of the catalytic surface, rapidly dehydrogenating to methoxy and formate species [1]. Taking into account transient isotopic studies, it is indicated that the mechanism of methanol steam reforming reaction involves the transformation of methoxy species (CH_3O*) to formaldehyde (CH_2O*), dioxomethylene (CH2OO*) and eventually to formate (HCOO*) species, which finally decomposed to CO_2 and H_2 [2].

Significance of work

Identifying the key intermediate species for methanol steam reforming and developing more efficient Cu-based catalysts is a significant topic for applying in situ hydrogen production.

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Efficient and Reuseable [Silica@iminophosphine-Fe] Hybrids for H_2-Production from Formic acid and Formaldehyde

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Keywords: H_2 production, Formic Acid, Formaldehyde, Fe-catalysts

Introduction

The use of hybrids, which are mainly developed of homogeneous catalysts grafted on supporting materials, have already shown their potential in various catalytic processes, because they combine advantages of homogeneous catalysts, such as high activity and selectivity, with those of materials, such as recyclability. Catalytic H_2 production via dehydrogenation of C1 organic molecules targeting its use in fuel cells is a contemporary scientific issue directly connected with climate crisis. Within this, there is a need for highly stable, efficient and reusable heterogeneous catalytic systems at low cost, for green energy production [1,2].

Experimental

Iminophosphine hybrid [SiO_2@benzNP] [3] and its reduced analogue [SiO_2@benzNHP] were synthesized, covalently grafted on colloidal SiO_2, and fully characterized by FT-IR, TGA, ssNMR, BET analysis. They were used for *in-situ* synthesis of [SiO_2@benzNP-Fe] and [SiO_2@benzNHP-Fe] catalytic complexes for H_2 production from formic acid (HCOOH) and formaldehyde (HCH=O), at 80°C. The identification of the [$H_2 + CO_2$] gases, produced during catalytic experiments, was performed using Gas Chromatography; it's highlighted that CO production was not observed.

Results and discussion

The [SiO_2@benzNP-Fe] hybrid in propylene carbonate and in the presence of a tetradentate phosphine yielded from FA 12L of gases with 36,000 TONs and it was functional for 3 successive uses. Under the same experimental conditions, the corresponding [SiO_2@benzNHP-Fe] analogue presented higher performance, producing 18,5L of gasses (TONs>61,000), and higher durability than the previous one, being re-used 5 times, without further metal addition. These Fe-hybrids have been also evaluated, without any base, in aqueous formaldehyde dehydrogenation, which occurs via methanediol intermediate formation; the [SiO_2@benzNHP-Fe] provided 1.3L of H_2 (TON>3,500) within 3 consecutive uses, *vs* the [SiO_2@benzNP-Fe] which presented 4 times lower catalytic performance. Overall, the reduction of C=N bond of iminophosphine ligand seems to endow the [SiO_2@benzNHP-Fe] catalyst with enhanced reactivity and stability in both formic acid and formaldehyde dehydrogenation.

Significance of work

The hybrids [SiO_2@benzNP-Fe] and [SiO_2@benzNHP-Fe] are among the first examples, which are active and reuseable in formic acid and formaldehyde dehydrogenation catalysis.

Acknowledgments

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Hellenic Foundation for Research & Innovation

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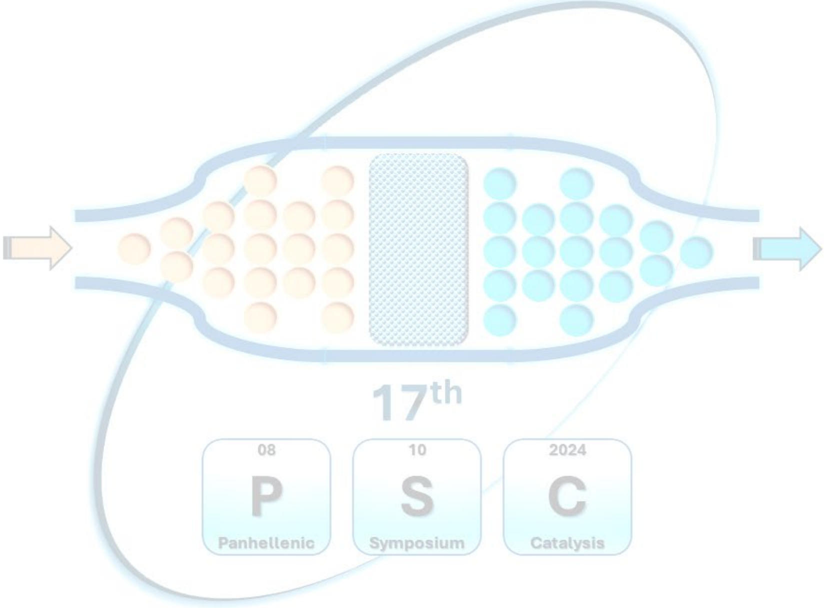
Session 5: Catalytic Conversion of CO/CO_2 into Fuels and Chemicals



From earth material to energy production: Ni-based modified halloysite catalysts for CO_2 methanation

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Keywords: CO_2 methanation; Ni-based catalyst; Oxygen vacancy; XAS

Introduction

CO_2 methanation has emerged as one of the promising approaches to produce valuable products, and chemicals. In this study, we focused on tuning the surface of natural halloysite clay as a support for Ni-based catalysts comprising of Ce-O, Ce-Cu-O and Ce-La-O modifiers.

Experimental

All the catalysts were synthesized via simple wet-impregnation and their microstructure, surface coordination environment, redox behavior and acid/base properties were analyzed. The interaction between Ni^0 nanoparticles and interfacial sites was unveiled along with their catalytic performance.

Results and discussion

HRTEM analysis demonstrated that modification of the Hal layer promotes high dispersion of Ni nanoparticles, predominantly exposing Ni^0 (111) facets. Specifically, Hal modification with Ce and La reduced the size of Ni particles to ~9 nm. XPS analysis revealed the co-presence of Ce^{3+} and Ce^{4+} on the surface, which significantly enhances CO_2 activation. Furthermore, XAS studies provided insights into the structural properties and surface interactions at the unit cell scale. The Ni/10La10CeHal catalyst exhibited superior oxidation resistance and achieved the highest CO_2 conversion (67%) among all studied catalysts, with a $Y_{CH4} = 61\%$ and $S_{CH4} = 91\%$ at 450°C, surpassing other catalysts in the study. Notably, Ni/10La10CeHal maintained a steady $X_{CO2} = 65\%$ over a 50 h on stream test at 450°C.

Significance of work

This work investigates the utilization of modified naturally occurring halloysite (aluminosilicate clay) nanotubes with various transition (Cu^{2+}) and rare-earth (Ce^{4+}, La^{3+}) metals as dopants; the latter are critical promoters of the support material for Ni-based catalysts in the CO_2 methanation reaction. These modification impacts on the catalyst's basicity, oxygen vacancies, Ni dispersion, and metal-support interactions was assessed along with the catalytic performance.

Multi-cyclic stability of Ru/Na_2O/Al_2O_3 dual-function materials for the integrated capture and methanation of CO_2

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Keywords: CO_2 capture and methanation; Dual-function materials; Material synthesis; Stability.

Introduction

The process of integrated CO_2 capture and methanation has gained significant research interest in recent years, as a means to couple these two separate processes into a single integrated process, that is operated isothermally, often using a single material, i.e., a dual-function material (DFM) [1].

Experimental

The support in RuNAl_PC was prepared via Pechini sol-gel, whereas a commercial Al_2O_3 support was used in RuNAl_Comm. The "Na_2O" and Ru phases were then introduced via wet impregnation. The materials were characterized and tested in a reactor with isothermal steps (300 °C) of CO_2 capture (different feeds), Ar purge and CO_2 methanation (10% H_2/Ar) for 10 cycles. The CO_2 capture feed was either: 10% CO_2/Ar (ideal), 10% CO_2, 10% O_2/Ar, or 10% CO_2, 10% O_2, 15% H_2O/Ar (simulated flue gas).

Results and discussion

RuNAl_PC, with the support prepared via Pechini, was tested for 10 cycles with the three different feeds during CO_2 capture. Under ideal operation (CO_2 capture with 10% CO_2/Ar), the stabilized CH_4 yield is approx. 0.45 mmol/g, with a small deactivation, whereas the CO yield and desorbed CO_2 is minor. For operation with O_2, CH_4 yield is slightly lower at 0.42 mmol/g, while the amount of desorbed CO_2 is higher. In the co-presence of O_2 and H_2O (simulated flue gas), the performance is similar as without H_2O (stabilized CH_4 yield at 0.41 mmol/g). On the other hand, RuNAl_Comm prepared with the commercial support displays much lower CH_4 yield values (0.34 mmol/g CH_4 yield at the 10th cycle).

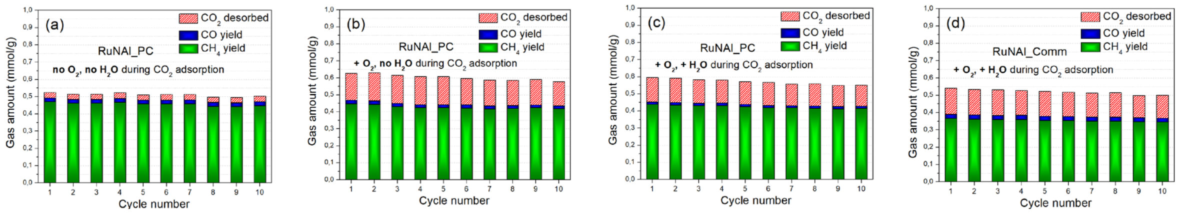

Fig. 1. CH_4 yield, CO yield and amount of desorbed CO_2 for the DFMs with different CO_2 capture gas feeds.

Significance of work

This work showcases the potential to further optimize the benchmark Ru/Na_2O/Al_2O_3 DFM formulation by varying the support synthesis method and studies the effect of different gas components in the CO_2 capture feed, from ideal conditions (CO_2/Ar) to more realistic conditions (co-presence of O_2 and H_2O).

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CO_2 hydrogenation over 3d transition metals supported on ceria nanoparticles

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Keywords: CO_2 hydrogenation, transition metals, ceria nanorods, structure-performance relationships.

Introduction

CO_2 hydrogenation is studied over M/CeO_2-nanorods (NR), employing first row 3d transition metals as active phases (M: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn with M/Ce atomic ratio of 0.25).

Experimental

CeO_2-NR was hydrothermally synthesized and M/CeO_2 (M: Ti, V, Cr, Mn, Fe, Co, Ni, Cu) catalysts were synthesized by the wet impregnation method [1]. The materials were characterized by various techniques and evaluated in the hydrogenation of CO_2 (WHSV = 30 $L\cdot g^{-1}\cdot h^{-1}$, H_2:CO_2 = 4, P = 1 bar).

Results and discussion

A volcano-type dependence of CO_2 hydrogenation activity and selectivity was disclosed as a function of metal entity (Ti – Zn) with a maximum for the Ni-based sample. Ni/CeO_2 is extremely active (~90% conversion at 300 °C) and fully selective to methane, followed by Co/CeO_2. The CO_2 conversion performance follows the trend: Ni > Co > Cu > Fe > Zn > Cr ≈ Ti ≈ V ≈ Mn.

Significance of work

CO_2 hydrogenation activity and selectivity can be closely related to the intrinsic electronic features of each metal in relation to their ability to activate CO_2 and dissociate H_2.

Acknowledgments

This research has been co-financed by the European Union NextGenerationEU under the call RESEARCH – CREATE – INNOVATE 16971 Recovery and Resilience Facility (project code: TAEDK-06169).

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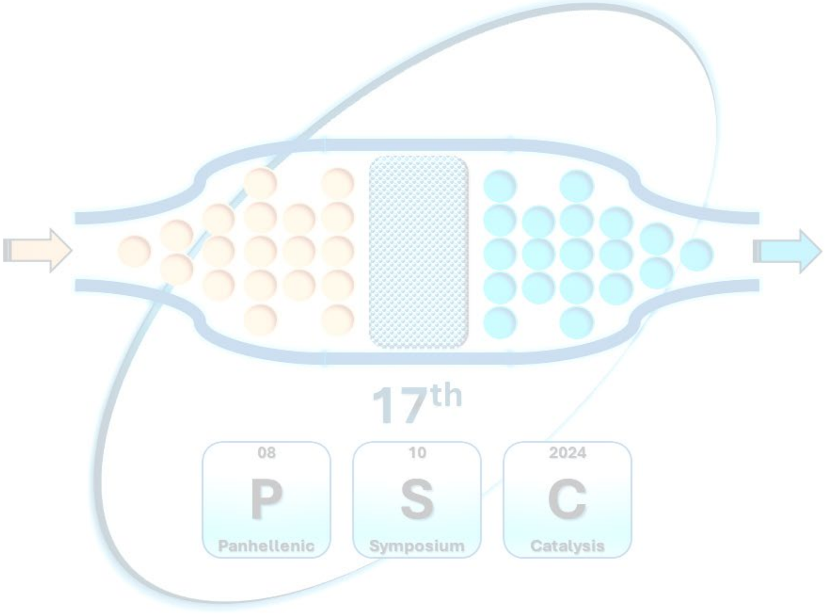
Session 6: Catalytic Conversion of CO/CO_2 into Fuels and Chemicals



Effect of Zeolite Type for Water Removal in Sorption-Enhanced CO_2 Hydrogenation to Methanol

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Keywords: Zeolite adsorbents, CO_2 hydrogenation, methanol, sorption-enhancement

Introduction

Addressing the thermodynamic constraints in CO_2-derived methanol synthesis is crucial. Continuous water removal through the use of solid adsorbents can lead to significant intensification of methanol production [1]. In this work, we focus on assessing the suitability of different zeolites for use in SE CO_2 hydrogenation by probing their adsorption/desorption behaviour and by determining their reaction performance, as well as stability and cyclability.

Experimental

We investigated four zeolites (LTA-3A, LTA-4A, LTA-5A, and FAU-13X) using a thermogravimetric setup with mass spectrometry to determine the water and methanol adsorption capacity and kinetics. High-pressure sorption-enhanced (SE) experiments were conducted at 250 °C and 70 bar, using mechanical mixtures of a commercial $CuO/ZnO/Al_2O_3$ catalyst with the sorbents, to study the correlation between adsorptive properties and performance in CO_2 hydrogenation. In addition, the regeneration and cyclic performance of the zeolites was assessed by conducting three consecutive reaction (sorption) - regeneration (desorption) cycles.

Results and discussion

All zeolites exhibit substantial adsorption capacity for both water and methanol. As expected, capacity decreases with temperature but remains important even at the high levels of the reaction temperature. At 250 °C, zeolite 13X demonstrates the highest water adsorption capacity followed by zeolite 4A. Exposure to methanol vapor leads to higher weight uptakes, indicating that the zeolites possess sites where methanol preferentially adsorbs. In the presence of both methanol and water, co-adsorption of both occurs. A positive correlation between the adsorption/desorption properties and the performance in high-pressure SE CO_2 hydrogenation experiments is observed. Zeolites' addition leads to a substantial increase in CO_2 conversion (48-56 %) and methanol yield (63-70 %), with the greatest enhancement occuring in the presence of zeolites 4A and 13X. However, in multiple reaction-regeneration cycles, zeolite 13X exhibits notably the worst stability, followed by 5A and 3A. The desorption profiles of the zeolites in combination with the textural and structural properties pre- and post- use offer valuable insight on their stability. Zeolite 4A, emerges as the most promising sorbent for the process due to the enhanced methanol production and the increased stability over consecutive reaction-regeneration cycles. Work is currently in progress to further intensify the process by synthesizing a bi-functional Cu/4A material which combines both the catalytic and the sorption properties in a single particle.

Significance of work

The study contributes to understand the key properties and parameters that improve or hinder sorption/regeneration performance of zeolite-based water sorbents, as an essential component towards the engineering of better sorbents for intensified sorption-enhanced processes.

Acknowledgments

This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE.

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CO_2 hydrogenation to Light Olefins over Iron Oxide Nanoparticles of Distinct Morphology

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Keywords: CO_2 hydrogenation, Light olefins Production, Iron Oxide catalysts, Magnetite

Introduction

The current focus on CO_2 hydrogenation for light olefins production offers a sustainable and energy-efficient route compared to the currently employed carbon-intensive traditional methods. This approach contributes to clean energy transition by recycling CO_2 emissions and facilitates the production of carbon-negative platform chemicals [1].

Experimental

Iron oxide nanoparticles were hydrothermally synthesized to obtain distinct morphologies, such as iron nanoclusters and nanospheres. The samples were characterized by various techniques and evaluated in the hydrogenation reaction of CO_2 ($WHSV = 6\ L\cdot g^{-1}\cdot h^{-1}$, $H_2:CO_2 = 3$, $P = 20$ bar).

Results and discussion

The obtained results showed that Fe_3O_4 nanoparticles, rather than Fe_2O_3, were more selective towards light olefins production. Additionally, a significant effect of particle's morphology was revealed, with iron oxide nanoclusters exhibiting the optimum performance in terms of olefins yield.

Significance of work

The key role of structural and morphological properties of iron nanoparticles on CO_2 hydrogenation to light olefins was disclosed, paving the way to the rational design of highly efficient iron-based catalysts.

Acknowledgments

This research has been co-financed by the European Union NextGenerationEU under the call RESEARCH – CREATE – INNOVATE 16971 Recovery and Resilience Facility (project code: TAEDK-06169).

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Kinetic and mechanistic implications of CO_2-assisted ethane dehydrogenation over Fe-based catalysts

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Keywords: CO_2 valorization, ethylene, reaction mechanism, oxidative dehydrogenation.

Introduction

CO_2-assisted ethane dehydrogenation (CO_2 -EDH) is a promising carbon economy process for CO_2 valorization, converting C_2H_6 and CO_2 to valuable C_2H_4 and CO respectively. Iron oxide-based catalysts have been found to be selective towards the C-H bond cleavage, attaining a single-pass ethylene yield of ~21 %, at 650°C [1]. In the present work, the nature of active sites of iron oxide-based catalysts is investigated, along with the kinetic and mechanistic implications on the best Fe-based candidate.

Experimental

a) Mechanistic insights: The mechanism of CO_2-EDH reaction was examined via a series of isotopic experiments, using $^{18}O_2$ for exchange of the catalyst oxygen, C_2H_6 and the isotope $C^{18}O_2$ as feedstock, at 101.3kPa and a Quadrupole Mass Spectrometer (MS) as the analytical device. b) Kinetic experiments: All the experiments at varying operating conditions were conducted at the same fixed bed reactor unit under conditions ensuring that the resistances of external and internal mass transfer limitations were negligible, while Agilent® 7890A GC system was used for online analysis.

Results and discussion

Fe-700(5h) catalyst exhibited 90% selectivity towards ethylene production, at 23.3% ethane conversion level, during CO_2-EDH at 650°C, which was attributed to a structural modification of Mg atoms geometry, as it was revealed by XRS data at Mg $L_{2,3}$ edge. A series of isotopic labelling experiments were conducted in order to get insights into the dominant reaction mechanism for CO_2 -EDH on Fe-700(5h) catalyst. The main proposed reaction mechanisms for CO_2-EDH are: 1) a direct redox mechanism that occurs in-situ under reaction conditions, where the lattice oxygen of the material participates in order to produce C_2H_4 and H_2O, and then it is replenished by CO_2. 2) an indirect mechanism in which the catalyst acts as a dehydrogenation catalyst, producing C_2H_4 and H_2, while CO_2 participates in a next step via the RWGS reaction. The formation of $H^{18}O_2$ was not observed during any of the experiments performed, while the main observed products being C_2H_4, $C^{18}O$, and H_2, indicating towards the indirect mechanism during CO_2 -EDH using iron oxide-based materials at temperature range of 600-650°C. A preliminary kinetic model was developed using the power-law model for the competitive reactions of CO_2-EDH and ethane dry reforming. Similar reaction orders, ~1, were calculated for the ethane consumption in both reactions, while CO_2 partial pressure appeared to not affect ethylene production during CO_2-EDH. A more advanced kinetic model, that takes into consideration other possible reaction mechanisms, is under development.

Significance of work

High CO_2 conversion in tandem with high C_2H_4 yield, at a relatively low temperature of 650°C.

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Effect of H_2O in CO methanation reaction over Co/Al_2O_3 catalyst studied by transient isotopic experiments

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Keywords: methanation reaction, effect of H_2O, SSITKA-MS, SSITKA-DRIFTS

Introduction

Water is the main product of CO methanation reaction and its influence on the catalytic performance has attracted much attention [1]. Due to the lower activity of Co-based catalysts in water-gas shift, the concentration of water increases with residence time; thus, the impact of water is of significant concern. The effect of water has been reported to be positive, negative, or negligible.

Experimental

SSITKA-mass spectrometry and SSITKS-DRIFTS experiments were employed to determine the surface coverage, chemical composition and structure of active intermediates and inactive species. To follow the carbon-path of CO methanation reaction at 230°C, the step-gas switch: 4 vol% ^{12}CO/8 vol% H_2/x vol% H_2O/Ar (t = 6 h) → 4 vol% ^{13}CO/8 vol% H_2/ x vol% H_2O/1 vol% Kr/Ar (x = 0, 2.5, 5) was performed. The experiments were conducted with or without treatment with H_2O (x vol% H_2O/He, x = 2.5 and 5) before the SSITKA switch.

Results and discussion

SSITKA-DRIFTS results reveal that adsorbed CO on Co are active intermediate species, while only a small amount of CH_x are active intermediates. Inactive species include -C_xH_y and formates on alumina surface [2]. H_2O does not affect the chemical structure of active intermediate species.
The concentration of active CO slightly increases with a small amount of H_2O in the feed but decreases with higher amount of H_2O or treatment with H_2O before SSITKA switches. The surface coverage of CH_x-s (θ_{CHx}) remains approximately constant, while τ_{CHx} decreased and k_{eff} increased ($k_{eff} = k_{CHx}\ \theta_H$), indicating that k_{CHx} or θ_H increases in the presence of H_2O. Thus, H_2O increases the rate of CH_x hydrogenation.

Significance of work

Our results show that H_2O does not affect the chemical structure of active or inactive species, but it increases the rate of CH_x hydrogenation.

Acknowledgments

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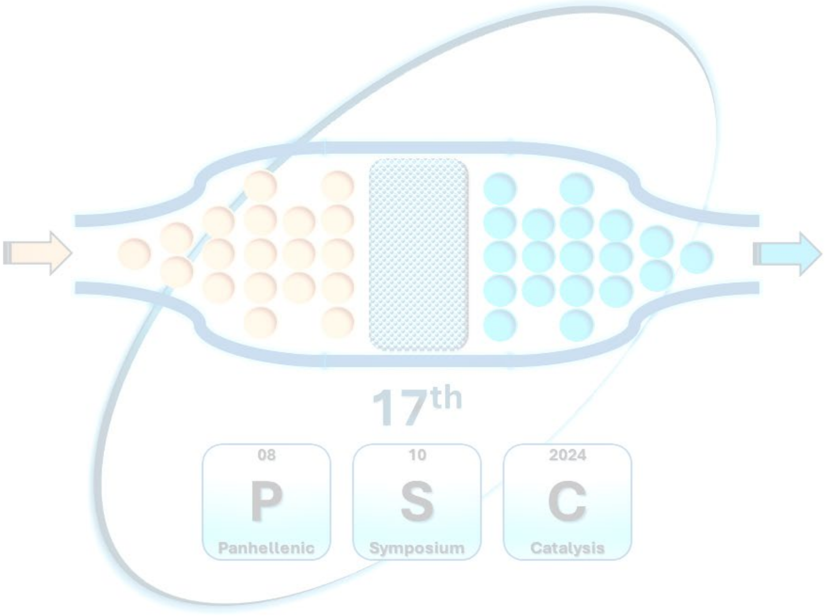
Session 7: Fuels Production and Biomass Conversion



Elaborated rice husk biochar as support of Mo-Ni catalysts used for green diesel production

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Keywords: Biochar; Ni-catalysts; green diesel; hydrotreatment.

Introduction

Nowadays, innovating sustainable solutions concerning biomass conversion to biofuels is a very important issue in which heterogeneous catalysts play a key role. The selection of the support (e.g. Al_2O_3 [1], SiO_2 [2], TiO_2 [3], zeolites [4], active carbon [5,6]) is crucial for the performance of such catalysts. In this work, active carbon produced by rice husk pyrolysis (biochar, BRH) has been activated by acidic and alkali treatment and has been used as support for Mo-Ni catalysts, which were evaluated in the hydrotreatment of waste cooking oil (wco) for green diesel (GD) production.

Experimental

Mo-Ni catalysts with various metal loadings supported on acidic and/or alkali treated BRH were synthesized by wet impregnation. Supports and catalysts were thoroughly physiochemically characterized and were evaluated in a high-pressure semi-batch reactor for the transformation of wco to GD.

Results and discussion

A Mo-Ni catalyst containing 20 wt.% metals ($\frac{Ni}{Ni+Mo} = 0.9$) supported on BRH activated first by alkali treatment and then by acidic one proved the most effective for the title process. This is due to its balanced acidity, high surface area and active surface as well as of its suitable pore size distribution.

Significance of work

Biochar makes the corresponding catalysts green and sustainable satisfying the circular economy principles.

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Optimization and upscale catalytic hydrogenation of biomass-derived glucose rich streams to sugar alcohols

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Keywords: biomass, enzymatic hydrolysis, hydrogenation, hydrogenolysis, sorbitol

Introduction

The majority of chemicals and fuels are made from fossil carbon sources. Using abundant and renewable natural resources, including lignocellulosic biomass from forestry and agriculture leftovers, has been proposed as a sustainable solution for the production of a variety of value-added chemicals, like sorbitol, glycerol, ethylene glycol, etc. In a modern biorefinery, the first step of biomass pretreatment/fractionation is of paramount importance, but chemo-catalysis applies to the majority of down-stream processes for the conversion of sugars and phenolics to valuable chemicals and fuels.

Experimental

The biomass (beech wood sawdust) fractionation was performed via the Organosolv process. The cellulose pulp produced, was hydrolyzed using Cellic Ctec 2 enzyme in order to produce a concentrated glucose stream. The hydrogenolysis reaction was performed in a 100 ml HT/HP autoclave stirred batch reactor. The reaction was upscaled to a 5L semi-pilot reactor with the same characteristics as the 100 ml one. All the catalysts and reaction products were analyzed by XRD, BET, TEM, HPLC, etc.

Results and discussion

In this work, we studied the performance of Ru and Pt catalysts supported on micro/mesoporous activated carbon, in the hydrogenation and hydrogenolysis of real glucose-rich-streams produced from lignocellulosic biomass pretreatment at a range of hydrogenation temperatures (120–180°C), at relatively low hydrogen pressure of 3MPa and for different reaction times (1–5h). It was shown that Ru is significantly more selective towards sorbitol compared to Pt. For example, the 5wt.% Ru/AC catalyst afforded sorbitol yield of over 90wt.% (at 99.9wt.% conversion) compared to 60wt.% (at 90.2wt.% conversion) obtained by the corresponding Pt catalyst, at the optimum condition, the latter being also selective towards glycerol and propane-1,2-diol.

Significance of work

This work focuses on the optimization of sugar alcohols (sorbitol, diols, glycols) production with Ru or Pt supported catalysts and the upscaling of the process using real glucose-rich biorefinery feedstocks.

Acknowledgments

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Green diesel production over promoted nickel catalysts supported on palygorskite

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Keywords: Palygorskite, Promoted nickel catalysts, Green diesel, Waste cooking oil.

Introduction

Nowadays, the rapid global increase in the human population and social development has resulted in energy and environmental crisis due to the extensive usage of fossil fuels as a main energy source. This fact has motivated the scientific communtity for searching new renewable and sustainable fossil fuels, biofuels. Green diesel can become a great potential to be a sustainable replacement for fossil fuel through selective deoxygenation (SDO) of waste cooking oils (WCO) [1]. Furthermore, enhancing the production of biofuels would require a significant number of catalysts. Scientists are becoming more and more interested in the use of accesible, inexpensive minerals as supports for heterogeneous catalysts [2]. In this work, nickel catalysts, promoted by different metals (Mo, W, Fe) supported on the natural cheap mineral palygorskite, were evaluated for green diesel production.

Experimental/methodology

The raw material, palygorskite, was cleaned by the clay fraction method. Four nickel catalysts were synthesized via deposition-precipitation method with urea as precipitation agent, at high temperature: a monometallic nickel catalyst with 30 wt. % Ni (Ni/Pal), and three bimetallic nickel catalysts, with molybdenum (MoNi/Pal), tungsten (WNi/Pal) and iron (FeNi/Pal) as a promoter. All promoted catalysts had 30 wt. % total active phases loading and atomic ratio Ni/(Ni+Me)=0.95 (Me: Mo, W or Fe). The final catalysts were obtained by reduction of the catalysts precursors with H_2 stream (30 mL/min) at 500^{O}C for 2.5 hours. The reduced catalysts were characterized using N_2 sorption isotherms, XRD and NH_3-TPD. Precursor samples (before reduction) were characterized by H_2-TPR. Ni/Pal and MoNi/Pal were evaluated in the SDO of WCO at 310 ^{o}C, hydrogen pressure 40 bar and reactant volume to catalyst mass equal to 100 mL / 1 g. Then, MoNi/Pal was evaluated to four different temperatures: 330, 350, 370 and 390 ^{o}C. At optimal temperature, 370 ^{o}C, the amount of catalyst was duplicated in order to maximize green diesel production. At these conditions, the WNi/Pal and FeNi/Pal catalysts were also evaluated in order to investigate the promoter effect.

Results and discussion

It was found that the addition of Mo enhanced significantly the production of hydrocarbons in the diesel range (C_{15}-C_{18}) in the liquid product (from 23 to 45 wt %). This is attributed to the well known promoted action of Mo [3] as well as to the increase of the active surface of Ni in the promoted catalyst. The optimum temperature of the SDO reaction, with the MoNi/Pal catalyst, proved to be 370 ^{o}C, where a value of 80% in hydrocarbons in the liquid product was achieved. In the same temperature, double mass of catalyst was examinated and green diesel in the liquid product reached 94%. At the same conditions the WNi/Pal catalyst produced slightly smaller amount of hydrocarbons (89%). These results demonstrate similar promoting action of tungsten with molybdenum, which has been also observed in other catalytic systems [4]. The FeNi/Pal catalyst produced 82% hydrocarbons but 5 wt. % of these hydrocarbons dispose lower number of carbon atoms than diesel hydrocarbons.

Significance of work

Promoted nickel catalysts supported on palygorskite were synthesized and evaluated in the SDO reaction for the first time. It was shown that they can successfully be used as low cost and very efficient natural catalysts for green diesel production from waste cooking oils.

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Hydrous hydrazine decomposition over Rh/Al_2O_3 catalyst: CFD studies

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Keywords: hydrous hydrazine, hydrogen, batch, CFD

Introduction

Hydrous hydrazine ($N_2H_4.H_2O$) is a great hydrogen carrier due to its high hydrogen content and stability. Its decomposition can produce hydrogen (H_2), but it can also generate ammonia (NH_3) which must be avoided [1]. Thus, it is critical to develop efficient catalysts to achieve high H_2 yield. This study investigates the catalytic decomposition of hydrous hydrazine, employing a commercial 0.5 wt% Rh/Al_2O_3. Both experimental and computational fluid dynamics (CFD) studies were conducted, varying parameters to optimise conditions for high H_2 yield and to explore the systems uniformity.

Experimental

The experiments were conducted in a batch system, varying different parameters such as stirring rate, temperature, catalyst mass and NaOH concentration. TEM and XRD characterisation techniques were performed on the catalyst. COMSOL Multiphysics was used for the CFD studies, for the validation of the experimental results and the further investigation of the system.

Results and discussion

TEM revealed that the Rh particles (2.46 nm) are uniformly dispersed in the support. XRD did not reveal any signal of Rh, verifying the presence of well dispersed particles on the support, in agreement with TEM analysis. Experimental and computational 0D models were in a great agreement for all studied parameters with optimal conditions of 1400 rpm stirring rate, temperature of 70 °C, substrate to metal molar ratio of 1000:1 and a NaOH of 0.5 M with H_2 yield over 90% in each case. 2D CFD simulations were also performed, showcasing velocity and temperature distribution over time as well as the dispersion of $N_2H_4.H_2O$ solution and catalytic particles, emphasizing on the importance of efficient mixing for optimal reaction performance. Studies were also conducted with a $Ir/NiO-TiO_2$ catalyst to compare the catalytic performance and extra CFD for the optimisation of the batch system.

Significance of work

This work provides valuables insights into optimising the catalytic decomposition of $N_2H_4.H_2O$ for H_2 generation, combining experimental results with CFD simulations, not only to validate experimental data but also to understand and enhance system performance pursuing sustainable energy solutions.

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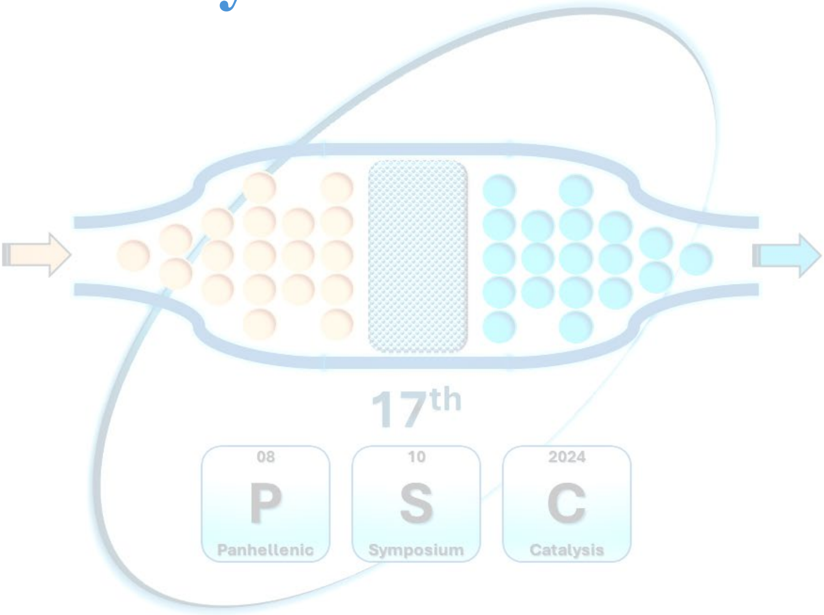
Session 8: Nanomaterials Sustainability



Digitalization in Catalysis: Accelerating the microkinetic model development by automation tools

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Keywords: research data management, automation tools, microkinetic modeling, simulation

Introduction

The development of a microkinetic model (MKM) is a multi-step process that requires considerable expertise, a wide variety of experimental techniques, substantial computational resources and time. In this work, we highlight a selection of digital tools that focus on the automation of these steps. These tools address diverse aspects, including the efficient storage of experimental research data that allows easy retrieval and reuse, to the establishment of automated workflows that harness state-of-the-art numerical solvers and algorithms that reduce manual effort.

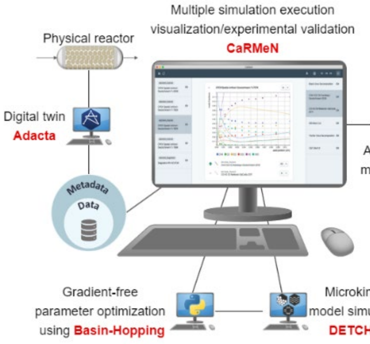

Fig. 1: Interconnection of the various digital tools for kinetic studies [2].

Results and discussion

In Fig. 1 the schematic overview of the concept of the automatized workflow in microkinetic modelling is presented. The software Adacta allows efficient data archiving and search possibilities by creating a digital twin of the experimental setup for measuring the catalytic activity. The digital components are associated to the physical components and their measurements allowing the tracing of the time-stamped measured data [1]. This approach allowed to keep track of the history of the experimental setup in a timeline visualization, providing overview of the setup and the measurements even to the researchers not directly involved in the data generation. The Reaction Mechanism Generator (RMG) automatically predict DFT-based reaction mechanisms. CaRMeN [2,3] enables the selection of multiple chemical models and multiple experimental datasets to automatically execute simulations with the simulation tool DETCHEM [3] and provide a comparison view of experiment and simulation data in one step. An optimization algorithm [4] towards specific kinetic experiments accelerates the process of the model development while addressing phenomena such as support effects.

Significance of work

Interconnecting novel digital tools will accelerate modeling of reaction kinetics in catalysis and boost reactor and process development. A key issue is the efficient archiving and reuse of research data.

Acknowledgments

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Synthesis of Palladium-based nanoparticles with tuneable sizes for catalytic applications

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Keywords: (microreactors, nanotechnology).

Introduction

Metallic palladium and palladium-based nanoparticles have been extensively studied in a wide range of catalytic applications, including their use in air pollution remediation catalysts in the automotive industry[1,2]. However, the relationships between their catalytic activity and size and composition remains unknown due to the dynamic structure of the nanoparticles under catalytic conditions. This work demonstrates the continuous synthesis of palladium-based nanoparticles with controllable sizes and a narrow size distribution using continuous flow microreactors for catalytic applications.

Experimental

Flow microreactors are used for the continuous synthesis of Pd-based nanoparticles, where the reactants were injected using syringe pumps at a controlled flow rate and both reactants molar concentrations were kept constant. In this study, the 3D configuration of microreactors enables continuous colloidal synthesis of palladium oxide nanoparticles through hydrolysis and palladium nanoparticles through reduction methods. The combination of laminar flow in the microreactors (characterised by low Reynolds numbers) and the promotion of transitional flows (i.e. Langragian turbulence) through 3D configurations leads to a narrow residence times which is translated into narrow size distributions even in the absence of steric capping ligands.[3]

Results and discussion

In this study, Pd-based nanoparticles with tunable sizes below 10 nm are synthesised. The results reveal the higher instability of the Pd nanoparticles with respect to PdO counterparts in the absence of capping ligands. In this work, we demonstrate that manipulation of initial precursor speciation can greatly affect the stability of resulting nanoparticles and allowing their synthesis in the absence of in-situ capping ligands and stabilisers. Tunable sizes of these Pd-based nanoparticles are synthesised, deposited onto ceria supports and used as model catalysts for three-way catalysis. The variation in nanoparticles size of active metal affects the number of uncoordinated sites available for the reactions to occur and the different species of Pd-based nanoparticles present on the surface.

Significance of work

This new method enables for the first time, the elucidation of size-activity relationships, decoupling size and supports effects. In addition, the easy scale-up of the method can lead to a new way of designing and manufacturing catalysts.

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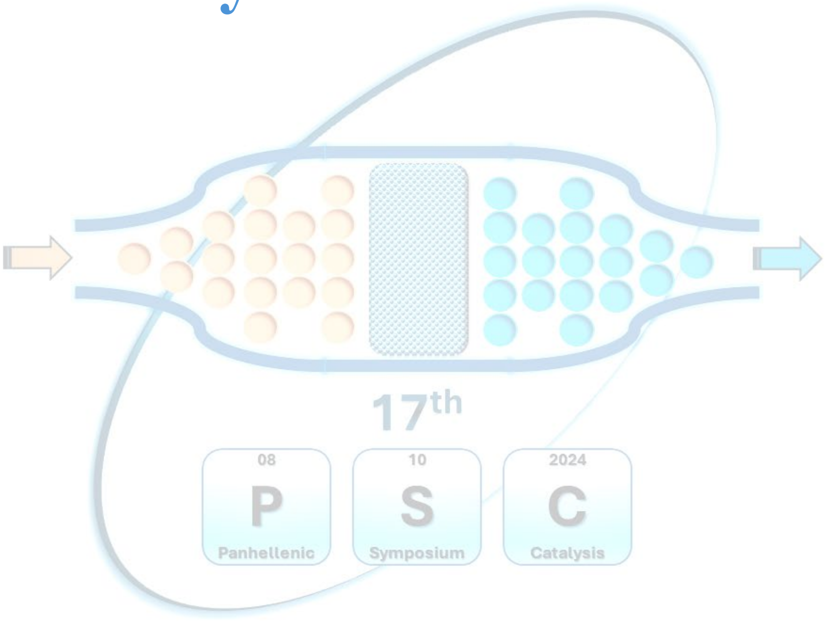
Session 9: Energy and Materials Sustainability



Sustainable catalysts for Dry Reforming of Methane obtained from recovered Pt

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Keywords: Dry Reforming of Methane, Platinum Group Metals (PGMs), PGM-Based Catalysts

Introduction

Dry reforming of Methane (DRM) is considered as one of the valuable technologies able to convert the two green-house gases CO_2 and CH_4 into a syngas, a mixture of H_2 and CO in a H_2/CO ratio suitable for utilization in the Fischer-Tropsch process of valuable chemicals.

Experimental

CeO_2 and $BaCe_{0.6}Zr_{0.2}Gd_{0.2}O_3$ supports synthesized by two different routes have been impregnated with a Pt containing leachate solution of spent diesel oxidation catalysts (DOCs) obtained by a mild hydrometallurgical route [1]. For comparison, a synthetic acidic solution of commercial Pt black powders was used. Catalysts were characterized by X-Ray Diffraction, Field Emission Scanning Electron Microscopy, Thermogravimetric Analysis, Brunauer-Emmett-Teller, Temperature Programmed Reduction and Desorption analyses. DRM tests were carried out in a fixed bed reactor.

Results and discussion

Aim of this study is to demonstrate the feasibility of the synthesis of innovative and sustainable catalysts using a leachate solution containing Pt coming directly from the recovery of spent DOCs without further purification. Catalysts showed a high conversion efficiency of CO_2 and CH_4 and a H_2/CO ratio close to 1 for Pt/CeO_2 catalyst.

Significance of work

To our knowledge, this is the first pioneering work in which catalysts obtained from real Pt leachate solutions were successfully obtained on different supports for application in the DRM reaction.

Acknowledgments

This paper is based on the project activities of H2020-MSCA-RISE-2020 101007669: Chemistry of Platinum Group Metals, CHemPGM and Italian PTR 22-24 (Ricerca di Sistema Elettrico), Progetto 1.6.

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Continuous slurry phase hydrotreating of heavy oils with Mo-based dispersed catalysts on pilot-scale

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Keywords: Dispersed catalyst, Mo-octoate, Heavy Oils, Slurry Reactor

Introduction

In recent years, there has been an increased interest in upgrading technologies for low-value unconventional heavy oils from bio-, waste-, and fossil origin [1]. Slurry phase hydrocracking processes, employing transition metal-based dispersed catalysts, can successfully upgrade such difficult feedstocks and overcome the coking and plugging issues often encountered with fixed-bed reactors [2]. In the present study, we investigate the hydrotreatment of Vacuum Gas Oil (VGO) in the presence of Mo-based dispersed catalysts in a continuous slurry-type reactor.

Experimental

The slurry phase hydrocracking of Vacuum Gas Oil (VGO), selected as model feedstock, was performed in a continuous high-pressure unit equipped with a 500 mL CSTR reactor, under constant pressure 100 bar, temperature 400 °C, LHSV 0.17 h^{-1} and H_2/oil volumetric ratio 940 NL/L. Non-catalytic and catalytic tests were performed with oil-soluble Mo-octoate (15 wt.% Mo) at 1000 ppmw Mo. After reaction, the products were separated into gas, liquid, and solid fractions. The gas products were analyzed with GC. The solid was washed with toluene, dried and analyzed. Extensive analysis of the liquid product (elemental analysis, density, SimDis etc.) was conducted to determine the fuel properties.

Results and discussion

The continuous catalytic and non-catalytic tests were operated for over 60- and 85-h time-on-stream, respectively, without any operability issues. With increasing time-on-stream, the liquid dispersed catalyst reduces sulfur gradually from ~45% to ~ 60%, while the thermal test achieves lower HDS degree (~ 20%). Analysis of the solid product from the tests with liquid Mo-catalyst evidenced the formation of MoS_2 nanoparticles, responsible for the hydrosulfurization activity. In terms of hydrocracking, the residue, diesel, and gasoline fractions are similar in catalytic and non-catalytic tests, suggesting that cracking mainly occurs thermally in agreement with literature [3].

Significance of work

The present study aims to the development of slurry phase processes, and novel catalysts for the catalytic hydrotreating of heavy oils from bio-, waste-, and fossil origin to high-quality products, that in the long-term could be even implemented on an industrial scale.

Acknowledgments

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Optimized in-situ catalytic upgrading of plastic waste pyrolysis oils to naphtha-range hydrocarbons

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Keywords: (Thermochemical recycling, in-situ py-oil upgrading; Fast pyrolysis).

Introduction

Plastic waste poses a growing environmental threat. Thermochemical recycling, specifically fast pyrolysis, offers an alternative to incineration or landfilling [1]. This study investigates in-situ catalytic upgrading of py-oil derived from various plastics using aluminosilicate (ZSM-5, Beta, USY, MOR, FER) and mixed-oxide catalysts, to improve naphtha-range hydrocarbon yields.

Experimental

Experiments were conducted on a fixed-bed reactor (450-600 °C, under N_2 flow) with a 10/1 plastic/catalyst ratio. Prior to pyrolysis, catalyst screening and thermal decomposition of the plastics were investigated using TGA (25-700 °C, N_2). The composition of the condensed py-oil was analyzed by GC-MS/FID, while the gaseous products were quantified by GC-FID/TCD. Characterization of fresh and spent catalysts employed XRD, N_2 sorption, FTIR-Pyr and other relative techniques.

Results and discussion

TGA screening revealed distinct decomposition profiles for plastics. PET and PS decomposed earlier (420-440 °C) compared to PE, and PP (454-477 °C). Zeolites significantly lowered decomposition temperatures up to 77 °C. Non-catalytic polyolefins pyrolysis yielded mostly waxes (93 wt.%-450 °C). However, Brønsted acidic catalysts favoured lighter py-oil (up to 65 wt.%) production and gases (up to 40 wt.%). Py-oil composition shifts from heavier compounds (C_{16+}) to the desired naphtha range (C_5-C_{11}), with increased olefinic and aromatic content, indicating significant cracking and secondary reactions. Product yields can be adjusted by process parameters (i.e. pyrolysis temperature and catalyst-to-feed ratio) while py-oil and gas composition can be tuned by balancing catalysts' the amount/type/strength of acid sites with their micro/mesoporosity.

Significance of work

This work highlights the potential of catalytic fast pyrolysis to efficiently convert plastic waste into high-value added naphtha-range hydrocarbons, essential feedstock to produce virgin plastics, providing a sustainable solution for plastic waste management and promoting circular economy.

Acknowledgments

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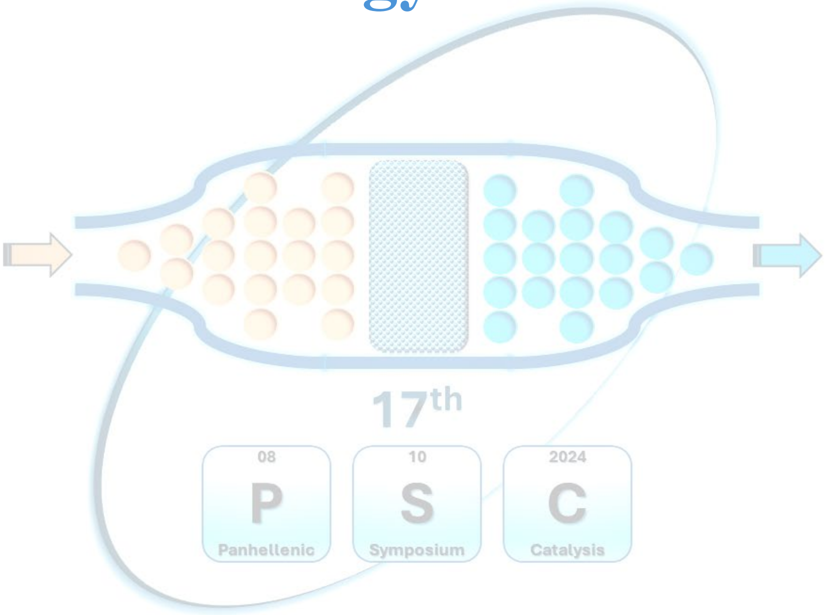

Chemical looping ammonia production: Investigating nitrogen carriers promoted with transition metal catalysts

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Keywords: Ammonia production, Chemical looping, Nitrogen carriers

Introduction

Demand of ammonia is projected to increase in the coming years, with NH_3 being a precursor for fertilisers and a potential hydrogen carrier. The dominant method for producing ammonia couples the Haber-Bosch process, operating at >100 bar, with steam reforming of methane. However, the associated high energy demand and carbon emissions trigger the necessity for more sustainable production routes. Chemical looping ammonia production (CLAP) offers a promising alternative route, operating at or near atmospheric pressure. CLAP involves two-step process: (1) hydrogenation of a solid material termed a nitrogen carrier, which donates nitrogen to reaction and produce ammonia, and (2) regeneration of the nitrogen-depleted carrier by exposing it to nitrogen [1]. Our thermodynamic screening identified LiH and BaH_2 hydrides as promising materials for CLAP [2], while our experiments showed relatively slow kinetics of these materials for nitrogen fixation and ammonia production. Hence, this work evaluates transition metal catalysts to improve the activity of LiH and BaH_2.

Experimental

Materials were prepared by grinding equivalent weights of LiH or BaH_2 with Co, V, Mn or Ni in a glovebox filled with Ar. Temperature-programmed nitrogenation with thermogravimetry (TGA) aimed to investigate the nitrogen capacity, and temperature at which materials uptake nitrogen. The kinetics of nitrogen fixation were evaluated in a batch reactor with experiments at atmospheric pressure and at 300-500°C.

Results and discussion

Barium-based materials led to faster nitrogen fixation than lithium-ones, reaching near-complete conversion in the TGA experiments, albeit with lower gravimetric nitrogen capacity. Reactions of hydrides with nitrogen formed $Li_{2.7}NH$ and BaNH imides, as confirmed by X-ray diffraction. The addition of transition metals, especially of Co, lowered the activation energy for nitrogen fixation in comparison to bare hydrides, verifying the enhanced kinetics. Our ongoing study considers bimetallic configurations of transition metals and evaluation of the hydrogenation activity and stability in cyclic CLAP experiments.

Significance of work

The step-wise CLAP approach overcomes the thermodynamic constraints of the direct ammonia synthesis, allowing operation at milder conditions. Transition metals enhance the performance of nitrogen carriers used in CLAP, further highlighting the potential of the proposed technology.

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Valorizing pyrolysis gases back to monomers

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Keywords: Plastic Recycling, Pyrolysis, cross-metathesis, Propylene production, Tungsten oxide

Introduction

Pyrolysis is a promising method for valorizing mixed plastic waste (MPW) to value-added products. This aligns with the European plastics industry's current transition toward net-zero carbon emissions and circularity goals by 2050 [1]. Pyrolysis yields three main products: solids (chars), liquids (pyrolysis oil) and non-condensable pyrolysis gases (NCPGs). NCPGs mainly contain light olefins such as ethylene, propylene, and C_4 alkenes; nevertheless, they are commonly used for their calorific value [2]. This study suggests catalytic valorization of ethylene and 1-butene, the main constituents of NCPGs, via metathesis reaction for propylene production. The goal is to isomerize 1-butene to 2-butene (Eq.1) and subsequently react it with ethylene to produce propylene (Eq. 2).

$1\text{-}C_4H_8 \rightleftharpoons 2\text{-}C_4H_8$ (Eq. 1)
$C_2H_4 + 2\text{-}C_4H_8 \rightleftharpoons 2C_3H_6$ (Eq. 2)

Experimental

WO_3-based catalysts were prepared by the wet impregnation of Aluminum modified MCM41 (30). Catalytic activity measurements were conducted, using a quartz reactor, in a continuous flow unit. Ethylene and 1-butene were introduced into the fixed bed reactor and the effect of WO_3 loading, temperature, reactant partial pressure and residence time were explored. Ex-situ and in-situ characterization techniques were applied to the fresh and used catalysts.

Results and discussion

The parametric study performed in this work pointed out the role of acidity on the isomerization of 1-butene to 2-butene which is the limited reactant of the cross-metathesis reaction towards propylene. The Al-MCM-41(30), with the highest content of Al, showed the highest isomerization activity. The presence of WO_3 on Al-MCM-41(30) proved to be essential for the cross-metathesis reaction towards propylene. The optimization of the WO_3 loading was carried out and showed that 20%WO_3/Al-MCM-41(30) catalyst results in the highest activity and selectivity, with the lowest carbon deposition.

Significance of work

Valorizing NCPGs rather than using them solely for their calorific value to enhance carbon circularity.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 859885.

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Application of mechanochemistry toward sustainable recycling of spent automotive catalysts

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Keywords: Mechanochemistry, spent automotive catalysts, platinum group metals (PGMs).

Introduction

This paper presents the research activities on the recovery of PGMs from secondary sources and further reuse of the recovered PGMs for the synthesis of new catalysts in order to secure the PGMs value chain and to achieve carbon neutrality.

Experimental

Treated materials are bathes of spent automotive catalysts, prepared by MONOLITHOS Ltd. Mechanical activation was performed using planetary ball-mill (PM-100, Retsch, Germany) under an ambient atmosphere. Characterization methods, exploited to analyze treated materials include X-ray diffraction, X-ray photoelectron spectroscopy, Thermal analysis, Scanning electron microscopy with energy dispersive X-ray spectroscopy and Fourier-transform infrared spectroscopy.

Results and discussion

Numerous mechanochemical treatment conditions were tested in order to optimize PGM recovery. The investigation clearly shows, that the utilization of mechanochemistry for PGMs recovery allows optimizing the processing technology, enhancing the PGMs recycling rate and increasing the ecological friendliness and sustainability. Chemical transformations induced by mechanical forces in the treated solid waste led to recovery of the studied chemically inert chemical elements in one-pot processing of spent catalysts using readily available inexpensive salts and avoiding the use of aggressive chemicals, high temperatures and pressures.

Significance of work

Mechanochemistry was successfully applied for PGM recovery and reuse. Thus, technologically optimized, waste-less, energy-saving and room-temperature methodology for a direct PGM activation and recycling was obtained in consideration with the green and sustainable principles.

Acknowledgments

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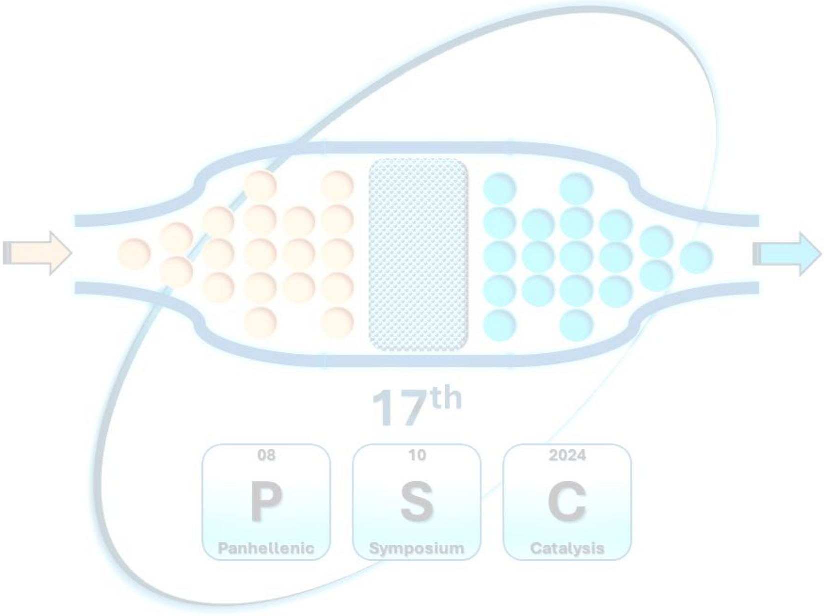
Poster Presentations



Production of liquid fuel precursors *via* aldol condensation of bio-derived compounds using solid Lewis acids

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Keywords: Aldol condensation, Furfural, Lewis acids, Biofuels

Introduction

Concerns regarding the future depletion of fossil fuels as well as the increasing environmental pollution have spurred research into the production of alternative fuels (biofuels). Lignocellulosic biomass (LB), consisting of cellulose, hemicellulose and lignin, is considered as a promising, abundant and renewable feedstock. Furfural, a key platform chemical from LB, can be upgraded to FAc (C8) and F_2Ac (C13) products *via* aldol condensation reaction with acetone. This acid/base catalyzed reaction combined with a solid catalysts allows for a greener process, in comparison with homogeneous catalysts, i.e. NaOH. Metal-incorporated zeolites, such as Sn-Beta, with tunable Lewis/Brønsted acidity, demonstrate exceptional properties and activity in the aldol condensation reaction [1].

Experimental

An optimization study was conducted using model acetone and furfural compounds over zeolitic catalysts in a 50 mL autoclave stirred batch reactor. Sn-Beta zeolites were obtained from the full or partial de-alumination of commercial H-Beta (Si/Al=12.5), followed by Sn-incorporation (1, 2 & 5%) via the Solid State Ion Exchange method [2]. For the solvent-free aldol condensation reaction we used a furfural/acetone (FF:Ac) molar ratio of 1:10, and a catalyst to furfural (Cat:FF) mass ratio ranging from 0.1 to 0.3. Experimental conditions, temperature and time, varied from 100 to 160°C and 2 to 6h. Feeds and products were analyzed by GC-MS and GC-FID while solid catalysts were characterized by XRD, XPS, N_2 Physisorption, ICP-OES, UV-Vis, acidity measurements etc.

Results and discussion

The optimal reaction conditions for achieving high selectivity towards FAc (C8) and F_2Ac (C13) products (50% and 4.5% at ~76% furfural conversion) using 2%Sn-Beta catalyst were 145°C, 4h and 0.2 Cat:FF mass ratio. A lower selectivity (~10%) for side products diacetone alcohol (DAA) and mesityl oxide was also detected by GC-MS. Sn-Beta remains active for 3 catalytic runs with constant C8 selectivity and with 30% decrease in conversion, likely due to carbonaceous species formation as investigated by TGA analysis, showing ~30% mass loss at 550°C. The Sn-Beta catalyst exhibited higher selectivity to the C8 monomer product, with C13 dimer selectivity increasing to 10% only by adjusting the FF:Ac molar ratio. Complementary XRD, XPS, ICP-OES and UV-Vis characterization confirmed the successful synthesis of Beta zeolite materials with tetrahedrally coordinated framework Sn sites and the absence of extra-framework SnO_2 species.

Acknowledgments

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Catalytic hydrogenolysis of plastic wastes towards sustainable chemical recycling

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Keywords: plastic wastes, hydrogenolysis, hydrocarbons

Introduction

During the last years, the extensive utilization of single-use plastics and the ineffective recycle (10%) arose various environmental issues. The most widely used plastics (80%) are PET, PE (LDPE/HDPE), PS and PP with high chemical upcycling potential towards chemicals and fuels. Chemical upcycling of plastics is performed via thermochemical and catalytic processes, such as pyrolysis and gasification, while hydrogenolysis has recently emerged as one of the most efficient processes providing a liquid product enriched in hydrocarbons. Within this context, this work focuses on the catalytic hydrogenolysis of various pristine plastics and mixtures over bifunctional catalysts.

Experimental

The catalytic hydrogenolysis was performed in a batch stirred autoclave reactor, in the temperature range 200-280 °C, for 1-5 h, under 10-70 bar H_2 pressure, using metallic catalysts (Ru, Pt, Ni) supported on activated carbon or oxides. The composition of the liquid product was determined via GC-MS and GC-FID analysis, while the gaseous products were analyzed via GC-TCD/FID.

Results and discussion

The conversion of plastics and the composition of the liquid products proved to be affected by the reaction conditions and the catalysts properties. In general, higher reaction temperatures and prolonged reaction times enhanced the conversion of plastics towards liquids but also gases (C_1-C_4). Indicatively, the non-catalytic hydrogenolysis of LDPE led to low conversion (6.5%) while using bifunctional catalysts the conversion increased to 91-98%. Furthermore, 5%Ru/AC enhanced the C-C bonds cleavage towards n-alkanes (71 wt.%) with C_9-C_{33}. On the other hand, the acid sites of 10%Ni/BETA induced hydrocracking reactions towards lower carbon number alkanes C_5-C_{15} (20.4 wt.%), BTX aromatics (14.3 wt.%) via aromatization reactions and (alkyl)cycloalkanes (14.1 wt.%).

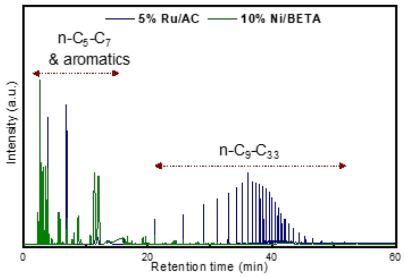

Figure 1. GC-FID spectra of liquid products formed via the hydrogenolysis of LDPE.

Significance of work

This work provides a significant insight into the chemical recycling of plastic wastes via catalytic hydrogenolysis toward hydrocarbons.

Acknowledgments

This project is carried out within the framework of the National Recovery and Resilience Plan Greece 2.0, funded by the European Union NextGenerationEU (Implementation Body HFRI).

Catalytic processes for production of alternative marine fuels with low carbon footprint

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Keywords: Alternative fuels; maritime sector; decarbonization

Introduction

More than 90% of goods are transported with large cargo ships fueled with residual heavy fuel oil (HFO) or very low sulfur fuel oil (VLSFO). HFO has a particularly high viscosity and need to be heated above 90°C to achieve a proper flow, requiring additional on-board processing steps (heating system, water and sludge removal, filters, etc.). Despite the additional cost of equipment and energy, HFO remains one of the most economical marine fuels [1]. However, the increasingly stringent targets set by the International Maritime Organization (IMO) for both greenhouse gas (GHG) emissions reduction and cleaner, zero-sulfur fuels create significant challenges for meeting these goals. In this work different technologies for production of alternative fuels are investigated, including hydrogen, ammonia, methanol, biofuels (biodiesel, crude biooil) for a potential application in maritime sector. LNG, a transitional fuel in this sector is also investigated for comparison.

Methodology

Five cases on alternative fuel production are studied considering not only the overall GHG and SO_x emissions of each process, but also the production cost, the technology readiness level (TRL) and scalability of each process and the potential replacement of fossil fuels based on the production capacity. Different subcases are also investigated, including blue and green hydrogen and ammonia production and their capability to decarbonize this sector, green methanol production via hydrogenation of captured CO_2 or via renewable synthesis gas and production of biodiesel and refined biooil for direct use in single or dual-fuel internal combustion engines (ICE). Required modifications of the fuel combustion systems or refitting engines and applying different systems (e.g. fuel cells) are also taken into account.

Results and discussion

Among alternative and transitional fuels, biodiesel and LNG present the highest potential as marine fuels, mainly as blends with HFO and VLSFO. Other fuels such as methanol or ammonia can be used to a smaller degree, taking advantage of latest generation of diesel engine technologies, with the premature state of their supply infrastructure and the high production cost however being the main challenges.

Acknowledgments

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Greece 2.0
NATIONAL RECOVERY AND RESILIENCE PLAN

Funded by the European Union
NextGenerationEU

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Experimental investigation of reactor type and operating variables in the catalytic upgrading of plastic pyrolysis oil

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Keywords: (plastic pyrolysis oil, catalytic cracking, Ru/ZSM5, ZSM5, naphtha)

Introduction

Plastic recycling remains a challenge, with a substantial portion of recycled plastics ending up in landfills or polluting oceans. Chemical upcycling and especially pyrolysis process can be a viable option as it can convert all types of plastics to a product mixture which can be either used as fuel or as source of monomers. The study aims to catalytically upgrade pyrolysis products by selectively decomposing the heavy fraction of pyrolysis oil into naphtha-range hydrocarbons.

Experimental

Hexadecane was selected as representative compound of the heavy fraction of plastic pyrolysis oil and was used as feed for the experiments which were conducted using batch and fixed bed reactors. Two catalysts were employed, the parent ZSM5 (Si/Al=25) and another one promoted with 2.15 wt% Ru. The tests in the batch reactor, were conducted at 300°C, high pressure 20bar (in N_2 or H_2 atmosphere) to ensure that the reactions proceed in the liquid phase while that of fixed bed at atmospheric pressure. Gases and liquids were collected, catalyst separated. Analysis of gaseous and liquid products was performed employing fours GSs equipped with suitable columns and detectors.

Results and discussion

Hexadecane conversion at 300°C under batch conditions highly depends on the type of catalyst and the atmosphere used. The presence of Ru and the reducing atmosphere favour the feed conversion which reaches 62wt% after 2h of testing. The liquid products formed are highly paraffinic in the range of C5-C11 and comprise ~90wt% of the total products. The gaseous products consist mostly of C3 and C4 with dominance of propane. The liquid/gas selectivity remains almost constant irrespective of the catalyst and the atmosphere. Deposition of intermediates and coke like compounds was detected which however do not surpass 0.3wt% of the feed. In the fixed-bed reactor, where reactions occur in gaseous phase, the effect of temperature and residence time on the same indicators was studied. Increasing temperature from 250-350°C enhances total conversion and productivity but increases selectivity towards gas products (C_3-C_4) from 40-60 wt% at the expense of liquid products which comprise of light hydrocarbons (C_5-C_7). Residence time, despite being very short (0.078-0.15s), linearly increases total conversion up to 97wt% and productivity without changing the gas/liquids selectivity.

Significance of work

The heavy fraction of plastic pyrolysis oil can be efficiently upgraded at mild temperature over ZSM5 catalysts yielding a liquid product with optimum composition in naphtha range as shown by the tests conducted in fixed bed and batch reactors with n-hexadecane as model compound.

Acknowledgements

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Boron promoted Ni-Al_2O_3 catalysts for green diesel production

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Keywords: Boron promotion; Ni-catalysts; green diesel; hydrotreatment.

Introduction

The role of metallic and metal oxide promoters in metallic nickel catalysts used for green diesel production has been recently reviewed [1]. Boron is a non-metallic promoter usually used for transition metal-based catalysts (Ni, Cu etc.) as it alters the electronic environment of metal ions enhancing metal dispersion and coking resistance [2-4]. In this work a series of Ni/Al_2O_3 catalysts doped with various amounts of B_2O_3 were studied for the transformation of waste cooking oil (wco) into renewable diesel.

Experimental

Ni/Al_2O_3 catalysts with 57.5 wt.% Ni doped with 0, 2.5 and 5 wt.% B_2O_3 were synthesized by co-precipitation, were thoroughly characterized by various physiochemical techniques and were evaluated in a high-pressure semi-batch reactor for the transformation of wco to renewable diesel (RD).

Results and discussion

Boron addition improved the textural characteristics of the Ni catalysts, enhanced the metal dispersion, metal-support interaction and surface acid sites population. Figure 1 shows that all catalysts studied achieved almost complete wco conversion and the catalyst with 2.5 wt.% B_2O_3 proved to be the most efficient for RD production due to its high population of weak acid sites, the high pore volume and the no-formation of inactive nickel aluminate species.

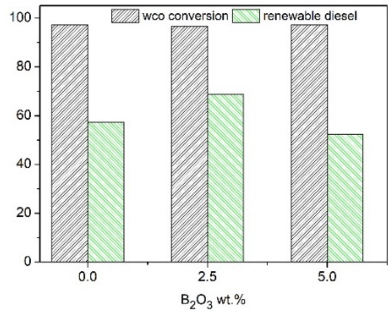

Figure 1. Conversion of wco and RD yield

Significance of work

Catalyst development is key factor for RD production.

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CeO_2-Al_2O_3 supported Mo-Ni catalysts for green diesel production

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Keywords: CeO_2-Al_2O_3; Ni-catalysts; green diesel; hydrotreatment.

Introduction

The role of support in Ni based catalysts used for green diesel production is of crucial importance as it regulates the acidity of the catalyst, the supported phase support interaction and finally the catalysts performance [1]. Mixed CeO_2-Al_2O_3 supports have been studied for preparing Ni catalysts used for hydrogen involving reactions, especially for dry reforming and CO_2 hydrogenation [2,3]. It has been proved that ceria addition enhances the catalysts stability. In this work we studied the influence of ceria addition on the efficiency for green diesel production and physicochemical characteristics of Mo-Ni/CeO_2-Al_2O_3.

Experimental

Mo-Ni/CeO_2-Al_2O_3 catalysts with 60 wt.% active metals and $\frac{Ni}{Ni+Mo} = 0.9$ were synthesized by co-precipitation. The CeO_2 content varied between 0 and 10 wt. %. The catalysts were thoroughly characterized by various physiochemical techniques and were evaluated in a high-pressure semi-batch reactor for the transformation of wco to green diesel (GD).

Results and discussion

CeO_2 incorporation in the Al_2O_3 support altered the physicochemical characteristics, mainly the acidity and the reducibility of the final catalysts influencing their catalytic performance. Although, an increase in the GD production did not observe, the catalyst containing 2.5 wt. % CeO_2 proved to be the most stable prohibiting the coke formation.

Significance of work

The key role of the support nature for Mo-Ni/CeO_2-Al_2O_3 catalysts has been proved.

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Biosolids derived biochars for CO_2 sorption

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Keywords: biomass conversion, biochar, CO_2 adsorption.

Introduction

Biochar, a carbon-rich material produced through the pyrolysis of organic wastes, has gained significant attention for its potential in environmental management and carbon sequestration. Previous studies have demonstrated that biochar's physicochemical properties, such as porosity and surface chemistry, play a critical role in its effectiveness for soil enhancement, pollutant adsorption, and greenhouse gas mitigation. Despite this, there remains a need to further explore and compare biochars derived from diverse biowastes to fully understand their properties and optimize their applications. This study addresses this gap by investigating biochars from sludge (SB), manure (MB), and spent coffee grounds (SCB), providing a comparative analysis of their structural and chemical features.

Experimental

Biochars were finely ground and sieved to a particle size of less than 125 µm, and characterized using a series of analytical techniques, including SEM, BET, FTIR, and CO_2-TPD analyses.

Results and discussion

The FT-IR spectra of the three biochars revealed the presence of hydroxyl groups, N–H, C–H (both aliphatic and aromatic), C–O/C, and Si-O bonds. The FT-IR spectra of MB and SB were attributed to the organic fractions of the biowastes, including polysaccharides, proteins, carbonyls, and aliphatic/aromatic hydrocarbons. In contrast, the FT-IR spectra of SCB were primarily attributed to the decomposition products of cellulose, hemicellulose, and lignin. According to the TG curves, MB and SB exhibited maximum weight losses in two distinct steps, whereas SCB showed a single, steep weight loss step between 350 and 500 °C. The porous structure of the derived biochars varied: SB and MB had mesopores (2–50 nm), while SCB had macropores (>50 nm), characterized by different shapes and sizes. Pores were generally more prominent in SCB, which displayed a honeycomb-like morphology with cylindrical crevices interconnected by large tubes, whereas SB and MB exhibited a tubular pore structure with particles or substances adhering to their walls, resulting in a dense and tightly packed microstructure with observable fragments and voids. The BET method revealed that the surface area of the raw materials was considerably low (< 0.1 m^2/g). However, the surface area of the produced biochars increased to 14.03 m^2/g for MB, 3.98 m^2/g for SB, and 1.53 m^2/g for SCB. The temperature of maximum desorption (Tmax, °C) varied among the samples during CO_2-TPD analysis. Multiple desorption peaks were observed, with the major peak for SCB centered at 125 °C, compared to peaks for SB and MB at temperatures above 500 °C. This suggests a significant quantity of surface basic sites on SB and MB compared to SCB. The quantity of basic sites (µmol/g) was determined by integrating the CO_2 desorption curve. The estimated values were 0.71 µmol/g for SB, 0.55 µmol/g for MB, and 0.38 µmol/g for SCB from a 5% CO_2/He gas mixture. These results indicate that SCB, with its macropore structure and lower surface area, exhibits the least CO_2 adsorption.

Significance of work

This study provides valuable insights into the structural and chemical properties of biochar derived from different biowastes, highlighting their potential for optimized carbon sequestration and environmental applications. By comparing the adsorption characteristics and porosity of biochars, this work contributes to the development of more efficient and sustainable biochar production strategies.

Catalytic hydrodeoxygenation of erythritol towards green butadiene production

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Keywords: Butadiene, erythritol, hydrodeoxygenation

Introduction

In petrochemical industry, the demand of 1,3-butadiene (BD) to produce synthetic rubbers has dramatically increased. With the majority of it being produced from fossil-based processes, new sustainable processes are required [1]. Erythritol, an industrially fermentation product, can serve as feedstock to manufacture BD. This study aims at the development of a suitable catalytic material for the effective conversion of erythritol to BD through hydrodeoxygenation (HDO). As catalysts based on transition metal oxides are considered promising candidates, a series of Re, Mo and mixed Mo-Re based catalysts were synthesized and evaluated in batch reactor. The effect of operating conditions over the most promising catalyst was further explored.

Experimental

Rhenium based catalysts (2-5-20wt%) supported on a commercially available black carbon (BC) Vulcan XC72 (Cabot) were prepared by wet impregnation method as previously described [2], while mixed Mo-Re catalysts (5%Mo-10%Re,10%Re-5%Mo) were prepared with successive impregnation following the same procedure. The catalysts were evaluated in liquid phase under batch conditions using 5wt% erythritol in 1,4-dioxane at specified reaction conditions (T=140°C, P_{in,H_2}=60bar, cat/sub=0.56, t=5h). The main physicochemical properties of the materials were determined by using XRD, H_2-TPR and XPS.

Results and Discussion

The results indicated that catalysts with lower Re loadings (2,5 and 5 %) are very active towards butenes, the hydrogenation product of BD, however at relatively low conversion levels (9 and 18%, respectively). On the contrary, over 20Re/BC, both conversion (65%) and BD selectivity (88%) are highly favored. This is attributed to different structure of the materials, as according to XRD, Re is fully crystallized as Re_3O_{10} over 20Re/BC, while for lower loadings the structure turns to amorphous. To avoid using high Re loadings on accounts of its high cost, the impregnation of Mo was further studied at lower Re loadings. Not only the conversion is enhanced, but BD selectivity as well indicating that the presence of Mo contributes to maintain the C=C bond of BD due to its mild hydrogenation activity [2]. A maximum 93% BD selectivity was achieved over 5Mo-10Re/BC at 140 °C and 60 bar H_2 pressure. The effect of operating parameters indicated the presence of H_2 as key factor for BD production. XPS confirmed the presence of Mo^{6+}, Re^{7+}, Re^{6+} and Re^{4+} on the catalyst surface which are most likely the active sites. These species host both redox and acid sites as confirmed by CH_3OH-TPSR tests.

Significance of work

The work explores the use of sustainable feedstock (erythritol) to produce butadiene, a very important olefin extensively produced from fossil-based processes. Mo-Re based catalysts were proved to be very active in complete deoxygenation of the polyol with high selectivity at 140 °C under H_2 pressure.

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Zeolite-catalyzed organosolv fractionation of lignocellulosic biomass

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Keywords: zeolites, organosolv, biomass, biorefinery

Introduction

Lignocellulosic biomass is a vital renewable feedstock for sustainable bioenergy and bioproducts. Organosolv fractionation is an efficient pretreatment method that separates lignin, hemicellulose, and cellulose, enhancing their usability in biorefineries. Previously, we developed an alternative oxidative organosolv process, which we further optimized using solid catalysts. In this work, we tested different zeolite types and compared their efficiency in fractionating wheat straw.

Experimental

The feedstock, wheat straw from Northern Greece, was processed using Y SAR 5, Mordenite SAR 20, and Ferrierite SAR 20 zeolites purchased from Zeolyst. Catalytic oxidative organosolv reactions occurred in a 975 mL autoclave with 25 g feedstock, 500 g H_2O:EtOH (1:1), and various catalyst-to-feed (C/F) ratios from 0.1 to 1. The reactor was pressurized with 16 bar O_2 and run at 150 °C for 2 hours. Non-catalytic runs at 150 °C and 175 °C were also conducted for comparison.

Results and discussion

The type of zeolite significantly affected wheat straw fractionation efficiency. Mordenite catalyzed both acid hydrolysis and oxidation reactions, boosting lignin removal from 42% to 86% and hemicellulose removal from 15% to 87% at an optimal C/F ratio of 0.5-0.6. Ferrierite mainly catalyzed acid hydrolysis, achieving moderate lignin (72%) and hemicellulose (78%) removal. Y facilitated both reactions but was less effective than Mordenite. The latter produced high-purity cellulosic pulps (>80% cellulose), with lower hemicellulose content than non-catalytic oxidative organosolv at 175 °C. Pulps from catalytic runs exhibited improved saccharification potential during enzymatic hydrolysis to produce glucose.

Significance of work

The results are a promising step towards a greener, low-severity organosolv technology that utilizes recoverable catalysts.

Acknowledgments

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Organosolv fractionation of lignocellulosic biomass catalyzed by supported and non-supported heteropoly acids

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Keywords: heteropoly acids, activated carbon, organosolv, biomass.

Introduction

Organosolv fractionation (OS) is an efficient method employed for the pretreatment of lignocellulosic biomass, a renewable resource for the production of sustainable bioenergy and biobased products. OS can lead to the efficient isolation of biomass constituents, namely lignin, hemicellulose and cellulose, improving thus their valorization in biorefinery applications. We have previously developed an alternative oxidative OS process, which was further optimized by using heteropoly acids (POMs) as homogenous catalysts. In this work, those POMS were supported on two activated carbons (ACs) with varying acidity and porosity properties in order to be evaluated in wheat straw fractionation.

Experimental

The feedstock, wheat straw from Northern Greece, was processed using ACs purchased from NORIT, three homogenous POMs (phosphotungstic, phosphomolybdic and tungstosilicic acid) purchased from Sigma-Aldrich, and solid acid catalysts synthesized after modification of ACs with the respective POMs. All catalysts were characterized regarding their acidity, porosity and structural properties. Catalytic oxidative organosolv reactions occurred in a 975 mL autoclave with 25 g feedstock, 500 g H_2O:EtOH (1:1), and various catalyst-to-feed (C/F) ratios ranging from 0.1 to 1. The reactor was pressurized with 16 bar O_2 and run at 150 °C for 2 hours. Non-catalytic runs at 150 °C and 175 °C were also conducted for comparison.

Results and discussion

POMs successfully promoted delignification and hemicellulose removal compared to the oxidative OS process in the absence of catalyst. Homogenous POMs were compared with the respective supported solid acid catalysts, while the type of the support, the type and loading of the POM were also studied as it concerns catalytic efficiency during fractionation in both acid hydrolysis and oxidation reactions. Both ACs were also tested for comparison reasons.

Significance of work

The results are a promising step towards the development of a low-severity OS fractionation technology for the efficient pretreatment of lignocellulosic biomass.

Acknowledgments

The work was carried out in the framework of H.F.R.I's call "Basic research Financing (Horizontal support of all Sciences)" under the National Recovery and Resilience Plan "Greece 2.0" funded by the European Union – NextGenerationEU (H.F.R.I. Project Number: 015795).

Hydrodeoxygenation of lignin model compounds and bio-oils

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Keywords: lignin bio-oils, hydrodeoxygenation, bifunctional catalysts, aviation fuels

Introduction

Lignin, a biomass-derived phenolic/aromatic macromolecule, can be converted to phenolic bio-oils via fast pyrolysis or hydrogenolysis which can be further upgraded via hydrodeoxygenation (HDO) to road/aviation fuels (C_7-C_{12}). This work aims to investigate the HDO of model phenolic compounds, surrogate mixtures and real pyrolysis bio-oils over Ni-based bifunctional, non sulfided catalysts [1].

Experimental

The experiments were performed in a high-pressure batch autoclave reactor with hexadecane as a solvent to simulate co-processing with petroleum fractions. Initially, the process was optimized in terms of temperature, time, H_2 pressure and type of phenolic compound. Surrogate mixtures were used to simulate the light fraction of lignin bio-oils, while heavy fractions of Miscanthus alkali lignin bio-oils were produced on a twin-screw pilot-scale reactor. Nickel-based catalysts supported on zeolites with different micro/mesoporous and acidic properties were used as catalysts.

Results and discussion

The hydrodeoxygenation of phenol was performed under mild reaction conditions (220°C, 1 h, 50 bar H_2) and the main products were cyclohexane and its isomer, methylcyclopentane. Regarding the effect of phenolic/aromatic ring substituent groups, the additional -OH or -CH_3 led to full conversion with high cyclohexane and methylcyclohexane yield, respectively. On the other hand, the addition of one or more methoxy (-OCH_3) groups induced lower conversion and gradual decrease of cyclohexane yield due to steric hindrance. Under the above optimized mild conditions, HDO of surrogate mixture of alkoxy/alkyl phenols afforded almost complete hydrodeoxygenation towards 75 wt.% alkylcycloalkanes with C_6-C_{12}. For the heavy fraction of lignin bio-oils, more intense conditions were required (320-400°C, 3-8 h and 50-80 bar H_2) to induce substantial deoxygenation of phenols towards (alkyl)cyclohexanes and aromatics. Regarding the catalyst stability, despite the formation of coke, the metallic structure and the porous properties were not significantly influenced and the catalysts were reused for at least three successive catalytic cycles.

Significance of work

This work provides a systematic study of the hydrodeoxygenation mechanism of simple and complex phenolics-constituents of the light lignin bio-oil fractions, as well as insights towards the potential of heavy lignin bio-oil HDO for cycloalkanes enriched hydrocarbon fuels.

Acknowledgments

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Chemo-catalytic hydrogenation of bio-succinic acid to value-added diols

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Keywords: catalysis, biomass, bio-succinic acid, diols

Introduction

Diols are important chemicals serving as monomers to a wide variety of (biobased) polyesters/plastics. 1,4-butanediol is currently being produced via biocatalytic transformation of (bio)succinic acid while the chemo-catalytic hydrogenation of succinic acid to 1,4-BDO is still a challenge.

Experimental

Bio-succinic acid was produced and kindly provided by Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB), via biocatalytic process. The chemo-catalytic hydrogenation reaction of succinic acid was performed on a 100 mL HT/HP autoclave stirred batch reactor, using different metal catalysts (Ru, Pt, Re, etc.) supported on micro/mesoporous activated carbons (AC). All the catalysts and reaction products were analyzed by XRD, BET, TEM, HPLC, etc.

Results and discussion

The conversion of glucose to SA was performed by ATB via fermentation using the *A. succinogenes* B1 microorganism and achieving high SA productivity, as described previously [1]. This bio-succinic acid, as well as commercial succinic acid, were used as feedstock for the production of 1,4-BDO via catalytic hydrogenation. Indicatively, with the use of 5%Ru/AC at 250°C, 12h reaction time and catalyst to feed ratio of 0.4, a yield (mol carbon based) of 15% 1,3-PDO, 10% 1,4-BDO, 13% g-GBL and 3% n-Propanol was achieved (at 70% wt. conversion), while at 220°C and 12h the corresponding yields were 10% 1,3-PDO, 8% 1,4-BDO, 9% g-GBL, 4% n-Propanol and 2% THF (at 68% wt. conversion).

Significance of work

This work focuses on the chemo-catalytic production of value-added diols (e.g. 1,4-BDO, 1,3-PDO, etc.) via hydrogenation of bio-succinic acid.

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Controlling CH_4 and CO products distribution of CO_2 hydrogenation reaction over Ni/MCM-41 catalysts via the preparation method.

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Keywords: CO_2 recycle, Ni monometallic catalysts, mesoporous MCM-41 silica, CO_2 methanation

Abstract

The catalytic reduction of CO_2 is an effective way to control industrial CO_2 emissions and receives special attention nowadays due to the urgent environmental need to mitigate global warming and climate change [1]. During CO_2 reduction by H_2, CO_2 methanation ($CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$) is thermodynamically favored at low temperatures (200–500 ° C), while higher temperatures favor CO production through the reverse water gas shift reaction (RWGS), ($CO_2 + H_2 \leftrightarrow CO + H_2O$), turning the catalytic process to a syngas production rather than a methanation one. Herein the CO_2 hydrogenation reaction is investigated over Ni catalyst supported on mesoporous MCM-41 silica. Two different synthetic methods, specifically one-pot synthesis and impregnation were followed for the preparation of the Ni-based catalysts of this study. Both support and catalysts were thoroughly characterized by several techniques and the catalysts were evaluated in the CO_2 methanation reaction at the temperature interval 200-650 °C. The CO_2 methanation efficiency of Ni catalysts was found to be strongly dependent on the catalyst preparation method used: One-pot synthesis provided catalysts almost completely ineffective for methanation, but very effective for the reverse-water–gas-shift (RWGS) reaction producing syngas at low temperatures. In striking contrast, compositionally identical Ni catalysts prepared by impregnation were efficient in CO_2 methanation. This was found to be mainly related to the size of Ni crystallites formed during catalyst synthesis. Specifically, large Ni particles (formed when using one-pot synthesis method) favor CO production, while small Ni nanoparticles (formed when using impregnation method for catalyst synthesis) favor methanation. According to the present findings, the Ni-MCM-41 system can be used as a simple and effectively controllable system for the preparation of versatile catalysts that can be directed to produce either syngas or methane.

Acknowledgments

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The effect of Ni particle size on CO_2 methanation over Ni/Ce-Ti-O: Operando transient isotopic studies

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Keywords: CO_2 hydrogenation, Ni particle size, doped-CeO_2 carrier; mechanistic study.

Introduction

CO_2 methanation ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) is a catalytic process that tackles greenhouse gas emissions and stores renewable energy. In this study, x wt% Ni (x = 2.5, 5, 10, and 15) supported on $Ce_{0.8}Ti_{0.2}O_{2-\delta}$ solid solution were synthesized to investigate key kinetic and mechanistic aspects related to the effect of Ni particle size on the methanation process, aiming to clarify the fundamental kinetics and mechanism(s) of CO_2 methanation (e.g., formate vs. CO hydrogenation route) [1].

Experimental

The $Ce_{0.8}Ti_{0.2}O_{2-\delta}$ support was prepared using a modified citrate sol-gel synthesis, and Ni metal was deposited via wet-impregnation [2]. The catalytic activity was evaluated in the 200-500°C range and P = 1 atm with 10% CO_2/40% H_2/He feed gas composition. Operando SSITKA-DRIFTS-MS step gas switches were conducted at 300°C, namely: 10% $^{12}CO_2$/40% H_2 (2 h) → 10% $^{13}CO_2$/40% H_2 (10 min) → 10% $^{12}CO_2$/40% H_2 (10 min) → 10% $^{12}CO_2$/40% D_2 (t) followed by a switch to 40% H_2/He.

Results and discussions

In this study, the effect of Ni particle size (d_{Ni} = 10-28 nm) of Ni/$Ce_{0.8}Ti_{0.2}O_{2-\delta}$ on CO_2 methanation reaction kinetics and mechanisms were investigated. The apparent activation energy (Ea) of CO_2 conversion is presented in Fig. 1A. The TOF for CO_2 conversion shows a minimum at d_{Ni} = 15 nm, while CO and CH_4 formation present maximum at 22.5 nm with a slight drop at 28 nm. SSITKA-MS studies at 300°C showed how d_{Ni} influences: (a) surface coverage (θ) of reversibly chemisorbed CO_2-s and active C-containing intermediates for CH_4 (Fig. 1B), and (b) mean residence time (τ) of active species in the CH_4 path.

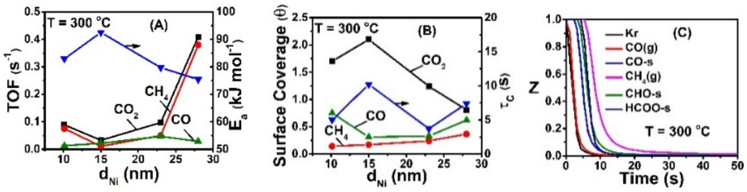

Figure 1. Dependence of Ea and TOF (CO_2, CO, and CH_4) on d_{Ni} (A); (B) Surface coverage of active C-containing intermediates and reversibly adsorbed CO_2-s; and (C) evidence of rival methanation mechanisms.

SSITKA-DRIFTS spectra showed that CHO-s, only present for d_{Ni} of 28 nm, didn't show red isotopic shift in the $^{13}CO_2/H_2$ treatment. The dynamics of depletion of adsorbed species and $^{12}CH_4$(g) during the operando $^{13}CO_2$-SSITKA experiment are presented in Fig. 1C (d_{Ni} = 28 nm). The decay response suggests formyl and formate species as active intermediates at 300°C, following a "CO hydrogenation" and "formate" route, respectively. For d_{Ni} < 28 nm, the former mechanism prevails, matching the TOF_{CH4}/TOF_{CO} relationship with d_{Ni} (Fig. 1A).

Significance of work

Kinetic studies and operando SSITKA-DRIFTS/MS experiments revealed that synergistic effects between Ni metal (H-assisted CH_xO hydrogenation to CH_4) and doped-CeO_2 support (activate CO_2 to formate) favoured on large Ni particles leading to a very active CO_2 hydrogenation catalyst.

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Impact of the support on the activity and stability of Ir catalysts under the Dry Reforming of Methane conditions.

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Keywords: Dry Reforming of Methane, Ir, Syngas, ceria-zirconia mixed oxides, greenhouse gases

Uncontrolled emissions of greenhouse gases cause global warming and subsequent climate change. Dry Reforming of Methane (DRM) is a promising catalytic process as it converts two major greenhouse gases (CH_4 and CO_2) into synthesis gas ($CO+H_2$), providing an efficient way to directly use biogas and recycle CO_2 emissions [1]. Syngas is a key feedstock for the petrochemical industry for producing liquid fuels, blue hydrogen, and high-value chemicals. The biggest challenges of the DRM process in practical applications are catalyst deactivation due to thermal sintering and carbon deposition [1]. In this study, the effect of support on the DRM performance (activity and selectivity) of Ir nanoparticles, carbon deposition phenomena, and their stability under reaction (at 500-750°C) and/or after oxidative thermal aging conditions is investigated. Supports studied include γ-Al_2O_3, Alumina-Ceria-Zirconia (ACZ), and Ceria-Zirconia (CZ). Their textural, structural and physicochemical properties, as well as those of the corresponding supported Ir catalysts, were determined using various techniques, such as BET, XRD, HRTEM, H_2-TPR, H_2-chemisorption, ICP-OES, and TPO. All catalysts studied were found to be highly stable under DRM conditions, while the carbon deposition rate was particularly low for all, although there seemed to be a clear decreasing trend in carbon deposition: Ir/γ-Al_2O_3 > Ir/ACZ > Ir/CZ. It was also found that Ir/CZ and Ir/ACZ catalysts, due to their high population of oxygen defects (oxygen vacancies), favor the conversion of CO_2, thereby producing syngas enriched in CO. They also promote carbon removal through a bifunctional reaction mechanism. It was also demonstrated that supports with sufficient mobile lattice oxygen enhance the resistance to agglomeration of sensitive Ir crystallites, even under intense (~750°C) oxidative thermal aging conditions. In summary, Ir nanoparticles dispersed on CZ-based supports appear to be highly promising catalysts for the DRM reaction at low temperatures.

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Effect of Ni particle size on the CO_2 methanation performance of Ni/CeO_2 catalysts

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Keywords: CO_2 hydrogenation, Ni/CeO_2, Citric acid assisted synthesis, Ni dispersion

Introduction

In recent decades, CO_2 hydrogenation to methane has emerged as a promising approach to mitigate the consequences of global warming, utilizing both industrial CO_2 emissions and green H_2 [1]. To explore this potential, nickel-nanoceria catalysts were investigated due to their advantageous properties, including enhanced redox features, abundant oxygen vacancies, and peculiar metal-support interactions.

Experimental

CeO_2-nanorods (NR) were hydrothermally synthesized. Ni/CeO_2 catalysts were subsequently prepared via a citric acid (CA)-assisted wet impregnation method in order to obtain NiCe-x (x=CA:Ni molar ratio). The materials were characterized by various techniques and evaluated in the hydrogenation of CO_2 (WHSV = $30\ L\cdot g^{-1}\cdot h^{-1}$, $H_2:CO_2 = 4$, P = 1 bar).

Results and discussion

This work explores the intricate relationship between Ni particle size, catalyst interfacial environment, and CO_2 methanation activity. Although the extent of Ni-ceria periphery plays a crucial role, a compromise between relatively large Ni crystallites and the surrounding interfacial environment appears necessary to maximize CO_2 methanation activity. This is evidenced by the maximization of TOF and interfacial rate (r_p) at a Ni particle size of approximately 10 nm.

Significance of work

This study highlights the structure sensitivity of CO_2 methanation revealing the significance of achieving a delicate balance between the interfacial area and the Ni crystallite size. This finding shed light on the principles of catalyst design, facilitating the fine-tuning of CO_2 methanation systems.

Acknowledgments

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Effect of alkali promotion on a $LaCuFeO_3$ catalyst for the CO_2 hydrogenation reaction

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Keywords: CO_2 hydrogenation, Cu-Fe catalysts, alkali promotion, coupling reaction.

Introduction

The production of C_{2+} products from CO_2 hydrogenation addresses concerns over climate change and simultaneously generates valuable chemicals [1]. Due to the higher importance of C_{2+} in comparison with the C_1 chemicals research interest is shifting towards these products, necessitating the design of more active, selective and stable catalysts. This study reports on the effect of alkali promotion on a CuFe catalyst for the hydrogenation of CO_2 to alcohols.

Experimental

The $LaCu_{0.2}Fe_{0.8}O_3$ catalyst was prepared by a citrate sol-gel method (citric acid:metal ions= 1.5:1) while the K-promoted (0.5 and 1%wt) $LaCu_{0.2}Fe_{0.8}O_3$ catalysts were prepared by a simply wet impregnation process. The final catalysts were denoted as 0.5K-$LaCu_{0.2}Fe_{0.8}O_3$ and 1K-$LaCu_{0.2}Fe_{0.8}O_3$. The catalysts were also characterized by H_2-TPR, N_2-adsoption/desorption, XRD and TEM. The catalytic experiments were carried out in a fixed-bed reactor (CO_2:H_2:N_2= 23.5:70.5:6, T= 250°C, P= 30bar and WHSV= 3600ml/gh). Prior to the reaction, the catalysts were reduced at 450°C for 1h under the flow of 50ml/min H_2 in atmospheric pressure.

Results and discussion

The addition of small quantities of K (0.5%) as a promoter enhanced the selectivity (39.5% vs 24.4%) towards C_{2+} products (C_{2-4}, $C_{2-4}^{=}$ and ethanol) reducing also the unwanted CO. Generally, the addition of an alkali metal as a promoter seems to be crucial as it regulates the production of the intermediate species and prevents their excessive hydrogenation leading to the formation of C-C bond on the surface of the catalyst. However, the excessive addition of alkali metal has a negative effect on the dissociation of H_2 inhibiting the formation of alcohols and C_{2+}.

Significance of work

The synthesis of C_{2+} chemicals from CO_2 is seen as a promising approach to mitigating global climate change while simultaneously producing high-value chemicals for various applications, such as fuels. This work represents an effort to shift the selectivity of a catalyst from C_1 products towards the production of C_{2+} products.

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CFD Simulations for the CO_2 Hydrogenation in Packed Bed Reactor

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Keywords: CFD modelling, CO_2 hydrogenation, hydrocarbons, packed bed reactor.

Introduction

Greenhouse gas emissions are massive concern for scientists to minimize the effect of global warming. The development of carbon capture and utilization (CCU) technologies attempt to reduce the release of CO_2 emissions in the atmosphere [1]. CO_2 utilization constitutes a circular carbon economy process by the conversion of CO_2 into gas and liquid fossil fuel, chemicals and materials [2]. In this work, we aim to develop a CFD model to validate the observed experimental results according to the hydrogenation of CO_2 to CH_4 and higher hydrocarbons (HH) and alcohols.

Experimental

CFD simulations were used to determine the transport phenomena of heterogeneous flows within the reactor. 1D configurations were designed assuming that the gradients of concentrations and temperatures take place only in the axial directions. For this work, it was included the mass balance equation for the diffusion and convection of species in the packed bed and the mass balance equation for the species inside the catalyst.

Results and discussion

In this study, the obtained experimental results were used to design a robust CFD model and to validate them. A monometallic and a bimetallic DFM catalysts were used for the CH_4 formation, and a Fe-Cu based catalyst for the HH and alcohol generation. Additional studies occurred theoretically in order to optimize the performance of each reaction.

Significance of work

In this work, a robust CFD model was developed to validate the experimental data and predict the effect of different parameters on the CH_4 and HH and alcohols concentration.

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Molten proton conductor fuel cell modules with internal reforming of methanol

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Keywords: Hydrogen; fuel cell stack; methanol reformer; molten proton conductor.

Introduction

Cu-based catalysts are commonly utilized to produce H_2 via methanol steam reforming (MSR) process. The integration of MSR process with high temperature PEM fuel cells through the concept of the internal reforming methanol fuel cell (IRMFC) is considered as an attractive arrangement especially for mobile or portable applications. In this work, the functionality of IRMFC modules with molten proton conductor ($CsH_5(PO_4)_2$) electrolyte membrane, is demonstrated under transient conditions at 220 °C.

Experimental

Lab-synthesized $CuZnGaAlO_x$ and commercial HiFUEL R120 ($CuZnAlO_x$) catalysts were employed for the reformers (100 mg/cm^2). Gold-plated aluminum plates with double serpentine flow fields were constructed. A commercial GDE (HT 140E, Advent) with 1 mg Pt/cm^2 and a $CsH_5(PO_4)_2$-doped PBI membrane were assembled to form MEAs of 10-26 cm^2 active area. The fuel cell modules (single cell and 4MEAs-4Reformers stack) were integrated and tested at 220°C under H_2 and H_2O/MeOH mixtures.

Results and discussion

The open circuit voltage (OCV) remained higher than 1.0 V through all startup/shutdown cycles for all the tested modules. At 0.1 A/cm^2, the fuel cell stack provided 2564 mV (641 mV per cell) after the end of thermal cycles at 220 °C, and 2460 mV (615 mV per cell) after the completion of on-off cycles.

Significance of work

Successful integration and testing of the fuel cell modules operating at 220 °C under on-off cycles.

Acknowledgments

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Performance and stability of $La_{0.75}Sr_{0.25}Cr_{0.9}Fe_{0.1}O_{3-\delta}$ as anode electrode in SOFCs fueled with methane mixtures

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Keywords: Solid Oxide Fuel Cell - SOFC, methane, syngas, lanthanum strontium iron chromite.

Introduction

Solid Oxide Fuel Cells (SOFCs) are high temperature electrochemical devices that convert chemical energy directly to electrical. SOFCs can utilize biogas, consisting mainly of CH_4 and CO_2, through dry reforming to produce electricity and syngas (H_2 and CO). However, the direct use of CH_4 inevitably leads to the formation of carbon deposits on the state-of-the-art nickel-based electrocatalysts, thus posing a significant challenge for the efficient, long-term and stable operation of biogas fuelled SOFCs [1]. Thus, research efforts are focused on developing alternative materials with mixed ionic-electronic conductivity (MIEC) to prevent carbon deposition. Among them, perovskite-type materials, which hinder carbon deposition, have been investigated [2]. In the present work, the perovskite-structured material $La_{0.75}Sr_{0.25}Cr_{0.9}Fe_{0.1}O_{3-\delta}$ (LSCF0.1) is studied, as anode electrode in fuel cells operating at the temperature range of 700-850°C fed with CH_4 and CH_4-CO_2-H_2-H_2O mixtures.

Experimental

LSCF0.1 was synthesized by the modified citrate sol-gel method [3]. All electrodes and layers were applied by screen printing. A standard sintering protocol was followed for each layer/electrode after screen printing. Button-type cells with a geometric anode and cathode electrode area of ~0.8 cm^2 were prepared. Electrochemical characterization and performance evaluation of cells was realized in a ProbostatTM (NorECs) cell test fixture. Gases were fed through mass flowmeters (Bronkhorst). A galvanostat/potentiostat, equipped with a frequency response analyzer, was used for the DC polarization and AC electrochemical impedance spectroscopy measurements. The anode outlet gas was analyzed by means of a gas chromatograph, a mass spectrometer and an infrared analyzer.

Results and discussion

Cells bearing novel LSCF0.1 anodes demonstrated exceptional performance surpassing the state-of-the-art benchmarks, along with outstanding stability under the investigated reaction conditions. Particularly noteworthy was their resilience when operated on pure CH_4, which clearly highlights their superiority compared to the Ni-based electrodes, which are unable to withstand such conditions.

Acknowledgments

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Engineering of photocatalytic Cu_2O/Cu^0-TiO_2 nanohybrids by Flame Spray Pyrolysis (F.S.P.): The role of Cu-atoms *versus* Cu-nanophases

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Keywords: Hydrogen production, Flame Spray Pyrolysis, Cu-nanoparticles, Cu-atoms

Introduction

Climate change has been described as one of the biggest problems faced by humankind dictating the establishment of alternative means for energy production[1]. In this direction, converting solar energy through photocatalysis into valuable fuels such as hydrogen (H_2) and carbon-based fuels by water splitting and CO_2 reduction respectively has emerged as a promising strategy[2,3].

In the present work, we have studied the properties of Cu_2O/Cu^0-TiO_2 nanohybrids with controllable Cu percentages as H_2 production photocatalyst. Engineering of the Cu_2O/Cu^0-TiO_2 nanohybrids has been achieved by an innovative Flame Spray Pyrolysis technology that we have developed herein.

Results and discussion

A novel Spray Injection-F.S.P. technology was developed that allows deposition of atoms e.g. Cu^{2+}, on TiO_2 nanoparticles formed in as separate flame[4]. By adjusting the FSP parameters and process design we were able to produce a library of nanohybrids i.e. to transition from Cu-oxide nanoparticles to Cu-nano-clusters and finally to Cu-atoms, deposited on 15nm TiO_2 nanoparticles. This allowed scalable one-step production of Cu_2O/Cu^0-TiO_2 nanohybrids with controllable Cu percentages. Based on XRD results we verify the presence, the percentage, and the nature of Cu-nanophases. We investigate the role of Cu-loading and the nature of Cu, i.e., Cu-nanoparticles or atomically dispersed, in photocatalytic H_2 production from H_2O. *In situ* Electron Paramagnetic Resonance spectroscopy has bene used as state-of-the art tool to study the coordination environment of Cu^{2+} on TiO_2 and provide quantitative information on photoinduced hole-electron dynamics.

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Engineering of Single- Bismuth-Atom Decorated $NaTaO_3$ Nanoparticles by One-Step Flame Spray Pyrolysis for Enhanced Photocatalytic Hydrogen Production.

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Keywords: $NaTaO_3$ nanoparticles, Bismuth Deposition, Flame Spray Pyrolysis, H_2 Photocatalysis

Introduction

In the quest for sustainable hydrogen energy solutions, the development of efficient photocatalysts is critical. Among the various photocatalysts, the $NaTaO_3$ perovskite is considered one of the most efficient photocatalysts for the water-splitting reaction under UV radiation, since $NaTaO_3$ possesses a sufficiently negative conduction band edge potential relative to the H_2/H_2O reduction level (conduction band-edge, E_{CB}=−1.06vsNHE).[1],[2]

Results and discussion

Herein, we have synthesized $NaTaO_3$ nanoparticles decorated with different loadings either of single bismuth (Bi^{3+}) atoms or clusters, via Flame Spray Pyrolysis (FSP) technology. In particular, to achieve the bismuth deposition on the $NaTaO_3$ particles in a one-step FSP process, a novel spray injection system has been used. This technique enables the rapid production of Bi:$NaTaO_3$ nanoparticles with controllable nanosize, crystallinity, interface, and metal ion deposition (from single atoms to clusters), which significantly enhances their photocatalytic properties. The so-produced Bi:$NaTaO_3$ catalysts were evaluated X-ray diffraction (XRD), Raman spectroscopy, N_2 porosimetry, and transmission electron microscopy (TEM). A systematic study of photocatalytic H_2 production from water, allows a comprehension of the role of Bi-atoms/clusters/particles in the Bi:$NaTaO_3$ catalysts demonstrating enhanced H_2-produciton performance in comparison with the pristine $NaTaO_3$.

Acknowledgments

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Enhancing Public Health Through Nano-photocatalytic Materials with Antibacterial and IR Reflectance Properties

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Keywords: photocatalysis, nanomaterials, antimicrobial, antiviral

Introduction

Photocatalytic materials and coatings represent an advanced approach in the fight against microbial contamination and excessive infrared radiation (IR), with significant benefits for public health, hygiene and living conditions. Upon light activation, the use of photocatalysts generate antimicrobial properties by disrupting the structural genetic material of bacteria and viruses. [1] Advances in nanotechnology have made possible the development of highly efficient photocatalytic coatings, demonstrating fast pathogen inactivation and high reflectivity index to excessive radiation, enabling their application as coatings to surfaces, such as hospital/dwellings' walls, and protective equipment.

Experimental

The research methodology focuses on the formulation and coating testing of metal (Ag/Cu)- and nitrogen-doped titanium dioxide (TiO_2) nanocatalysts, for their antimicrobial and IR reflection properties, respectively. The screening method for the produced metal-doped nanoparticles is standardized with photocatalytic degradation of methylene blue in visible light, and the testing of N-doped ones with visual observation (change of color) and IR reflectance studies (ATR-FTIR measurements). Finally, the optimization of the concentration of particles in the paint took place in order to achieve maximum antimicrobial efficiency.

Results and discussion

The results provide insights into the functionality of the novel photocatalytic nanoparticles and their practical applications in enhancing antimicrobial and reflectivity properties of coatings. The results show that the metal-doped TiO_2 anatase nanoparticles at concentrations of 0.1% Cu/TiO_2 and 0.25% Ag/TiO_2 have shown the best performance. Specifically, the first type is capable of deactivating 99.99% of bacteria in less than 24 hours when integrated into a paint. The N-doped TiO_2 nanoparticles prepared using the optimized concentration of N-dopant with TiO_2 anatase nanoparticles (urea 3:1 ratio, <500 nm size) provided significant IR reflectance as well as solar reflectance properties.

Significance of work

By exploring the interactions between these nanocatalysts in the intended applications, the research aims to provide sustainable and effective solutions for infection control and heat resistance through prevention of IR exposure at healthcare facilities, public spaces, and the transportation sector.

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Evaluation of biogenic CO_2 off-gases impurities as methanol synthesis catalyst poisons

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Keywords: $CuO/ZnO/Al_2O_3$, CO_2 hydrogenation, methanol, biogenic CO_2, impurities, poisoning

Introduction

Waterborne transport represents around 3 - 4 % of all EU GHG emissions [1] and is currently driven primarily by diesel engines. Green methanol can be used as marine fuel without major modifications, enabling mitigation of GHG from shipping. Thus, the interest in green methanol from CO_2 as an energy carrier via carbon capture and utilization (CCU) technologies has increased sharply. However, methanol production via CO_2 originating from off-gases poses challenges due to the various impurities present in such streams that could irreversibly deactivate the methanol synthesis catalyst. We found in previous work [2] that typical contaminants of steel-work emissions, namely S, N, Na, Ca and Fe, reduce the activity of a $CuO/ZnO/Al_2O_3$ catalyst by blocking part of the Cu active sites. In this work, we focus on the effect of typical impurities in bio-CO_2 emission streams, i.e. from biogas production plants, pulp and paper industries etc., on the Cu-based methanol synthesis catalyst.

Experimental

The most common contaminants found in biogenic off-gases are N (NO_x, NH_3, N_2O, HCN) and S (H_2S, SO_x, COS, DMS) species, oxygenates (acids, ketones, etc.), H/C and alkali and heavy metals. Following previously developed protocols [1], a commercial $CuO/ZnO/Al_2O_3$ catalyst is poisoned with suitable concentrations of selected contaminants. To accurately control the concentration of impurities on the catalyst surface, the catalyst is poisoned ex-situ with known amounts of key contaminants. Finally, the poisoned and untreated samples are characterized and tested under CO_2/H_2 mixture in a high pressure dual fixed-bed reactor unit at industrially relevant reaction conditions as a function of time on stream.

Results and discussion

Preliminary physicochemical characterizations of the fresh and poisoned catalyst reveal the successful poisoning of the samples. The stability test conducted as benchmark using the un-poisoned sample of $CuO/ZnO/Al_2O_3$ catalyst reveals a mild deactivation slope with increasing time-on-stream. The poisoned catalysts are currently being tested to assess the extent and type of deactivation caused by the different impurities.

Significance of work

The study explores the effect of commonly found impurities on a $CuO/ZnO/Al_2O_3$ catalyst to explore the viability of using bio-CO_2 as feedstock for methanol production.

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Evaluation of total catalytic oxidation of light hydrocarbons under lean conditions over $La_{1-x}Sr_xMnO_3$ perovskites.

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Keywords: CH_4, VOCs, perovskites, LSM, lean burn conditions

In recent years, urbanization and industrialization have degraded ambient air quality. Both the increasing use of natural gas - as an environmentally friendly source of energy- and various industrial activities contribute to the increase of unburned CH_4 and volatile organic compounds (VOCs) emissions, enhancing the "greenhouse effect" and the formation of secondary pollutants and photochemical smog [1],[2]. Catalytic oxidation is considered a simple and economical strategy for the removal of CH_4 and VOCs, and for this reason the development of highly active and thermally stable catalysts for their total oxidation is a research topic of high environmental interest [1], [2]. In present work, $La_{1-x}Sr_xMnO_3$ perovskites were studied under the total catalytic oxidation of hydrocarbons, CH_4, C_3H_8 and C_3H_6. Specifically, the effect of the gradual partial replacement of La by Sr was investigated (for x = 0, 0.3, 0.5 and 0.7) under O_2 excess conditions, and under different pre-treatment protocols: (a) pre-reduction, (b) pre-oxidation and (c) after oxidative aging at high temperatures. Moreover, various characterization techniques such as BET, XRD and H_2-TPR were implemented to correlate materials structure properties with their catalytic activity. LSM perovskites were found to exhibit good catalytic activity and thermal stability in the catalytic oxidation of light HCs. Furthermore, significant differences (volcano-type) of their catalytic activity (up to ~300°C in terms of T_{50}) were observed in relation to the composition of the perovskite as well as reverse hysteresis phenomena during heating/cooling cycles [2].

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CO_2-assisted oxidative dehydrogenation of propane over Ga_2O_3-SiO_2, Ga_2O_3-TiO_2 and Ga_2O_3-Al_2O_3 catalysts

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Keywords: oxidative dehydrogenation of propane, propylene, CO_2, composite metal oxides.

Introduction. Among various processes that have been proposed for the production of propylene (C_3H_6), which ranks among the most critical building blocks for the industrial production of numerous chemical compounds, is the oxidative dehydrogenation of propane (C_3H_8) using a mild oxidant like CO_2 (ODP-CO_2). This approach is considered to be attractive due to (a) the abundant availability of C_3H_8 contained in shale gas condensates which can be easily extracted in large scale and (b) the utilization of CO_2 which participates both in C_3H_8 conversion towards C_3H_6 and the consumption of H_2 via the RWGS reaction, contributing to the reduction of CO_2 emissions and therefore, the mitigation of global warming [1]. In the present study, the influence of the support nature (Al_2O_3, TiO_2, SiO_2) on the activity and stability of supported Ga_2O_3 catalysts was investigated for the CO_2-ODP reaction.

Experimental. Gallium based composite metal oxides (10%Ga_2O_3-M_xO_y) were synthesized by the incipient wetness impregnation method and characterized employing BET, XRD, CO_2-TPD, TPO, TGA, TEM and SEM techniques. Catalytic performance tests were carried out in the temperature range of 500-750 °C using a CO_2:C_3H_8 molar ratio of 5:1.

Results and discussion. Catalytic activity was found to be higher when gallium oxide was dispersed on alumina support. Although this catalyst was characterized by the highest acid site density, surface acidity does not seem to be the key physicochemical property determining ODP activity. A moderate surface basicity was found to be beneficial for the achievement of high C_3H_6 yields at temperatures of practical interest. Ga_2O_3-TiO_2 and Ga_2O_3-SiO_2 exhibited sufficient stability for 35 hours on stream at 660 and 710 °C, contrary to Ga_2O_3-Al_2O_3 which although was found to be stable at 710 °C it was gradually deactivated when the reaction occurred at 600 °C. Coke formation was favored over Ga_2O_3-Al_2O_3 catalyst which may be related to the higher surface acidity of this sample and be responsible for its deactivation with time. SEM images and elemental mapping obtained from both the as prepared and used samples showed that Ga and M (M: Si, Ti, Al) were uniformly present even after prolonged catalyst interaction with the gas stream. EDS analysis indicated that carbon formation was accelerated with increasing reaction temperature. No carbon formation was detected by conducting TEM and XRD experiments over all "spent" catalysts providing evidence that the so formed carbon was amorphous.

Significance of work. The significance of this work lies in (a) the development of active catalysts with sufficient stability for 35 hours on stream contrary to previous studies where a rapid catalyst deactivation was observed and (b) the identification of key physicochemical properties that determines catalytic activity and catalysts' tendency to coke formation.

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Fe-Molecular Catalyst on Activated Carbon Matrix for H_2-Production from Formic Acid: a Self-Reconstructed Catalyst during Process

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Keywords: H_2 production, FADH catalysis, activated carbon, Fe catalysts

Introduction

Hydrogen possesses a notably high energy density of approximately 120 MJ/Kg, nearly 2.6 times greater than that of gasoline and it is a promising candidate for sustainable energy production. Hydrogen can be produced *in situ* by catalytic dehydrogenation of Liquid Organic Hydrogen Carriers (LOHCs) such as Formic Acid. Complexes of precious (Ir, Ru, Rh) and transition (Fe, Ni) metals have shown promise catalytic behavior in FA dehydrogenation [1]. Catalyst grafting on matrices can endow them with robustness and recyclability [2], [3]. Activated charcoal, characterized by its high surface area, chemical inertness, and amenability to regeneration processes such as thermal reactivation, seems to be a good choice of support matrix. Within this, a Fe-imidazole based complex was attached to activated carbon matrix and the results on the use of the hybrid material, AC_{ox}@imiFe, in FADH catalysis for H_2-production are presented herein.

Results and discussion

The hybrid catalyst AC_{ox}@imiFe, was effectively synthesized and characterized by Raman, FT-IR, EPR, and SEM analysis. When AC_{ox}@imiFe is combined with a polydentate phosphine and FA in propylene carbonate, the generated system is an effective and highly recyclable catalyst for H_2-production providing 22.1 lt H_2 and 428,880 TON within 5 h from 53 ml FA. This performance is obtained over 8 reuses and, interestingly, an enhancement in reactivity is noted with each reuse. The observed increase in catalyst's performance was correlated with structural changes of AC_{ox}@imiFe material, which undergoes a self-reconstruction during catalysis resulting in positive impact on its performance. The presented study underscores the potential of carbon matrices in conjunction with molecular non-noble metal catalysts in FADH catalysis for *in situ* H_2-production.

Acknowledgments

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H_2-Production from FADH Catalysis by SiO_2@NP(Ph)$_2$-Fe using Formic Acid pretreated by silk fiber

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Keywords: formic acid, dehydrogenation, Fe catalyst, grafting, silk fiber

Introduction

The excess desire for energy, mostly powered from fossil fuels, is rapidly causing environmental problems such as global warming, leading to a shift towards renewable energy sources. Currently, H_2 is being introduced as a sustainable energy source however it is not available for immediate use, but it can be obtained from other molecules known as Liquid Organic Hydrogen Carriers (LOHC) such as formic acid[1]. Formic acid (FA) is attracting attention as a hydrogen storage carrier due to its high hydrogen energy content and its potential to produce H_2 via catalytic dehydrogenation (FADH catalysis). Traditionally, homogeneous catalysts have been used but as the science is developing research is focused on heterogeneous catalysts for separation and reusability purposes while metal centers tend to be more earth-abundant and cost efficient such as non-noble metals[2][3]. Herein, we developed a SiO_2@NP(Ph)$_2$-Fe catalyst for formic acid dehydrogenation. The used FA undergoes pretreatment via Silk Fiber, process which boosts catalytic H_2-production.

Results and discussion

A SiO_2@NP(Ph)$_2$ hybrid was developed by covalently grafting of NP-ligand on SiO_2 matrix and fully characterized. The coupling of SiO_2@NP(Ph)$_2$ with Fe^{II} and their combination with polyphosphine PP3 results in [Fe^{II}/SiO_2@NP(Ph)$_2$/PP_3] catalytic system which was evaluated for FADH catalysis providing a consumption of 8mL formic acid, achieving a turnover number (TON) of 19.246 and turnover frequency (TOF) of 6.071. To enhance the catalytic system's performance, FA was initially treated with silk fiber, which possess an abundance of NH_2 groups on its surface, for deprotonation. This treatment significantly improved the catalytic outcome compared to using commercially available formic acid. Consequently, a total of 12mL formic acid was consumed, achieving TON=27.970 and TOF=7.911. This corresponds with our previous research, which suggests that NH_2 groups promote the formation of $HCOO^-$ anion through FA deprotonation. The coordination of these anions to the Fe-center initiates the catalytic cycle, leading to efficient H_2 production.

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Engineering of Ag@SiO$_2$ Films via Flame Spray Pyrolysis as Plasmonic Boosters of Catalytic H$_2$ Production from HCOOH

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Keywords: Nanofilms, Plasmonics, Flame Spray Pyrolysis, Photocatalytic H_2O splitting

Introduction

Plasmonic nanoparticles are nanoscale metallic particles that their performance is based on interaction between electromagnetic waves and collective oscillations of free electrons, known as surface plasmons, at the interface of metals and dielectric materials. Silver (Ag) is the best performing plasmonic material, however, under contact with liquid solvent, e.g. H_2O may undergo oxidation. We have shown that nano-coating with SiO_2 can protect Ag at the same time preserving its photoactivity.[1–3] Herein, we have developed plasmonic Ag@SiO$_2$ films utilizing the Flame Spray Pyrolysis (FSP) methodology. Our aim was to explore to performance of these Ag@SiO$_2$ films as boosters of catalytic H_2 production from HCOOH by molecular catalysts.[4]

Results

Nanofilms, were produced in one step via FSP as follows: first the Ag@SiO$_2$ particles were formed in the flame of the FSP nozzle. Glass substrates were positioned on the particle upstream flow and the particles were allowed to deposit. By controlling the flame-conditions (deposition time) and the positioning of the substrate, we have produced a library of Ag@SiO$_2$ films of various thicknesses. SEM analysis show that the so-formed films were of thickness in the range 200 nm to 5 μm. The physicochemical and surface characterizations of the films were carried out using XRD and Raman spectroscopy. We evaluated these films in molecular catalysis as enhancers of H_2 production from HCOOH, observing remarkable performance.

Acknowledgments

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Evaluation of the performance of Ni-Co bimetallic oxygen carriers in sorption enhanced chemical looping steam CH_4 reforming

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Keywords: H_2 production; steam reforming of methane; chemical looping; bimetallic oxygen carriers

Introduction

The main industrial route for H_2 production, steam reforming of natural gas, consists of an energy-intensive, multistep process with high CO_2 emissions. Aiming to intensify the industrial reforming process, Sorption-Enhanced Chemical Looping Steam Methane Reforming (SE-CL-SMR) has been proposed, which combines reforming with the chemical loops of a CaO-based CO_2 sorbent and a NiO-based oxygen carrier (OC). During the reforming stage of the SE-CL-SMR process, reduced NiO serves as reforming catalyst, while CaO enables the *in-situ* capture of produced CO_2 via the exothermic carbonation reaction and production of high purity H under near autothermal conditions. During the second stage, the endothermic $CaCO_3$ calcination is driven by the OC reoxidation [1-3]. This work aimed to improve the coupling of calcination and oxidation reactions by introducing Co in the NiO-based OC lattice.

Experimental

Bimetallic OCs composed of 40 wt% Ni-Co oxides/ZrO_2 were prepared via a sol-gel combustion route [2]. SE-CL-SMR experiments were conducted in a fixed bed reactor over a mechanical mixture of OC and a CaO-based CO_2 sorbent [3]. The materials were exposed to CH_4/steam during reforming stage at 650 °C. The feed was then switched to air to carry out the OC reoxidation and drive the $CaCO_3$ calcination. Previous results with a 40 wt% NiO/ZrO_2 derived via wet impregnation were used as a benchmark [1].

Results and discussion

During the reforming stage of SE-CL-SMR experiments, the OC could be reduced by CH_4 feed, forming a Ni-Co alloy, which acted as a reforming catalyst for 94% CH_4 conversion and H_2 generation with 94% purity in the regime of efficient capture of the CO_2 sorbent. After switching to air (calcination/oxidation stage), the heat generated by the OC reoxidation increased the temperature of the bed thus decomposing autothermally part of $CaCO_3$. Co addition led to enhanced oxidation kinetics of the bimetallic OC, resulting in higher degree of autothermicity (40.6%), defined as the CO_2 fraction released adiabatically during OC oxidation, compared to the monometallic NiO/ZrO_2 (28.6%).

Significance of work

Bimetallic (Ni-Co) oxygen carriers/catalysts were utilized for an alternative reforming process coupled with calcium and chemical loops, resulting in high-purity H_2 production at the relatively low temperature of 650 °C with simultaneous CO_2 capture and reduced energy requirements. Commercialization of such intensified routes could allow blue H_2 to continue playing a key role in the energy transition period.

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Water-Gas Shift reaction over Pt catalysts supported on CeO_2 and GDC of different nano-configurations

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Keywords: WGS; Pt/CeO_2; Pt/GDC; nanorods

Introduction

The Water-Gas Shift (WGS) reaction is an effective approach for the production of H_2 and the removal of CO required in several practical applications including ammonia synthesis, Fischer–Tropsch synthesis and fuel cells. Fe–Cr and Cu–Zn based catalysts have been traditionally used for the WGS reaction. However, several disadvantages including catalysts pyrophoricity, particles sintering, chromium toxicity and the need for long-time activation procedures, have turned the attention towards the development of alternative WGS catalysts. In the present study, the catalytic performance for the WGS reaction of Pt (0.5 wt.%) catalysts supported on CeO_2 and GDC carriers, synthesized employing two different methods leading to materials with different nano-morphologies, was investigated and compared with counterpart catalysts dispersed on commercial CeO_2 and GDC supports.

Experimental

CeO_2 and GDC carriers were synthesized by the hydrothermal and co-precipitation synthesis methods, whereas supported Pt catalysts were prepared following the wet impregnation method and characterized by BET, XRD, TEM, SEM, and H_2-TPR techniques. Catalytic activity experiments were conducted in the temperature range of 250-650 ^oC with a feed composition consisting of $10\%H_2+10\%CO+5\%CO_2+35\%H_2O/Ar$. *In-situ* DRIFTS experiments were also carried out under WGS reaction conditions.

Results and discussion

TEM and SEM analysis demonstrated that the use of hydrothermal and co-precipitation methods led to CeO_2 and GDC carriers with nanorod and nanoparticle structures, respectively. It was found that the shape of the support strongly affects the physicochemical properties of catalysts and therefore, their WGS activity. Pt particles dispersed on the nanorod-shaped CeO_2 or GDC presented higher specific surface area, lower primary crystallite size and enhanced oxygen storage capacity leading to higher WGS activity compared to the conventional CeO_2 or GDC supports characterized by nanoparticles of irregular shapes and/or the corresponding commercially available carriers. Optimum activity was observed for Pt dispersed on GDC nanorods which also exhibited satisfactory stability with time on stream. The enhanced redox properties of nanorod-shaped metal oxide supports contribute to the creation of more active sites at the metal-support interface leading to an increase of the WGS activity.

Significance of work

The significance of this work lies in the development of CeO_2 and GDC carriers of different nano-morphologies with enhanced WGS activity and stability when used as supports for Pt catalysts. The determination of the physicochemical properties that are strongly affected by the shape of catalyst's support and their correlation with both WGS activity and reaction pathway was of great importance.

Acknowledgments

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Low temperature steam reforming of methanol over CuZn oxide catalysts

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Keywords: Hydrogen, Methanol Steam Reforming; copper; hydrothermal; flame spray pyrolysis

Introduction

Hydrogen can be easily produced on-site or on-board via methanol steam reforming (MSR) over commercially available CuZn(Al)O_x catalysts operating between 200 and 300°C with high hydrogen yields and very low CO selectivity, though suffering from sintering and pyrophoricity phenomena [1]. In order to promote high dispersion and stabilization of the active metallic copper sites and operation at lower temperatures (<200°C), various CuZn-based catalysts were developed in this work.

Experimental

CuZnO_x catalysts with 40 wt.% CuO were synthesized via (i) hydrothermal method (HTM) at 120-180°C for 24 h, and (ii) Double-Nozzle (DN) Flame Spray Pyrolysis (FSP) method, and doped with various oxides. The catalysts were tested under MSR conditions at 160-280 °C (W_{cat} = 0.3 g, F_T = 70 ccm, S/C ratio = 1.1-1.5, MeOH = 6.5-46%). Gas streams were monitored with a GC/MS system. Mapping of the physicochemical properties was done via N_2 adsorption, XRD, XPS, Raman, TPR, S/TEM and DRIFTS.

Results and discussion

Highly efficient CuZn-based catalysts were synthesized via hydrothermal method at 120°C with Na_2CO_3 as precipitating agent. These catalysts were able to operate at temperatures as low as 160°C with traces of CO produced, thus promoting the operation of internal reforming methanol fuel cells. Remarkable activity was also obtained by the FSP sample, showing lower CO selectivity as compared with the commercial catalyst. In-situ DRIFTS studies highlighted that the reaction follows the pathway of dehydrogenation of methanol to CH3O* and HCOO*, then being decomposed to CO_2 and H_2.

Significance of work

Efficient operation of methanol reforming catalysts at low temperature levels (<200°C) provides an attractive option for high temperature PEM fuel cells.

Acknowledgments

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Gas-phase synthesis of metal nitrides via atmospheric spark ablation

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Keywords: metal nitrides, spark ablation, aerosol nanoparticles, catalysis

Introduction

Metal nitrides are gaining significant attention in the field of catalysis due to their unique properties, which include excellent thermal stability and good electrical conductivity. These materials exhibit remarkable catalytic activity across a range of chemical reactions [1,2], making them versatile and valuable in industrial applications.

Spark ablation is a gas-phase synthesis method for generating nanoparticles (NPs) from conductive materials in the form of electrodes [3]. The process relies on spark discharges forming a plasma between two conductive electrodes, heating them up and consequently evaporating small amounts of the material they consist of. The resulting vapours are subsequently quenched and carried away by a gas flow, forming NPs upon nucleation and growth.

Experimental

Here we use spark ablation operated at atmospheric pressure using N_2 as a carrier gas to produce different metal nitrides, including Titanium Nitride (TiN), Aluminum Nitride (AlN), among others.

Results and discussion

Figure 1 shows the XRD spectra of cubic TiN and hexagonal/cubic AlN. The primary particle size of the synthesized metal nitrides was estimated to be in the range of 14-18 nm.

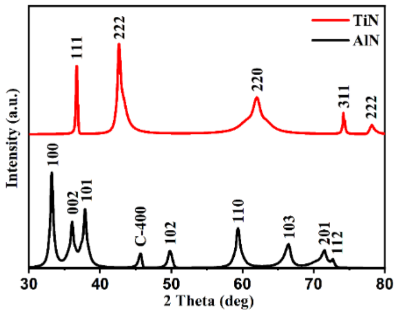

Figure 1. X-ray diffraction patterns of Aluminum and Titanium Nitrides produced via Spark ablation.

Significance of work

The successful synthesis of metal nitrides via the spark discharge generator represents a significant advancement in the field, contributing to the exploration of unconventional synthetic routes and the enhancement of material properties for future technological innovations.

Acknowledgments

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Synthesis of a hybrid SiO_2@NP(*t*-Bu)$_2$-Fe catalyst for H_2 production from formic acid: a polymeric-sponge as low-cost cocatalytic agent

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Keywords: H_2 production, formic acid, Fe-catalyst, grafting, artificial sponge

Introduction

Most energy sources used today are depleted much more quickly than naturally replenished on Earth. Given this situation, there is increasing emphasis on transitioning to environmentally friendly renewable sources, a trend supported by both academic research and industrial initiatives[1]. In this scenario, hydrogen has become an appealing clean energy carrier because of its high energy density, environmental compatibility, and versatility across various applications. Until now, Liquid Organic Hydrogen Carriers (LOHCs) have garnered significant interest due to their ease of storage and transportation; specifically formic acid (FA) presents advantageous physiochemical properties and low toxicity enabling safe and easy handling, transportation, and storage[2]. Notably, FA can be reversibly produced by hydrogenating carbon dioxide and then dehydrogenated, making it an appealing candidate for a hydrogen carrier. Numerous studies have been conducted to develop highly effective homogeneous and heterogeneous catalysts that can selectively produce H_2 and CO_2 from FA under mild conditions[3].

Results and discussion

A hybrid material was developed by covalently attaching an NP ligand on the surface of a SiO_2 matrix. The catalytic system which includes the hybrid material, a metal precursor Fe^{2+} and a phosphine ligand (PP_3) and is denoted as [SiO_2@NP(t-Bu)$_2$-Fe/PP_3], was evaluated in formic acid dehydrogenation catalysis (FADH) for H_2-production; for comparison reasons, the homogeneous system [Fe^{2+}/NP(t-Bu)$_2$/PP_3] was also examined. The heterogeneous catalytic system produced V_{H2+CO2}=7lt in 4h and showed TONs of 16506,4 and TOFs of 5502,13h^{-1}, while the homogeneous system achieved TONs of 10913,3 and TOFs of 3037,8h^{-1} and produced V_{H2+CO2}= 4lt in 3h. To enhance the hydrogen production rate in the heterogeneous system, FA was pretreated with a commercial polymeric-sponge such as melamine sponge (MS), which was modified via imidazole (MS@Im) for deprotonation. After this pretreatment, the catalytic system showed higher TONs and TOFs. Comparing the latter catalytic system with the non-deprotonated, the reaction rate increased from 50 to 70ml/min and TOFs from 5502.13 to 6100h^{-1}.

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Nanosize Effects on Catalytic OH-Radical Production by Fe-Oxide Nanoparticles

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Keywords: Fe-oxides, Nanosize, Catalytic OH-radicals, Electron Paramagnetic Resonance

Fe-oxides are efficient in catalytic production of Reactive Oxygen Species (ROS).[1] When the size is downscaled to nanosize, the reactivity is severely affected. Herein, we have investigated the role of nanosize of Fe-oxides on catalytic OH-radical production from H_2O_2 in conjunction with light-irradiation. The nanomaterials have been produced using Flame Spray Pyrolysis (FSP) technology. Then, we used in-situ XRD analysis of the materials under various thermal treatment protocols. In-situ OH-radical generation has been studied by Electron Paramagnetic Resonance (EPR) spectroscopy under protocols including H_2O_2 and UV-Vis light irradiation.[2] Quantitative analysis and kinetic profiles of ROS generation have been mapped. Our data reveal a strong interrelation of nano-crystal phase transition and the catalytic OH production dynamics.[3]

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