



Abstract book

**Workshop on Catalytic Reactions with Ion Transfer
through Interfaces**

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Plenary Lectures

PL1

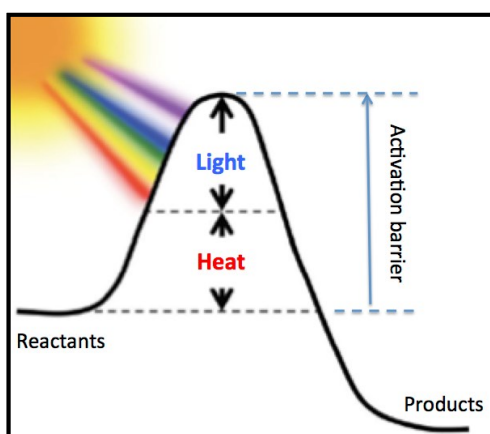
Photocatalytic enhancement of thermal catalytic reactions

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Abstract: Many heterogeneous catalytic reactions require significant energy input to overcome the activation energy barrier. This energy input is generally provided by heating the catalyst bed to high enough temperatures where significant conversion of reactants can be achieved. However, for exothermic reactions, the equilibrium becomes less favorable as the temperature is increased. This raises the question to what extent it may be possible to increase the rates of thermal catalytic reactions in the gas phase by photocatalytic enhancement so that high conversion levels can be reached at lower temperatures where the equilibrium is more favorable.



In this lecture, we explore the interplay between thermal and photocatalytic activation of reactants, with particular emphasis on how photogenerated charge carriers in photocatalytic materials are affected by temperature [1,2]. We discuss how charge carrier lifetimes can be adjusted by modifying radiative and nonradiative charge carrier recombination through appropriate design of photocatalytic materials and reactor systems.

Practical examples include photocatalytically enhanced oxidation reactions on titania-supported metal catalyst and on core@shell catalysts that facilitate the transfer of oxygen ions from the porous shell material to the catalytically active core. For photocatalytically enhanced hydrogen transfer reactions, we evaluate the feasibility of hydrogen generation via vapor phase water splitting and compare it with electrolysis using proton-exchange membranes.

Key words: Photocatalysis, Oxygen transfer, Hydrogen transfer, PEM electrolysis

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PL2

Oxygen surface exchange kinetics of mixed ionic-electronic conducting oxides

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Abstract: High-temperature electrochemical devices such as solid oxide fuel cells, solid oxide electrolysis cells, oxygen separation membranes and membrane reactors based upon fast oxygen ionic conducting oxides have the potential to provide great economic and ecological benefits. One of the challenges of researchers in this field is to develop materials showing fast oxygen ionic transport *and* fast surface exchange kinetics under given operating conditions. It is therefore important to gain a fundamental understanding of the factors controlling oxygen surface exchange, such as defect chemistry and defect-related properties, degree of oxygen non-stoichiometry, surface composition and grain boundary properties. Basic engineering parameters (e.g., firing temperature, atmosphere and duration) determine morphology, microstructure and surface composition of the materials, and may therefore also be of influence. The oxygen exchange activity for a given material may be enhanced via infiltration and/or surface decoration with exchange-active second phases.

Main characterization techniques used to determine the oxygen surface exchange kinetics of fast ionic conducting oxides include ^{18}O - ^{16}O isotopic exchange depth profiling method (IEDP), ^{18}O - ^{16}O isotopic exchange gas phase analysis (IE-GPA), ^{18}O - ^{16}O isotopic exchange pulse technique (PIE), electrical conductivity relaxation (ECR), electrochemical impedance spectroscopy under controlled atmosphere (humidity and $p\text{O}_2$). Data from, e.g., low energy ion scattering (LEIS) and X-ray photo electron spectroscopy (XPS) is used to relate the observed oxygen exchange kinetics to the surface and near-surface composition of the materials.

Major aim of my lecture is to present recent progress and challenges of studies towards understanding the oxygen surface exchange kinetics of single-phase and composite mixed ionic-electronic conducting oxides.

Key words: Oxygen surface exchange, mixed conductors, isotopic exchange, electrical conductivity relaxation, LEIS

PL3

Development of Solid Oxide Fuel Cell Systems for Utilization of Ammonia as Energy Carrier

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Abstract: Among various hydrogen carries, ammonia is one of the promising candidates because of its high hydrogen density and boiling point and ease in liquefaction and transportation. The reaction temperature of ammonia cracking to nitrogen and hydrogen, being about 600°C or higher, is close to the operating temperature of solid oxide fuel cells (SOFCs). A demonstration of the stack-level ammonia-fueled SOFC systems is an important step for the actual utilization of ammonia-fueled SOFCs. In this study, 200 W class and 1 kW class SOFC stacks were applied for ammonia fueled generation systems.

Catalysts for decomposition of ammonia has been developed. The activity of Ni/Y₂O₃ and SrO modified Ni/Y₂O₃ for ammonia cracking was sufficiently high for combination with SOFCs.

A catalyst based on Co-Ce-Zr composite oxide has been developed for autothermal ammonia cracking. Autothermal cracking of ammonia is characterized by fast start-up in the exothermic condition. The start-up time required from the initiation of electrical heating to the achievement of the steady state was 130 s.

Ammonia fueled SOFC stack systems were evaluated. The cell consisted of a Ni/ZrO₂-based fuel electrode, ZrO₂-based electrolyte, and perovskite-type oxide air electrode. The stack composed of 10 single cells was evaluated from its I–V and I–P characteristics at 770°C. Four fuel supply systems were connected to the stack, i.e., 1) direct supply of dry ammonia, 2) the ammonia cracker, 3) the autothermal ammonia cracker, 4) The mixture of hydrogen and nitrogen with a composition of 3 to 1 for comparison. For the direct ammonia fueled stack, the supplied ammonia was almost completely decomposed into hydrogen and nitrogen over the anode. The electrical power achieved with this 10-cell stack was about 250 W. The performances for the SOFC stack was comparable for four fuel supply systems.

The stack consisting of 30 single cells was tested at *ca.* 750°C. Since the performance of the cells has been improved, the power per cell in this stack has also been improved as compared with the cells used in the 10-cell stack. The power of 1073 W can be achieved with the supply of dry ammonia at the current of 50 A which was almost the same as the supply of 3H₂+N₂ mixture at the same current. The average cell voltage at this operation point was 0.715 V. The DC efficiency was 52.3% at the fuel utilization of 80%. The 1 kW class stack was successfully operated for 1000 h. The 1kW-class stack was also operated by supplying the reacted gas from autothermal ammonia decomposition reactor.

This work was supported by the Council for Science, Technology and Innovation (CSTI) Cross-ministerial Strategic Innovation Promotion Program (SIP) “energy carrier” (Funding agency: JST).

Key words: solid oxide fuel cell, ammonia, energy carrier, cracking, fuel cell stack

PL4**Mixed Protonic-Electronic Membrane Reactors;
Converting Hydrocarbon Resources and CO₂ to Fuels**Eric Wachsman*

Abstract: Membrane reactor technology holds the promise to circumvent thermodynamic equilibrium limitations by in-situ removal of product species, resulting in improved chemical yields. Recent advances in mixed-conducting oxide-membrane technology present the possibility for a dramatic reduction in the cost of converting petroleum, coal and biomass derived feed stocks to hydrogen and other “value added” hydrocarbons. We have developed novel membrane reactor technology, based on high temperature proton conductors, that can convert a wide range of hydrocarbons to pure H₂, and syngas for synthesis of liquid fuels and chemical feed stocks. By simultaneous H₂ permeation and catalysis, we have demonstrated the ability to increase water gas shift yields >70% over thermodynamic limitations. Similarly, we have demonstrated increases in steam reforming yields, and the ability to reform CH₄ with CO₂.

More recently we have developed single-step gas to liquid reactors that convert natural gas to C²⁺ products with high yields and no unwanted oxidation byproducts. The direct utilization of CH₄ and CO₂ to simultaneously produce C²⁺ hydrocarbons (C₂ and aromatics) and syngas (CO and H₂) on opposite sides of a mixed protonic-electronic conducting SrCe_{0.7}Zr_{0.2}Eu_{0.1}O_{3-δ} membrane reactor is demonstrated. On one side (interior) of the membrane reactor, direct non-oxidative methane conversion (DNMC) over an iron/silica catalyst produces C²⁺ hydrocarbons and H₂. On the other side (outer surface) of the membrane, permeated H₂ (driving the DNMC reaction) reacts with a CO₂ sweep gas to form CO and water via the reverse water gas shift (RWGS) reaction. This novel single H₂-permeable membrane reactor simultaneously addresses both reduction of greenhouse gas (CO₂ and CH₄) emissions as well as production of value-added hydrocarbon products (C²⁺, CO, and H₂) with in situ gas separation.

Keynote Lectures

K1

Layer-Engineered Functional Inorganic-Organic Materials and Interfaces through ALD/MLD

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Abstract: The combined ALD/MLD technique is strongly emerging as a viable technology for the fabrication of new types of metal-organic materials and inorganic-organic interfaces. The technique is derived from the ALD (atomic layer deposition) technology commercially used for the fabrication of high-quality inorganic thin films, and from its less exploited counterpart for purely organic thin films, i.e. MLD (molecular layer deposition). In ALD/MLD the hybrid thin film is grown from gaseous metal and organic precursors through surface-saturated reactions which enables the hybrid film growth with atomic/molecular level precision. We have already developed well-controlled ALD/MLD processes for a wide palette of metal (alkali/alkaline earth metals, d-block transition metals and lanthanides) and organic (arenes, pyridines, nucleobases, azo molecules, etc.) constituents.^[1-3] Also, the technique is capable of yielding in-situ crystalline thin films of structures similar to those known for so-called coordination polymer or metal-organic framework (MOF) materials synthesized from solutions, or even entirely new compositions/structures.^[1,4,5] An exciting example of the latter case is the crystalline lithium quinone thin films; the structure contains the Li⁺ cations in a coordinatively unsaturated three-fold coordination, which explains why it can not be synthesized through conventional solution synthesis. This material was long wanted though, as it is a promising organic cathode material for Li-ion microbattery with ultrathin layers.^[6] Another interesting approach enabled by ALD/MLD is to build superlattices or gradient materials with precisely tailored inorganic-organic interface frequencies. Such layer-engineered thin films are useful for example for bandgap tuning,^[7] and phonon blocking,^[8] needed e.g. for enhanced thermoelectric energy harvesting. In this lecture, I discuss the fundamentals and future application possibilities of ALD/MLD.

Key words: Atomic layer deposition, Molecular layer deposition, Metal-organic materials, Inorganic-organic interfaces, Energy harvesting and storage

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K2

Interfaces in batteries, a hot topic for the long-term large-scale research initiative in Europe

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Abstract: There are many complex reactions taking place at interfaces in batteries in general and in lithium (LIB) and sodium-ion batteries (SIB) in particular. Some of these are unique for each battery type. For SIBs there are similar reactions taking place as in LIBs.

In this presentation, investigations of the electrolyte/electrode interface, including the solid-electrolyte interphase (SEI) on the anode and the cathode electrolyte interface (CEI) on the cathode, will be discussed. The discussion will be based on the spectroscopy, such as hard X-ray Photoelectron Spectroscopy (HAXPES) and ambient pressure PES, in order to elucidate the chemical composition as a function of depth profiling of the interfaces. A special focus is how interfaces are influenced by electrochemical cycling and how this influence the performance of the respective type of battery. We have investigated different categories of electrode materials: i.e. conversion, alloying, and insertion anodes as well as metal-oxide and phosphate cathodes. This presentation will describe how the methodology of the experiments has improved and how we start to be able to look at dynamic properties due to the development of ambient pressure PES [1,2,3].

To understand and control interfacial reactions in batteries is one of the most important long-term issues to address, as defined by European battery-research community in the large-scale research initiative BATTERY 2030+ [4]. It is one of the most important obstacles to solve when it comes to make the ultra-high performance batteries of the future. If safe batteries with higher energy and/or power with a lifetime longer than 10 years could be made, it would be beneficial for a fossil-free society with a sustainable transport sector.

Key words: interface, SEI, battery, BATTERY 2030+, battery life-time

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K3

Design of Plasmonic Catalysts for Efficient H₂ Production from Hydrogen Carrier Molecules

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Abstract: The Hydrogen is regarded as a promising fuel. Ammonia borane (NH₃BH₃) and formic acid (HCOOH) containing high hydrogen content are attractive candidates as chemical hydrogen carrier molecules. In the exploitation of highly efficient nanocatalysts, special attention has been drawn to the plasmonic nanostructures, including conventional noble metals and non-conventional semiconductor nanocrystals¹⁻⁸. Plasmonic nanostructures are capable of utilization of abundant solar energy by localized surface plasmon resonance (LSPR). LSPR can be described as the collective oscillation of valence electrons for establishing a resonance between the photons and surface electrons of nanoparticles (NPs), driven by the electromagnetic field of incident light. Such LSPR has promising applications in the energy conversion and storage. In this study, we demonstrated that the plasmonic nanostructures, bimetallic Pd/Ag NPs on SBA-15 mesoporous silica, Pd/MoO_{3-x} nanosheet hybrid, core-shell Au@Pd NPs supported on titanium doped zirconium based amine-functionalized MOFs (UiO-66(Zr_{100-x}Ti_x)), can be used as highly efficient catalysts under visible light for H₂ production from NH₃BH₃ and HCOOH. The moderate control of electron density of Pd metal and surface acid-basic properties of support are key factors to realize efficient H₂ production.



Figure 1. Plasmonic Ag/SBA-15 catalysts.



Figure 2. Plasmonic Pd/MoO_{3-x} catalysts.

Key words: Plasmonic Catalysts, H₂ Production, Hydrogen Carrier, Ag NPs, MOF

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K4**Li⁺ transfer through the SiC/Si and Si₃N₄/Si layer to inhibit the Chemical Formation Reaction of Li₂SiF₆ for Stable Si-based Anode**

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Abstract: Silicon-based (Si-based) materials are the promising anode candidates for the next generation lithium-ion battery. However, the poor cycle performance has hindered their practical applications. Herein, a fresh and fundamental reason for the rapid capacity decay of silicon-based materials was proclaimed. Silicon can chemically react with lithium hexafluorophosphate (LiPF₆) and generate lithium hexafluorosilicate (Li₂SiF₆) aggregations constantly during cycling. Moreover, nano carbon on the surface of silicon acted as a catalyst to accelerate such detrimental reaction. Herein, taking advantage of high strength and toughness of silicon carbide (SiC) as well as Si₃N₄ ceramics, SiC or Si₃N₄ layer was rationally introduced between inner silicon and outer carbon to inhibit the chemical formation reaction of Li₂SiF₆. The side reaction rate reduced by 10 times than that of Si, and 300 times than that of Si@C, attributed to the increased activation energy of Li₂SiF₆ formation reaction. The Li⁺ diffusion coefficient is found as high as 1.078×10⁻⁹ cm²/s, 5 times higher than Si indicating an obvious promotion of Li⁺ diffusion. The Si@SiC@C maintained a specific capacity of 980 mAh g⁻¹ at the current density of 1 A g⁻¹ after 800 cycles with the initial Coulombic efficiency (ICE) over 88.5%. This egg structure to enhance both Li⁺ and electron conductive provide a new way to improve anode materials for better performance.

K5

Challenge to overcome carbon corrosion in supercapacitors

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Abstract: Supercapacitors are rechargeable devices with the advantages of high power density and long-term stability despite their disadvantage of low energy density, compared with secondary batteries. Conventionally, activated carbons (ACs) are used as electrode materials, but their stability is not sufficient for use in objectives such as automobiles, as they require a high voltage and high temperature operation. There are two major methods to expand the working voltage of symmetric supercapacitors: (1) the development of stable electrolytes such as ionic liquids and (2) the development of stable carbon materials. The former has been intensively investigated, whereas very stable electrolytes are too expensive for practical applications. On the other hand, the latter including the study on the mechanism of corrosion reactions has been less studied because of difficulty in precise control of complex porous carbon structures.

In order to develop highly durable carbon materials, it is first necessary to understand the mechanism of the carbon corrosion reactions. However, there have been only a limited number of studies because of the very complex structures of porous carbons including ACs. Thus, on the first topic, our recent work on the carbon corrosion sites^[1] is presented. A variety of carbon materials are analyzed with many characterization techniques such as X-ray diffraction, Raman spectroscopy, N₂ adsorption, magnetic susceptibility measurement, and temperature programmed desorption up to 1800 °C, to find out the origin of corrosion reactions in an organic electrolyte. While carbon crystallinity and porosity are not directly related to the positive-electrode corrosion, a good correlation is found between the corrosion charge and the number of carbon edge sites terminated by H and oxygen-functional groups which are decomposed and release CO. On the second topic, the development of super-stable carbon material is presented. The material is a seamless mesoporous carbon sheet consisting of continuous graphene walls.^[2] The sheet contains very few carbon edge sites (only 4% of the number present in conventional activated carbons) despite its high specific surface area (1500 m² g⁻¹), and it is possible to use it to assemble symmetric supercapacitors with excellent stability under 3.5 V@60 °C and 4.4 V@25 °C conditions, even using a conventional electrolyte (1 M Et₃MeNBF₄/propylene carbonate). Moreover, high-voltage operation at 4.4 V results in a 2.7 times higher energy density compared to that achieved using conventional activated carbons.

Key words: supercapacitors; carbon corrosion; graphene

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K6

Coupling Catalysis and Membrane

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Abstract: The application of catalytic inorganic membrane reactors show great promise for industrial processes to produce value-added chemicals owing to high thermal and chemical stability. A catalytic membrane reactor combines Reaction and separation in one unit and also synergistically enhances the membrane permeability and catalyst activity, resulting in process intensification. The selective removal of one of the products during the reaction often leads to enhance the yield of reaction by shifting the thermodynamic equilibrium according to Le Chatelier's principle. Gas separation membranes represent one of the most significant developments in the inorganic membrane decompose area, such as perovskite membranes, Pd/Pd alloy membranes and dual-phase ceramic-carbonate membranes. This lecture will summarize important application and development of O₂ permeable, H₂ permeable and CO₂ permeable catalytic inorganic membrane reactors for various reactions, such as partial oxidation of methane (POM), oxidative dry reforming of methane (ODRM), oxidative coupling of methane (OCM), water gas shift (WGS), propane dehydrogenation (PDH) reaction, CO₂ methanation reaction, reverse water gas shift (RWGS) and NO_x decomposition (DeNO_x). The performance, advantages and challenges of catalytic membrane reactors for various reactions are summarized and discussed.

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K7

Electro-Catalysis at the atomic scale

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Abstract: The chemical industry should in the future be based on renewable energy. Therefore, material development for environmentally friendly, electrocatalytic production of valuable chemicals is needed.

Chemicals could be produced using safe, cheap, more environmentally friendly and more abundant reactants than today. The products could be provided on demand at the place where they are needed, reducing expensive and hazardous transport of chemicals. However, stable, efficient and selective catalysts have to be discovered. This requires insight into the surface chemistry at the atomic scale.

The challenge of discovering new catalyst materials is twofold: Firstly, the properties or descriptors of the wanted catalyst have to be identified. Secondly, real materials with the wanted properties should be found.

I will give examples of determining descriptors for different reactions and a method for identify promising catalyst materials based on high entropy alloy, which is a new class of materials with the promise to change the way we discover interesting catalyst materials.

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K8**A Carbon Neutral Approach to Long Duration Energy Storage through Manipulated Interfaces for Enhanced Carbon Dioxide Electrolysis**

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Abstract: Large-scale energy storage is a key enabling technology for the wide spread adoption of renewable generation on the power grid. The intermittent nature of renewable generation leads to instability in the grid and large-scale energy storage has been shown to be an effective solution for multiple grid applications with different power and duration requirements. Although several storage technologies are capable of providing storage on the order of minutes to hours, very few can provide long duration storage (days to weeks) with the exception of pumped hydro. The lack of long duration storage will require fossil fuel based generation to provide power during the absence of renewable resources that extend beyond a day. One promising technology for long duration energy storage is P2X (power to fuels or chemical) which is based on the electrochemical conversion of reactants through electrolysis. The utilization of carbon dioxide from industrial waste streams offers both a reactant source for chemical based storage and can allow significant reductions in global carbon dioxide emissions. Solid oxide electrolysis is a highly efficient, high temperature approach that reduces polarization losses and best utilizes process heat; however, the technology is relatively unrefined currently for carbon dioxide electrolysis. In most electrochemical systems, the interfaces between active components are usually of great importance in determining the performance and lifetime of any energy materials application. Here we report a generic approach of interface engineering to achieve active interfaces at nanoscale by a synergistic control of materials functions and interface architectures. The composite cathodes with in situ grown interfaces demonstrate significantly enhanced carbon dioxide electrolysis and improved durability. With these results we also investigate a multi-energy systems scenario for chemical production as energy storage that can lead to increased exergy when compared to singular processes. A first-cut economic model will also be presented to demonstrate the economic viability of the overall process.

Key words: carbon dioxide, electrolysis, interface engineering, energy storage

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Oral presentations

O1

Anti-photocorrosion 2-D layer over CdS for hydrogen generation

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Abstract: CdS is a promising visible-light responsive photocatalyst. However, the serious photocorrosion limits its application in photocatalytic water splitting to generate hydrogen. Here we report a novel strategy to overcome the disadvantage of CdS photocorrosion by fabricating peroxide decomposing active MnO₂ thin-layer over CdS nanowires (NWs) and assembling oxygen separation artificial gill to remove nascent formed oxygen in the dispersion. In the meantime, the using non-noble metal NiSe quantum dots (QDs) co-catalyst, NiSe/MnO₂-CdS photocatalysts shows excellent photocatalytic over-all water splitting activity and remarkable stability under visible light irradiation without addition of any sacrifice reagent, 455.0 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ of hydrogen evolution reaction (HER) rate and 5.20% of apparent quantum efficiency (AQEs) at 430 nm. Removing nascent formed O₂ from water by artificial gill can prevent the oxygen leading CdS photocorrosion. Photoluminescence spectra and photoelectrochemical measurements indicate that loading NiSe QDs and coating MnO₂ thin-layer can also improve transfer of the photogenerated charges in CdS. MnO₂ thin-layer can decompose formed hydrogen peroxide and enhance water splitting. Our results can provide a new method for designing and fabricating more stable and efficient CdS-based nanocomposite photocatalysts toward versatile solar energy conversion.

Key words: Over-all water splitting, Fabricating peroxide decomposing active MnO₂ thin-layer, Inhibition of CdS photocorrosion, Replacing noble metal co-catalyst with NiSe QDs, Remove nascent formed oxygen by artificial gill

O2

Particulate photocatalysts and their reaction systems for large-scale solar hydrogen production by water splitting

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Abstract: Sunlight-driven water splitting has been studied actively for production of renewable solar hydrogen as a storable and transportable energy carrier [1,2]. Both the efficiency and the scalability of water-splitting systems are essential factors for practical utilization of renewable solar hydrogen because of the low areal density of solar energy. Particulate photocatalyst systems do not involve any secure electric circuit and can be spread over wide areas by inexpensive processes potentially. Therefore, it is important to activate particulate photocatalysts and develop their reaction systems. In this talk, the latest progress in photocatalytic materials and reactors and concepts toward large-scale demonstration will be presented.

Various oxides, (oxy)nitrides, and (oxy)chalcogenides have been investigated [3]. Ta₃N₅ has a band structure suitable for water splitting under visible irradiation of up to 600 nm; however, overall water splitting had not been achieved because of high densities of trap states until recently. The authors' group has developed a Ta₃N₅ photocatalyst active in overall water splitting via one-step excitation under visible light [4]. Ta₃N₅ single crystal nanorods are directly evolved on KTaO₃ particles by short-time nitridation accompanied by gradual evaporation of K contents (Fig. 1). Ta₃N₅ single crystal nanorods have low defect densities and can utilize photoexcited carriers in the water splitting reaction after loading with appropriate cocatalysts.

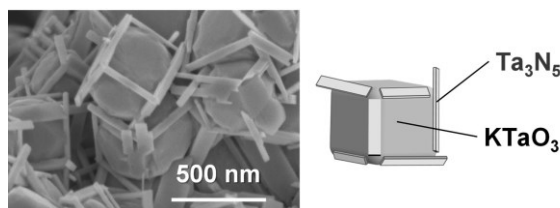


Figure 1. Ta₃N₅ single crystal nanorods evolved on KTaO₃.

Two different photocatalysts can also be combined so that hydrogen and oxygen are generated on the respective photocatalysts. The authors' group has developed particulate photocatalyst sheets consisting of the hydrogen evolution photocatalyst (HEP) and the oxygen evolution photocatalyst (OEP) embedded into conductive layers by particle transfer (Fig. 2) [5,6]. A photocatalyst sheet consisting of La- and Rh-codoped SrTiO₃ as a HEP and Mo-doped BiVO₄ as an OEP embedded into a carbon conductor exhibits a solar-to-hydrogen energy conversion efficiency (STH) of 1.0% at ambient pressure. A photocatalyst sheet can also be fabricated inexpensively by printing ink of photocatalysts containing inert and transparent conductive colloids [7]. Some (oxy)chalcogenides and (oxy)nitrides with longer absorption edge wavelengths have also been shown to be applicable as the HEP and the OEP of particulate photocatalyst sheets recently.

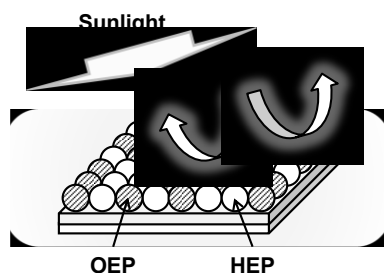


Figure 2. Water splitting on a particulate photocatalyst sheet. Reprinted with permission from ref. [1]. Copyright © 2017, Royal Society of Chemistry.

The authors' group has been developing panel-type reactors that accommodate photocatalyst sheets effectively as shown in Fig. 3 [8]. Al-doped SrTiO₃ photocatalyst sheets contained in a panel-type reactor split water and release gas bubbles at a rate corresponding to a solar-to-hydrogen energy conversion efficiency of 10% under intense UV illumination when the water depth is 1 mm and even thinner. A 1-m²-sized photocatalyst panel reactor splits water under natural sunlight irradiation without a significant loss of the intrinsic activity of the photocatalyst sheets. Panel-type reactors can accommodate various kinds of photocatalysts sheets and are expected to be built using light and inexpensive materials, thus being suitable for large-scale solar hydrogen production from water.

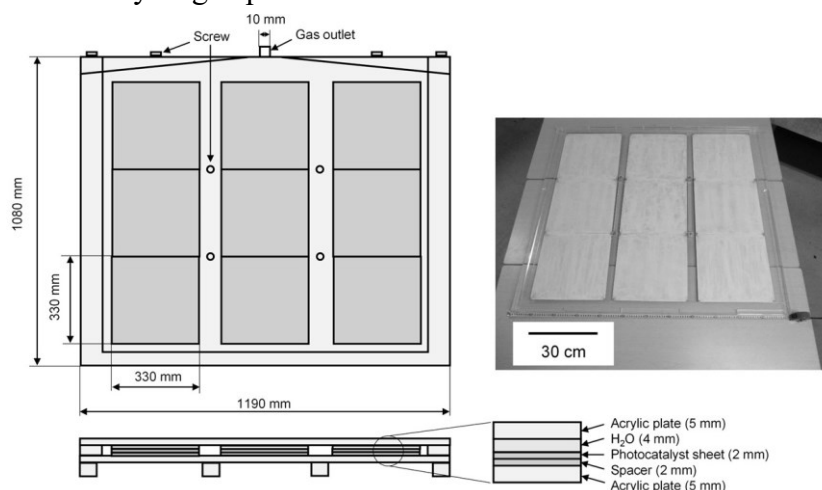


Figure 3. A 1-m²-sized photocatalyst panel reactor accommodating photocatalyst sheets. Reprinted with permission from [8]. Copyright © 2017 Elsevier Inc.

Key words: semiconductor, photocatalyst sheet, panel reactor

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O3

Tunable Covalent Triazine-Based Frameworks (CTF-0) for Visible-Light-Driven Hydrogen and Oxygen Generation from Water Splitting

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Abstract: Covalent triazine-based frameworks (CTFs), a group of semiconductive polymers, have been identified for photocatalytic water splitting recently. Their adjustable band gap and facile processing offer great potential for discovery and development. Here, we present a series of CTF-0 materials fabricated by two different approaches, a microwave-assisted synthesis and an ionothermal method, for water splitting driven by visible-light irradiation. The material (CTF-0-M2) synthesized by microwave technology shows a high photocatalytic activity for hydrogen evolution (up to 7010 $\mu\text{mol h}^{-1} \text{g}^{-1}$), which is 7 times higher than another (CTF-0-I) prepared by conventional ionothermal trimerization under identical photocatalytic conditions. This leads to a high turnover number (TON) of 726 with respect to the platinum cocatalyst after seven cycles under visible light. We attribute this to the narrowed band gap, the most negative conduction band, and the rapid photogenerated charge separation and transfer. On the other hand, the material prepared by the ionothermal method is the most efficient one for oxygen evolution. CTF-0-I initially produces ca. 6 times greater volumes of oxygen gas than CTF-0-M2 under identical experimental conditions. CTF-0-I presents an apparent quantum efficiency (AQY) of 5.2% at 420 nm for oxygen production without any cocatalyst. The activity for water oxidation exceeds that of most reported CTFs due to a large driving force for oxidation and a large number of active sites. Our findings indicate that the band positions and the interlayer stacking structures of CTF-0 were modulated by varying synthesis conditions. These modulations impact the optical and redox properties, resulting in an enhanced performance for photocatalytic hydrogen and oxygen evolution, confirmed by first-principles calculations.

Key words: covalent triazine-based frameworks, oxygen evolution, hydrogen evolution, visible-light-driven photocatalysis, water splitting

O4

Metal-Organic Frameworks/Gels for Oxygen Electrocatalysis

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Abstract: The growing pollution and energy crisis call for the development of clean energy, such as hydrogen fuel cells, water electrolyzers and metal-air batteries, in order to reduce the dependence on fossil fuels. In such clean energy devices, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the key processes in determining the practical performance. Unfortunately, the reactions involve multiple proton and charge transfer steps, thus suffering from sluggish kinetics and resulting in high efficiency penalties. To address the issues, rational design of platinum group metal (PGM)-free catalysts with ORR/OER performance comparable or even superior to PGM is desirable.

Metal-organic frameworks (MOFs) are porous crystalline materials with repeated metal-organic ligations uniformly distributed throughout the frameworks, thus constructing into high surface areas and accessible metal sites. MOFs have tunable compositions and pore structures, for instance, by introducing a secondary metal or different length of organic linkers, respectively. The unique properties enable MOFs to be promising for oxygen electrocatalysis, in pristine phases or as self-sacrificial templates. Besides MOFs, another class of metal-organic coordinated materials that are of great interest is called metal-organic gels (MOGs). MOGs are viscoelastic solid-like materials assembled by metal-organic coordination in conjunction with other interactions. MOGs possess great inclusion properties, design flexibility and ease in synthesis, highlighting themselves as precursors for producing ORR/OER electrocatalysts.

In this presentation, a series of MOFs/MOGs and their applications in oxygen electrocatalysis will be introduced. MOFs/MOGs as well as their derived materials were synthesized through various strategies. The catalytic performance of the catalysts was evaluated in alkaline/acidic half-cells, a proton exchange H₂-O₂ fuel cell and an aprotic Li-O₂ battery. Several catalysts exhibited electrocatalytic activity comparable or even greater than that of a commercial Pt/C or IrO₂ benchmark. Rational design of MOFs/MOGs offers a general solution for production of highly effective PGM-free electrocatalysts.

Key words: Metal-organic frameworks, oxygen reduction reaction, oxygen evolution reaction, electrocatalysis

O5

Solid electrochemical energy storage for aqueous redox flow batteries via molecular wiring

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Abstract: Solid redox active materials such as Prussian blue analogues can be used as electrochemical energy storage materials to enhance the capacity of redox flow batteries [1-3]. We have recently demonstrated this concept for aqueous organic flow batteries, achieved stable cycling performances with high Coulombic efficiency and significant capacity enhancement [4]. The crucial step is the redox reaction of the solid material with the soluble redox active organic species, coupled with the intercalation of the K^+ ion into the solid. This reaction has been investigated both experimentally and by finite element simulations to understand better the limiting factors. The catalytic effect of conductive additives such as carbon nanotubes is discussed.

Key words: aqueous organic redox flow batteries, solid charge storage material, redox mediator, Prussian blue analogue

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O6

Efforts in finding the active species for non-aqueous redox flow battery

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Abstract: With the rapid development of renewable energy power generation technologies such as solar and wind, energy storage technologies have been intensively explored. Among them, redox flow battery (RFB) exhibits various unique advantages such as long lifetime, simple structure, decoupled power and energy, etc. Due to its exceptional flexibility and scalability, it is considered to be a promising large-scale energy storage technology. A number of aqueous RFB systems, such as all-vanadium RFB, have been successfully demonstrated. However, they still encounter the inherent limitation of low energy density ($< 25 \text{ Wh L}^{-1}$) due to the low cell potential ($< 2\text{V}$) caused by the narrow electrochemical window of water. To address this issue, non-aqueous RFB (NARFB) has been proposed. Benefit from the wide electrochemical window of the organic solvents, the open circuit voltage (OCV) of NARFB can be as wide as $>4 \text{ V}$, thus enables high energy density.

The active species are vital components for RFB which determine the total performance of the battery. Compared to conventional aqueous RFBs that primarily employ metal-based and halogen-based active species, NARFB has a wide option of active materials based on organometallic and metal-free organic substances, which possess unique characteristics such as molecular diversity and structural adjustability. These significant advantages provide possibility to monitor the solubility and the potential of the active species and thus effectively optimizing the performance of the battery. Organometallic-based active species have been developed due to their excellent electrochemical performance, however, there are still hurdles to be addressed such as low solubility and ligand decomposition. Metal-free organic material is another alternatives to achieving high energy density. The incomparable advantages of simple composition and earth abundance make it possible to screen for electroactive molecules with the equivalent weight below the threshold value of $150 \text{ g mol}^{-1} \text{ e}^{-1}$ and thus facilitate achieving the cost target of \$100 per kWh.

Key words: Electrochemical energy storage; non-aqueous redox flow battery; active species

O7

Design and Synthesis of TiO₂-based Photocatalysts for CO₂ Reduction with H₂O

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Abstract: Titanium dioxide (TiO₂) has been widely used and studied in the field of photocatalysis research, due to its super properties including cheap, nontoxic, abundant and resistant to photocorrosion. The photocatalytic reduction of CO₂ with water to chemical energy-rich molecule is a significant way to utilize solar energy and reduce the emission of CO₂ [1].

In this talk, I will summarize the recent results of our group for the photoreduction of CO₂ with water over TiO₂-based photocatalysts [2-8]. Firstly, we introduced La to the TiO₂ by surface modification and the obtained La-TiO₂ catalysts showed enhanced photocatalytic CH₄ selectivity [3]. Secondly, based on the results of three-dimensionally ordered macroporous (3DOM) structure with diffuse light effect, we have successfully synthesized high-efficient photocatalysts of 3DOM TiO₂-supported binary noble metals or Pt(Au)@CdS core-shell structural nanoparticles by the gas bubbling-assisted membrane reduction-precipitation (GBMR/P) method [4-6]. 3DOM structure can enhance the light-harvesting efficiency and the all-solid-state Z-scheme system with CdS(shell)-Pt(core)-TiO₂(support) nanojunction is favourable for the separation of photogenerated electrons and holes. Thirdly, we report a novel fabrication of core-shell-structured photocatalysts of Pt/TiO₂-nanocrystals wrapped by reduced graphene oxide (rGO) sheets ((Pt/TiO₂)@rGO). [7,8] The all-solid-state electron multiple transmission (EMT) system is not only favorable for the vectorial electron transfer of TiO₂→Pt→rGO and enhancing the separation efficiency of photogenerated electrons and holes, but also the surface residual hydroxyl and extended π bond of wrapping rGO sheets can improve the adsorption and activation capabilities for CO₂ reactant. Such as, (Pt/TiO₂)@rGO-2 catalyst shows the highest formation rate of CH₄ is 41.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and the selectivity of CO₂ conversion to CH₄ product is 99.1 % [7].

Key words: TiO₂; 3DOM structure; Pt; Core-shell structure; Z-scheme system

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O8

Amorphous metal oxides as catalysts for oxygen evolution reaction

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Abstract: High performance catalysts for oxygen evolution reaction (OER) are of great significance for the electrochemical water splitting due to its sluggish kinetics involving four protons and four electrons. The recent years have witnessed the rapid development of OER catalysts. Increasing evidences have demonstrated that the amorphous metal oxides can show higher OER activity compared with their crystalline counterparts. We have prepared a series of amorphous metal oxides by photochemical metal-organic deposition ^[1-4]. The resultant metal oxides show superior catalytic activity in terms of Tafel slope, onset overpotential (η), and $\eta@1$ and 10 mA cm^{-2} . The relationship between the composition and the activity will be built. The challenges with such catalysts will also be discussed.

Key words: Oxygen evolution reaction, amorphous materials, eletrocatalysis, catalytic activity

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O9

Coupling of catalytic reactions in mixed ionic-electronic conducting membrane reactor

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Abstract: In past decades, a series of perovskite-type membranes and dual phase ceramic membranes with mixed oxygen ion and electronic conductivity were developed for the selective oxidation of light hydrocarbons or ammonia. Different to the co-feed partial oxidation process in packed bed reactors, the oxygen activation in oxygen transporting membrane reactor takes place on air side, and the selective oxidation reaction proceeds on the other side of membrane. The supply of active oxygen species O* for the partial oxidation on membrane surface can be finely controlled by tuning the composition of membrane materials and operation conditions. In our recent work, the improved methane aromatization and ethane dehydrogenation were achieved in mixed oxygen ion and electronic conducting membrane reactor, benefiting from the controllable supply of oxygen species. In addition, we have recently demonstrated the coupling of two reactions on the opposite sides of the membrane reactor, such as water splitting with the partial oxidation of methane/oxidative dehydrogenation of ethane. In this talk, the catalytic and separation performance of mixed conducting membranes will be discussed under the reaction conditions. The effect of catalytic layer onto the membrane surface on the performance towards the selective oxidation of methane and ethane will be demonstrated. In the coupling strategies, not only the reactions on both sides of the membrane reactor are industrially interesting, but also the reactor performance has been significantly improved, which contributes to the concept of process intensification.

Key words: Mixed ionic-electronic conducting membrane, selective oxidation, oxygen permeation, oxygen species, catalytic membrane reactor

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O10

Enhanced Performance of Pd Catalysts for Selective Hydrogenation of Acetylene by Modifying the Subsurface Structure

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Abstract: Selective hydrogenation of acetylene is commercially used to remove trace acetylene in ethylene produced from the cracking of naphtha and thus avoid the deactivation of the ethylene polymerization catalyst.^[1] Pd catalysts are highly active for the acetylene hydrogenation, but their easily formed subsurface hydrogen during the hydrogenation process results in the over-hydrogenation to ethane.^[2] Herein, we modified the subsurface structure of the Pd catalyst by employing carbon nanotube (CNT) as the support toward the suppressed subsurface H and hence the enhanced catalytic performance. The multiple characterizations including the X-ray absorption spectroscopy techniques reveal the presence of the subsurface carbon within the Pd catalysts (**Figure 1a** and **1b**), which suppresses the formation of subsurface H and increases the Pd electron density. The adsorption of acetylene and ethylene over the electron-rich Pd surface have been shown to be weakened, contributing to the enhanced activity and selectivity (**Figure 1c** and **1d**). The insights demonstrated here could pave a way for development of highly efficient yet stable Pd-based catalysts for the reaction.

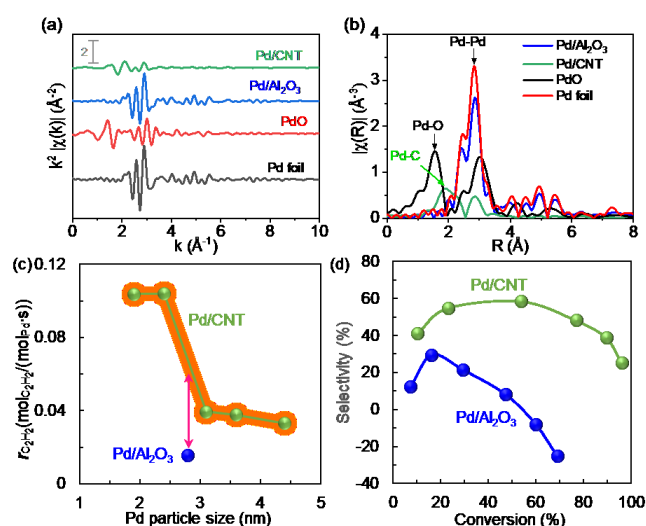


Figure 1. (a) EXAFS oscillation functions at the Pd K-edge and (b) Fourier transforms of the EXAFS spectra of Pd foil, PdO, Pd/Al₂O₃ and Pd/CNT catalysts. (c) Reaction rates of differently sized Pd/CNT and Pd/Al₂O₃ catalysts. (d) Ethylene selectivity versus acetylene conversion over the similarly sized Pd/CNT and Pd/Al₂O₃ catalysts.

Key words: Acetylene hydrogenation, subsurface C, subsurface H, Pd catalyst

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O11

Numerical Assessment of Interfacial Heat Transfer Profile in Contacting Materials: A 3-Mode Perspective

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Abstract: The purpose of this study is to apply a novel transient finite difference equation (FDE) for the determination of the interfacial heat transfer profile in a variety of contact configuration. The numerical FDE computation result is compared with the experimental data obtained using the Beck's inverse technique given in Ref. [1]. Following the experimental data, the temperature profile is analyzed at the punch-blank-die interface. The numerical computation was rendered in Java language. The specification of the boundary condition for the continuum problem in similar and dissimilar materials was considered; and a computerization algorithm for the discretization and solution was also implemented. In addition, A NSYS simulation was used in analyzing the temperature field of a CAD geometry which simulates a hot-stamping process with chemically passive interaction in a range of operating conditions. The modeling scheme justifies a multi-analytic methodology for the determination of the interfacial heat transfer (IHT) profile relative to generic-assumption-based consideration of proprietary software algorithm.

Key words: Transient, finite difference, computerization, interface, heat transfer

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O12

Isobutane Alkylation Kinetics Catalyzed by Sulfuric Acid Based on Carbonium Ion Mechanism

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Abstract: The alkylate, has the advantages of high-octane number, low vapor pressure, and zero content of olefins and aromatics that allow it to become a desirable blending component for high-quality gasoline [1]. It is well accepted that the isobutane alkylation reaction proceeds following the classic carbonium ion mechanism, in which the hydride transfer from isobutane to TMP^+ across the acid/hydrocarbon interface is the rate-controlling step [2, 3]. Considerable efforts have been made to fully understanding the mechanism, providing the fundamental insight of the isobutane alkylation [3]. However, due to simultaneously considerable reactions occurring in the alkylation system and the exist of more than three dozen isoparaffins that are hard to detect owing to the effective analysis method limits, few literature was devoted to the isobutane alkylation kinetics with sulfuric acid as catalyst to explain the formation pathway of several key components in alkylate, such as trimethylpentanes (TMPs), dimethylhexanes (DMHs), and heavy ends (HEs).

In this work the alkylation kinetics of isobutane with mixed C4 olefins using sulfuric acid as catalyst were investigated under conditions of industrial interest. The kinetic model was established on the basis of the carbonium ion mechanism with three key components in alkylate being measured, including TMPs, DMHs, and HEs. Meanwhile, the reaction pathways for polymerization of C4 olefins to produce HEs were modified and the isomerization reaction between butenes was fully considered in this model. According to the result of alkylation experiments, the concentration changes of three key components in alkylate were well predicted by the kinetic model with satisfactory agreement between experiments and model calculations. The reliability of the kinetic model was verified by the isobutane alkylation experiments with mixed C4 olefins with different compositions, confirming the good transferability of the model regardless of the species of butenes in the feed.

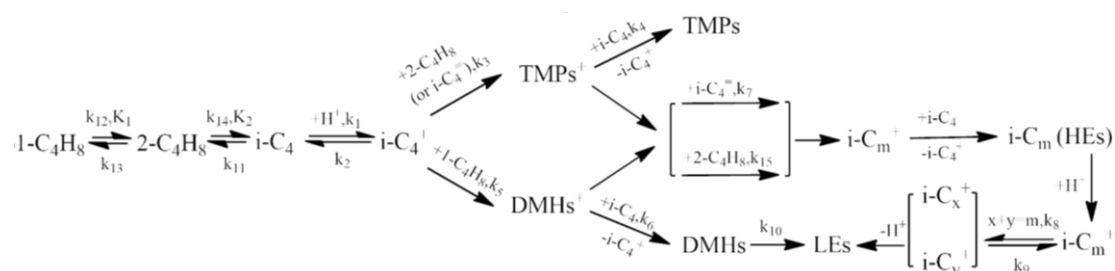


Figure 1. Diagram of the reaction pathway network.

Key words: carbonium ion mechanism, isobutane alkylation, hydride transfer

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O13**Light-to-electricity conversion & stability enhancement by charge transfer catalysis at metal chalcogenide film electrode/electrolyte interface**

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Abstract: Attachment of electro-active species to the surface of a given semiconductor (SC) electrode permanently affects its photo-electrochemical (PEC) properties. Depending on the charge of the electro-active species, the flat band potentials may be shifted up (more negative) or down (more positive). The shift value depends on the applied ion charge density at the surface. Up to 300 mV shifting has been achieved here [1, 2]. Moreover, the electro-active species behaves as charge transfer catalyst across the solid/liquid junction. This increases the charge (holes or electrons depending on the type of the SC) transfer rate between the SC electrode and the redox couple. By doing so, the SC electrode can be stabilized for photo-degradation. All such advantages can be gained simply by attaching the proper electro-active materials to the proper SC electrode. The attachment can be performed by either chemical linkage [1] or by embedding the electro-active material inside a polymer matrix [2]. The new technique has been successfully applied to monolithic and to polycrystalline SC electrode systems. Monolithic n-GaAs electrode showed up to eight fold enhancement in conversion efficiency. Polycrystalline film electrodes, involving nano-particles of semiconductors (CuS, CuSe, CdSe, CdTe, and others), are globally known to be unstable and yield low conversion efficiency (in the order of 1.0% or less) under PEC conditions [1-4]. Such new types of electrodes have been examined here by the new technique. Conversion efficiency values of 4.4, 8.0, 15.0% and 18.0% have been observed from CdSe, CdTe, CuS and CuSe film electrodes, respectively [5-7]. The CuS and CuSe film efficiencies are beyond values expected by the US DOE for the year 2020, and have not been reported for pristine metal chalcogenide film electrodes before. This presentation will show a critical survey of our results observed throughout the last 15 years, as compared to other literature. The new model proposed for the efficiency and stability enhancement will also be rigorously presented. Future prospects of this work will also be discussed.

Key words: Thin film electrodes, Conversion efficiency enhancement, Stability enhancement, Charge transfer catalysis, Photoelectrochemistry.

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O14

Molecular level modelling of electrochemical reactions

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Abstract: I will present an overview of density functional theory (DFT) based molecular modelling of hydrogen and oxygen evolution reactions (HER and OER). The emphasis is on the fast screening type modelling (ΔG) of various catalyst. We have studied HER on several different catalyst, including carbon nanotube (CNT) based materials [1], MoS₂ [2] and Ni₂P [3]. In addition, the OER can be studied with ΔG -type models [4]. In all these studies, the role of catalyst doping has been addressed. On MoS₂ and Ni₂P, the metal doping has been considered and in CNT the N doping has been studied in detailed [1,4]. Some remarks of the limitations of the ΔG model and models with explicit water molecules will be discussed. Overall, the molecular modelling of electrochemical reactions is under intense development and many new methods have been introduced recently. One of them is the use of constrained-DFT for studying coupled electron-proton transfer reaction [5].

Key words: Density Functional theory, hydrogen evolution reaction, oxygen evolution reaction, catalysis

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O15

Perovskite anodes for solid oxide fuel cells fed with CH₄

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Abstract: Anodes catalyzing electrochemical oxidation of fuels such as H₂ and hydrocarbons are key components in solid oxide fuel cells (SOFCs), which require high activity and sufficient ionic and electronic conductivities. Perovskite oxides exhibit a high structural flexibility with a wide non-stoichiometric window, facilitating the optimization of their electrical and catalytic properties with appropriate substitution. In recent years, double perovskite PrBaMn₂O_{5+δ} and its derivatives have been developed, which show promising performance with H₂ and C₃H₈ as fuels [1]. In our previous work, Fe and Co co-doped LaBaMn₂O_{5+δ} is studied as the anode of SOFCs with CH₄ as fuel. With that anode, a single cell supported by a 300-μm-thick La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} electrolyte layer exhibits a maximum power density (P_{\max}) of 503 mW cm⁻² at 850 °C and a durability of more than 200 hours [2]. In this work, the catalytic activity of the anode is further improved when Mn in the anode is fully substituted by Fe, i.e., La_{0.5}Ba_{0.5}FeO_{3-δ}, which shows a high catalytic activity for electrochemical oxidation. The rate limiting step of the anode process is found to be the electronic conduction, which is accelerated with the dope of F. The P_{\max} of a single cell reaches 809 mW cm⁻² at 850 °C with CH₄ as the fuel.

Keywords: Solid oxide fuel cell, anode, methane, lanthanum ferrite

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O16**The nickel zeolite catalyst for hydrocracking of algal oil – the impact of zeolite’s framework on catalytic activity**

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Abstract: Because the availability of non-renewable sources of fossil fuel is limited and they are slowly running out the scientists search alternative technologies of fuel production and their renewable sources. The Bio-Jet fuel can be obtained in catalytic hydrocracking of vegetable oils such as: palm oil, soybean oil, sunflower oil etc. However these oils are also the food oils, what in the face of global hunger can be seen as disadvantage in their application in fuel production. This causes that scientists began to consider the use of algal oil as a source of fuel production. Because the catalytic hydrocracking process demands using of bifunctional, acidic catalytic system, the various zeolites modified by transition metals are tested. In this work, the influence of the preparation method, framework and porous size of zeolite in NiBeta zeolite and NiZSM-5 catalysts on their catalytic activity in hydrocracking of two kinds of algal oil (Fucus Algae and Spirulina Algae) towards aviation fuel were investigated. The physicochemical properties of catalysts were determined with using UV-Vis, XRD, TPR, TPD, TEM. The hydrocracking process was carried out in autoclave at 260°C with various hydrogen pressure of 50 Barr for 2 hours. The preliminary studies show that the more active are catalysts with smaller amount of nickel in systems and the presence of nickel in framework of BEA zeolite seems to be key factor in activity of NiBEA zeolites in hydrocracking processes.

Key words: ZSM-5 zeolite, Beta zeolite, nickel catalysts, algal oil, Bio-Jet fuel

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O17

Hydrodeoxygenation of Dibenzofuran over Pt(111) Surface: A DFT Study

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Abstract: Catalytic hydrodeoxygenation is an efficient way to remove the oxygen atom and upgrade the quality of low temperature coal tar and coal liquefaction oil.^{1,2} However, limited knowledge about the mechanism of hydrodeoxygenation stymies the rational design of more efficient and stable catalysts.³ In this study, density functional theory calculations were performed to understand the reaction mechanism of hydrodeoxygenation of dibenzofuran on the Pt(111) surface. Calculated energetics and activation barriers (Figure 1) indicate that the ring-opening reaction of five-membered ring in tetrahydrodibenzofuran is easier (TS1, 0.40 eV) than hexahydrodibenzofuran (TS2, 1.25 eV). This could be ascribed to the stronger interaction with the Pt(111) surface and little deformation energy of tetrahydrodibenzofuran. Then the intermediates are hydrogenated to 2-cyclohexylphenol (CHPOH). The nonconsecutive hydrogenation of CHPOH could result in a multiple radical species. Thus, CHPOH is prone to go through the nonconsecutive hydrogenation rather than consecutive hydrogenation. The dehydroxylation reaction of the intermediate formed by adding five H atoms to the phenyl ring of CHPOH has a lower energy barrier (TS3, 1.53 eV). However, the dehydroxylation reaction of cyclohexylcyclohexanol has a higher energy barrier (TS4, 2.04 eV). For the hydrodeoxygenation of DBF on Pt(111) surface, the dehydroxylation reaction is the rate-determining step. We hope these investigations can provide a theoretical basis for designing new catalysts for HDO of coal based oils.

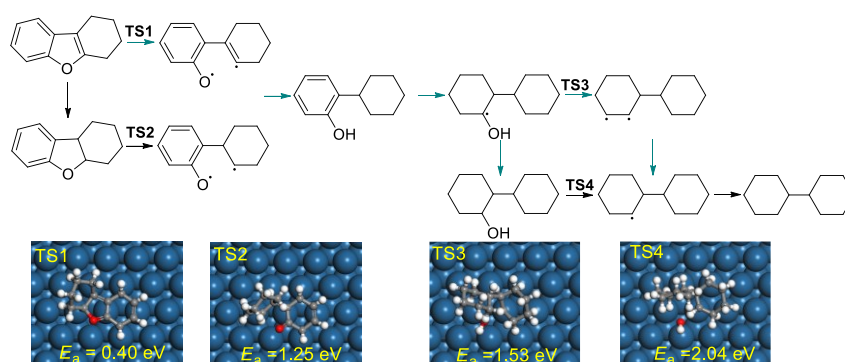


Figure 1: The possible pathways of the hydrodeoxygenation of tetrahydrodibenzofuran. Some transition state structures and corresponding energy barriers also are shown.

Key words: Hydrodeoxygenation, dibenzofuran, Pt(111), density functional theory

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O18

Role of H Diffusion on the Reduction Behavior of VO_x/CeO₂ Catalyst

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Abstract: Fast H diffusion appears at the interfaces of VO_x/CeO₂ catalyst, which have caused considerable attention in the oxide dehydrogenation of hydrocarbons in the atmosphere of CO₂. In this work, we employed the DFT method to probe the detailed effect of H diffusion on the reduction behavior of VO_x/CeO₂ catalyst during the Mars-van Krevelen mechanism. By taking the phenomenon of H diffusion into account, we mapped out different paths of H₂O formation which is the intrinsic reason for catalysts reduction on four oxygen sites, O(1), O(2), O(3), and O(4), located at the interface. Our results show that H₂O is more favorable to form on the O(3) site on the support CeO₂(111) surface, instead of limiting on the active site on VO_x cluster, after H₂O desorption from the surface, leaving a vacant site on O(3), however, the configuration of VO₂/CeO₂(111)-defect with the vacancy on O(3) is found to be unstable, VO₂ cluster exhibits a spontaneously fall down with the O(2) be incorporated into the O(3) vacancy, correspondingly be reduced to VO. In addition, H diffusion cannot be found on other supported VO_x catalyst, such as VO_x/TiO₂ and VO_x/α-Al₂O₃.

Therefore, a hypothesis can be made, if the diffused H on O(3) can be released or eliminated by reaction with some oxidants, in this reaction system, CO₂ as a soft oxidant is a good candidate, the reduction of VO_x/CeO₂(111) and moreover the deactivation of catalysts may be blocked. This would be a new direction of developing a novel catalyst for the ODH of ethylbenzene or other hydrocarbons with CO₂. Herein, it is should be noted that previous studies use the formation energy to evaluate the activity of VO_x/CeO₂(111) catalyst, causing the ignorance of the important role of H diffusion in the reduction behavior for a long time.

Key words: H diffusion, reduction, VO_x/CeO₂

O19

Iron-based Mixed Composites as Active and Durable Oxygen Evolution Electrocatalysts

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Abstract: Electrocatalytic oxygen evolution reaction (OER) is a key step to efficient overall water splitting for renewable energy production and storage.^[1] Active catalysts are required to accelerate the sluggish kinetics of OER, which involves in four-electron transfer steps. NiFeO_xH_y and CoFeO_xH_y are among the best OER catalysts in alkaline condition.^[2] Recent studies have found that Fe rather than Ni or Co acts as the fast kinetics site for OER.^[3, 4] Both the energy barriers for Fe-oxo formation and O-O bonding process on Fe sites are low enough to render a low overpotential. Therefore, it is of great potential to design new OER catalysts by replacing Co and Ni with other transition metal.

Herein, we have developed a series of Fe-based oxide catalysts with high activity and long-term stability. Fe-W composite catalysts show a faster OER kinetics than Fe₂O₃ and WO₃ in alkaline condition. Despite the dissolution of Fe and W species, a phase reforming process of FeWO₄ to W-substituted γ -FeOOH occurred during OER, leading to an overpotential of 0.38 V and a long-term current duration for FeW catalysts. Introduction of Nb to iron oxide could further lower the overpotential to 0.34 V for OER and showed a robust stability for over 100 hours. Unlike WO_x species, NbO_x is highly resistive against dissolution and dispersed in the surrounding of γ -FeOOH to affect the OER process. Density function theory plus Hubbard U (DFT+U) results indicated that the energetics of Fe-OH to Fe-O elementary step were notably reduced with either W or Nb substitution. The presence of W or Nb in the surrounding of Fe octahedra can mitigate the over-strong affinity of Fe towards OH intermediate. Both experimental and theoretical results evidenced that low overpotential and high stability corresponded to Fe-based active sites in the mixed composites.

Key words: Electrocatalysis, oxygen evolution reaction, iron oxide, density function theory

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O20

Photocatalytic Hydrogen Production by RGO/ZnIn₂S₄ under Visible Light with Simultaneous Organic Amine Degradation

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Abstract: The problems of environmental pollution and energy shortage have become increasingly pressing^{1, 2}. In this work, the study of photocatalytic hydrogen production by RGO/ZnIn₂S₄ with simultaneous degradation of organic amines was carried out in the presence of the organic amines in wastewater. The results showed that, the order of H₂ production activity of RGO/ZnIn₂S₄ in six organic amine solutions was N(CH₂CH₃)₃ > N(HOCH₂CH₂)₃ > N(CH₃)₃ > HO(CH₂)₂NH₂ > C₆H₅-N₂ > CO(NH₂)₂, and the highest H₂ production was in N(CH₂CH₃)₃ (triethylamine) solution, being 1597 μmol·g⁻¹·h⁻¹, 2.6 times as high as using the aqueous solution mixture of Na₂S and Na₂SO₃ as sacrificial agent. When N(CH₂CH₃)₃ in wastewater is used as sacrificial agent, hydrogen production and degradation of N(CH₂CH₃)₃ can occur simultaneously and the relationship between the concentration of N(CH₂CH₃)₃ and the H₂ production was in accordance with the Langmuir equation.

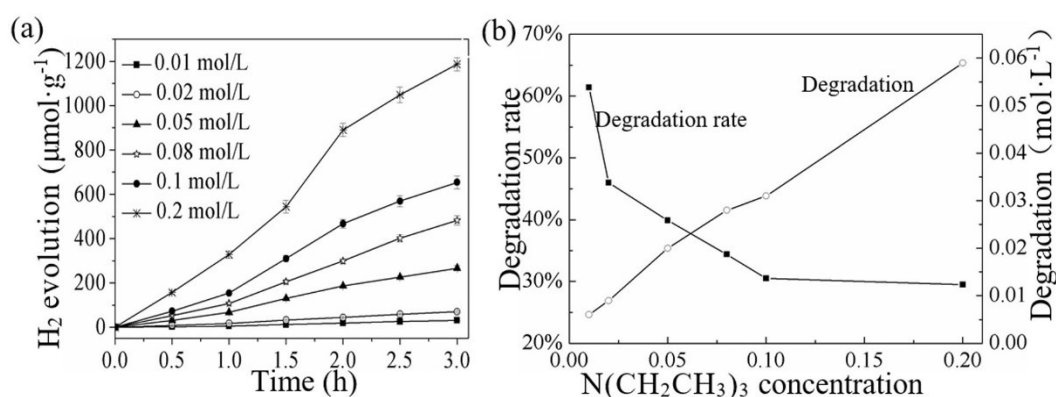


Fig. 1 Simultaneous H₂ production and organic degradation in low trimethylamine-concentration solutions.

Key words: RGO/ZnIn₂S₄; visible light; H₂ production; organic amine degradation

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O21

Hydrogen generation via LNG reforming process on nickel catalysts

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Abstract: The growing demand for fossil fuels and depletion of their resources leads to an increase in their prices. In addition, the ever-growing limitations of greenhouse gas emissions into the atmosphere caused, that many research centers are working on the development of alternative energy sources. The solution of this problem is hydrogen. The energy produced from fuel cells powered by hydrogen is one of the possibilities technologies that do not harm the environment [1-4].

The main aim of this work was to determine the correlation between the physicochemical properties of nickel catalysts and their activity in the oxygen-steam reforming of LNG reaction. In order to achieve the intended purpose of the presented work, nickel was deposited on mono- CeO_2 , ZrO_2 , La_2O_3 and binary oxides ($\text{CeO}_2\text{-ZrO}_2$, $\text{La}_2\text{O}_3\text{-CeO}_2$, $\text{ZrO}_2\text{-La}_2\text{O}_3$) with different loadings (5%, 10%, 20%, 30% wt. of Ni). All of the listed catalytic systems were obtained by wet impregnation method and their physicochemical properties were determined using the following research techniques: TPD- NH_3 , TPR- H_2 , XRD, BET, SEM-EDS, ToF-SIMS. The catalytic activity of the prepared catalysts, whose composition was confirmed by XRD and SEM-EDS, was extensively studied in the oxygen-steam reforming of LNG using a quartz microreactor under atmospheric pressure. The main component of LNG is methane, whose content ranges from 88.4 to 99.7% and its other components include ethane (0.1-13.4%), propane (0-3, 7%), C_4 (0-1.5%) and nitrogen (0-0.8%). Therefore the catalytic tests in reforming process were carried out using only CH_4 as a model mixture of Liquid natural gas. The activity tests confirmed that the reactivity of the catalysts depends not only on the percentage of nickel, but also on the catalysts reducibility, acidity and their specific surface area.

Key words: Hydrogen generation, monometallic nickel catalysts, reforming of LNG

ACKNOWLEDGMENTS

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O22**MO₂ (M=Ti, Ce) embedded carbon nanofibers as an effective support of PtRu catalyst for direct methanol fuel cells**

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Abstract: As an anode catalyst for direct methanol fuel cells, PtRu nanoparticles supported on carbon nanofiber in which TiO₂ or CeO₂ fine particles are embedded (PtRu/TECNF or PtRu/CECNF) has been proposed [1-2]. These catalysts showed two to three times higher mass activity for methanol oxidation reaction compared to that of the conventional catalyst, PtRu/C. Those high activities were explained by the embedded structure that could enhance the positive interaction between Pt and the metal oxide nanoparticles. In order to investigate the mechanism of the interaction between Pt based nanoparticles and the metal oxide particles (TiO₂), CO-pulse adsorption and CO-TPD were conducted for Pt based catalysts with different supports including PtRu/TECNF, PtRu/C and Pt/C. CO₂ production with the initial CO-pulse supply was observed only for PtRu/TECNF. This result could be explained by a reaction mechanism, Mars and van Krevelen mechanism, that the oxygen vacancies of the metal oxide particles take part in the CO oxidation to CO₂. Hence, introduction of the oxygen vacancies of the metal oxide particles of the TECNF or CECNF support by a proper method is expected to realize a further increased methanol oxidation activity of PtRu/TECNF or PtRu/CECNF. On the other hand, high-energy ion-beam irradiation is known to generate oxygen vacancies and an increased electron conductivity to CeO₂ [3]. Based on the above results and discussion, high-energy ion-beam irradiation was introduced for CECNF in order to add oxygen vacancies to the metal oxides (CeO₂) and further enhance the catalytic activity at the PtRu/CECNF. The ion beam irradiation enhanced the mass activity of the PtRu catalyst at a certain range of the irradiation density, fluence, depending on the sort of ion beam. The addition of the oxygen vacancy to the metal oxide was suggested by the reduction of particle size of the metal oxide and also the change in the elemental composition of oxygen and carbon of the CECNF support measured by Energy Dispersive X-ray spectrometry (EDX). An increase in the lattice distance of CeO₂ crystal by the ion beam irradiation was also confirmed by X-ray diffraction (XRD). Since the increase of the lattice distance correlated with the increase of the mass activity, it suggested that the oxygen vacancy related to the methanol oxidation reaction on the PtRu catalyst supported on the CeO₂ embedded carbon nanofiber supports.

Key words: catalyst support, methanol oxidation reaction, metal support interaction, CO pulse adsorption, ion beam irradiation.

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O23**Catalytic requirements for proper electrolyte reactions in single-layer ceramic nanocomposite fuel cells**

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Abstract: Converting the chemical energy of the fuel directly to electricity in ceramic nanocomposite fuel cells (CNFCs) allows flexible and clean electricity generation with high efficiency. Conventional three-layer (anode, electrolyte and cathode) CNFCs have high compatibility requirements for the materials used, mostly due to thermal expansion to prevent the cells from cracking. This issue can be solved by developing a single-layer material that work as all three components simultaneously. Such material is required to catalyze both anode and cathode reactions and transport ions through the cell. A composite material consisting of lithium nickel zinc oxide and doped cerium oxide has been found to fulfill these requirements and reach high electrochemical performance at 550 °C [1].

Here the factors affecting the catalytic properties of single-layer fuel cell electrodes are studied. Using lithium nickel cobalt aluminium oxide as current collector has been found to improve the catalytic activity [1]. Increasing the porosity of the fuel cell more potential reaction sites are created, but too high porosity may cause direct gas mixing through the cell. Moreover, the effect of implementing alkali carbonates to doped ceria to improve the ionic conductivity of the cell [2] is studied.

Key words: ceramic, fuel cell, nanocomposite, single-layer, ionic-transport

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O24

Structure decoration of high performance double perovskite anode materials for SOFCs

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Abstract: Solid oxide fuel cell (SOFC) is all-solid-state energy conversion device that converts directly chemical energy stored in fuel into electricity. It is considered to be one of the cleanest and most efficient energy technologies in 21st century. Significant efforts have been devoted to developing high-performance electrode materials with the aim of increasing the power density of SOFC stacks. Ceramic anode materials have many advantages over the traditional Ni/YSZ (yttrium stabilized zirconia) in terms of reaction active site, structural stability, carbon deposition and sulfur poisoning [1]. To enhance the electrochemical activity of ceramic anode, *in situ* exsolution of highly catalytic nanoparticles and lattice tailoring strategies are employed in this work to enhance the electrochemical performance of anode materials.

A series of double perovskites $\text{Sr}_2\text{FeMo}_{0.65}\text{M}_{0.35}\text{O}_6$ (SFMM, $M = \text{Co}, \text{Ni}, \text{Cu}$) with outstanding performance are developed. Through *in situ* exsolution, several metallic nanoparticle catalysts decorated ceramics were prepared. The maximum power densities (MPD) of electrolyte supported single cells with SFMCo and SFMNi anodes reach 820, and 960 mW cm^{-2} in wet H_2 at 850 °C, respectively [2]. The SFMNi anode meanwhile shows good coking resistance in wet CH_4 . A novel double perovskite $\text{Sr}_2\text{FeMo}_{2/3}\text{Mg}_{1/3}\text{O}_{6-\delta}$ was designed and prepared. The structure study shows that the doped Mg actually takes the Fe-site, leading to the formation of a number of anti-site defects and the presence of $\text{Fe}_B\text{-O-Fe}_B'$ bonds. In an electrolyte (300 μm) supported single cell, the $\text{Sr}_2\text{FeMo}_{2/3}\text{Mg}_{1/3}\text{O}_{6-\delta}$ anode demonstrates excellent cell performance with MPD of 1038 and 1316 mW cm^{-2} at 850 and 900 °C, respectively [3]. The designed double perovskites are attractive anode materials for SOFCs.

Key words: Double perovskite, Structure decoration, Electrochemical properties, Anode, SOFC

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O25

Semiconductor and heterostructure materials function for both electrolyte and electrocatalyst in novel fuel cells

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Abstract: Over hundred years, scientists have designed and searched for ionic conductivity by ionic conducting materials, but challenge unsolved. Typically, solid oxide fuel cell (SOFC), yttrium stabilized zirconia (YSZ) electrolyte, which needs high operational temperature above 700 °C to reach required ionic conductivity, for SOFC technology over several decades, not yet commercially. The YSZ can be now replaced by semiconductor or its heterostructure with higher ionic conductivity. Thus better fuel cell performances have been demonstrated bellow 600°C as shown in Figure 1.

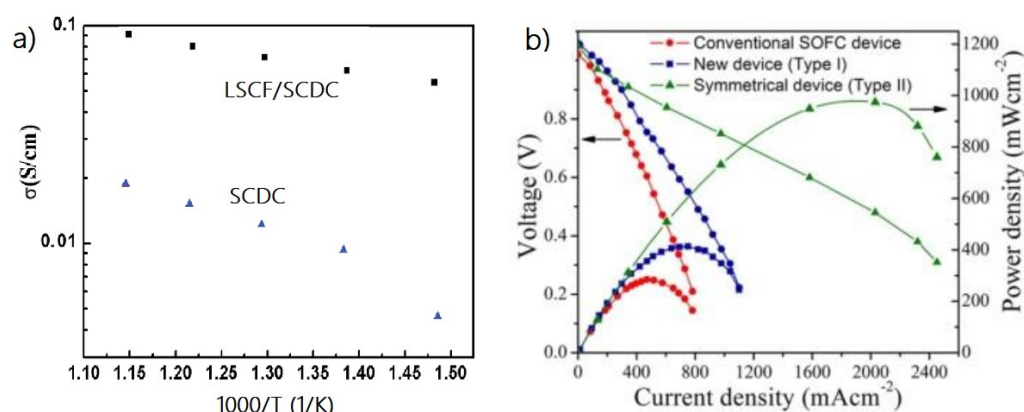


Figure 1 Ionic conductivities (a) and fuel cell performances (b) between ionic SrCa-codoped ceria (SCDC) and a semiconductor LaSrFeCoO_3 and SCDC heterostructure nanocomposite. Type I: LSCF/SDC membrane fuel cell; Type II: the fuel cell designed by/band alignment compared to conventional SCDC electrolyte fuel cell (b).

New scientific understanding has been established between conventional ionic electrolyte-based fuel cell and semiconductor-based device. Figure 2 displays fuel cells from anode, electrolyte and cathode device [1] to semiconductor-ionic fuel cell based on semiconductor heterostructure nanocomposites with both electrolyte and electrocatalyst functions. The fuel cell redox, i.e. hydrogen oxidation and oxygen reduction reactions can then be realized from macro-scale [1] to nano-scale on particles [2].

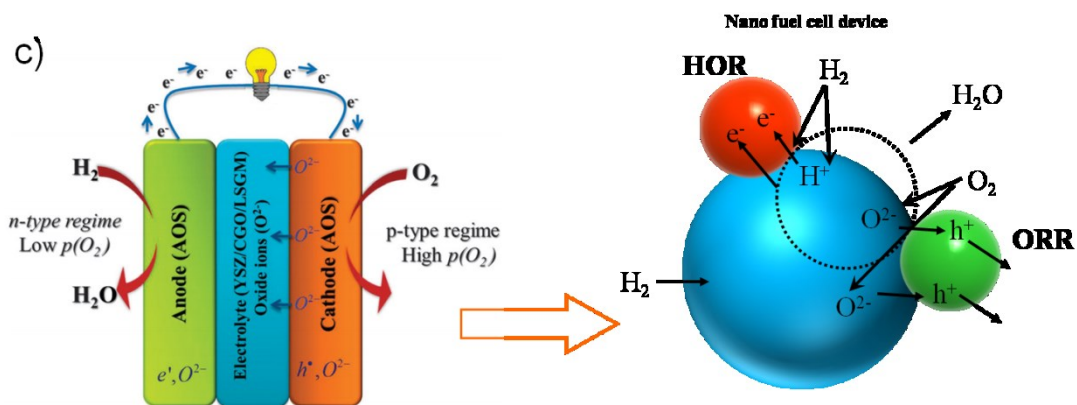


Figure 2 Conventional anode, electrolyte and cathode fuel cell can be realized by semiconductor-ionic heterostructure nanocomposite device

Tuning semiconductors and heterostructure nanocomposites to ionic conductivity and high electrocatalyst can be developed as a very effective approach to develop high ionic conducting and electrocatalyst materials for new generation fuel cell technologies and fundamentals of Semiconductor Electrochemistry. A number of novel devices have been demonstrated by various semiconductor junctions, e.g. bulk hetero p-n junction, planar p-n junction, Schottky junction, all are designed by energy bands and alignments. [2-4]

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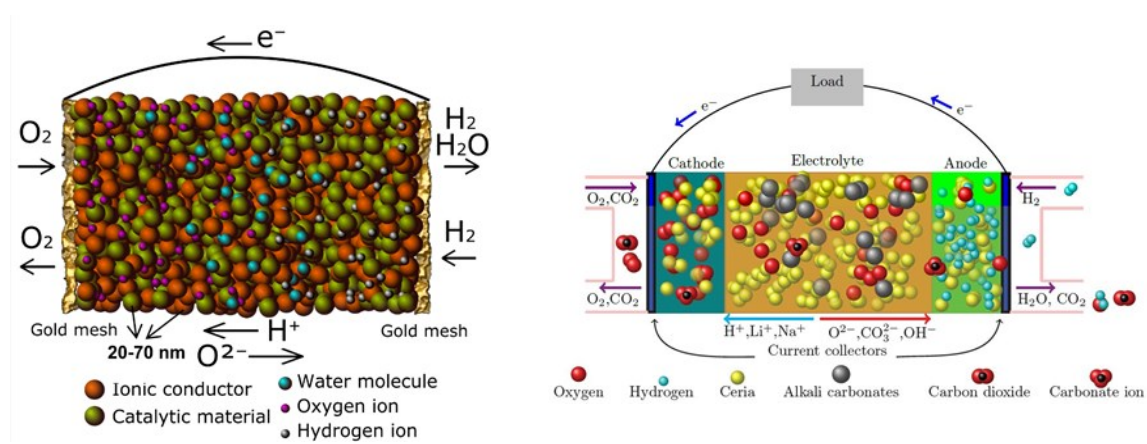
Cutting-edge nanocomposite fuel cell research and challenges

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Abstract: A continual improvement in the synthesis of nanocomposite materials have revolutionized the ceramic fuel cells with improved performance at a lower temperature (400-600°C) [1,2]. With the help of an optimized composition of electrolyte material, a record high ionic conductivity of 0.55 S/cm has been achieved at 550°C [3]. Furthermore, this improved ionic conductivity of the nanocomposite materials resulted in an improved fuel cell performance of 1.1 W/cm² at 550°C in a conventional three-layer cell structure [3]. Electrochemical impedance spectroscopy reveals that the performance of these cells can be further improved by decreasing the Ohmic losses in the electrolyte layer and polarization losses due to the electrode processes [3,4]. Modern printing techniques enables deposition of thin electrolyte layers of high ionic conductivity nanocomposite materials and optimized electrode layers to achieve beyond the state-of-the-art performance. Application of these promising nanomaterials in single layer cell configuration resulted in around 0.8 W/cm² [5]. A systematic study is conducted to understand the mechanisms in the cells.



Key words: ceramic, nanocomposite, ionic transport, printing, electrode reactions

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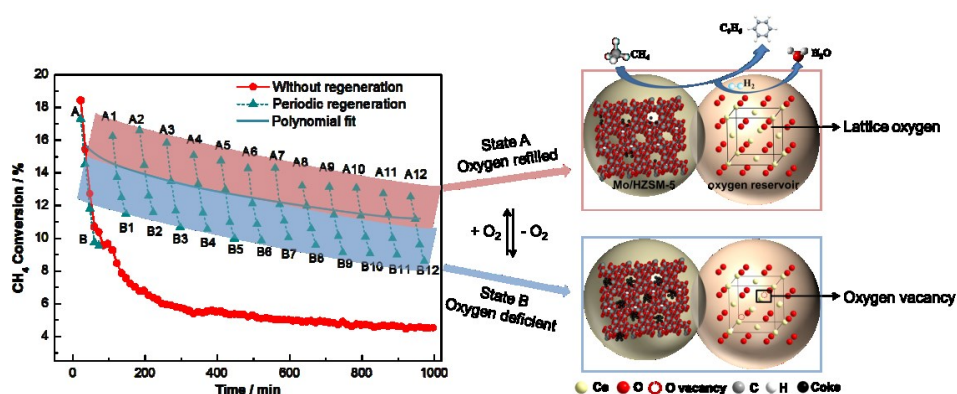
Ion-conducting oxides intensified alkane aromatization over zeolite catalysts

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Abstract: Dehydroaromatization reaction is regarded as a promising route in view of its simple and direct conversion of light alkanes, such as CH_4 and C_2H_6 , to aromatic hydrocarbons. However, equilibrium-limited per-pass conversion and rapid catalyst deactivation due to extensive deposition of coke are two obstacles in commercialization. One strategy to overcome the equilibrium has focused on the introduction of oxygen into reaction. Unfortunately, non-selective gaseous oxygen results in irreversible deep oxidation of hydrocarbons to CO_x , and higher alkane conversion is thus always compromised with lower aromatic selectivity. In the previous works, we reported that the methane aromatization in the membrane reactor with oxygen dosing gives a better yield of aromatic compounds and a longer durability. Recently, a novel composite catalyst was proposed for the first time for the alkane aromatization reaction in a fixed bed reactor, involving an established zeolite catalyst for dehydroaromatization of alkane, and an oxygen reservoir, such as oxygen ion conducting metal-doped ceria and mixed oxygen ion and electronic conducting perovskite oxides, to in situ supply lattice oxygen species. The concerted action of this composite catalysts leads to improved aromatic yield and catalyst stability. For example, in the catalytic aromatization of methane, the CH_4 conversion and aromatic selectivity after 100 min of operation over this composite catalyst can be increased by $\sim 62\%$ and 83% with respect to the Mo/HZSM-5 reference, respectively. In addition, the redox properties of oxygen reservoirs and their high selectivity towards hydrogen oxidation enable an efficient periodic alkane aromatization reaction/regeneration process, leading to improved methane aromatization. This isothermal and regenerable process opens new opportunities for rational development of improved catalyst formulations and for optimizing reactor configurations.

Key words: aromatization, light alkane, ion-conducting oxides, regeneration



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O28

The Synthesis of Highly Dispersed Ni@MCM-41 for Hydrogenation of Naphthalene at Low Temperature

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Abstract: Polycyclic aromatic hydrocarbons (PAHs), a class of harmful compounds to the environment and human beings, present in diesel lead to diesel with a lower cetane number and increased particulate pollutants in exhaust gases. Hydrogenation of aromatic compounds is an effective way to remove PAHs.^[1] Nevertheless, this is an exothermic reaction and low reaction temperature is more beneficial to the conversion of aromatics. According to many published papers, supported noble metal catalysts exhibit excellent hydrogenation performance.^[2,3] Traditional nickel-based hydrogenation catalysts are not very active and stable in hydrodearomatization. How to improve the low temperature activity and stability of supported Ni catalyst remains a significant challenge. Here, we demonstrate a simple and efficient method for the synthesis of Ni nanoparticles in MCM-41 channels. The obtained Ni@MCM-41 catalyst exhibits improved activity for the hydrogenation of naphthalene to decalin at very low reaction temperatures.

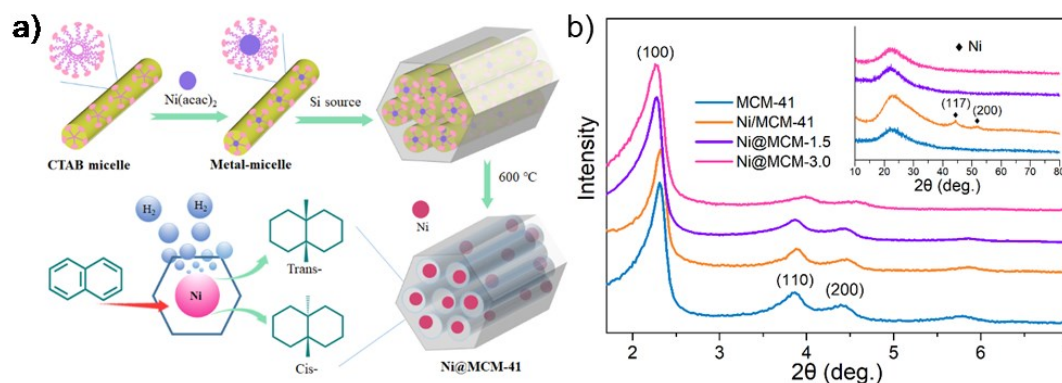


Fig. 1 a) Illustration of the Ni@MCM-41 synthesis and HDA reaction, b) XRD patterns of MCM-41, Ni/MCM-41, and Ni@MCM-x (x=1.5, 3.0).

Key words: MCM-41, hydrogenation, hydrodearomatization, naphthalene

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O29**Platinum electrocatalysts with ultra-low metal loadings for promoting hydrogen evolution reaction**Taneli Rajala, Rasmus Kronberg, Kari Laasonen, Tanja Kallio**Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland**E-mail of corresponding author: tanja.kallio@aalto.fi*

Abstract: Solar and wind based energy supply will increase from the current level by more than one decade by the year 2040 [1], which lays foundation for the hydrogen economy concept where hydrogen serves as an energy carrier. Hydrogen utilization requires, however, introduction of efficient, durable and economically feasible electrochemical conversion of electrical energy into hydrogen bond energy. Electrochemical water splitting can meet these expectations if its key components, electrocatalysts, can be improved.

Today scarce platinum group metals (PGMs) are utilized to electrocatalyze the hydrogen evolution reaction. In addition to PGM availability and cost issues, these electrocatalysts suffer from inadequate durability because of the altering operation conditions induced by intermittent nature of solar and wind energy technologies.

Single-walled carbon nanotubes (SWNTs) have several beneficial properties needed for electrochemical applications: high conductivity, good chemical and electrochemical durability and appropriate properties for fabricating 3D electrodes [2]. Here, the unique morphology of SWNTs contributes to achieve material with ultra-low loadings Pt nanowires (PtNW). For the hydrogen evolution reaction (HER) in aqueous electrolyte, with ultralow Pt content of $340 \text{ ng}_{\text{Pt}} \text{ cm}^{-2}$ this kind of a material reaches catalytic activity comparable to that of state-of-the-art supported Pt with a notably higher Pt content ($38,000 \text{ ng}_{\text{Pt}} \text{ cm}^{-2}$). Furthermore, at the cathode of a proton-exchange-membrane electrolyzer generating stable voltage for more than 2,000 h at high current density it successfully competes with the state-of-the-art construction but with one tenth of Pt mass loading.

The high activity and excellent durability is attributed to favorable PtNW interaction with the SWNTs as well as exposed PtNW edge-sites which adsorb hydrogen optimally and help to alleviate repulsive interactions on the nanowire surface. In addition, the metallic nature of Pt, morphological effects and enhanced surface wetting contribute positively to the performance.

Key words: hydrogen evolution, ultralow Pt, Pt nanowire, carbon nanotube

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O30**Enhanced Visible-Light-Driven Hydrogen Evolution of Ultrathin Narrow Band-gap g-C₃N₄ Nanosheets**

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Abstract: To broaden the light response range of semiconductor photocatalysts and improve the efficiency of photocatalytic reaction is the focus of the production of clean hydrogen energy through solar photocatalytic water splitting. Metal-free graphitic carbon nitride (g-C₃N₄) is an efficient visible light-driven photocatalytic material. In this study, a kind of narrow band-gap g-C₃N₄ has been synthesized by optimizing the synthesis temperature. And then a two-step method of ultrasonication and calcination treatment was used to synthesize ultrathin g-C₃N₄ nanosheets with much bigger specific surface area. The results of characterization analysis indicate that the as-prepared ultrathin narrow band-gap g-C₃N₄ nanosheets show great light absorbance in visible light and high photogenerated charge separation capability. And the as-prepared ultrathin g-C₃N₄ nanosheets exhibit significantly enhanced photocatalytic performance for photocatalytic hydrogen evolution under visible light ($\lambda > 480$ nm).

Key words: Graphitic carbon nitride, Band structure turning, Ultrathin nanosheets, Hydrogen evolution.

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O19

Pickering emulsion interface for continuous-flow catalysis reactionsMing Zhang, Hengquan Yang*

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Abstract: Heterogenization of homogeneous catalysts is of both scientific and industrial interest because it could be helpful for the recovery of homogeneous catalysts and the product purification. However, the immobilized catalysts often suffer from lower activity and selectivity. To address these limitations, my group focuses on developing efficient methods to continuously process reactions involving homogeneous catalysts, nano-metal catalysts and enzymes based on Pickering emulsions (particle-stabilized emulsions), as shown in Figure 1.¹⁻⁹ Homogeneous catalysts and enzymes are confined in micron-sized water or ionic liquid (IL) droplets without need for any modification. Such droplets are packed in a column reactor like particulate catalysts in conventional fixed-bed reactors. The catalysts are thus “immobilized” in the column reactor, while the interstices among the droplets allow the oil phase and substrates dissolved in it to flow down. During passage through the column reactor the reactants contact the catalyst at droplet interfaces or within the droplets, where catalytic reactions occur. Case studies including enzymatic chiral reactions, CuI-catalyzed cycloaddition, cyclization of citronellal, cyanosilylation reactions, and transesterification reactions demonstrate its generality and versatility. Impressively, this system not only exhibits outstanding durability over 4000 h and excellent selectivity, but also significantly enhances catalysis efficiency in comparison to their batch homogeneous counterparts.

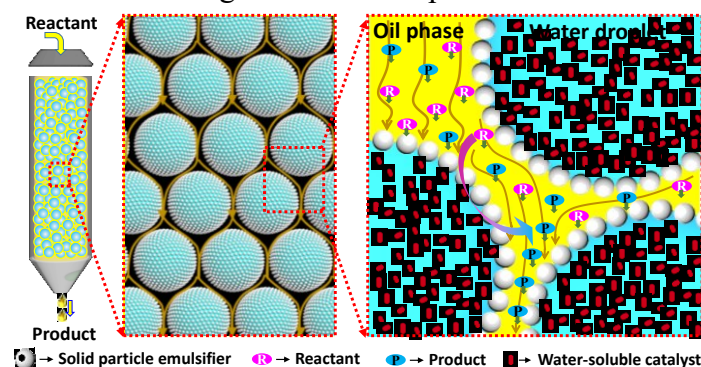


Figure 1 Schematic illustration of the droplet-based continuous-flow reactions

Key words: Pickering emulsion, Interface, Continuous-flow, Catalysis

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O32**Electrochemical reduction of CO₂ to synthesis gas on CNT supported Cu_xZn_{1-x}O catalysts**

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Abstract: Electrochemical CO₂ reduction is a promising method for the production of CO₂ neutral fuels and chemicals from renewable electricity. ZnO supported on CNT is a low-cost electro catalyst that can produce syngas from CO₂ and H₂O. A rational catalyst design strategy for further improvement of the ZnO/CNT catalyst is to dope with copper to strengthen the binding energy of the CO intermediate, which could improve the activity. In this work, a series of CuZnO/CNT catalysts with intimate Cu and Zn contact and various Cu loadings are prepared. By varying the copper content we show that the synergy of copper and zinc improves the activity for CO formation, and the optimal copper content is 20 at%. On hydrogen evolution, the addition of copper has a two-fold effect. This reaction is enhanced by the reduced ZnO particle size obtained when copper is added, but at similar particle sizes of ZnO, a suppression is observed with increasing copper content as CO evolution is enhanced. Stability tests showed that pure ZnO phase is more stable than metallic copper on ZnO. Compared with polycrystalline silver, the CuZnO/CNT catalysts are more active for syngas formation at a useful CO: H₂ composition. This work demonstrates that the viability of DFT based rational design of electrochemical CO₂ reduction catalyst. By varying CuZnO composition as well as crystallite size, one is able to tune the electrochemical reduction activity towards CO and H₂, and therefore achieve desired syngas ratio.

Key words: Electrochemical CO₂ reduction, Hydrogen evolution, Catalysis, Carbon nanotubes, Copper, Zinc

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O33

Unlocking the Energy and Chemicals in Plant Biomass

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Abstract: An important current focus of research in biology, chemistry, engineering, agriculture, and environmental sciences is the development of clean technologies that utilize cellulosic biomass as a renewable resource to the largest extent possible in a biorefinery setting to produce sustainable liquid transportation fuels and chemicals. Of all sustainable resources, only biomass can be transformed into organic fuels and chemicals that can integrate well into our current transportation infrastructure with the inherent convenience, cost, and efficiency advantages of current fuels. Cellulosic biomass can be converted to fuels and chemicals through aqueous-phase processes involving carbohydrates-derived and lignin-derived reactive intermediates deconstructed from these structural components within biomass. Conversion of all major biopolymers within biomass, including lignin in addition to cellulose and hemicellulose, offers promising opportunities for enhancing the overall operational efficiency, carbon conversion yield, economic viability, and sustainability of biofuels production. Despite the potential, the conversion of lignin to biofuels has proven to be challenging. This is especially true for the simultaneous production of monomeric sugars and reactive lignin useful for fermentation and/or catalytic upgrading. Biochemical conversion processes that utilize heat, chemicals, and enzymes to deconstruct biomass into its reactive intermediates at high yields necessary for catalytic upgrading and/or fermentation into useful biofuels and chemicals are still expensive and slow. Thus, biological and/or catalytically upgrading processes that can achieve high biofuel yields from these reactive intermediates at low cost need to be developed.

In this talk, an overview of state-of-the-art technologies for the advanced biofuels production as well as Prof. Yang's recent research and development on both catalytic and biological pathways to upgrade lignin to jet fuel, chemicals, and materials will be discussed.

O34**Metal Nanoparticles Enveloped within Zeolite Crystals as Stable and Selective Catalysts**

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Abstract: Metal nanoparticles are dominant among catalysts used for technological applications. Because they are expensive, dispersions in the form of nanoparticles on porous supports are often used to maximize the metal surface area and the number of atoms accessible for catalysis. A major challenge during application is catalyst deactivation, which results from metal sintering and surface area loss, accompanied by the formation of surface-covering deposits of coke. Regeneration of supported metal catalysts is complex and expensive, often requiring metal leaching, purification and redeposition. To minimize sintering, researchers have learned to strengthen metal-support interactions and, alternatively, have coated the metals with thin shells of porous oxides or carbon. However, the pores are poorly controlled, and many active sites remain covered and do not participate in reactions. In addition, the selectivity in these supported catalysts are also not easy to be controlled.

Here, we demonstrate a general methodology for zeolite encapsulation of metal nanoparticles to prevent metal sintering. The resultant catalysts exhibit extraordinary sinter resistance in the high-temperature water-gas shift (WGS) reaction at 300 °C, CO oxidation at 200 °C, oxidative reforming of methane at 600 °C and CO₂ hydrogenation at 350 °C. In addition, the zeolite micropores are selective for molecular diffusion, which are very favorable for selective catalytic conversion of reactants and selective formation of products. As a result, metal nanoparticles enveloped within zeolite crystals are very stable and selective catalysts, compared with those reported previously.

O35

Modeling of Isobutane Alkylation Using Composite Ionic Liquid as Catalyst

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Abstract: The alkylate produced by strong acid-catalyzed alkylation is an ideal blending component for high-quality gasoline^[1]. Ionic liquids (ILs), with the advantages of negligible vapor pressure, strong chemical stability, and adjustable acidity, have been widely investigated as catalyst of isobutane alkylation. It is well accepted that the isobutane alkylation reaction proceeds following the classic carbonium ion mechanism regardless of the catalyst, including H₂SO₄, HF or ILs, in which the hydride transfer from isobutane to TMP ions across the acid/hydrocarbon interface is the rate-controlling step^[2,3]. For the H₂SO₄-catalyzed alkylation, considerable classical researches have been reported to better understand the reaction mechanism and kinetics^[4]. However, there exists little literature focusing on the kinetics of IL-catalyzed alkylation, especially CIL-alkylation.

In this work, the CIL-catalyzed isobutane alkylation was investigated over the temperature range of 270.2–288.2 K. The optimized reaction time of CIL-catalyzed alkylation was found to be less than 30 s, much shorter than the traditional H₂SO₄-catalyzed one. Based on the carbonium ion mechanism, the kinetic model was further developed, in which three key groups in alkylates and the hydride transfer were fully considered. The rate constant related to the formation of TMPs in the CIL alkylation is more than two orders of magnitude larger than that in the H₂SO₄ alkylation. The enhancement of rate constants of the CIL alkylation can be attributed to the higher solubility and diffusion of isobutane in the IL, which are confirmed by MD simulations. On the basis of the kinetic model, the model prediction of CIL reactor was achieved successfully.

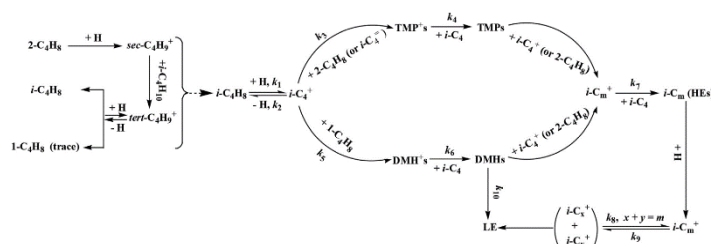


Figure 1 Diagram of CIL-catalyzed alkylation reaction pathway network

Key words: carbonium ion mechanism, isobutane alkylation, ionic liquid, molecular dynamic simulation

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O36**First-Principles Evidence and Experimental Verifications on Enhanced Photoelectrocatalytic Efficiency by double Schottky Junctions**Xinyong Li¹

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Abstract: The bimetallic nanostructures have attracted significant attention due to their unique optical, electronic, magnetic and catalytic properties. Ruthenium (Ru) and Palladium (Pd) NPs catalytic materials have shown marvelous activity in catalysis including photocatalytic hydrodechlorination (HDC) due to their physico-chemical characteristics including specific ability and capability for tremendously facilitating the hydrogenolysis of C-Cl bonds over the interface of Ru and Pd co-catalysts, and deeply uncovering the metal-support interaction via first principle DFT calculations etc. is crucial for further understanding the mechanism of photoelectrocatalytic reductive dechlorinations (PECRD) of PCCs.

Herein, with the aim of molecular designing efficient light harvesting nanomaterials with marvelous activity, stability and recyclability towards highly efficient environmental eliminations and green energy conversions in terms the point view of future practical applications, novel palladium (Pd) and ruthenium (Ru) Bimetal Quantum Dots (BQDs) co-anchored on Titania nanotube (NTs) arrays electrodes bearing double Schottky junction with superior Photoelectrochemical (PE) conversions and PECRD properties were successfully developed and constructed by facial two-step electrochemical strategy. A remarkable enhancement of PE conversion efficiency of 14.10 % as compared to that of the pure TiO₂ NAEs (0.45 %) in the Ru-Pd BQDs/TiO₂ NAEs composites with double Schottky barrier has been successfully achieved, and PCP species could be PECRD over 90% under the optimum conditions. The First-Principles DFT studies revealed that in the Ru-Pd bimetal-semiconductor composites with double Schottky junctions, the number of impurity (i.e., co-anchored Ru-Pd BQDs) energy levels near Fermi surface increased and some were overlapped with original energy level, promoting electron energy transition and reduces the band gap. Meanwhile, after Ru and Pd bimetal co-anchored, the reduction potential of the CB is more negative and the Fermi level moved from to the bottom of the bands which suggesting the composite systems a better reduction capability. Besides, the surface derivation including anchoring of bimetal BQDs into Titania NTs could incur an up band bending and a double Schottky barrier promoting electron energy transition and reduces the band gap, which will significantly promote the interfacial charge carriers separation and transfers. Overall, this work shall provide brand new insight for molecular design of BQDs assembled onto Tatiana NTs composites with superior performance both for environmental eliminations and green energy conversions.

Poster presentations

P1

Hydrogen generation via LNG reforming process on nickel catalysts

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Abstract: The growing demand for fossil fuels and depletion of their resources leads to an increase in their prices. In addition, the ever-growing limitations of greenhouse gas emissions into the atmosphere caused, that many research centers are working on the development of alternative energy sources. The solution of this problem is hydrogen. The energy produced from fuel cells powered by hydrogen is one of the possibilities technologies that do not harm the environment [1-4].

The main aim of this work was to determine the correlation between the physicochemical properties of nickel catalysts and their activity in the oxygen-steam reforming of LNG reaction. In order to achieve the intended purpose of the presented work, nickel was deposited on mono- CeO₂, ZrO₂, La₂O₃ and binary oxides (CeO₂-ZrO₂, La₂O₃-CeO₂, ZrO₂-La₂O₃) with different loadings (5%, 10%, 20%, 30% wt. of Ni). All of the listed catalytic systems were obtained by wet impregnation method and their physicochemical properties were determined using the following research techniques: TPD-NH₃, TPR-H₂, XRD, BET, SEM-EDS, ToF-SIMS. The catalytic activity of the prepared catalysts, whose composition was confirmed by XRD and SEM-EDS, was extensively studied in the oxygen-steam reforming of LNG using a quartz microreactor under atmospheric pressure. The main component of LNG is methane, whose content ranges from 88.4 to 99.7% and its other components include ethane (0.1-13.4%), propane (0-3, 7%), C₄ (0-1.5%) and nitrogen (0-0.8%). Therefore the catalytic tests in reforming process were carried out using only CH₄ as a model mixture of Liquid natural gas. The activity tests confirmed that the reactivity of the catalysts depends not only on the percentage of nickel, but also on the catalysts reducibility, acidity and their specific surface area.

Key words: Hydrogen generation, monometallic nickel catalysts, reforming of LNG

ACKNOWLEDGMENTS

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P2**Preparation and Catalytic Reactions with the Excellent Proton Transfer of Porous Hybrid Resin Solid Acid**

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Abstract: First of all, the supported hybrid resin solid acid catalysts were prepared by loading of organic monomers on inorganic porous material, polymerization and sulfonation. Characterization of the catalysts found that compared with Amberlyst-15, the obtained resin catalysts have a larger surface area and total pore capacity, especially of catalysts used ENO-PC (combined micro-mesopore carbon) as a carrier. The acid-base titration results show that the catalysts have a lower acid content, but higher acid content per unit mass of resin acid. Their thermal stability is slightly higher than that of Amberlyst-15. When the same carrier was used, with the raise of the concentration of organic monomers, the catalyst prepared would have higher content of resin loaded, lower specific surface area and pore volume, the higher acid content and the lower thermal stability. The carrier also plays an important role in the preparation of the catalyst. MCM-41 formed used as carrier, the prepared catalysts have a lower load of resin content compared with catalysts that used MCM-41 powder as carrier in the same conditions.

Then, the catalytic activity of the catalyst was evaluated. It is found that the conversion mainly depends on the acid content and the surface area. The catalytic reactions relate with the proton transfer between reactants and catalyst surface, which decides the utilization efficiency of the sulfonic acid groups over the solid acid catalyst. When the pore volume of obtained catalyst is small, the conversion mainly depends on the acid content of the catalysts, such as catalyst used MCM-41 as the carrier. When the pore volume of obtained catalyst is large, the conversion often depends on its pore structure character, such as catalyst used ENO-PC as the carrier. With the big molecules as reactants, the pore structure character has a great impact on the selectivity of the reaction. ENO-PC supported hybrid resin catalyst has the high reaction selectivity in the esterification of benzyl alcohol and hexanoic acid, mainly due to the micropore was prior loaded, then the proportion of mesopore got higher.

Compared with Amberlyst-15, supported hybrid resin catalysts have higher catalytic activity although its acid content is lower. It is because they have higher surface area, which makes the reactants contact with the acid groups easier, facilitating the proton transfer between reactants and catalyst surface to activate reactants greatly. So they have a much higher butanol yield per sulfonic acid group than Amberlyst-15, which shows higher active site turnover frequency.

Key words: hybrid resin, proton transfer, catalytic activity, pore structure, acid content

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P3

Cu migration of Cu-SAPO-34 catalyst for NH₃-SCR of NO_x during high temperature hydrothermal aging treatment

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Abstract: NH₃-SCR is considered as one of the most effective technologies for eliminating NO_x from stationary combustion and diesel vehicle emissions. Cu-CHA zeolite has been proved highly effective for DeNO_x in terms of high activity and high hydrothermal stability. A lot of efforts have been devoted to the Cu-CHA type catalysts including Cu-SSZ-13 and Cu-SAPO-34 [1,2].

This work investigates the migration behavior of the Cu species in two kinds of Cu-SAPO-34 catalysts, prepared by different methods (one-pot (OP) method and ion-exchange (IE) method), during hydrothermal treatment (10 %H₂O/air, 750 °C for 16 or 24 h) and the resultant effect on the selective catalytic reduction of NO_x by ammonia (NH₃-SCR). A certain amount of CuO exists at the outside and inner of the crystallites in the as-prepared IE sample, whereas copper is mainly atomically dispersed as isolated Cu²⁺ in the OP sample. After hydrothermal treatment for 16 h, the amount of the inner nanosized CuO in the IE sample decreases and the copper disperses to form more isolated Cu²⁺. However, the surface CuO particles increase at the expense of isolated Cu²⁺ with extending hydrothermal treatment to 24 h. Aggregation of the Cu²⁺ species also happens during the aging treatment over the OP sample. The increase of the amount of the isolated Cu²⁺ enhances the low-temperature (< 350 °C) NH₃-SCR activity. However, the increased amount of the surface CuO particles in the aged samples promotes the nonselective NH₃ oxidation reaction in the high temperature range and thus resulting in lower SCR activity.

Key words: NH₃-SCR, Hydrothermal treatment, Cu-SAPO-34, One-pot method, Ion-exchange method

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P4

Modification of microbial fuel cell anodes using graphene-like MoS₂ nanosheets

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Abstract: To enhance the performance and reduce the cost of the anodes, graphene-like molybdenum disulfide nanosheets with a lateral size about 200 nm are successfully synthesized via a simple one-step hydrothermal method, and used to modify carbon cloth and stainless-steel fiber felt in this paper. Equipped with the graphene-like molybdenum disulfide modified carbon cloth and stainless-steel fiber felt anodes, the corresponding microbial fuel cell obtains its maximum power density of 960.4 mW m⁻² and 713.6 mW m⁻² which are 1.7 times and 3.6 times of the unmodified counterparts, respectively. The experiments show that the modification not only can offer large specific surface area and good biocompatibility for biofilm growth, but also makes the anode surface more accessible for microbes' colonization and substrate transfer and thus reduces polarization loss considerably. The results reveal that the graphene-like materials, especially those like graphene-like molybdenum disulfide, are promising materials for excellent and cost-effective anode modification.

Key words: graphene-like molybdenum disulfide, nanosheets, microbial fuel cells, anode modification

1. Introduction

MFC technology has yet been hindered by its low power output and high material costs and for conventional dual-chamber MFC the anode is the key factor for improving MFC's performance. Molybdenum disulfide (MoS₂) is a new 2D-layered material that is analogue to graphene. Graphene-like MoS₂ (GL-MoS₂)⁰ is of a layer structured material. Being inspired by the unique physicochemical properties of nanosheets MoS₂ and the excellent performance of graphene modified MFCs, GL-MoS₂ nanosheets was synthesized through one-step hydrothermal method and were first used to modify CC and stainless- steel fiber felt for fabricating the MFC anode in this paper. The performances of the GL-MoS₂-modified stainless-steel fiber felt and the GL-MoS₂-modified CC anode were tested and assembled into a two-chamber MFC, respectively. The power generation performance of GL-MoS₂-modified anode of MFCs was obtained and the experimental results demonstrated the great application prospects of GL-MoS₂ nanosheets for increasing the specific surface area, enhancing the colonization of EABs, making the electrode more biocompatible, and thus improving the power density output and at same time, reducing the overall electrode cost.

2. Experimental

2.1 Preparation of GL-MoS₂

Analytically pure ammonium molybdate tetrahydrate was purchased from Sinopharm Chemical Reagent Co. Ltd. China, and thiourea of analytical grade from Fuchen Chemical Reagent Co. Ltd. China. GL-MoS₂ was synthesized via one-step hydrothermal process as follows⁰⁰: (NH₄)₆Mo₇O₂₄·4H₂O (3 mmol, 3.708 g) and CH₄N₂S (90 mmol, 6.852 g) without any further purification were fully dissolved in 105 ml deionized water by magnetic stirring for 30min, and then transferred into Teflon-lined stainless-steel autoclave at 200 °C for 24 h. After the suspension was cooled to room temperature naturally, MoS₂ was obtained by a centrifugal machine with a speed of 10000 rpm, and then were rinsed by ethanol and deionized water in sequence, and finally dried under vacuum at 60 °C for 6 h before use.

2.2 Experimental details

Experimental details such as electrode fabrication and characterization, MFC construction and operation, surface morphology and surface chemistry are omitted here and referred to our previous publications^[3,4].

3. Main results and conclusions

XRD and SEM were carried out to characterized the anodes and EDS was used to confirm the modification element changed. Voltage output of various MFCs were obtained, and power curve and polarization curves were also made of the anodes; Polarization curves of anode and cathode were determined; and electrochemical analysis was used to explain the measured performance of the MFCs.

GL-MoS₂ nanosheets have been synthesized via a convenient one-step hydrothermal method and were used to modify the CC and the SSFF anodes of MFC. The GL-MoS₂-modified CC and SSFF anodes obtain their maximum power density of 960.4 mW m⁻² and 713.6 mW m⁻² which are 1.7 and 3.6 times of their unmodified counterparts, respectively. The great improvement is mainly stemmed from the large specific surface area of the GL-MoS₂ nanosheets, good biocompatibility for a comfortable habitation, and probably also its adsorption ability for rapidly integrating with bacterial biofilm. Our experimental results prove that the one-step hydrothermal method for GL-MoS₂ modification is simple, reliable and cost effective.

Acknowledgments

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P5

Protonation Characteristics of Layered $A_x\text{CoO}_2$ ($A = \text{Li, Na}$) Phases

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Abstract: The hexagonal CoO_2 layer^[1] is an important constituent of a number of functional multilayered materials such as the Li_xCoO_2 positive electrode in Li-ion batteries^[2] and the Na_xCoO_2 p-type thermoelectric component in the next-generation energy harvesting devices.^[3] Moreover, the discovery of superconductivity for the water-containing $\text{Na}_{0.3}\text{CoO}_2(\text{H}_2\text{O})_{1.3}$ ^[4] highlighted the potential of the CoO_2 layer to host unexpected new physical phenomena and functionalities. There have been a handful of occasional publications over the years reporting the formation of alkali-metal free H_yCoO_2 through solution reactions where the alkali metal layers between successive CoO_2 layers in Na_xCoO_2 or LiCoO_2 are replaced by protons.^[5,6] However, there is no comprehensive understanding of the protonation tendency of the CoO_2 -layer based materials. We have now systematically investigated the de-intercalation of different types of intervening layers within the CoO_2 -layer stacks and the subsequent intercalation of protons. Using an extensive series of CoO_2 -layer based materials, we demonstrate that the protonation is a very characteristic feature for the CoO_2 layer. The crystal structure and precise composition of the resultant H_yCoO_2 phase are shown to depend on the starting material. Among the prototype systems studied, Na_xCoO_2 (independent of x) yielded hexagonal H_yCoO_2 , while LiCoO_2 yielded trigonal H_yCoO_2 . It is also possible to prepare CoO_2 -layer stacks where the intervening layers consist of different mixtures of alkali metal ions and protons; we demonstrated this with partial Na-extraction from Na_xCoO_2 down to $x = 0.10$ by immersing Na_xCoO_2 in different aqueous solutions; protons were found to be simultaneously incorporated into the Na_xCoO_2 lattice, presumably to balance the charge. Moreover, revealed was that the water-containing $\text{Na}_x\text{CoO}_2(\text{H}_2\text{O})_z$ has a tendency to contain additional protons. Hence, as the protonation seems to be a rather typical feature of the CoO_2 layer, and as it is likely to affect not only the crystal-chemical properties but also the electrochemical and physical properties and important functionalities of the CoO_2 -layer based materials, our work should be of both fundamental and more practical impact.

Key words: Multilayered oxides, $A_x\text{CoO}_2$, Alkali-metal extraction, Proton intercalation, Li-ion battery, Thermoelectrics

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P6**A Study of Magnetic Controlled Gas-liquid-solid Reactor with Surface Modified Core-shell Catalyst**

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Abstract: The slurry bubble column reactor (SBCR) is widely used in coal chemical industry for catalytic reactions including Fischer-Tropsch (F-T) synthesis. It can realize the on-line addition of catalyst and continuous operation. Therefore it effectively reduces the operating cost and improves the capacity of the device. However, the fluid turbulence in the reactor is intense and the catalyst is easily broken into fine powders to be consumed and deactivated. Furthermore, it is very difficult to separate catalyst from liquid phase mainly containing products. How to keep the advantages of slurry reactor at the same time removing the disadvantage of catalyst loss easily is a hot topic in the interdisciplinary field of chemical engineering, machinery and physics. We developed a magnetic controlled gas-liquid-solid SBCR with the function of coupling separation and catalytic reaction is proposed. A cold-model reactor was built with one set of electromagnetic coil with controllable external magnetic field. A core-shell structure iron oxide/silica composite magnetic microsphere type F-T synthesis catalyst was prepared with precipitation method. The behavior of above catalyst in that reactor was studied with N₂ gas and light F-T oil under magnetic strength. The triple-phase boundary (TPB) was studied with a model and verified in the experiments. The catalysts were characterized with XRD, VSM, and TEM. It shows that under the optimized experimental conditions, core-shell coated magnetic particles with a shell thickness of 100-150 nm can be obtained and combined to form composite magnetic microspheres with average particle size of 50 μm, uniform particle size and good spherical regularity.

Key words: Magnetic controlled gas-liquid-solid reactor, triple-phase boundary, core-shell coating, composite magnetic microspheres, Fischer-Tropsch synthesis

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P7**Promoting effect of nickel and lanthanum on Cu-ZSM-5****catalyst in NO direct decomposition**Miao Wei^a, Mengke Liu^a, Yongdan Li^{a,b*}

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Abstract: NO direct decomposition to N₂ and O₂ is an ideal route for NO removal because of the simple reacting network with no additional reductant. Ion-exchanged ZSM-5, especially the copper ion-exchanged ZSM-5 (Cu-ZSM-5) is active for NO direct decomposition in the temperature range of 300-600°C. However, its activity should be further improved. Doping Cu-ZSM-5 is considered as an effective strategy.

Herein, a number of M-Cu-ZSM-5 (M = La, Ni, La-Ni) samples were prepared via an aqueous solution ion-exchange method. The results show that the activity of NO decomposition decreases in the order of La-Ni-Cu-ZSM-5 > Ni-Cu-ZSM-5 > Cu-ZSM-5 > La-Cu-ZSM-5. The co-doping of La and Ni or single doping of Ni is beneficial for improving the activity of Cu-ZSM-5. The O₂-TPD results indicate that La effectively improves the dispersion of the Cu species to form more Cu²⁺ ions whilst Ni is likely to facilitate the implantation of Cu²⁺ to form (Cu²⁺-O²⁻-Cu²⁺)²⁺ dimers. The synergistic effect of La and Ni contributes to the increased (Cu²⁺-O²⁻-Cu²⁺)²⁺ content in the co-doped sample, thus enhancing the NO decomposition activity in the temperature range of 350-550 °C.

Key words: Cu-ZSM-5, NO decomposition, Emission control, Ni and La doping

P8

Electrochemical properties and loss mechanisms of all-organic non-aqueous redox flow battery

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Abstract: Redox flow batteries (RFBs) are considered as one of the most promising large-scale energy storage technology, reliance on facile and reversible reactants, and potentially simpler manufacture. Aqueous RFBs have made remarkable progress in commercial applications due to their long cycling life so far. And non-aqueous RFBs utilize the broader electrochemical stability window of non-aqueous solvent, which provide a promising higher energy density than conventional aqueous RFBs. Non-aqueous Redox flow batteries are considered as one of the most promising high energy density energy storage technology but have not yet been commercialized because of their poor cyclability. For commercialization, the research of the loss mechanisms is necessary. Here we using 2,1,3-benzothiadiazole (BzNSN) and 2,5-di-tert-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene (DBMMB) as anolyte and catholyte redox materials, respectively, which both have high solubility and electrochemical reversibility; and the synthesized ionic liquids, Tetraethylammonium bis(trifluoromethylsulfonyl)imide (TEATFSI), as the supporting electrolyte. Membrane is one of the crucial factors which influence the feasibility of the flow cell. Here we test the cycling performance with three Daramic porous separators and all of them exhibit a good performance. The 100 mM BzNSN/DBMMB in 0.5 M TEATFSI/MeCN flow cell achieves the discharge plateau of 2.50 V and a VE of 95.7%, which are highest reported thus far. And a good capacity retention (material utilization of ~80%), yielding a VE of 94.0%, CE of 85.7% and EE of 80.6% for 100 cycles at the current density of 20 mA cm⁻² are obtained by using Daramic 250 porous separators. Otherwise, the loss mechanisms are studied for the first time by an in-house designed flow cell testing. Mixed-reactant electrolyte can mitigate the crossover effect to some degree, and both leakage and chemical decomposition should be responsible for the capacity degradation during cycling.

Key words: Non-aqueous Redox flow battery; Redox-active organic materials; Capacity degradation; Loss mechanisms

P9

Amorphous ZnFeO_x as cocatalyst for Ti-doped hematite for photoelectrochemical water splitting

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Abstract: Clean and renewable energy such as hydrogen is a promising alternative to fossil energy. Hydrogen can be produced by photoelectrochemical (PEC) water splitting. Hematite (α -Fe₂O₃) stands out as an alternative photoanode due to its stability, abundance and suitable band gap for visible light absorption. However, the poor conductivity and sluggish surface reaction kinetics seriously affect the PEC activity. By Ti-doping and amorphous co-catalyst loading, this work shows that the PEC activity of α -Fe₂O₃ film can be significantly enhanced. The photocurrent of the resultant modified α -Fe₂O₃ film reaches 1.33 mA cm⁻² at 1.23 V vs. RHE and the turn-on voltage shifts to the cathodic side by 110 mV compared to the pure hematite.

Key words: Photoelectrochemical water splitting, α -Fe₂O₃, Ti-doping, amorphous ZnFeO_x

P10

Research progresses of Photoanodes for Photoelectrochemical Water Splitting

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Abstract: Under the background of shortage of fossil energy and environmental pollution, researchers are looking for cleaner and more efficient energy. Photoelectrochemical (PEC) water splitting has become the research direction of researchers [1-6]. In this work, some basic principles of photoelectrochemical catalysis are described. The recent progresses in the photoanodes including Fe₂O₃ and TiO₂ for PEC water splitting are reviewed. The challenges with PEC water splitting are also discussed.

Key words: Photoelectrochemical water splitting, photoanodes

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P11**Improve the activity of oxygen in $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ with the doping of Pr**

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Abstract: Solid oxide fuel cell (SOFC), a kind of energy converting device, has been long studied due to its high efficiency and low emission. NiO-Ce_{0.8}Sm_{0.2}O_{2-δ} (SDC) is the most commonly used anode material in SOFC. It has good chemical and thermal compatibility with the electrolyte. However, its catalytic performance is not good enough in the intermediate temperature region (500-700 °C) when hydrocarbons are used as fuels. Recently, CePr oxide has been widely used as the catalyst in CO oxidation and soot combustion, and the doping of praseodymium increases the oxygen storage capacity^[1]. In this work, Pr is incorporated into SDC as the ceramic phase in the anode of SOFCs. The results of thermogravimetry analysis and CH₃OH temperature programmed surface reaction demonstrate the improvement of the activity of surface oxygen species. The performance of a single cell with the modified anode is improved significantly with methanol as the fuel.

Key words: Praseodymium doping, Oxygen storage capacity, Active oxygen

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P12

Selection and optimization of stable heterocyclic aromatics for nonaqueous redox flow battery

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Abstract: Redox flow battery (RFB) is a promising electrochemical energy storage technology which is suitable for the storage of intermittent energy such as solar and wind energy. The most remarkable advantage of RFBs is their independent tunability of energy storage and power delivery. Nonaqueous RFBs (NARFBs) can reach a high cell potential without the limitation of the electrochemical window of water, and lower the cost by using cheap but effective materials. However, NARFBs have not yet been mature and few appropriate organic active species can be applied so far. Heterocyclic aromatics have similar properties to aromatics, which can delocalize electrons and stabilize neutral species as well as radical cations and radical anions, which are regarded as promising active species. The introduction of heteroatoms, especially O, N, and S, which have high electronegativity, will improve the stability of the system. In this work, electrochemical properties of heterocyclic aromatics, including phenothiazine, thianthrene, carbazole and phthalimide, are studied. Substituent groups are introduced to the heteroatoms and benzene rings through organic synthesis methods. The redox potential, solubility and stability of active species are tuned with both electron donating groups and electron withdrawing groups, which can functionalize the molecules and improve the performance of RFBs.

Key words: Redox flow battery; Energy storage; Heterocyclic aromatics; Substituent groups

P13

Layered perovskite oxide with *in situ* exsolved nanoparticles as a highly stable and efficient anode for solid oxide fuel cellsNianjun Hou^{a,b}, Yicheng Zhao^{a,b*}, Yongdan Li^{a,b,c*}^a School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, China^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin, 300072, China^c Department of Chemical and Metallurgical Engineering, Aalto University, Kemistintie 1, FI-00076 Aalto, Finland

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Abstract: Solid oxide fuel cells (SOFCs) with a high energy conversion efficiency and low emissions are considered as promising substitutes for traditional thermal power generators [1]. Methane is a potential fuel for SOFCs due to its abundant reserves. Meanwhile, the high H/C ratio of methane leads to low CO₂ emissions compared with other hydrocarbons. However, the symmetrical tetrahedron structure of methane results in strong carbon-hydrogen bonds with an average dissociation energy of about 440 kJ mol⁻¹. [2] Meanwhile, the conventional Ni based anode suffers from agglomeration, sulfur poisoning and carbon coking with hydrocarbon fuels. Thus, the development of novel anode materials with high activity and stability is essential for practical application. *In situ* exsolution has been developed as a strategy to prepare perovskite oxides with uniformly dispersed nanometallic particles. [3] Recently, A-site ordered PrBaMn₂O_{5+d} has been reported as a promising anode with high electrical conductivity and good catalytic activity for the electrochemical oxidation of both hydrogen and hydrocarbons. [4] In this work, La_{0.5}Ba_{0.5}Mn_{1-2x}Co_xFe_xO_{3-δ} (x=0, 0.05, 0.1) has been synthesized with the Pechini method and investigated as an anode material of SOFCs with H₂ and methane as fuels. The structure of the anode converts from a mixture of cubic and hexagonal phases to a perovskite structure with core-shell nanoparticles on the surface after reduction. The *in situ* exsolution process of the metals on the B sites is studied with an X-ray photoelectron spectrometer, a thermogravimetric analyzer and a transmission electron microscope. The doping of Co and Fe into B sites effectively improve the performance of the single cell with H₂ as the fuel. A single cell with La_{0.5}Ba_{0.5}Mn_{0.8}Co_{0.1}Fe_{0.1}O_{3-δ} anode and a 300-μm-thick La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} electrolyte layer exhibits a maximum power density (P_{\max}) of 98, 210, 383, 653 and 1479 mW cm⁻² with wet H₂ as the fuel at 650, 700, 750, 800 and 850 °C, respectively, and achieves P_{\max} of 145, 236 and 503 mW cm⁻² at 750, 800 and 850 °C, respectively when fueled with wet CH₄. Moreover, the anode exhibits a high coking resistance, and no remarkable degradation of the performance is observed when the cell is operated with methane as the fuel for more than 200 hours.

Key words: Solid oxide fuel cell, Perovskite, Anode, *In situ* exsolution**References**

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P14

Doped $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ Double Perovskite as Fuel Electrode for Solid Oxide Steam Electrolysis Cell

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Abstract: Solid oxide electrolysis cell (SOEC) is one of the most promising approaches to producing chemicals (e.g., H_2 , CO and hydrocarbons) using electricity [1]. As high-temperature (800-1000 °C) accelerates the rate of steam electrolysis reaction, non-noble metal materials can be used as electrodes of SOECs. Meanwhile, steam electrolysis process is environmentally friendly with no emission [2]. Ni-based cermet has been extensively used as fuel electrodes of SOECs because of its excellent catalytic activity. However, it experiences serious agglomeration of Ni particles and sulfur poison problems [3]. Recently, doped $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ with in situ exsolved core-shell nanoparticles has been developed as an anode material of solid oxide fuel cells, which shows a good catalytic activity and stability in both hydrogen and methane atmospheres [4]. In this work, $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ and $\text{La}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.8}\text{Co}_x\text{Fe}_{0.2-x}\text{O}_{3-\delta}$ ($x=0, 0.1, 0.2$) have been synthesized with the Pechini method and studied as the cathode material of a SOEC. The XRD results show that the structure of the material converts from a mixture of cubic and hexagonal phases to a tetragonal structure after reduction. The results of iodometry and thermogravimetry demonstrate that the doping of Co and Fe increases the oxygen vacancy content, and thus effectively improves the electrochemical performance of the cathode. A single cell with the configuration $\text{La}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.8}\text{Co}_{0.1}\text{Fe}_{0.1}\text{O}_{3-\delta} \mid \text{La}_{0.4}\text{Ce}_{0.6}\text{O}_2 \mid \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (300 μm -thick) $\mid \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ exhibits a current density of 2.1 A cm^{-2} at a voltage of 1.5 V at 850 °C.

Keywords: Solid oxide electrolysis cell, Perovskite oxides, Steam electrolysis, Fuel electrode

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P15**Construction of Cu₂O-based photocatalyst with enhanced photocatalytic activity and stability under visible light**Xue Luan¹, Qiuyang Huang¹, Cuijuan Zhang^{1*}, Yongdan Li^{*1,2}

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Abstract: Although large research efforts have been devoted to the photoelectrochemical (PEC) water splitting in the past several decades, the lack of efficient, stable and earth-abundant photoelectrodes remains a bottleneck for its practical application. Cuprous oxide (Cu₂O) is attracting increasing attention as cathode for PEC water splitting owing to appropriate band gap (2.0 eV), high theoretical solar to hydrogen conversion efficiency (18%) and high power conversion efficiency (20%), abundance, and environmental friendliness. However, a serious challenge with Cu₂O is its limited chemical stability in aqueous environments, i.e., photocorrosion. Herein, we present a simple and low-cost approach to prepare a highly stable Cu₂O-based photocathode. This work demonstrates the potential of earth-abundant light-harvesting material as catalysts for solar hydrogen production.

Key words: Cu₂O, photocathode, solar water splitting

P16

An all-iron non-aqueous redox flow battery

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Abstract: Redox flow battery (RFB) is a promising electrochemical energy storage device which stores its energy in the redox-active materials dissolved in liquid electrolytes circulating between the external reservoirs and the cell compartments. Compared to the traditional aqueous flow battery, non-aqueous redox flow battery (NARFB) holds the promise of achieving higher energy density owing to its broader electrochemical window. However, the cycling performance and battery efficiency is generally limited due to the low solubility of active materials in organic solvents and high resistance of the organic system. To address these issues, we demonstrate a NARFB based on organometallic complexes of iron (ferrocene) with a high solubility in acetonitrile. The anolyte active material was modified through molecular engineering to increase its solubility. Both anolyte and catholyte active materials are iron-based species to mitigate cross-contamination. A porous separator (Daramic) and an anion-exchange membrane were used in this organic flow battery. The cell shows a stable performance during 100 charge-discharge circles at a current density of 10 mA cm⁻² with both membranes, which is superior to most of other NARFB systems. Benefit from the superior chemical stability and fast kinetics of the active materials, the battery achieves a high cycle performance with a stable Coulomb efficiency around 98.7%, voltage efficiency of around 84.5% and energy efficiency of around 83.4% over 100 cycles with an anion-exchange membrane. These results indicate that the iron-based metal-organics non-aqueous redox flow battery is quite promising.

Key words: Electrochemical energy storage; Redox flow battery; Organometallic materials

P17

Water splitting: amorphous $\text{Fe}_y\text{Ni}_{1-y}\text{O}_x$ oxides as efficient electrocatalyst for oxygen evolution reaction

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Abstract: Water splitting into hydrogen and oxygen by electrolysis using electricity from renewable energy such as solar and wind is a promising way to store the excess electrical power and to produce high-purity hydrogen. The main challenge for water electrolysis, however, is the high overpotential required especially for the oxygen evolution reaction (OER). Developing efficient and cost-effective electrocatalysts for the OER is an appealing yet challenging work. The layered NiFe double hydroxides show high OER activity. Increasing evidences have proved that the amorphous metal oxides have higher OER activity than their crystalline counterparts. Herein, we prepared the amorphous nickel-iron oxide by the photochemical metal-organic deposition (PMOD) method. The resultant NiFe-oxides deliver 1 and 10 mA cm⁻² current density at the overpotential of 193 and 283 mV, respectively, for the OER in alkaline electrolyte. When the amorphous oxides are loaded onto the nickel foam, the overpotential can be further decreased.

Key words: Water splitting, oxygen evolution reaction, amorphous materials, nickel-iron oxide

P18**Amorphous $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ as efficient electrocatalyst for oxygen evolution reaction**

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Abstract: Recent years have witnessed the rapid development of catalysts for water electrolysis since this reaction is a promising strategy to address the intermittency of renewable energy such as solar and wind and to produce hydrogen of high energy density. However, the sluggish oxygen evolution reaction (OER) involving four-electron and four-proton transfer always jeopardizes the water splitting efficiency. Correspondingly, it is greatly desirable to develop catalysts of high OER activity.

The crystalline cobalt-based catalysts have been widely studied due to their high OER activity. Increasing reports show that the amorphous metal oxides have higher OER activity compared with their crystalline counterparts because of the more coordinately unsaturated surface sites, isotropic and single-phase nature. Herein, we access the amorphous $\text{Co}_{1-y}\text{Ce}_y\text{O}_x$ catalysts on fluorine doped tin oxide by the photochemical metal-organic deposition method. The results show that cerium doping greatly improves the catalytic activity of cobalt oxide. The overpotential at a current density of 10 mA cm^{-2} of $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x$ is 353 mV compared with 390 mV for CoO_x in 0.1 M KOH. The charge transfer processes for the OER is remarkably enhanced by Ce-doping. $\text{Co}_{0.9}\text{Ce}_{0.1}\text{O}_x$ was loaded onto nickel foam to further develop high performance OER catalysts.

Key words: water splitting, oxygen evolution reaction, amorphous materials, cobalt oxide

P19

Preparations and Photocatalytic Performances of Cesium Lead Bromide Quantum Dots and Its Water-resistant Composites

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Abstract: Recently, inorganic metal halide perovskite CsPbBr₃ has gained considerable attention in the field of solar energy utilization ^[1] duo to its beneficial optoelectronic properties such as high absorption coefficient, wide absorption range, direct and adjustable bandgap, and low-cost processability ^[2]. Additionally, perovskite CsPbBr₃ has a narrow band gap of 2.26 eV making it to have good visible light absorption capacity. They indicate that CsPbBr₃ may have great potential in photocatalysis. However, only limited reports have focused on their photocatalytic properties. For example, Xing et al ^[3] reported the photocatalytic reduction of CO₂ by CsPbBr₃ nanoparticles. However, the practical applications of CsPbX₃ nanocrystals (NCs) have been limited by their poor stability in water and air condition. The improvement of their water resistance/stability is essential for the wide applications.

Herein, we firstly prepared CsPbBr₃ quantum dots by anti-solvent precipitation and the role of water on the phase transformation is intensively investigated. The prepared CsPbBr₃ has been firstly applied in the photocatalytic degradation of antibiotics in ethanol solution as model degradation. The prepared CsPbBr₃ showed good photocatalytic performance and good stability in ethanol and reaction mechanism is also proposed. The prepared photocatalyst should have potential applications in the removal of pollutants in organic system.

Furthermore, core-shell CsPbBr₃@SiO₂ structure has been successfully synthesized by using CsPbBr₃ QDs as the core and SiO₂ as the shell from a simple precipitation coating method. The experimental parameters influencing the formation of CsPbBr₃@SiO₂ have been intensively studied and the best strategy for obtaining the stable CsPbBr₃@SiO₂ composite has been achieved. The phase transformation is studied and a formation mechanism is discussed from the well characterizations. It is interesting to find that the prepare sample is very stable and can work as an efficient photocatalyst for the degradation of antibiotic residues in water. The active species responsible for the photocatalytic process are identified and a reaction mechanism is suggested in the end. This opens new application of CsPbBr₃ in water.

In summary, the inorganic halide perovskite could play roles in photodegradation of refractory pollutants and open novel applications by designing new structures.

Key words: CsPbBr₃ quantum dots; Photocatalytic activity; CsPbBr₃@SiO₂ composite; Phase transformation

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P20**Electrochemical Study of Titanate Based catalyst in Direct Carbon Fuel Cell using Walnut and Almond Shells Biochar Fuel**

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Abstract: The direct carbon fuel cell (DCFC) is an efficient device that converts the carbon fuel directly into electricity with 100% theoretical efficiency contrary to practical efficiency around 60 %[1,2]. In this paper four perovskite anode materials $\text{La}_{0.3}\text{Sr}_{0.7}\text{M}_{0.07}\text{Ti}_{0.93}\text{O}_{3-\square}$ (M = Ni, Fe, Co, Zn) have been prepared using sol-gel technique to measure the performance of the device using solid fuel. These materials have shown reasonable stability and conductivity at 700 °C. Walnut and almond shell biochar fuels have been examined in DCFC at the temperature range 400-700 °C. Further structural analysis of as-prepared anode material using XRD technique reveals a single cubic perovskite structure with average crystallite size roughly 47 nm. In addition, Elemental analysis (EDX) has shown high carbon content and low nitrogen and sulfur contents in the obtained biochar. Subsequently, the superior stability of as-prepared anode materials is evident by thermogravimetric analysis (TGA) in pure N₂ gas atmosphere. Conversely, the LSFT anode has shown the highest conductivity of 7.53 Scm⁻¹ at 700 °C. The obtained power density for LSFT anode mixed in sub-bituminous coal, walnut and almond shells biochar is of 68, 55, 48 mWcm⁻² respectively. A significant improvement in performance of DCFC (78mWcm⁻²) was achieved using sub-bituminous coal.

Keywords: Perovskite, Walnut Shell, Almond Shells, Electrical Conductivity, Power Density

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P21

Effects of Surface Modification on the Reactivity of Activated Carbon in Direct Carbon Fuel Cells

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Abstract: A direct carbon fuel cell (DCFC) is the only fuel cell type that converts the chemical energy stored in solid carbon, which could be obtained from coal and biomass, into electricity directly via an electrochemical route with a higher energy efficiency and less pollution than conventional coal-fired power plants [1, 2]. In this work, the effect of the surface properties of carbon fuel on its electrochemical oxidation reactivity is investigated. Activated carbon (AC) is pre-treated with HNO₃ and NaOH, respectively, which both increase the oxygen content and decrease the graphitization degree of AC. The amount of hydroxyl groups on the surface of AC increases after the treatments with HNO₃ and NaOH, and then decreases during the subsequent heating process in an inert atmosphere. On the contrary, the carbonyl and quinone groups on the surface of the activated carbon remain stable during the heating process. The activated carbon treated with HNO₃ shows the highest reactivity towards oxidation and reverse Boudouard reactions due to its lowest graphitization degree and highest oxygen content. The performance of the cell supported by a 380- μm -thick yttria stabilized zirconia (YSZ) electrolyte layer with 60 mol% La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃-40 mol% Gd₂O₃ doped CeO₂ as the electrodes is investigated with various fuels. The cell with AC-HNO₃ as the fuel exhibits the lowest polarization and the highest maximum power density of 128 mW cm⁻² at 800 °C.

Keywords: Direct carbon fuel cell, Activated carbon, Surface modification, Electrochemical oxidation, Oxygen functional groups

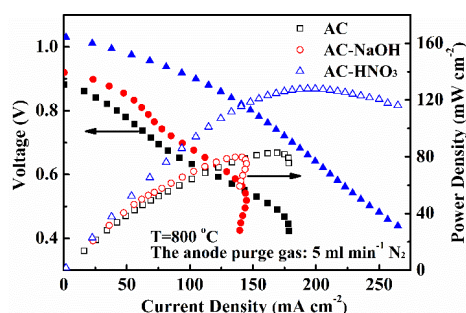


Fig. 1. *I-V* and *I-P* curves of single cells with various carbon fuels and 5 ml min⁻¹ N₂ as the anode purge gas at 800 °C.

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P22**Interaction analysis of Ni–perovskite and its application as an anode for syngas-fueled solid oxide fuel cells**

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Abstract: Solid oxide fuel cells (SOFCs) are promising energy converting devices with a high efficiency and little emission [1-2]. Recently, the PrBaMn₂O_{5+d} perovskite with uniformly exsolved metal particles has been reported as an outstanding anode for hydrocarbon-fueled fuel cell. Besides, interaction and effects of Ni–perovskite such as Ni–SrTi_{0.7}Fe_{0.3}O_{3-δ} and Ni–La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ (LSCF) have been studied and showed promising activity in methane steam reforming reaction and ethanol-fueled fuel cell [3-4]. Based on these ideas, Ni being alloyed or formation of other intermetallic compound with exsolved nano-metal particles from supported perovskite might bring about novel catalytic effects. In this work, Ni–La_{0.6}Sr_{0.4}FeO_{3-δ} (Ni-LSF) powder was synthesized by impregnating 10 wt.% Ni on LSF powder. The cell with Ni-LSF anode and Ce_{0.8}Sm_{0.2}O_{1.9}-carbonate composite electrolyte shows a maximum power density of 587 mW cm⁻² at 700 °C with syngas as fuel. The performance and stability were measured with H₂ and syngas as fuel, respectively. Furthermore, the structure and the morphology of the Ni-LSF material before and after reduction were characterized with XRD and SEM. The exsolution phenomenon of the Fe metal particles and interaction with Ni were investigated with XPS and TEM. Moreover, the anode surface after stability test was studied with TG and SEM-Mapping.

Key words: anode, catalyst, hydrocarbon fuel, SOFC, perovskite

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P23

ZnO nanoclusters supported on dealuminated zeolite β as a novel catalyst for direct dehydrogenation of propane to propylene

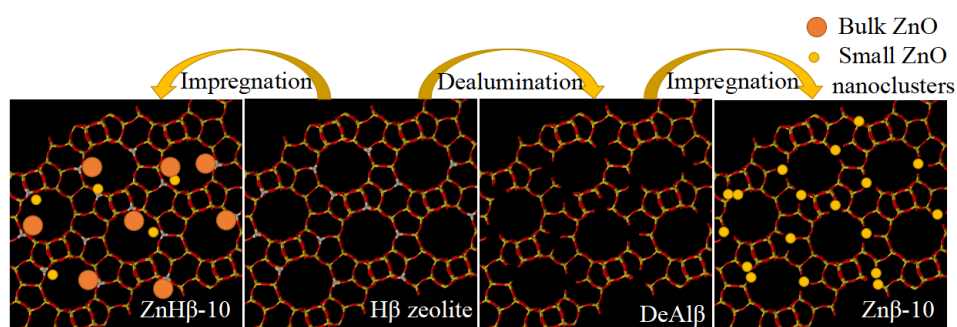
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Abstract: Small ZnO nanoclusters supported on dealuminated β zeolite were prepared and evaluated for catalyzing direct dehydrogenation of propane to propylene (PDH), exhibiting high catalytic performance. N_2 sorption, XRD, TEM, ^{27}Al and ^{28}Si MAS NMR, IR, XRF, DR UV-vis, XPS, and NH_3 -TPD techniques were employed to characterize the physicochemical properties of this novel catalyst system. It is found that the Zn species can be accommodated in the vacant T-atom sites of dealuminated β zeolite due to the reaction of aqueous zinc acetate solution with silanol groups, and thus, producing massive small ZnO nanoclusters as active phases in PDH. Additionally, dealuminated β zeolite can greatly depress side reactions attributable to the absence of strong acid sites, thereby guaranteeing high catalytic activity, propylene selectivity and stability. As a result, the optimal catalyst of 10 wt% Zn loaded on dealuminated β zeolite exhibits a high initial propane conversion of around 53% and a superior propylene selectivity of about 93% at a space velocity of $4000\text{ cm}^3\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$, together with the high stability and satisfactory reusability. This study may open a new way to design and synthesize highly active PDH catalysts with high selectivity and stability.



Key words: active sites, dealuminated zeolite β , propane dehydrogenation, propylene, ZnO