

Thursday Evening Poster Sessions, October 25, 2018

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room Hall B - Session HC-ThP

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic Poster Session

HC-ThP-1 Analyses of Nano-Crystalline Structure in Precipitated Iron-Based Catalysts for Fischer-Tropsch Synthesis, Dong Hyun Chun, G Rhim, J Park, Korea Institute of Energy Research, Republic of Korea; C Kim, Kookmin University, Republic of Korea; J Bae, M Youn, H Jeong, S Kang, H Lee, J Yang, H Jung, Korea Institute of Energy Research, Republic of Korea

FTS (Fischer-Tropsch synthesis) is a process invented by two German researchers, Franz Fischer and Hans Tropsch, in the 1920s, which catalytically convert syngas ($H_2 + CO$) into hydrocarbon products: $nCO + \{2n(+1)\}H_2 \rightarrow C_nH_{2n(+2)} + nH_2O$. Iron-based catalysts are highly promising for the FTS due to their high activity and low cost. A precipitation technique is one of the commercially proven methods for preparation of iron-based FTS catalysts as this technique can easily generate nano-crystalline particles. In general, the as-prepared precipitated iron-based catalysts are known to be composed of hematite ($\alpha-Fe_2O_3$) that are inactive for the FTS. Thus, the as-prepared catalysts must be subjected to a proper activation treatment to change the as-prepared catalysts into active phases such as Fe_5C_2 and Fe_2C . This means that the crystal structure of as-prepared catalysts and their reduction and carburization behavior can critically influence the catalytic performance of precipitated iron-based FTS catalysts. But, it is very difficult to reveal the exact relationship among the crystal structure of as-prepared catalysts, their reduction and carburization behavior, and the catalytic performance for FTS because high-performance iron-based FTS catalysts are usually composed of a mixture of several iron species with nano-crystalline structure. In this presentation, we analyzed the crystal structure of precipitated iron-based FTS catalysts in detail by X-ray diffraction and Mössbauer spectroscopy. We found that a significant amount of ferrihydrite ($FeOOH \cdot nH_2O$, $0 < n < 1$) can coexist with hematite in the as-prepared catalysts, which depends on the precipitation conditions. Furthermore, we revealed that the ferrihydrite plays a crucial role in determining the catalytic performance as well as the reduction and carburization behavior of the catalysts.

HC-ThP-2 In situ Infrared and Catalytic Reaction Studies of Active Sites on Pt Nanoparticles Supported on Nanosponge Oxides under CO oxidation, Sunyoung Oh, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; C Jung, Institute for Basic Science (IBS), Republic of Korea; H Ha, Chungnam National University, Republic of Korea; C Jo, Institute for Basic Science (IBS), Republic of Korea; S Moon, Y Kim, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; W Doh, Institute for Basic Science (IBS), Republic of Korea; H Kim, Chungnam National University, Republic of Korea; R Ryoo, J Park, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Platinum-based heterogeneous catalysts are mostly used in various commercial chemical processes because of their highly catalytic activity influenced by the metal-oxide interaction. To design the rational catalysts with high performance, it is crucial to understand the reaction pathway. Here, Pt nanoparticles supported on nanosponge oxides such as TiO_2 and SnO_2 with advantage of high surface area, thermal stability, and quite high interfacial sites were synthesized and utilized in CO oxidation reaction to prove the interaction of the metal and support. CO oxidation results show high activity for Pt supported on TiO_2 nanosponge catalyst, which is associated to the O_2 dissociation at the Pt/ TiO_2 perimeter sites. *In situ* infrared (IR) spectroscopic observation indicates that oxygen molecule bond is activated at the Pt/ TiO_2 interface by neighbor CO molecules on the Pt surface. The computational calculations for proposed reaction mechanism for O_2 activation at Pt/ TiO_2 interface are consistent with experiment results. In contrast, we directly observe that absence of adsorbed CO on Pt surface for Pt/ SnO_2 catalyst by using IR because the Pt surface as active site was covered with a shell of tin oxide after hydrogen pre-treatment. These results allow us to obtain the insight into the nature of metal-support interface between Pt and nanosponge oxide supports and reaction pathways of CO oxidation for Pt-based supported catalysts.

HC-ThP-3 Activity of Bimetallic Pt-Re Surfaces and Influence of the Support for the Water-Gas Shift Reaction, Amy Brandt¹, T Maddumapatabandi, D Shakya, S Farzandh, D Chen, University of South Carolina

Bimetallic Pt-Re clusters are systematically investigated on model supports in order to understand the effects of metal-metal interactions and metal-support interactions on cluster formation and catalytic activity for clean hydrogen production via the water-gas shift (WGS) reaction. Bimetallic catalysts have exhibited unique characteristics different from their single metal constituents, and interactions with the support are believed to have an influence on the chemistry taking place at the interface. Pure and bimetallic Pt-Re surfaces were prepared in ultrahigh vacuum (UHV) by vapor-deposition on model supports of $TiO_2(110)$, Pt(111), and highly oriented pyrolytic graphite (HOPG). WGS activity was studied in a UHV-coupled microreactor operating at a temperature of 160 °C and pressures of ~ 1 atm. On the TiO_2 support, bimetallic clusters consisting of Pt at the surface and Re residing subsurface were found to have the highest activity for the WGS reaction, with turnover frequencies (TOF) nearly twice as high as monometallic Pt on TiO_2 . The TOF on the Pt single crystal was lower than Pt clusters supported by TiO_2 . A Pt-Re alloy with pure Pt at the surface and Re residing subsurface showed enhanced activity over pure Pt(111). Pt clusters deposited on TiO_2 were investigated by scanning tunneling microscopy and found to have an increasing number of perimeter atoms compared to total atoms at decreasing Pt coverages. WGS experiments revealed a trend of increasing TOF for Pt coverages with increasing perimeter atom percentages, suggesting the Pt/ TiO_2 interfacial sites contribute to WGS activity. An alternative support of HOPG confirmed that Pt clusters on TiO_2 have a greater TOF than Pt clusters on HOPG for the WGS reaction. In contrast to bimetallic Pt-Re clusters on TiO_2 , Pt-Re clusters on HOPG consisted of higher concentrations of Re at the surface, leading to lower TOFs for Pt-Re clusters on HOPG than the monometallic Pt on HOPG surface.

HC-ThP-4 In-Operando Photoluminescence Imaging of a Single-Layer Molybdenum Disulfide Catalyst, Koichi Yamaguchi, University of California - Riverside; S Naghibi, W Coley, L Bartels, University of California, Riverside

MoS_2 is the key industrial catalyst for hydrodesulfurization (HDS) of crude oil. Atomistic investigation of the HDS reaction is hampered by the elevated pressures and temperatures required for HDS. There is close correlation between the current industrial catalyst material and model single-layer MoS_2 flakes. We developed a new experimental approach that relies on strong photoluminescence (PL) of monolayer MoS_2 that we grow efficiently on an inert SiO_2 substrate. We find that wide-field PL imaging is possible even under near in-operando condition and can serve as a reporter of the chemical state and spatial variation of the catalyst material. Our experiments proceed under up to 1atm of hydrogen, any volatile thiol, and at temperatures of up to 400 °C. Spatially resolved images allow us to distinguish between reactions at island edges and the basal plane; desulfurization and binding of organic species to the catalyst are reported as bleaching of the photoluminescence. Concomitant mass spectrometric analysis allows us to correlate the variation in the island PL with different reaction regimes.

HC-ThP-5 Efficient Photoelectrochemical Water Splitting in Band Edge Engineered Metal Oxide Heterostructure Photoanode for Solar Fuel Production, Nisha Kodan, Thin Film Laboratory, Department of Physics, IIT Delhi, India; A Singh, Division of Chemical Physics, Department of Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden; B Mehta, Thin Film Laboratory, Department of Physics, IIT Delhi, India

Solar induced splitting of water in a photoelectrochemical (PEC) cell into hydrogen and oxygen appears to be the most promising, economically viable and sustainable way for the production of hydrogen. PEC cells integrate solar energy harvesting and water electrolysis into a single event on photoactive material surfaces. The efficient separation of photogenerated electron-hole pairs and stability against corrosion are critical preconditions for a photoelectrode to achieve a high photoelectrochemical performance. However, the (photo)oxidation of water is a challenging electrochemical reaction demanding robust but inexpensive electrode materials. For large-scale photoelectrochemical (PEC) hydrogen production, systematic efforts towards design of inexpensive and stable semiconductor photoelectrode materials, permitting sustained splitting of water in PEC cells are desirable. Yet, finding an optimal material for PEC cell is a very difficult task due to three

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main requirements in a single material system: 1) chemical stability 2) visible light absorption and 3) band edges matching to redox levels of water. The band edge engineering strategy, i.e., band re-alignment in $\text{TiO}_2/\text{BiVO}_4$ and $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$ heterostructure was achieved by gas-phase modification technique i.e. hydrogenation of the top TiO_2 layer which strongly promotes interfacial interaction at the junction and leads to an effective interfacial charge separation and charge transport. The hydrogen treated $\text{TiO}_2/\text{BiVO}_4$ heterostructure photoanode exhibit significant enhancement of visible light absorption and improve the photoelectrochemical response with a photocurrent density of 4.44 mA/cm^2 as compared to pristine BiVO_4 (0.84 mA/cm^2) and $\text{TiO}_2/\text{BiVO}_4$ (0.28 mA/cm^2) photoanodes. Using electronic structure calculations, an alteration of the band alignment is predicted at the heterojunction from type I to type II by hydrogen treatment of the top TiO_2 layer which results in improved PEC performance of hydrogenated $\text{TiO}_2/\text{BiVO}_4$ heterostructure photoanode.

HC-ThP-6 Comparative Reactivity of Oxide and Metallic Phases on Rh(111), *R Farber, M Turano, W Walkosz, Christopher Smith, D Killelea, Loyola University Chicago*

Recently, the understanding of the role of surface oxides in catalytic activity has changed. Instead of being thought of as poisons, similar to bulk oxides, they are now believed to be effective promoters of selective catalysis. We have chosen to study oxidation on Rh(111) as a model system; Rh effectively promotes oxidation reactions and is a benchmark system for models of heterogeneously catalyzed chemistry. Using atomic oxygen (AO) as an oxidizing agent, high coverage oxygen adlayers and oxides can be formed under ultra-high vacuum (UHV) conditions. Careful control of the AO exposure parameters allowed for the selective growth of the RhO_2 surface oxide, surface adsorbed oxygen, and subsurface oxygen. Furthermore, formation of the RhO_2 surface oxide was shown to rely not only on the presence of defects, as evident by the selective growth along step edges (Figure 1), but also on high concentrations of oxygen absorbed below the surface of the metal.

Utilizing our surface preparation techniques to carefully prepare specific oxidized Rh(111) surfaces, we use carbon monoxide (CO) as a probe molecule to track surface structure specific reactivity via CO oxidation. Exposing RhO_2 to CO, TPD and STM are employed to gather information on CO_2 production, residual O_2 population, and surface structure evolution during CO oxidation reactions. In order to determine the actual reaction mechanism of CO oxidation on oxidized Rh(111), STM is needed to provide atomic scale resolution of the active surface adsorbates during the reaction progression, as shown in Figure 1. By combining spatially resolved structural information with CO_2 production and oxygen consumption, we will be able to identify which oxidic species and surface sites contribute to CO oxidation. This information will help in determining the exact reaction mechanism occurring during CO oxidation over an oxidized Rh surface.

HC-ThP-7 Hybrid Adsorbent Catalyst for Siloxane Removal: Fe-BEA Zeolites, *Alba Cabrera-Cadony, University of Girona, Spain; E Santos-Clotas, M Martin, University of Girona*

Different types of both natural and synthetic zeolites, covering a wide range of physical and chemical properties, were evaluated as adsorbents/catalyst for siloxane removal in lab-scale gas phase adsorption tests of octamethylcyclotetrasiloxane (D4). After bed exhaustion, wet oxidation processes were used for the regeneration of the spent zeolite samples, including ozonation and Fenton-like treatment of the Fe-amended zeolites using hydrogen peroxide. New adsorption tests were performed after these AOP-driven regeneration processes.

The results on the uptake of gaseous D4 by various zeolites led to the conclusion that BEA type materials presented the highest catalytic activity for the siloxane ring-opening and formation of α - ω -silanediols due to the high content of Bronsted and Lewis acidic sites. Those silanediols formed on the BEA surface were detached from the catalytic acidic sites when water was available, and were narrow enough to diffuse into the channels, hence enhancing the removal efficiency for D4.

The water soluble α - ω -silanediols formed by the catalytic activity of the iron exchanged Fe-BEA type zeolites during D4 adsorption were easily removed by wet regeneration treatment with water, however, the regeneration was incomplete, i.e. the adsorption capacity was partially recovered. Adding H_2O_2 in a heterogeneous Fenton-like regeneration treatment led to a complete recovery of the adsorption capacity of the Fe-zeolites samples.

However, on successive adsorption/regeneration cycles, the recyclability of the Fe-zeolites catalysts was hampered by the accumulation of

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carbonaceous materials on the material surface, which caused a loss of the catalytic activity, affecting both the adsorption and the regeneration stages.

Bronsted acidic sites (BAS) and Lewis acidic sites (LAS) promoted the D4 transformation into silanediols, as shown in Figure 1, which was the fundamental step that ruled the D4 uptake on the gas adsorption process. At the same time, the iron exchanged in Fe-BEA type zeolites promoted the catalytic activity towards Fenton-like reactions for the regeneration of the exhausted materials.

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