

## Nanomaterials

### Room Naupaka Salon 5 - Session NM-MoE

#### NanoCatalysis

Moderator: Fumitaro Ishikawa, Ehime University

#### 5:40pm NM-MoE-1 Strong Interactions Between the Admetal and Molybdenum Carbide Substrates for Catalyzing H<sub>2</sub> Related Reactions, *Chuan Shi*, Dalian University of Technology, China **INVITED**

Transition metal carbides (TMCs) are known to display catalytic properties similar with those of noble metals. The high activity of TMCs compared with their parent metals originates from a modification of the electronic properties from the addition of carbon, which in turn affects the binding strength and the reactivity of adsorbates. In the present talk, special interest will be focused on employing TMCs as a substrate to load another metal and the strong interactions between the admetal and the carbide. Several reactions involved will be discussed, including dry reforming of methane, water gas shift and reverse water gas shift reactions [1,2], as well as liquid phase reforming of methanol for H<sub>2</sub> production [3].

#### References:

[1] X. Zhang, X. Zhu, L. Lin, S. Yao, M. Zhang, X. Liu, X. Wang, Y.W. Li, C. Shi\*, D. Ma, "Highly Dispersed Copper over  $\beta$ -Mo<sub>2</sub>C as an Efficient and Stable Catalyst for the Reverse Water Gas Shift (RWGS) Reaction", *ACS Catalysis* 7 (2017) 912-918.

[2] S. Yao, X. Zhang, W. Zhou, R. Gao, W. Xu, Y. Ye, L. Lin, X. Wen, P. Liu, B. Chen, E. Crumlin, J. Guo, Z. Zuo, W. Li, J. Xie, L. Lu, C.J. Kiely, L. Gu, C. Shi\*, J.A. Rodriguez\*, D. Ma\*, "Atomic-layered Au clusters on  $\alpha$ -MoC as catalysts for the low-temperature water-gas shift reaction", *Science*, (2017). *Science*, 357, (2017) 389.

[3] L. Lin, W. Zhou, R. Gao, S. Yao, X. Zhang, W. Xu, S. Zheng, Z. Jiang, Q. Yu, Y.W. Li, C. Shi\*, X.D. Wen, D. Ma\*, "Low-temperature hydrogen production from water and methanol using Pt/ $\alpha$ -MoC catalysts", *Nature*, 544 (2017) 80-83

#### 6:20pm NM-MoE-3 Nanostructured MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> Powders and Films for Chemical-Looping Oxidative Dehydrogenation of Ethane, *H. Henry Lamb, P Novotný, S Yusuf, F Li*, North Carolina State University

Ethylene, a major petrochemical building block, is produced industrially by endothermic steam cracking of ethane and petroleum naphtha at 800-850°C. Catalytic oxidative dehydrogenation (ODH) of ethane offers huge potential for reductions in energy consumption and greenhouse gas emissions; however, ethane ODH using co-fed O<sub>2</sub> also requires costly cryogenic air separation [1]. As an alternative, we are investigating redox catalysts that operate in a cyclic mode (chemical looping, CL) and utilize lattice oxygen (O<sup>2-</sup>) as the sole oxidant [2-3]. One monolayer (1 ML) equivalent MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by conventional impregnation and calcination methods contain highly dispersed supported molybdate species and exhibit high ethylene selectivity (>95%) in CL-ODH at 500-550°C. In contrast, at higher MoO<sub>3</sub> loadings the Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> bulk phase predominates, as evidenced by Raman spectroscopy and x-ray diffraction (XRD); these catalysts have somewhat higher activity albeit 10-12% lower ethylene selectivity under equivalent conditions. X-ray photoelectron spectroscopy (XPS) studies indicate that high ethylene selectivity correlates with reduction of Mo<sup>VI</sup> to Mo<sup>V</sup>. The presence of Mo in lower oxidation states (+V, +IV) triggers H<sub>2</sub> and CH<sub>4</sub> generation resulting in selectivity loss. Interaction of molybdate species with the Al<sub>2</sub>O<sub>3</sub> support appears to decrease reducibility and enhance ethylene selectivity in CL-ODH. Even after extended reduction in ethane at 550°C, the monolayer catalyst retained about 25% Mo<sup>VI</sup>. In contrast, for 3 ML equivalent catalysts, surface Mo<sup>VI</sup> is rapidly consumed, and its concentration eventually approaches zero. To better elucidate the nature of the catalytically active sites, model catalysts consisting of nanostructured MoO<sub>3</sub> films on c-plane sapphire were deposited at 580°C by molecular beam epitaxy using a conventional Knudsen cell. The sapphire substrate after annealing at 700°C in UHV exhibited a streaky reflection high-energy electron diffraction (RHEED) pattern. Films deposited at short times (<1 min) were polycrystalline with relatively smooth surfaces (1.1 nm RMS roughness by atomic force microscopy). XPS revealed that MoO<sub>3</sub> films deposited *in vacuo* were oxygen-deficient. Surface asperities grew with deposition time and with annealing at 700°C in UHV. The catalytic properties of the films are currently under investigation using molecular beam methods.

#### References:

1. C.A. Gärtner, A.C. van Veen, J.A. Lercher, *ChemCatChem* 5 (2013) 3196-3217.

2. S. Yusuf, L. Neal, V. Haribal, M. Baldwin, H.H. Lamb, F. Li, *Appl. Catal. B* 232 (2018) 77-85.

3. P. Novotný, S. Yusuf, F. Li, and H.H. Lamb, *Catal. Today* (2018) in press.

#### 6:40pm NM-MoE-4 Fabrication of Visible Light Active Nanostructured TiO<sub>2</sub>/Cu<sub>2</sub>O Heterojunction Thin Films, *Anna Patricia Cristobal, M Ramos, A Montallana*, University of the Philippines, Philippines; *L Zhang, J Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China; *M Vasquez*, University of the Philippines, Philippines

Designing multiphase or multicomponent semiconductor heterojunctions is a promising strategy to enhance the performance of photocatalytic materials. Titanium dioxide (TiO<sub>2</sub>) is a material of interest as a photocatalytic material because of its availability, stability, and cost-effectiveness. However, one major drawback of TiO<sub>2</sub> is its wide band gap resulting to photocatalytic activity in the UV region only. Through heterojunction coupling of TiO<sub>2</sub> with a lower band gap semiconductor such as cuprous oxide (Cu<sub>2</sub>O) with a direct band gap of 2.17 eV, visible light active photocatalytic activity can be achieved. TiO<sub>2</sub>/Cu<sub>2</sub>O heterojunction thin films were assembled in a configuration wherein the junction of the coupled semiconductors is exposed to light irradiation for photocatalysis. This design ensures that photocatalytic reaction can occur in both semiconductors since they are exposed to the light source. A layer of TiO<sub>2</sub> thin film was deposited on (100) silicon (Si) substrate via reactive RF magnetron sputtering coupled with post deposition thermal annealing at 500°C. To form the heterojunction, ordered Cu clusters were patterned on top of the TiO<sub>2</sub> layer through a mask. The deposited Cu were transformed into Cu<sub>2</sub>O by thermal oxidation at 200°C in air atmosphere followed by slow cooling at a rate of 0.48°C/min. The TiO<sub>2</sub>/Cu<sub>2</sub>O heterojunction films were characterized using XRD and FE-SEM with EDS mapping. Photocatalytic performance was evaluated by visible light photodegradation of methylene blue dye as the test analyte. The XRD pattern of the TiO<sub>2</sub>/Cu<sub>2</sub>O heterojunction film indicated the existence of rutile and anatase phases of TiO<sub>2</sub> as well as the existence of mostly Cu<sub>2</sub>O phase. SEM image of the TiO<sub>2</sub>/Cu<sub>2</sub>O showed a patterned thin film design composed of a TiO<sub>2</sub> thin film layer decorated with grain-like Cu<sub>2</sub>O clusters that are approximately 500  $\mu$ m in diameter. At higher magnification, the TiO<sub>2</sub> thin film exhibited a porous columnar structure while the Cu<sub>2</sub>O is characterized by terraced grain-like structures. Using an effective thin film surface area of 1.0 cm x 2.5 cm, around 50% removal rate of methylene blue was observed in 6 h of visible light irradiation. This promising approach of designing immobilized heterojunction thin films offers a potential for wastewater treatment applications using visible light irradiation.

#### 7:00pm NM-MoE-5 Enhanced Photocatalytic Activity of Plasma-modified Electrospun PVA/TiO<sub>2</sub> Nanocomposites, *Arantxa Danielle Montallana, A Cristobal*, University of the Philippines, Philippines; *B Lai, J Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China; *M Vasquez*, University of the Philippines, Philippines

Poly(vinyl alcohol)/titanium oxide (PVA/TiO<sub>2</sub>) nanocomposites were successfully synthesized using the electrospinning method. 1% (w/v) <25 nm TiO<sub>2</sub> nanoparticles (NP) were dispersed in 12% (w/v) PVA solution and was electrospun using the following parameters: V = 15 kV, tip-to-collector distance = 15 cm, and flow rate = 0.5 mL/hr. The nanofibers were collected on an aluminum foil mounted to a 3 in diameter grounded electrode rotating at ~850 rpm. Scanning electron microscopy images revealed a smooth and continuous fiber morphology with average fiber diameter of 281.84  $\pm$  53.47 nm. Energy dispersive x-ray spectroscopy maps showed the dispersion of TiO<sub>2</sub> NPs in the nanofiber mats (NFMs). Raman spectral analysis showed TiO<sub>2</sub> peaks at 142.76, 394.64, 515.42, and 639.07 cm<sup>-1</sup> confirming the integration of the NPs in the NFM. No changes were observed in the PVA peak at 2911.7 cm<sup>-1</sup> after TiO<sub>2</sub> NP loading, implying that the addition of TiO<sub>2</sub> NPs did not alter the chemical composition of PVA and TiO<sub>2</sub>. The NFMs were irradiated with a 13.56 MHz radio frequency plasma system using oxygen gas for 1 min exposure time. Plasma exposure allowed the controlled etching of the nanofiber to expose the TiO<sub>2</sub> NP on the surface. Using a 3 x 3 cm<sup>2</sup> NFM, photodegradation of methylene blue (MB) as the test analyte under UV irradiation was conducted. UV-vis spectral analysis was used to monitor the change in concentration of MB. After 9 hr irradiation, pristine samples showed 83% removal of the dye while plasma-treated samples showed 90% removal rate. Using only TiO<sub>2</sub> NP, 95% removal efficiency was achieved after 4 hr UV irradiation. However, use of NPs only for photodegradation is not advisable since it

# Monday Afternoon, December 3, 2018

becomes difficult to collect and reuse the NPs. Thus, immobilizing the TiO<sub>2</sub> NPs would allow reusability of the photocatalytic nanocomposites.

7:40pm **NM-MoE-7 Large Scale Production of Nanoparticle Catalysts for Biomass Conversion Processes**, *E Roberts, L Wang*, University of Southern California; *F Baddour, D Ruddy, S Habas*, National Renewable Energy Laboratory, USA; *N Malmstadt, Richard Brutchey*, University of Southern California

In order to realize more sustainable routes for the conversion of biomass into useful liquid fuels, the use of lower-cost and more Earth-abundant catalysts is required. This necessitates the development of advanced catalysts that promote the desired transformations (e.g., hydrogenation, deoxygenation), while resisting deactivation, and that can be produced cost-effectively at relevant scales. Advances in the controlled synthesis of colloidal nanoparticle catalysts have resulted in the demonstration of promising catalytic performance for these materials, with Earth-abundant transition metal and transition metal carbide nanoparticles representing two such examples. Research by our team has focused on developing chemistry that enables precise control over nanoparticle catalyst phase and/or morphology. This presentation will focus on recent developments regarding the translation of these chemistries to continuous flow reactors for nanoparticle catalyst scale up. A key metric for scale up is ensuring that the resulting nanoparticles synthesized in flow are functionally equivalent to those produced in small (mL) batch reactors. The catalytic performance of these nanoparticles will be compared between those produced in batch and continuous flow, and further compared to their “bulk” material equivalents, for key transformations of model biomass compounds.

8:00pm **NM-MoE-8 Influence of a Tailored Nanoparticle Composite Cathode on Electrochemical Properties of Anode-Supported Solid Oxide Fuel Cells**, *Jong-Eun Hong, H Ishfaq, T Lim*, Korea Institute of Energy Research (KIER), South Korea; *S Lee*, Korea Institute of Energy Research (KIER), South Korea, South Korea; *K Lee*, DGIST, South Korea; *R Song*, Korea Institute of Energy Research (KIER), South Korea

Application of nanocatalysts to a solid oxide fuel cells cathode is expected to increase triple phase boundary (TPB) density and electrocatalytic reactivity to oxygen reduction reaction, resulting in performance improvement. Thus a conventional Sr- and Fe-doped LaCoO<sub>3</sub> (LSCF) based composite cathode was tailored with nanoparticles of a multi doped ceria that has an enhanced ionic conductivity and evaluated for electrochemical properties. In this study, Sm- and Nd-doped ceria (SNDC) nanoparticles were successfully prepared on the composite cathode via an in situ sol-gel process, which was confirmed by field emission scanning electron microscopy analysis. The tailored nanoparticle cathode indicated an increase in power density for a reduction of polarization resistance in anode supported SOFCs. It was attributed that more conductive nanoparticles led to enlarge the specific surface area and promote the reactivity for the cathode reaction.

## Author Index

### Bold page numbers indicate presenter

— B —

Baddour, F: NM-MoE-7, 2  
Brutchev, R: NM-MoE-7, **2**

— C —

Chu, J: NM-MoE-4, 1; NM-MoE-5, 1  
Cristobal, A: NM-MoE-4, **1**; NM-MoE-5, 1

— H —

Habas, S: NM-MoE-7, 2  
Hong, J: NM-MoE-8, **2**

— I —

Ishfaq, H: NM-MoE-8, 2

— L —

Lai, B: NM-MoE-5, 1

Lamb, H: NM-MoE-3, **1**

Lee, K: NM-MoE-8, 2

Lee, S: NM-MoE-8, 2

Li, F: NM-MoE-3, 1

Lim, T: NM-MoE-8, 2

— M —

Malmstadt, N: NM-MoE-7, 2

Montallana, A: NM-MoE-4, 1; NM-MoE-5, **1**

— N —

Novotný, P: NM-MoE-3, 1

— R —

Ramos, M: NM-MoE-4, 1

Roberts, E: NM-MoE-7, 2

Ruddy, D: NM-MoE-7, 2

— S —

Shi, C: NM-MoE-1, **1**

Song, R: NM-MoE-8, 2

— V —

Vasquez, M: NM-MoE-4, 1; NM-MoE-5, 1

— W —

Wang, L: NM-MoE-7, 2

— Y —

Yusuf, S: NM-MoE-3, 1

— Z —

Zhang, L: NM-MoE-4, 1