

Thu. Nov 11, 2021

Room-A

International sess.

[1A09-10] International sess.(1)

Chair: Toru Murayama (Tokyo Metropolitan Univ.)

1:00 PM - 2:00 PM Room-A (Room-A/Hakodate Areana)

[1A09] [Invited] Dehydrogenative conversion of small molecules -from alcohol electrolysis to methane polymerization-

○Hitoshi Ogihara¹ (1. Saitama Univ.)

1:00 PM - 1:30 PM

[1A10] [Invited] Precise synthesis, characterization, and reactivity of multi-functional catalysts

○Insoo Ro¹ (1. Seoul National University of Science and Technology)

1:30 PM - 2:00 PM

International sess.

[1A11-13] International sess.(2)

Chair: Takuma Higo (Waseda Univ.)

2:15 PM - 3:00 PM Room-A (Room-A/Hakodate Areana)

[1A11] Local structure of In-hydride species in zeolite and its reactivity for C₂H₆ dehydrogenation.

○Shunsaku Yasumura¹, Takashi Toyao^{1,2}, Zen Maeno¹, Ken-ichi Shimizu^{1,2} (1. Institute for catalysis, Hokkaido University, 2. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University)

2:15 PM - 2:30 PM

[1A12] Highly efficient removal of ethylene at 0 °C over Au-Pt/zeolite

○Minyue Lin¹, Haifeng Wang¹, Tetsuya Shishido¹, Hiroki Miura¹, Masatake Haruta¹, Toru Murayama^{1,2} (1. Tokyo Metropolitan University, 2. Yantai University)

2:30 PM - 2:45 PM

[1A13] Catalytic reduction of NO to ammonia by CO-H₂O over metal oxide supported catalysts

○Chaudhari Chaudhari Chandan¹, Keisuke Kobayashi¹, Yuichi Manaka^{1,2}, Tetsuya Nanba¹ (1. Fukushima Renewable Energy Inst., AIST, 2. Tokyo Inst. Tech.)

2:45 PM - 3:00 PM

International sess.

[1A14-16] International sess.(3)

Chair: Yasutaka Kuwahara (Osaka Univ.)

3:15 PM - 4:00 PM Room-A (Room-A/Hakodate Areana)

[1A14] Low-temperature conversion of methane to

methanol using carbon nanotubes supported catalyst

○Yingluo He¹, Guohui Yang¹, Noritatsu Tsubaki¹ (1. University of Toyama)

3:15 PM - 3:30 PM

[1A15] One-pot synthesis of HKUST-1 monolith for CO₂ adsorption

○Motomu Sakai¹, Hayata Hori², Ayaka Itoh³, Takaya Matsumoto⁴, Tsuyoshi Asano⁴, Masahiko Matsukata^{1,2,3,5}

(1. Research Organization for Nano & Life Innovation, Waseda University, 2. Department of Applied Chemistry, Graduate School of Advanced Science and Engineering, Waseda University, 3. Department of Applied Chemistry, Waseda University, 4. ENEOS Corporation, 5. Advanced Research Institute for Science and Engineering, Waseda University)

3:30 PM - 3:45 PM

[1A16] Zr doped Ni/CeO₂ prepared by Flame Spray Pyrolysis for CO₂ methanation

○Kakeru Fujiwara¹, Syugo Kayano¹, Dai Yoshioka² (1. Yamagata University Graduate school of Chemistry and Chemical Engineering, 2. Yamagata University Department of Chemistry and Chemical Engineering)

3:45 PM - 4:00 PM

Interenational sess.

[1A09-10] Interenational sess.(1)

Chair: Toru Murayama (Tokyo Metropolitan Univ.)

Thu. Nov 11, 2021 1:00 PM - 2:00 PM Room-A (Room-A/Hakodate Areana)

[1A09] [Invited] Dehydrogenative conversion of small molecules -from alcohol electrolysis to methane polymerization-

○Hitoshi Ogihara¹ (1. Saitama Univ.)

1:00 PM - 1:30 PM

[1A10] [Invited] Precise synthesis, characterization, and reactivity of multi-functional catalysts

○Insoo Ro¹ (1. Seoul National University of Science and Technology)

1:30 PM - 2:00 PM

Dehydrogenative conversion of small molecules – from alcohol electrolysis to methane polymerization

(Saitama Univ.) ○ Hitoshi Ogihara

1. Introduction

The conversions of small molecules to value-added chemicals are important processes in the chemical industry. This presentation will show several dehydrogenative conversions processes. One is the electrolysis of lower alcohols. We have developed electrolysis systems for the conversion of lower alcohols into esters, aldehydes, and acetals.^{1,2)} The feature of the system is to use membrane electrode assembly (MEA) as an electrolysis unit. As shown in Fig. 1, alcohols converted into esters, aldehydes, and acetals on the anode. Then, proton and electron transfer through a proton-exchange membrane (PEM) and an external circuit, respectively. Finally, the proton and electron are recombined on the cathode to generate hydrogen. The electrolysis using MEA can be a sustainable process for upgrading alcohols to chemicals because it can use renewable electricity and does not require chemical reagents (e. g., oxidants and electrolytes).

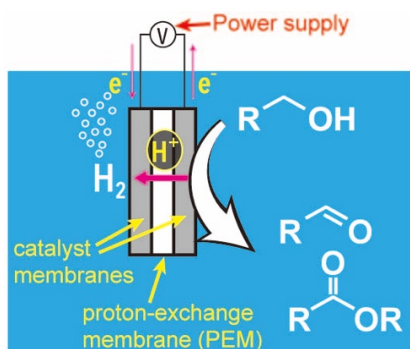


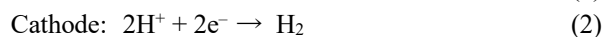
Fig. 1 Schematic diagram of electrolysis of alcohols using an MEA unit

Furthermore, we also studied the direct conversion of methane (CH_4) to C2 hydrocarbons and aromatics. CH_4 is expected to be used to produce essential chemicals, and recent developments in shale gas extraction technology are also supporting the use of natural gas in the chemical industry. However, CH_4 , which is the main component of natural gas, is highly stable due to its strong C–H bond and symmetric molecular structure, making it difficult to convert it into useful chemicals. In this presentation, some approaches to activate CH_4 molecules are reported.

2. Results and Discussion

2.1 Electrolysis of alcohols using an MEA unit

We have proposed processes to convert alcohols into chemicals via the dehydrogenative electrolysis using an MEA device. One example is the electrolysis of methanol (CH_3OH). We found that the electrolysis of pure CH_3OH using the MEA device selectively produced methyl formate,¹⁾ which is an important intermediate in the production of essential chemicals. The methyl formate and hydrogen are directly formed from CH_3OH according to Eqs 1 and 2. The average formation rate of methyl formate was $930 \text{ mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ and a turnover frequency was 468 h^{-1} . The productivity of methyl formate via pure CH_3OH electrolysis was comparable to previously reported systems such as heterogeneous catalysts and photocatalysts.



Next, we focused on ethanol ($\text{C}_2\text{H}_5\text{OH}$). The electrolysis of ethanol showed different behavior from CH_3OH electrolysis. In the electrolysis of pure $\text{C}_2\text{H}_5\text{OH}$, the main product was 1,1-diethoxyethane (DEE).²⁾ The formation scheme is shown in Fig. 2. Unlike CH_3OH , the electrochemical reaction of $\text{C}_2\text{H}_5\text{OH}$ is mainly produced acetaldehyde as follows:



where a Pt/C acted as an electrocatalyst, then, acetaldehyde is converted into DEE with the aid of PEM (Nafion, in this study). Nafion is known as a strong acid catalyst so that the Nafion promotes the following acetalization reaction.

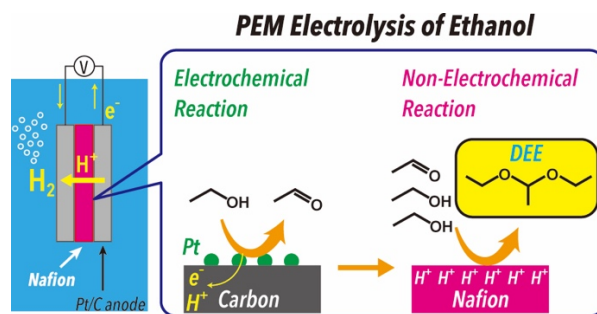


Fig. 2 Electrolysis of ethanol to form DEE.

DEE was produced at high faradaic efficiency (78 %) via the sequential electrochemical and nonelectrochemical reactions. The DEE formation rate was higher than that of previous reported systems.

So far, MEA has been widely used in the field of fuel cells and water electrolysis. Our work proposed that the MEA can be used as the electrolysis unit for upgrading alcohols into value-added chemicals (e.g., esters, aldehydes, and acetals).

2.2 Dehydrogenative polymerization of CH₄

Catalytic decomposition of CH₄ is a reaction that produces CO_x-free hydrogen.



We investigated the catalytic activity Pd-M alloy on the decomposition of CH₄ and found that Pd-Au and Pd-Si alloys promoted not only the decomposition of CH₄ but also coupling of CH₄ to produce C₂ hydrocarbons.^{3,4)}



Although the selectivity for C₂ hydrocarbons was not so high (~2%), this is the first report that valuable C₂ hydrocarbons can be co-produced during the decomposition of CH₄ to produce CO_x-free hydrogen.

In addition to the catalytic process, we proposed a new radical route to activate CH₄.⁵⁾ CH₄ is so stable molecule that it cannot be activated without catalysts even at high temperatures. As shown in Table 1, CH₄ was not converted at 800 °C in the absence of catalysts. In contrast, ethane (C₂H₆) is more reactive than CH₄; therefore, C₂H₆ was dehydrogenated into C₂H₄ and C₆H₆ etc. In such a case, CH₄ is expected to be an inert gas; however, mixtures of CH₄/C₂H₆ and of Ar/C₂H₆ showed different pyrolysis behaviors; the addition of CH₄ increased the formation of propylene, propane and toluene. To reveal the activation process of CH₄, we used ¹³C-labeled CH₄. Mass spectrometry analysis showed that carbon contained in

CH₄ was incorporated into the pyrolysis products. We assumed that CH₄ was attacked by radical species generated from pyrolysis of C₂H₆ and was converted into methyl radicals (Fig. 3). The CH₄-derived methyl radicals were incorporated into pyrolysis products via radical reactions.

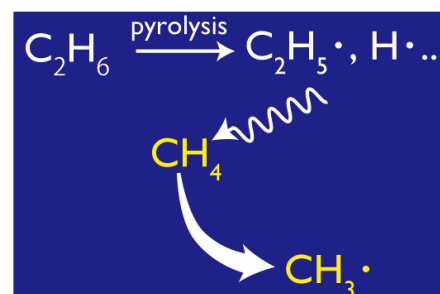


Fig. 3 Schematic diagram of CH₄ activation by radicals generated from the pyrolysis of C₂H₆.

3. Acknowledgement

This work was supported by JSPS KAKENHI (Grant Number 16K18287, 18K04832, and 21H01710), JST CREST (Grant Number JPMJCR15P4), the technology development project carried out in Japan Petroleum Energy Center (JPEC) under the commission of the Ministry of Economy, Trade and Industry (METI), and Tonen General Sekiyu Research/Development Encouragement & Scholarship Foundation.

References:

- 1) R. Kishi, H. Ogihara, M. Yoshida-Hirahara, K. Shibamura, I. Yamanaka, H. Kurokawa, *ACS Sustain. Chem. Eng.*, **2020**, 8, 11532–11540.
- 2) D. Kawaguchi, H. Ogihara, H. Kurokawa, *ChenSusChem*, in press.
- 3) H. Ogihara, N. Imai, M. Yoshida-Hirahara, H. Kurokawa, *Chem. Lett.*, **2020**, 49, 236-239.
- 4) H. Ogihara, N. Imai, H. Kurokawa, *Int. J. Hydrog. Energy*, **2020**, 45, 33612-33622.
- 5) H. Ogihara, H. Tajima, H. Kurokawa, *React. Chem. Eng.*, **2020**, 48, 1145-1147.

Table 1 dehydrogenative conversion of CH₄, C₂H₆, and CH₄/C₂H₆. T = 1073 K, catalyst mass = 0 g.

reactant gas	yield / μmol h ⁻¹								conv. / %	
	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	C ₃ H ₆	C ₆ H ₆	C ₇ H ₈	C ₈ H ₈	C ₁₀ H ₈	CH ₄	C ₂ H ₆
CH ₄	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.002	n/a
Ar/C ₂ H ₆	13027	303	2	113	192	0.9	2	10	n/a	90.6
CH ₄ /C ₂ H ₆	13611	266	24	595	125	3	2	4	-0.7	85.0

Precise Synthesis, Characterization, and Reactivity of Multi-functional Catalysts

Seoul National University of Science and Technology

Insoo Ro *

1. Introduction

Beyond the maximized atomic efficiencies and cost savings, atomically dispersed catalysts have attracted great attention in recent years due to the uniformity in active sites and careful regulation over local environments of active sites. Thus, it is interesting to investigate how the dispersed active site-support environment can be precisely engineered to control catalytic reactivity. In this work, we demonstrate control over the local coordination environment of atomically dispersed Rh on Al_2O_3 through a systematic tuning of interactions between Rh and ReO_x or WO_x species. Through this precise engineering of the local environment of atomically dispersed Rh species on an oxide support, it is shown that the local environment of the active site are significantly influenced, which in turn control ethylene hydroformylation reactivity. Whereas ReO_x were atomically dispersed on Al_2O_3 regardless of Re loading, the structure of WO_x on Al_2O_3 varied (atomically dispersed WO_x , polystungstate monolayer, to monoclinic WO_3 crystallites) by changing W loading, which influences the intrinsic reaction kinetics.

2. Experimental

Supported atomically dispersed Rh catalysts were prepared by a strong electrostatic adsorption method. Catalysts were characterized by a range of techniques, including UV-Vis and Raman spectroscopy, CO probe molecule infrared (IR), and transmission electron microscopy to understand the local structure and Rh charge state.

3. Results and Discussion

Figure 1 (a) and (b,c) show representative image of the $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and corresponding line scan intensity analysis of the two selected dimers, respectively. The difference in scattering intensity of Rh and Re species due to their different atomic mass (intensity $\propto Z^{1.5-2}$, where Z represents atomic number) evidences the formation of Rh-ReO_x atomically dispersed site pairs in $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$.

For ethylene hydroformylation, the propanal formation was greatly enhanced over $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$ relative to $\text{Rh}/\text{Al}_2\text{O}_3$, resulting in the higher selectivity toward propanal up to 63%. Interestingly, the selectivity toward propanal substantially changed depending on WO_x structure nearby dispersed Rh species. When Rh were localized with atomically dispersed WO_x ($\text{Rh}/1\text{WO}_x\text{-}$

Al_2O_3), the selectivity toward propanal is the higher (63%) than Rh on bare Al_2O_3 ($\text{Rh}/\text{Al}_2\text{O}_3$, 22%), a polystungstate monolayer ($\text{Rh}/2\text{WO}_x\text{-Al}_2\text{O}_3$, 43%) and monoclinic WO_3 crystallites ($\text{Rh}/8$ and $25\text{WO}_x\text{-Al}_2\text{O}_3$, 50%).

Kinetic experiments revealed that $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$ have higher CO reaction orders relative to $\text{Rh}/\text{Al}_2\text{O}_3$, indicating a decrease in the CO binding energy on Rh in Rh-ReO_x and Rh-WO_x co-localized structures, which was further evidence by CO temperature program desorption (TPD) characterization. This suggests that the promoted reactivity for $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$ and $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$ was primarily due to an increase in the concentration of vacant sites under reaction conditions. As shown in Figure 2, the CO reaction orders increased and became positive over $\text{Rh}/1$ and $3\text{WO}_x\text{-Al}_2\text{O}_3$, potentially suggesting that C_2H_4 adsorbed on atomically dispersed WO_x reacts with CO on nearby dispersed Rh. Two classes of active sites consisting of Rh and WO_x with an atomic intimacy allow a cooperative bifunctional mechanism when Rh is coordinated with atomically dispersed WO_x , consistent with previous report studies reporting atomically dispersed WO_x as active sites for olefin metathesis.

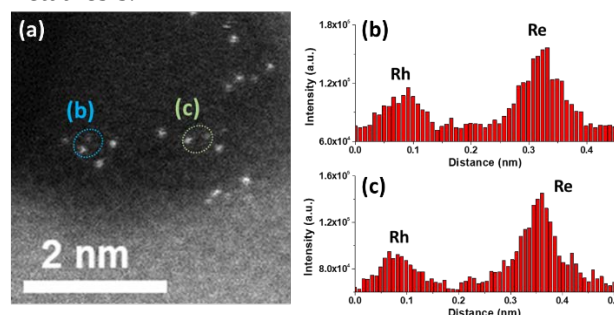


Figure 1. (a) HAADF STEM image of $\text{Rh}/\text{ReO}_x\text{-Al}_2\text{O}_3$. (b,c) Corresponding line scan intensity analysis of the two selected dimers shown in (a).

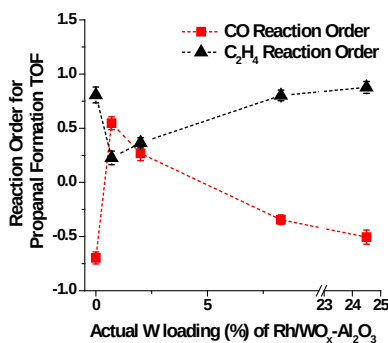


Figure 2. CO and C_2H_4 reaction orders for propanal formation TOF as a function of actual W loading of $\text{Rh}/\text{WO}_x\text{-Al}_2\text{O}_3$.

Interenational sess.

[1A11-13] Interenational sess.(2)

Chair:Takuma Higo(Waseda Univ.)

Thu. Nov 11, 2021 2:15 PM - 3:00 PM Room-A (Room-A/Hakodate Areana)

[1A11] Local structure of In-hydride species in zeolite and its reactivity for C₂H₆ dehydrogenation.

○Shunsaku Yasumura¹, Takashi Toyao^{1,2}, Zen Maeno¹, Ken-ichi Shimizu^{1,2} (1. Institute for catalysis, Hokkaido University, 2. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University)

2:15 PM - 2:30 PM

[1A12] Highly efficient removal of ethylene at 0 °C over Au-Pt/zeolite

○Minyue Lin¹, Haifeng Wang¹, Tetsuya Shishido¹, Hiroki Miura¹, Masatake Haruta¹, Toru Murayama^{1,2} (1. Tokyo Metropolitan University, 2. Yantai University)

2:30 PM - 2:45 PM

[1A13] Catalytic reduction of NO to ammonia by CO-H₂O over metal oxide supported catalysts

○Chaudhari Chaudhari Chandan¹, Keisuke Kobayashi¹, Yuichi Manaka^{1,2}, Tetsuya Nanba¹ (1. Fukushima Renewable Energy Inst., AIST, 2. Tokyo Inst. Tech.)

2:45 PM - 3:00 PM

Local structure of In-hydride species in zeolite and its reactivity for C₂H₆ dehydrogenation

(Institute for catalysis, Hokkaido University* · Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University**)○Shunsaku Yasumura*, Takashi Toyao*,**, Zen Maeno*, Ken-ichi Shimizu*,**

1. Introduction

Hydrides in/on solid materials have attracted significant attention in many research fields, including energy engineering, electrochemistry, and catalysis. Research on the synthesis, characterization, and catalytic function of the isolated surface hydrides is an attractive but formidable task.¹ In this study, in-situ IR and DFT calculation were carried out to find the formation of isolated In-hydride species in indium-exchanged CHA zeolite (In-CHA).² The catalytic ability of In-CHA on C₂H₆ non-oxidative dehydrogenation was examined, resulting in superior selectivity (96 %) and low coke formation during a long-term reaction (90h). By the combination of kinetic analysis and transition state (TS) calculation, it was elucidated that its catalytic performance was originated from the formation of not mono-hydride ([InH]²⁺) but di-hydride species ([InH₂]⁺) as active sites.

2. Experimental

In₂O₃ supported on the proton-type CHA (In₂O₃/CHA) was synthesized through impregnation of In(NO₃)₃·nH₂O (Kanto Chemical Co., Inc.) in the NH₄⁺-type CHA zeolite (Tosoh, SiO₂/Al₂O₃ = 22.3), followed by drying in an oven and calcination under air for 1 h at 773 K. Afterward, the reductive solid-state ion-exchange reaction of In₂O₃/CHA was conducted in the presence of H₂ at 773 K. For IR spectroscopic experiments, the In-CHA disk was prepared in-situ in a quartz reactor from a self-supported disk of In₂O₃/CHA. DFT calculations were performed using the Vienna ab initio simulation package (VASP) with a periodic boundary condition under the Kohn–Sham formulation.

3. Result and Discussion

The in-situ IR measurement of In-CHA treated with H₂ at 773 K (In-CHA(H₂)) was performed. The IR spectrum of In-CHA(H₂) exhibited a band with a maximum at 1720 cm⁻¹ (Figure 1a) arising from In–H stretching vibrations (ν(In–H)). This band remained unchanged even at 473 K. After H–D exchange reaction with D₂ at 373 K, ν(In–H) decreased and disappeared at 473 K. ν(In–H) appeared again by the following exposure to H₂ at 473 K. The gas-phase products were also analyzed by mass spectrometry during the H–D exchange reaction with an increase in the temperature from 313 to 473 K. The reaction of In-CHA(H₂) with D₂ afforded a positive peak for m/z = 3 with a negative peak for m/z = 4 around 373–473 K (Figure 1b), while a peak for m/z = 2 was hardly observed. A control experiment using proton-type CHA (H-CHA) instead of In-CHA (H₂-treated H-CHA with D₂) was conducted where no peak was observed for all signals,

supporting the occurrence of an H–D exchange reaction between In-hydrides and D₂.

In-CHA exhibited high selectivity (96 %) and durability for the nonoxidative ethane dehydrogenation without cofeeding of H₂. The activity and selectivity of In-CHA were maintained for at least 90 h, and the catalyst was reusable without loss of its efficiency. Based on the results of kinetic analysis and TS calculations, the formation of [InH₂]⁺ as active sites is responsible for the durable reaction due to the less formation of Bronsted acid sites and carbenium cations. More detailed reaction mechanisms and the relationship with the local structure of In-hydride species will be discussed

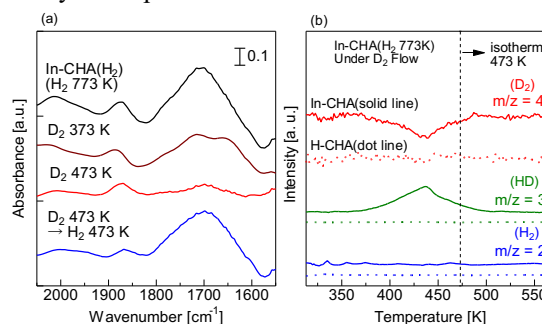


Figure 1 (a) FTIR spectra of In-CHA after H₂ treatment at 773 K (In-CHA(H₂)) and H–D exchange reactions. (b) Mass profiles for m/z = 2, 3, and 4 during H–D exchange reaction of In-CHA(H₂) (solid line) or H-CHA(H₂) (dot line) with D₂.

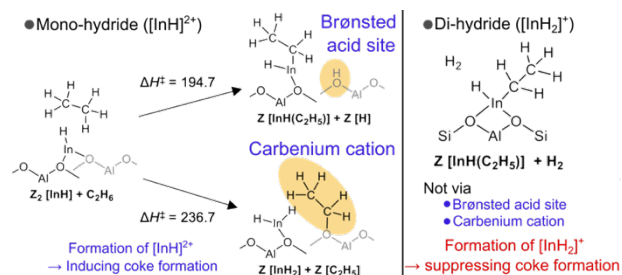


Figure 2 Reaction scheme of non-oxidative dehydrogenation of C₂H₆ on indium mono-hydride ([InH]²⁺) and di-hydride ([InH₂]⁺) species in zeolite.

References

- 1 C. Copéret, D. P. Estes, K. Larmier and K. Searles, *Chem. Rev.*, 2016, **116**, 8463.
- 2 Z. Maeno, S. Yasumura, X. Wu, M. Huang, C. Liu, T. Toyao and K. Shimizu, *J. Am. Chem. Soc.*, 2020, **142**, 4820.

Highly efficient removal of ethylene at 0 °C over Au-Pt/zeolite

(¹Tokyo Metropolitan University, ²Yantai University)

○Mingyue Lin^{*1}, Haifeng Wang^{*1}, Tetsuya Shishido^{*1}, Hiroki Miura^{*1},
Masatake Haruta^{*1}, Toru Murayama^{*1,2}

1. Introduction

Ethylene (C₂H₄) released from the plants could fasten the mature and deterioration of fresh fruits and vegetables even at low temperatures since it is a natural gaseous plant hormone. To prolong the storage time of the fresh plants during the transportation, removing trace amounts of C₂H₄ is important, and selective catalytic oxidation of C₂H₄ to CO₂ is an ideal method.¹ However, almost all of the reported catalysts would be deactivated due to the water adsorption, usually within 1 h. Therefore, it is necessary to develop a more effective material with a high C₂H₄ removal efficiency and long-term stability at low temperatures (0~5 °C).

Here, we report an Au-Pt/zeolite (ZHM20) with a highly active C₂H₄ removal efficiency (81%) and long-term stability (40 h) for C₂H₄ elimination at 0 °C.

2. Experimental

Mordenite 20 (ZHM20, SiO₂/Al₂O₃=18.3) provided by the Catalysis Society of Japan was used as the support. The loading amount of nanoparticles was prepared as 1wt%. Sol immobilization method² was applied to prepare ZHM20, Pt/ZHM20, Au/ZHM20, and Au_xPt_y/ZHM20 (*x* and *y* represent the molar ratio of Au and Pt, respectively) and they were calcined at 500 °C for 2 h before being used.

A fixed-bed flow reactor was used to conduct the C₂H₄ removal test. The sample (0.2 g) was firstly pretreated at 150 °C for 2 h under N₂ with a flow rate of 50 mL min⁻¹ before being evaluated under the reactant gas that contained 50 ppm C₂H₄, 20% O₂, and N₂ balance with a total flow rate of 10 mL min⁻¹. The inlet and outlet concentrations of C₂H₄ and CO₂ were analyzed by an online 490 Micro GC system (Agilent) for calculating the removal efficiency of C₂H₄ and the yield of CO₂.

3. Results and Discussion

As shown in Figure 1, the initial C₂H₄ removal efficiency over ZHM20 was 100% at 0 °C and it reached the maximum adsorption capacity after flowing 11 h of 50 ppm C₂H₄. The removal efficiency curves of Pt/ZHM20 and Au/ZHM20 were U-shaped. Initially, the removal efficiency was 100% and it decreased to 19% and 15% after 10 h-on-stream over Pt/ZHM20 and Au/ZHM20, respectively, which was the same with that observed from ZHM20, suggesting that this step might be owing to the adsorption of C₂H₄ on ZHM20. Then, the C₂H₄ removal efficiency increased until reaching the steady-state of 56% on Pt/ZHM20 and 45% on Au/ZHM20. Au₅₄Pt₄₆/ZHM20 also showed a U-shape removal efficiency curve, but the turning point time of 3.5 h was much shorter than the other two. Moreover, the C₂H₄ removal efficiency of Au₅₄Pt₄₆/ZHM20 at the steady-state was 81% and it lasted for as long as 40 h. According to the electronic state analysis, Au₅₄Pt₄₆/ZHM20 possessed electron-deficient Pt species and electron-rich Au species, which might be helpful for the faster adsorption and transformation of C₂H₄ on Au₅₄Pt₄₆ NPs than that on Au NPs and Pt NPs.

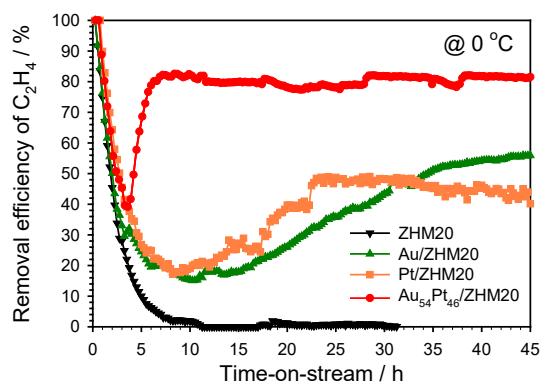


Figure 1. The removal efficiency of C₂H₄ with time-on-stream over ZHM20, Au/ZHM20, Pt/ZHM20, and Au₅₄Pt₄₆/ZHM20 at 0 °C.

- 1) C. Jiang, K. Hara, A. Fukuoka, *Angew. Chem. Int. Ed.*, 52(24), 6265 (2013)
- 2) H. Miura, Y. Tanaka, K. Nakahara, Y. Hachiya, K. Endo, T. Shishido, *Angew. Chem. Int. Ed.*, 130(21), 6244 (2018)

Catalytic reduction of NO to ammonia by H₂ or CO-H₂O over metal oxide supported catalyst.

(FREA¹, TIT₂) O.C. Chaudhari,¹ K. Kobayashi,¹ Y. Manaka^{1,2*} T. Nanba¹

1.Introduction

Ammonia is an important N-containing chemical which is used as fertilizer, starting material for heterocycles sthe synthesis and carbon-free fuel. Ammonia is synthesized industrially by Haber-Bosch method with high energy consumption. Ammonia synthesis from air pollutant NO is an attractive alternative to reduce the concentration of NO. Several reductants such as hydrocarbon, H₂ or CO-H₂O have reported for the transformation of NO to NH₃. Recently, our group developed Pt/TiO₂ catalyst for ammonia synthesis on NO-CO-H₂O reaction.¹ However, the activity of Pt/TiO₂ was not studied for NO-H₂ reaction. In this study, we investigated and optimized the catalytic activity of Pt/TiO₂ for NH₃ synthesis. Furthermore, the activity of Cu/CeO₂ catalyst at lower temperature (>200 °C) investigated for NO-CO-H₂O reaction.

2. Experimental

Supported metal catalysts were prepared by an incipient wetness method with different Pt or Cu precursors. TiO₂ or CeO₂ support was prepared by sol-gel method using different conditions. All catalysts were characterized by BET and CO adsorption. The catalytic activity was measured by a fixed-bed flow reactor. For NO-H₂ reaction, the feed gas was composed of 0.1 % NO, 0.3% H₂ ppm with dilution by Ar. For NO-CO-H₂O reaction, the feed gas was composed of 0.1 % NO, 0.3% CO and 1% H₂O ppm with dilution by Ar. The total flow was set to 250 mL/min. The product gases were analyzed online Fourier transform infrared spectroscopy and gas chromatography.

3. Results and Discussion

Initially, we synthesized Pt/TiO₂ catalyst using different precursor such as (NH₃)₄Pt(NO₃)₂, (NH₃)₄Pt(Cl)₂, (NH₃)₄Pt(OH)₂ and H₂PtCl₆ and tested for NO-H₂ reaction. All precursors showed full conversion (100 %) of NO. The catalytic activity of all four precursors for ammonia selectivity was almost

similar at lower temperature (100 °C-150 °C). When the temperature increased to 230 °C, H₂PtCl₄ showed superiority (99 %) for the synthesis of ammonia (Fig.1). Later, we investigated the effect of reduction temperature using different temperatures (400 °C, 500 °C and 600 °C). When Pt/TiO₂ catalyst prepared from H₂PtCl₄ precursor reduced at 400 °C, high yield of ammonia (98.9%) was obtained at 230 °C.

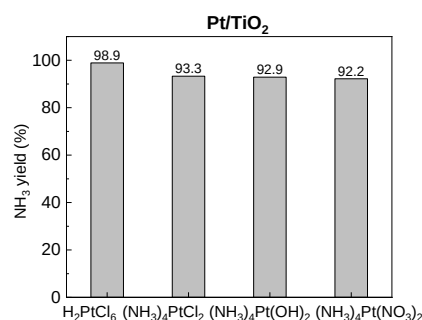


Fig. 1. The activity of Different Pt catalysts at 230 °C

For NO-CO-H₂O reaction, we examined Cu/CeO₂ catalysts prepared from different precursors at 150 °C. The catalyst prepared from Cu(NO₃)₂ precursor showed higher yield (72%) than other precursors.

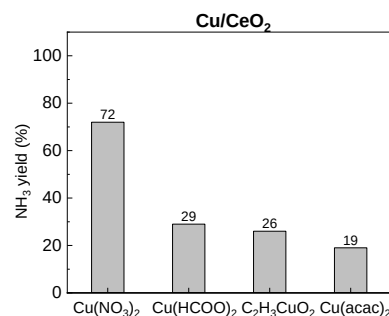


Fig. 2. The activity of Different Pt catalysts at 150 °C

In summary, Pt/TiO₂ prepared from H₂PtCl₆ found to be an active catalyst for ammonia synthesis over NO-H₂ reaction. In NO-CO-H₂O reaction, Cu/CeO₂ catalyst showed high activity for ammonia synthesis.

¹K. Kobayashi, R. Atsumi, Y. Manaka, H. Matsumoto, T. Nanba, *Catal. Sci. Technol.*, **9**, 289 (2019).

Interenational sess.

[1A14-16] Interenational sess.(3)

Chair:Yasutaka Kuwahara(Osaka Univ.)

Thu. Nov 11, 2021 3:15 PM - 4:00 PM Room-A (Room-A/Hakodate Areana)

[1A14] Low-temperature conversion of methane to methanol using carbon nanotubes supported catalyst

○Yingluo He¹, Guohui Yang¹, Noritatsu Tsubaki¹ (1. University of Toyama)

3:15 PM - 3:30 PM

[1A15] One-pot synthesis of HKUST-1 monolith for CO₂ adsorption

○Motomu Sakai¹, Hayata Hori², Ayaka Itoh³, Takaya Matsumoto⁴, Tsuyoshi Asano⁴, Masahiko Matsukata^{1,2,3,5} (1. Research Organization for Nano &Life Innovation, Waseda University, 2. Department of Applied Chemistry, Graduate School of Advanced Science and Engineering, Waseda University, 3. Department of Applied Chemistry, Waseda University, 4. ENEOS Corporation, 5. Advanced Research Institute for Science and Engineering, Waseda University)

3:30 PM - 3:45 PM

[1A16] Zr doped Ni/CeO₂ prepared by Flame Spray Pyrolysis for CO₂ methanation

○Kakeru Fujiwara¹, Syugo Kayano¹, Dai Yoshioka² (1. Yamagata University Graduate school of Chemistry and Chemical Engineering, 2. Yamagata University Department of Chemistry and Chemical Engineering)

3:45 PM - 4:00 PM

Low-temperature conversion of methane to methanol using carbon nanotubes supported catalyst

(University of Toyama) ○Yingluo He, Guohui Yang, Noritatsu Tsubaki

1. Introduction

Conversion of methane to methanol is performed by a two-step process under harsh reaction conditions in industry. The direct synthesis process of methanol from partial oxidation of methane has been studied for a few decades. However, it remains one of the considerable challenges in the sector of methane utilization.¹⁾ Herein, we report carbon nanotubes (CNTs) supported palladium-gold (Pd-Au) nanoparticles catalyst for this direct synthesis, which shows outstanding methanol selectivity and productivity at low temperature.^{2), 3)}

2. Experimental

2.1 Catalyst preparation

Commercial CNTs were pretreated by various acids to modify its surface properties. The supported Pd-Au catalysts were prepared by an incipient wetness impregnation method. The Pd and Au amount were 2.5 % wt respectively without explain.

2.2 Catalyst characterization

XRD, XPS, H₂-TPR, CO-PULSE, FE-SEM, HR-TEM measurements were performed to analyze the physical and chemical properties of our catalysts.

2.3 Catalytic tests

Catalyst tests for direct synthesis of methanol from methane were accomplished in a stainless-steel autoclave. The motor was vigorously stirred at 1200 rpm, the temperature was raised to 50 °C to start the reaction at the same time. After the 30 min reaction, the vessel was cooled by ice (< 10 °C), to avoid volatilization of the products.

3. Results and Discussion

The carbon materials such as carbon nanotubes (CNTs), activated carbon (AC), and reduced graphene oxide (rGO) are employed as the catalyst

support, and the palladium-gold (Pd-Au) nanoparticles are used as active center. By using oxygen/hydrogen mixture as oxidant in the direct synthesis, it is found that Pd-Au/CNTs catalyst shows outstanding methanol selectivity and productivity.

Table 1 Catalytic performance with different carbon supported Pd-Au nanoparticles catalyst

Catalyst	Total product (mmol/kg _{cat.})	MeOH Selectivity (%)	TON of MeOH ^b
Pd-Au/rGO	33.2	54.2	76.5
Pd-Au/AC	156.0	65.6	435.1
Pd-Au/CNTs	190.1	73.2	591.7
Pd-Au/CNTs-a	149.5	71.2	452.6
Pd-Au/CNTs-n	98.0	90.0	375.0

a: Reaction conditions: Time 30 min; Temp. 50 °C; Solvent H₂O 10 mL; Catalyst weight 30 mg; Feed gas CH₄/O₂/H₂/Ar; Total pressure 3.3 MPa.

b: mmoles of MeOH formed by per mole Pd metal.

Compared with the Pd-Au/CNTs, the Pd-Au/CNTs-n catalyst with a treatment of nitric acid on the CNTs support enhances the methanol selectivity obviously (Table 1), due to the changed surface oxygen species on the supports. In addition, our characterization results reveal that a weak interaction between Pd-Au nanoparticles and CNTs support is in favor of methanol productivity and selectivity.

This work offers a simple and effective strategy to directly synthesize methanol from methane partial oxidation under the mild conditions.

1) Hammond C, Forde M. M, Ab Rahim M. H, et al.; *Angew. Chemie - Int. Ed.*, **51**, 5129 (2012).

2) He Y, Luan C, et al.; *Catalysis Today*, **339**, 48 (2020).

3) He Y, Liang J, et al.; *Catalysis Today*, **352**, 104 (2020).

One-pot synthesis of HKUST-1 monolith for CO₂ adsorption

CO₂ 吸着用 HKUST-1 モノリスのワンポット合成

(早大ナノ・ライフ*・早大先進理工**・ENEOS 株式会社***・早大理工総研****)

○酒井 求*・堀隼太**・伊藤綾香**・松本隆也***・朝野 剛***・松方正彦*, **, ****

1. Introduction

Metal-organic-framework (MOF) is drawn attention as CO₂ adsorbent. Shape forming technology for powdery MOF is required in order to generate objects of millimetric dimensions with enough mechanical resistance for application in industry¹⁾. In this study, alumina tube and Cu cube were used as the metal source for MOF preparation and a part of them was directly converted into MOF monoliths. The preparation method of MOF monolith and its adsorption property were investigated.

2. Experimental

Two types of monoliths containing MOFs, HKUST-1 and MIL-96, were prepared. HNO₃, trimesic acid (TMA), and porous α -alumina tube were used as raw materials for MIL-96 preparation. Porous Cu cube was used for HKUST-1 preparation instead of α -alumina tube. Either alumina tube or Cu cube was placed into the aqueous solution of HNO₃ and TMA, and then hydrothermally treated by using glass-lined autoclave. The effect of these preparation conditions on the preparation of MOF monolith was studied.

MIL-96 powder was synthesized according to the literature²⁾ as reference material. HKUST-1 powder (Basolite C-300) was purchased from Sigma-aldrich.

CO₂ adsorption properties of prepared MOF powder and monoliths were measured by volumetric adsorption method (Belsorp-MAX, microtracBEL).

3. Results and discussion

The concentrations of HNO₃ and TMA and the conditions of hydrothermal treatment were widely changed. By the optimization of synthesis conditions, the contents of MIL-96 and HKUST-1 in monoliths increased up to 6.0 and 32 wt%, respectively.

Fig. 1 shows the morphological features of raw materials of metal sources and monoliths synthesized. The surface of alumina tube was fully covered with

MIL-96 crystals and the color of alumina tube changed to yellow. The surface of Cu cube was converted to HKUST-1 as well.

Fig. 2 shows the isotherms of CO₂ on MIL-96 and HKUST-1 monoliths and powders at 298 K. The adsorbed amount of CO₂ at 100 kPa on MIL-96 monoliths and powder were 140 and 95 cm³(STP) g⁻¹, respectively. HKUST-1 powder and monolith showed almost the same values of the CO₂ adsorbed amount, 99 cm³(STP) g⁻¹.

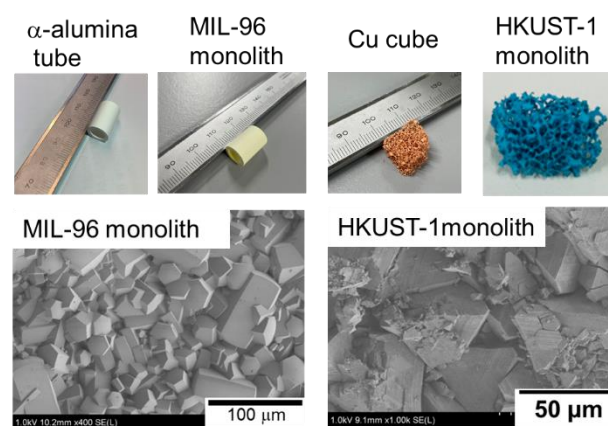


Fig. 1 Typical photo and FE-SEM images of α -alumina, MIL-96 monolith, Cu cube and HKUST-1 monolith.

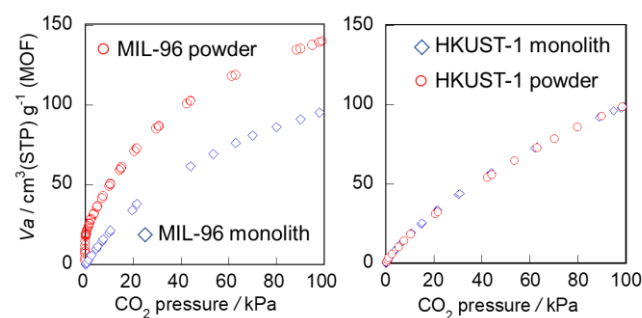


Fig. 2 CO₂ isotherms on MIL-96 and HKUST-1 at 298 K.

References

- 1) Bazer-Bachi, D., *et al.*, *Powder Technol.*, **255** (2014) 52-29.
- 2) Benoit, V. *et al.*, *J. Mater. Chem. A*, **6** (2018) 2081-2090.

Zr doped Ni/CeO₂ prepared by Flame spray pyrolysis for CO₂ methanation

(Yamagata University) Kakeru Fujiwara*, Syugo Kayano and Dai Yoshioka

1. Introduction

Utilization of CO₂ by converting it into CH₄ is sought because it reduces CO₂ emission to the environment and stores H₂ produced by renewable energies. So far, for this reaction, Ru supported on CeO₂ is one of the most active catalyst but its utilization is limited due to the cost of Ru. Alternatively, Ni has attracted the interest but it suffers from the low activity at low temperature (< 250 °C) compared to Ru catalysts. To address the issue, high Ni loading with keeping the size small is promising approach for maximizing the Ni surface area. Here, we successfully prepared highly-loaded NiO (60 wt% as Ni) on CeO₂ nanoparticles by flame spray pyrolysis (FSP). Furthermore, the effect of Zr doping to the Ni/CeO₂ catalyst for CO₂ methanation was investigated.

2. Experimental

Ni (60wt%) supported on Ce_{1-x}Zr_xO₂ (x = 0 and 0.1) was prepared by an FSP reactor [1]. Appropriate amount of Ni (II) acetate tetrahydrate (Wako, purity > 98.0%), Zr 2-ethylhexanoate in mineral spirits (Wako, 11.7-12.3% as Zr) and Ce (III) 2-ethylhexanoate, 49% in 2-ethylhexanoic acid (Alfa Aesar, Ce: 12%) were mixed with a mixture (1: 1) of 2-ethylhexanoic acid (Sigma-Aldrich, purity > 99%): methanol (Wako, Reagent Grade) to be the total metal concentration (Ni + Zr + Ce) of 0.2 M. The precursor solution was fed to the two-fluid spray nozzle at 3 mL min⁻¹, dispersed to a fine spray by 5 L_{STP} min⁻¹ of O₂ dispersant (technical grade). The spray was evaporated and combusted by a premixed CH₄/O₂ plot flame (1.5 L_{STP} min⁻¹/3.2 L_{STP} min⁻¹) to form particles. The particles were collected on a glass-fiber filter by a vacuum pump (Busch SV1040C). Also, 20 and 60 wt% of Ni was deposited on FSP-made pure CeO₂ by an impregnation method. Before the characterization and activity tests, all the catalysts were reduced in 5%H₂-Ar at 500°C for 1 h.

Catalytic activity was evaluated using a fixed bed reactor. The catalyst (100 mg) and SiC powder (400 mg) were filled into a quartz tube (inner/outer diameters of 6/8 mm). The catalyst was reduced at 500 °C for 1 h in 5% H₂-Ar (100 mL_{STP} min⁻¹), and subsequently, a reactant gas (CO₂/H₂/N₂ = 1/4/1) was fed to the catalyst at 60 mL_{STP} min⁻¹. The composition of the product was measured by a gas chromatograph equipped with a thermal conductivity detector.

3. Results and discussion

PXRD pattern of all the catalysts shows the peaks of fluorite CeO₂ at 28° and 33°. In the absence of Zr, the peak positions were identical while the Zr doping

shifts the peaks to the higher diffraction angle. Additionally, the peaks of monoclinic and tetragonal ZrO₂ were not detected. These facts indicate the preferable Zr doping to the CeO₂ lattice. EDX mapping (not shown) exhibited the size of Ni in FSP-made 60Ni/CeO₂ and 60Ni/Ce_{0.9}Zr_{0.1}O₂ was small (10-20 nm), despite the high Ni content (60 wt%).

Figure 2 shows the activity of FSP-made and wet-made catalysts for CO₂ methanation. The conversion of FSP-made 60Ni/CeO₂ was higher than that of wet-made ones. Notably, the Zr doing by FSP significantly enhanced the catalytic activity. In addition, by-product (CO) was not detected for all the tests. In conclusion, highly active and selective catalyst was developed by simultaneously achieving high Ni content (60wt%), small Ni size (10-20 nm) and Zr doping to CeO₂ by FSP.

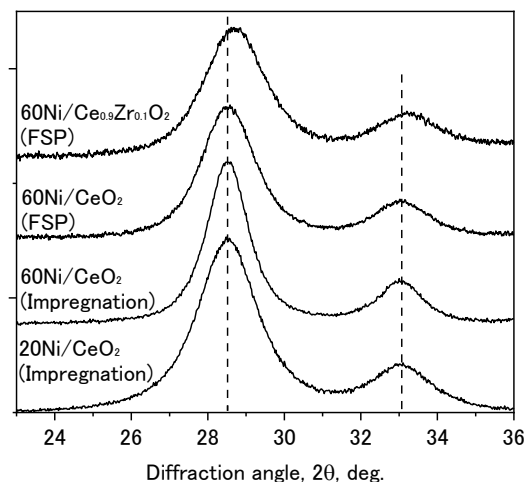


Fig. 1 PXRD patterns of FSP-made Ni/Ce_{1-x}Zr_xO₂ and wet-made Ni/CeO₂ particles

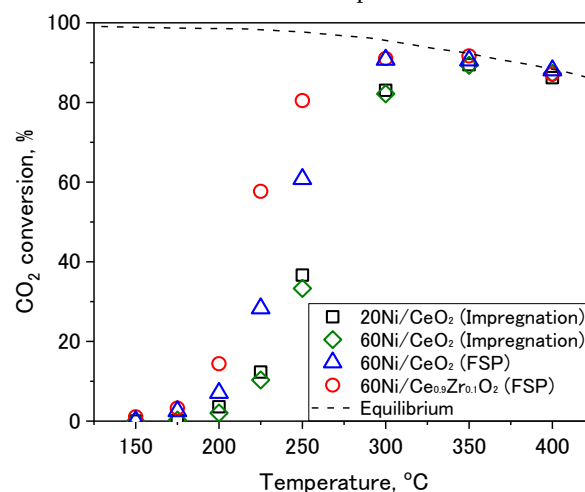


Fig. 2 Catalytic activity of FSP-made and wet-made catalysts for CO₂ methanation.

References

1. Fujiwara, K.; Tada, S.; Homma, T.; Sasaki, H.; Nishijima, M.; Kikuchi, R., *AIChE J.* **2019**, 65, e16717.