Fri. Oct 28, 2022

Room-F

Interenational sess.

[2F01-2F04] Interenational sess. (4) Chair:Naohiro Shimoda(Tokushima Univ.) 9:00 AM - 10:00 AM Room-F (13A Conf. room)

[2F01] CeO ₂ -supported bimetallic Ni-Ag catalyst for
ammonia synthesis from NO-CO-H ₂ O
Chandan Chaudhari ¹ , ⊖Yuichi Manaka ^{1,2} , Tetsuya
Nanba ¹ (1. Fukushima Renewable Energy Institute,
AIST, 2. School of Materials and Chemical Technology,
Tokyo Institute of Technology)
9:00 AM - 9:15 AM

[2F02] Plasmon-assisted hydrogenation and dehydrogenation reactions of noble metal nanoparticles

> ○Priyanka Verma¹, Kohsuke Mori², Yasutaka Kuwahara², Ryo Watanabe¹, Hiromi Yamashita², Choji Fukuhara¹ (1. Shizuoka University, 2. Osaka University)

9:15 AM - 9:30 AM

[2F03] Effect of Ca addition on the catalytic activity of BaTiO₃ for oxidative coupling of methane ORongguang Gan¹, Yoshihide Nishida¹, Massaki Haneda¹ (1. Nagoya Institute of Technology) 9:30 AM - 9:45 AM

 [2F04] CO₂ hydrogenation reaction over Pd-containing MWW zeolite catalyst
OWillie Yang¹, Shuhei Yasuda¹, Sridharan Balu², Muyuan Yu¹, Toshiki Kaseguma¹, Toshiyuki Yokoi¹ (1. Tokyo Institute of Technology, 2. National Taipei

University of Technology)

9:45 AM - 10:00 AM

Interenational sess.

[2F05-2F07] Interenational sess. (5) Chair:Ryo Watanabe(Shizuoka Univ.) 10:15 AM - 11:15 AM Room-F (13A Conf. room)

[2F05] Direct synthesis of carbamates as polyurethane raw materials from low-concentration of CO₂ equivalent to thermal power plant exhaust gas OHiroki Koizumi¹, Katsuhiko Takeuchi¹, Kazuhiro Matsumoto¹, Norihisa Fukaya¹, Kazuhiko Sato¹, Masahito Uchida², Seiji Matsumoto², Satoshi Hamura², Jun-Chul Choi¹ (1. National Institute of Advanced Industrial Science and Technology , 2. Tosoh Corporation)

10:15 AM - 10:30 AM

- [2F06] Design of efficient catalyst for higher alcohols synthesis via $\rm CO_2$ hydrogenation
 - ⊖Minghui Zhao¹, Nozomi Kawamoto¹, Kenji Kamiya¹,

Eika W. Qian¹ (1. Tokyo University of Agriculture and Technology)

10:30 AM - 10:45 AM

[2F07] [Invited] Oxidative coupling of methane over alkaline tungstate catalysts OKazuhiro Takanabe¹ (1. The University of Tokyo) 10:45 AM - 11:15 AM Interenational sess.

[2F01-2F04] Interenational sess. (4)

Chair:Naohiro Shimoda(Tokushima Univ.)

Fri. Oct 28, 2022 9:00 AM - 10:00 AM Room-F (13A Conf. room)

[2F01] CeO₂-supported bimetallic Ni-Ag catalyst for ammonia synthesis from NO-CO-H₂O Chandan Chaudhari¹, OYuichi Manaka^{1,2}, Tetsuya Nanba¹ (1. Fukushima Renewable Energy Institute, AIST, 2. School of Materials and Chemical Technology, Tokyo Institute of Technology)

9:00 AM - 9:15 AM

[2F02] Plasmon-assisted hydrogenation and dehydrogenation reactions of noble metal nanoparticles

OPriyanka Verma¹, Kohsuke Mori², Yasutaka Kuwahara², Ryo Watanabe¹, Hiromi Yamashita², Choji Fukuhara¹ (1. Shizuoka University, 2. Osaka University) 9:15 AM - 9:30 AM

[2F03] Effect of Ca addition on the catalytic activity of BaTiO₃ for oxidative coupling of methane

ORongguang Gan¹, Yoshihide Nishida¹, Massaki Haneda¹ (1. Nagoya Institute of Technology) 9:30 AM - 9:45 AM

[2F04] CO₂ hydrogenation reaction over Pd-containing MWW zeolite catalyst OWillie Yang¹, Shuhei Yasuda¹, Sridharan Balu², Muyuan Yu¹, Toshiki Kaseguma¹, Toshiyuki Yokoi¹ (1. Tokyo Institute of Technology, 2. National Taipei University of Technology) 9:45 AM - 10:00 AM

CeO₂ 担持 Ni-Ag 二元系触媒を用いた NO-CO-H₂O 反応によるアンモニア合成

CeO₂₋supported bimetallic Ni-Ag catalyst for ammonia synthesis from NO-CO-H₂O

(AIST¹, Tokyo Tech²) C. Chaudhari,¹ K. Kobayashi,¹ OY. Manaka,^{1,2*} T. Nanba¹

1.Introduction

The emission of NO is cause of various environmental problems such as acid rain and photochemical smog. Therefore, it is necessary to reduce the concentration of NO. Ammonia can be prepared from NO (Nitrogen oxide To Ammonia: NTA) which is an attractive alternative for NO abatement. Our group developed Pt/TiO₂ catalyst for ammonia synthesis on NO-CO-H₂O reaction.¹ However, the cost of Pt is a barrier for industrial applications. Recently, we developed Ni/CeO₂ catalyst for NTA reaction. Moderate yield (55%) of ammonia was obtained. In this study, we investigated the effect of second metal (M= Fe, Co, Cu, Ag) on the activity of Ni/CeO₂.

2. Experimental

CeO₂ support was purchased from Daichi Kigenso company and calcined at 700 °C for 4 h. 10 wt% Monometallic Ni or Ag and bimetallic 10 wt % Ni_xAg_{1-x} (x = 0.3, 0.5, 0.7) catalysts were prepared by an incipient wetness method with using different second metal. The catalysts were characterized by BET, XRD, H₂-TPR and CO-adsorption. The catalytic activity was measured by a fixed-bed flow reactor. 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 Discusion

Initially, we prepared 5Ni5Fe/CeO₂, 5Ni5Co/CeO₂, 5Ni5Cu/CeO₂ and 5Ni5Ag/CeO₂ catalysts and examined for NTA reaction. All catalysts showed full conversion (100%) of NO above 200 °C (Figure 1). 5Ni5Ag/CeO₂ showed high yield (62%) ammonia (Figure 2). Higher Ni or Ag concentration in NiAg /CeO₂catalyst was not favorable for ammonia formation. The activity of monometallic (Ni or Ag) and bimetallic (NiAg) was compared. Ag/CeO₂ was unable to produce below 300 °C. Ni/CeO₂ gave 55% yield of ammonia. Later, we investigated the effect of support using 5Ni5Ag. CeO_2 found to be effective support for ammonia synthesis. We characterized monometallic (Ni or Ag) and bimetallic (NiAg) to understand the difference in their activity.



Figure 1. NO conversion using bimetallic catalysts

XRD analysis revealed that Ni and Ag metal were in metallic state in all three catalysts. H₂-TPR profile of Ag/CeO₂ showed Ag₂O oxide was reduced at 172 °C which shifted to higher temperature (193 °C) in bimetallic NiAg catalyst. Ni/CeO₂ showed reduction at 453 °C which shifted to lower temperature (279 °C). CO-chemisorption showed metal dispersion was higher in bimetallic than monometallic catalysts.



In summary, 5Ni5Ag/CeO₂ catalyst exhibited high activity for NTA reaction.

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

Plasmon-assisted hydrogenation and dehydrogenation reactions of noble metal nanoparticles

(Shizuoka University^A • Osaka University^B) ○Priyanka Verma^A • Kohsuke Mori^B • Yasutaka Kuwahara^B • Ryo Watanabe^A • Hiromi Yamashita^B • Choji Fukuhara^A

1. Introduction

The localized surface plasmon resonance (LSPR) mediated enhanced chemical activity can be entitled as a promising strategy for efficient solar to chemical energy conversion.¹ To tune the selectivity of a desired product in a chemical reaction is of paramount importance yet a great challenge. Herein, a new strategy to effectively enhance the selectivity of the product formation under visible light irradiation is reported.² A series of Ag catalysts deposited on metal oxide support materials (TiO₂, ZrO₂, Al₂O₃ and CeO₂) along with their preparative techniques, optimum metal content ratio and effect of different wavelength of light is explored for the chemoselective reduction of *p*-nitrostyrene to *p*-aminostyrene under visible light irradiation.

2. Experimental

The catalyst was prepared by a simple impregnation method. 500 mg of metal oxide support materials (TiO₂, ZrO₂, CeO₂ and Al₂O₃) and sodium laurate (5 mg) was dispersed and ultrasonicated in 100 mL ethanol solution. The mixture was bubbled with argon gas in order to maintain inert atmosphere. Subsequently desired amount of aqueous AgNO₃ solution was added into the mixture and stirred continuously for 6 h. The suspension was evaporated under vacuum and the obtained powder was dried overnight at 80 °C. The obtained sample was named as Ag/M_xO_y and series of catalysts with varied amount of Ag (0.5, 1.0, 2.0 and 5.0 wt. %) were prepared.

3. Results and Discussion

The prepared catalysts were characterized by a range of physicochemical techniques including UV-vis, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). All samples exhibited the strong intrinsic plasmon peak at around 400 nm, attributing to the LSPR effect of Ag NPs. A single broad peak absorption suggests the spherical morphology of the prepared NPs which was further confirmed by TEM. The LSPR peak maximum was observed at 516, 450, 463, 430 nm for Ag/TiO₂, Ag/CeO₂, Ag/ZrO₂ and Ag/Al₂O₃, respectively. The Ag/TiO₂ absorption peak was found to be significantly red shifted in comparison to other catalysts. The average particle size of Ag/TiO2, Ag/ZrO2, Ag/Al2O3 and Ag/CeO₂ was found out to be 11.8 ± 3.4 , 6.84 ± 2.1 , 20.7 ± 5.2 and 9.0 ± 3.2 nm, respectively.

The chemoselective reduction reaction was carried out in ethanolic suspension at room temperature and pressure utilizing ammonia borane (AB) as an in-situ source of H₂.



Figure 1. (a) Effect of using different wavelengths of light (power = 66.7 mW) in the reaction conversion and selectivity utilizing Ag/TiO₂ (b) wavelength of performance increase in the *p*-AS selectivity over Ag/TiO₂ using LED light.

All catalysts displayed complete conversion with varied selectivity obtained for different catalysts. Under light irradiation conditions, the kinetics and overall selectivity was found to be significantly enhanced. Amongst all, Ag/TiO₂ displayed a maximum chemoselectivity of 81 % shown by Ag/TiO₂ under light irradiation conditions.

In order to have a detailed insight of the mechanism and absorption of light by plasmonic Ag NPs, the reactions on Ag/TiO₂ with LED light of different wavelengths and comparison of the obtained results in dark and under visible light irradiation conditions ($\lambda > 420$ nm) was reported (Figure 1a). The LED and their corresponding wavelengths employed in the present study are Blue (470 nm), Green (530 nm) and Red (627 nm). The order of catalytic activity follows the trend Green LED > Red LED > Blue LED > Dark conditions. The selectivities changed significantly upon varying the source of monochromatic LED light. The green LED was found to be the most effective amongst all. Figure 1 (b) summarizes the action spectrum in the performance increase over Ag/TiO₂ catalyst using monochromatic light. The increasing rate of catalytic performance activities was found to be highly consistent with the LSPR absorption intensity of Ag NPs. This result concludes that LSPR plays an important role in increasing the p-AS selectivity under light irradiation conditions. We hope that such plasmonic photocatalysts will assist in opening a new promising avenue in the visible-light-driven heterogeneous catalysis.

References

¹⁾ P. Verma, K. Mori, Y. Kuwahara, R. Raja, H. Yamashita, *Mater:* Adv., 2, 880 (2021).

²⁾ P. Verma, Y. Kuwahara, K. Mori, H. Yamashita, *Catal. Today*, 324, 83 (2019).

Effect of Ca addition on the catalytic activity of BaTiO₃ for oxidative coupling of methane

(Nagoya Institute of Technology) \bigcirc GAN Rongguang, NISHIDA Yoshihide, HANEDA Masaaki

1. Introduction

Oxidative coupling of methane (OCM) reaction has attracted extensive attention due to its energysaving and convenience process [1]. Although perovskite-type catalysts with high thermal stability are known to show the activity for OCM reaction, the C_2 yield is not high enough for industrial use due to the low activity and selectivity [2]. In this study, we investigated the additive effect of Ca on the catalytic performance of BaTiO₃ and found that the addition of small amount of Ca is effective to increase the C_2 yield. The detail experiments were performed to reveal the role of Ca.

2. Experimental

Catalysts were prepared by conventional impregnation method. Commercial BaTiO₃ powder was immersed with an aqueous solution of Ca(NO₃)₂·4H₂O, followed by evaporation to remove water. The obtained powders were dried at 110 °C and calcined at 900 °C for 8 h in air. The loading of Ca was set to $1 \sim 30$ wt%. The catalytic activity was evaluated using a flow reactor system. Catalyst (100 mg) was loaded into a tubular quartz reactor, and a gas mixture of CH₄/O₂/N₂ (20/5/20 mL/min) was introduced to the reactor. The steady-state activity was evaluated by analyzing the reaction/product gases with gas chromatography. As for the catalyst characterizations, XRD, BET surface area and O₂-TPD were carried out.

3. Results and Discussion

Fig. 1 shows the effect of Ca loading on the performance (CH₄ conversion, catalytic C_2 selectivity) of Ca-doped BaTiO₃ for OCM reaction at 650 °C. Not only CH₄ conversion but also C₂ selectivity were increased by addition of Ca up to 3 wt%. However, further increase in Ca loading caused a decrease in the activity. In Fig.1 is also shown the change in BET surface area as a function of Ca loading. Basically, BET surface area was gradually decreased with increasing Ca loading suggesting that BET surface area is not an important factor determining the catalytic activity of Ca-doped BaTiO₃.

In the range of Ca loading below 3 wt%, only the XRD peaks due to BaTiO₃ were observed. However, increase in the Ca loading up to 5 wt% caused an appearance of new peaks due to BaCaTiO₄, indicating the solid phase reaction between Ca additive and BaTiO₃. From the comparison with the catalytic performance shown in Fig.1, the formation of BaCaTiO₄ is negative effect on the catalytic performance of BaTiO₃.

In order to obtain an information on the role of Ca additive, O₂-TPD profiles from Ca-doped BaTiO₃ were measured. O₂ desorption from BaTiO₃ was found to be increased by the addition of Ca. The maximum amount of O₂ desorption was achieved for 3 wt% Ca-doped BaTiO₃. This is in agreement with the order of C₂ yield, suggesting that the Ca additive promotes the oxygen mobility on the surface of BaTiO₃. More detail experiments to discuss the promotional effect of Ca is now in progress.

This research is supported by CSC fundament.



Fig.1. Dependence of CH_4 conversion, C_2 selectivity for OCM reaction at 650 °C and BET surface area on Ca loading.

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- 1) J.H. Lunsford, Angew. Chem. Int. Ed., 34, 970-980 (1995).
- 2) L. Bai, F. Polo-Garzon, Z.H. Bao, S. Luo, B.M. Moskowitz,
- H. Tian, Z.L. Wu, ChemCatChem, 11, 2107-2117 (2019).

CO₂ hydrogenation reaction over Pd-containing **MWW** zeolite catalyst

(Tokyo Inst. Tech.) ○Willie Yang, Shuhei Yasuda, Sridharan Balu, Muyuan Yu, Toshiki Kaseguma, Toshiyuki Yokoi

1. Introduction

Different from the well-known ZSM-5 (**MFI**) catalyst, the MCM-22 (**MWW**) possesses three pore systems: the two-dimensional sinusoidal channels composed of slightly elliptical 10-MR, the characteristic of 12-MR supercages accessible through 10-MR windows, and pockets on its external surface [1]. Due to the distinctive pore structure, the MCM-22 zeolite has shown robust reaction performance in many catalytic processes such as MTO reaction. The group also consider this zeolite catalyst a potential support for CO_2 hydrogenation. Here in this work, the Pdcontaining MWW zeolite catalyst has been deployed for the CO2 hydrogenation reaction.

2. Experimental

A series of **MWW** typed aluminosilicate zeolite, MCM-22, were synthesized as the following method. First, the as-calcined sample was synthesized through hydrothermal synthesis at 150 °C from an aqueous gel of 1.0 SiO₂ : 0.15 Na₂O : 0.025 Al₂O₃ : 0.9 hexamethyleneimine (HMI) : 45 H₂O mol composition [1]. Then the ammonium-type, proton-type, and sodium-type sample were obtained through ion exchange and calcination. Finally, the 1 wt% of Pd was impregnated into the zeolite support by wet impregnation method. The final samples were obtained with the nomenclature of Pd/[M]-MWW-10 where and [M] represents the containing charge balance cations.

3. Results and discussion

layered

From the XRD results, the patterns of MCM-22 and Pd-containing MCM-22 are nearly identical. However, the diffraction peak attributed to PdO (101) particles was observed. The SEM images revealed the well-defined

morphology. Furthermore, the elemental compositions measured from EDX agreed well with the ICP-AES results.

To investigate the intrinsic molecular interactions between adsorbates and the catalyst statically and dynamically, the in-situ DRIFT measurements were performed. The sample was pre-treated in 20vol%H₂/N₂ at 400 °C for 1 hour. In Figure 1, chemisorption of CO2 on the Pd/MWW-10 samples with different Na contents were detected differently under the flow of 20vol%CO₂/H₂ at 250 °C. The band around 1640 cm⁻¹ of Pd/MWW-10 and Pd/Na-MWW-10 is considered as the carbonate species resulting from the sodium cations and trace amount of water molecules from aluminum-rich zeolites [2]. The dynamic evolution of intermediate species was also observed. During CO₂ hydrogenation, carbonate (1520 cm^{-1}), bicarbonate (1640 cm^{-1}), formate (1603 cm^{-1}), and CO (1800-2100 cm⁻¹) were identified as the key intermediates [3]. In the three samples, band related to each intermediates obtained different intensities implying a distinctive reaction pathways from each sodium content observed from DRIFT spectra. Thus, it can be concluded that the reaction mechanism can be controled by the adsorbate species and the relative position and the amount of sodium cations and Pd particles.

References:

1) Wang, Y., et al, *Journal of Catalysis*, 333, 17-28. (2016).

2) Cheung, O., et al, *ACS omega*, 5(39), 25371-25380 (2020).

3) Feng, K., et al, *Journal of Energy Chemistry*, 62, 153-171. (2021).



Figure 1 In-situ DRIFT measurements of the Pd-containing MWW zeolite catalysts under CO_2+H_2 gas flow at 250 °C.

Interenational sess.

[2F05-2F07] Interenational sess. (5)

Chair:Ryo Watanabe(Shizuoka Univ.)

Fri. Oct 28, 2022 10:15 AM - 11:15 AM Room-F (13A Conf. room)

[2F05]	Direct synthesis of carbamates as polyurethane raw materials from low- concentration of CO, equivalent to thermal power plant exhaust gas
	\bigcirc Hiroki Koizumi ¹ Katsubiko Takeuchi ¹ Kazubiro Matsumoto ¹ Noribisa Eukava ¹ Kazubiko Sato ¹
	, Masahito Uchida ² , Seiji Matsumoto ² , Satoshi Hamura ² , Jun-Chul Choi ¹ (1. National Institute
	of Advanced Industrial Science and Technology , 2. Tosoh Corporation)
	10:15 AM - 10:30 AM
[2F06]	Design of efficient catalyst for higher alcohols synthesis via CO ₂
	hydrogenation
	OMinghui Zhao ¹ , Nozomi Kawamoto ¹ , Kenji Kamiya ¹ , Eika W. Qian ¹ (1. Tokyo University of
	Agriculture and Technology)
	10:30 AM - 10:45 AM
[2F07]	[Invited] Oxidative coupling of methane over alkaline tungstate
	catalysts
	○Kazuhiro Takanabe ¹ (1. The University of Tokyo)

10:45 AM - 11:15 AM

Direct synthesis of carbamates as polyurethane raw materials from low-concentration of CO₂ equivalent to thermal power plant exhaust gas

(AIST*, Tosoh Corporation**) OHiroki Koizumi*, Katsuhiko Takeuchi*, Kazuhiro Matsumoto*, Norihisa Fukaya*, Kazuhiko Sato*, Masahito Uchida**, Seiji Matsumoto**, Satoshi Hamura**, Jun-Chul Choi*

1. Introduction

In the technologies of carbon dioxide (CO₂) capture and utilization (CCU), the usage of CO2 as a C1 source for organic syntheses is one effective approach to achieve CO₂ emission reduction. Among synthesizable compounds from CO₂, carbamates (RNHC(O)OR') are attractive because those can be converted into isocyanates as monomers of polyurethanes, which are widely used for such as automobile parts. We have reported synthesis of carbamates from CO₂ using and environmental-friendly regenerable amines reagents, $Ti(OR')_4$ or $Si(OR')_4$. Although these methods can provide high selectivity and high yields of carbamates, high-purity and high-pressure (~3.0 MPa at room temperature) of CO₂ are essential. In contrast, direct utilization of low-concentration and low-purity CO₂ such as exhaust gas of fire power plants is one ideal method owing to excluding energy-loss processes in purification, condensation, and compression. Therefore, we designed direct synthetic method of carbamates from low-concentration of CO₂ by the combination of regenerable reagent Ti(OR')₄ and CO₂ capture methods using 1.8-diazabicyclo[5.4.0]undec-7enc (DBU), which induces formation of two organic salts as CO₂ captured species: carbamate salt formed from amine with DBU and carbonate salt formed from alcohol with DBU (Scheme 1.)^[1].



2. Experimental

First, to capture CO_2 into a reaction solution as the two organic salts as shown in Scheme 1, 0.5 mL of NMP solution containing 2.0 mmol of monoamine or 1.0 mmol of diamine, 6.0 mmol of DBU, and 0.6 mL of ^{*n*}BuOH was bubbled by low-concentration of CO₂ for 20 min at 0.1 L/min in a stainless reactor (volume: 6 mL). Then, additional 2.5 mL of NMP and 2.0 mmol of Ti(O^{*n*}Bu)₄ were added to the reaction mixture. The reaction vessel was tightly sealed by a stainless lid with a gasket and then heated in an oil bath at 150 °C for 5 h. Yields of carbamates were determined by ¹H NMR using 1,3,5-trimetylbenzen as the internal standard.

3. Results and Discussion

Various carbamates were obtained in moderate to high yields by the reaction of $Ti(O^nBu)_4$ with the two organic salts formed from 15 vol%CO₂ (CO₂:N₂ = 15:85, v/v). Conducting the control experiments and the determination of amounts of captured CO₂ into the organic salts, we clarified that the yields of carbamates were correlated with the amounts of captured CO₂. The simultaneous formation of two organic salts was important to obtain the high yield of carbamates owing to increasing the amount of captured CO₂. This synthetic method could be applied to use of simulated exhaust gas (CO₂: 15 vol%, CO: 300 ppm, NO₂ and SO₂: 500 ppm, N₂: balanced), which is equivalent to exhaust gas of coal fired power plants including impurities. Using this simulated exhaust gas, dicarbamates as important precursors of industrially useful alkyl and aryl diisocyanates were obtained in 90% and 71% yields, respectively (Scheme 2).



Acknowledgement: This work is supported by NEDO Feasibility Study Program (Uncharted Territory Challenge 2050). Reference: [1] H. Koizumi *et al.*, ACS Sustainable Chem. Eng. **2022**, 10, 5507.

Design of efficient catalyst for higher alcohols synthesis via CO₂ hydrogenation

(Tokyo University of Agriculture and Technology^{*}) OMinghui Zhao^{*}, Nozomi Kawamoto^{*}, Kenji Kamiya^{*}, Eika W. Qian^{*}

1. Introduction

Directly synthesis of higher alcohols (HAs) via CO₂ hydrogenation has attracted considerable attention. However, suffered from the complicated kinetics and adverse thermodynamic properties, the poor yield of target product makes this route industrialization challenging. Hence. the development of an efficient catalyst for this reaction is of great importance. Considered from the perspective of sustainable and large-scale application, Co-based catalysts deserve more attention [1]. Meanwhile, the morphology of a catalyst also has influence on the catalytic performance and thus has been widely studied. Mesoporous metal oxides have been utilized due to the unique pore structure which could act as the channel to expose more active site and provide microenvironment conditions as nanoreactor [2]. In this work, we selected non-precious mesoporous cobalt based catalyst as the research subject. The MOF was utilized as a template for the catalyst synthesis. Also, the effect of alkali metal, the carbonization temperature and the promoter have been studied in this work.

2. Experimental

The catalysts were synthesized by using MOF as template which refers to build MOF containing target metal and calcinated under suitable condition. The catalytic performance of HAs production directly via CO₂ hydrogenation were then examined using a fixed-bed pressurized flow reaction system under the following conditions: 200 - 300 °C, 3 - 5 MPa, GHSV of 5000 h⁻¹ and H₂/CO₂ ratio of 3. The effects of morphology and promoter on the performance of catalysts were characterized by N₂ adsorption, X-ray photoelectron spectroscopy (XPS), and Temperature-programmed reduction (TPR).

3. Results and Discussion

The effect of promoter, the amount of potassium doping and the carbonization temperature

were studied in this work. Compared with the catalyst promoted by Ni, the Fe promoted catalyst exhibited a relatively high chain-growth probability. This could be ascribed to the appearance of FeC_x introduced by Fe metal. The HAs selectivity of catalyst with 0.5% K content increased to 2% which maybe explained by the electron transformation from K to Cobalt. As for the effect of carbonization temperature, as shown in fig.1, the catalyst carbonized at 400 °C possessed the best performance. The conversion rate and the selectivity to HAs both increased. This could be ascribed to the suitable amount of carbides appearing during the carbonization process.



Fig.1 (a) CO₂ conversion (b)Selectivity of CO (c) Selectivity of HAs alcohol (d) chain growth probability of catalyst carbonization at different temperature as a function of temperature. Calcinated at -- 300 °C, -- 400 °C, -- 500 °C.

[1] Xu et al., Advances in Higher Alcohol Synthesis from CO_2 Hydrogenation, Chem 2021; 7(4): 849.

[2] Zeng et al., Catalysts design for higher alcohols synthesis by CO₂ hydrogenation:Trends and future perspectives. Applied Catalysis B: Environmental 2021; 291 (2021): 120073.

Oxidative coupling of methane over alkali tungstate catalysts

(Univ. Tokyo) OKazuhiro Takanabe

The oxidative coupling of methane (OCM) is a promising direct route to make C_2 products from CH₄ using cofed O₂. It is generally agreed that the OCM process proceeds via a complex reaction network involving surface-catalyzed radical formation and its chain reaction in the gas phase.^{1,2}

Among many investigated catalysts for OCM, Mn-containing Na-tungstate containing catalysts exhibit excellent performance in the OCM. We discovered that the promotional effects on both rate and selectivity were attained over the catalyst in the presence of H₂O, which is one of the major products.³ On detailed microkinetic analysis study, it appears that the OH radical from reaction of O_2 and H_2O plays a key role in improving the performance. After composite variation, Mn species as a catalyst component is not essential for this OH-radical pathway although its presence is effective to improve the overall rate.⁵ The study also confirms that the tungstate is among the most effective anions as they hold the alkali active sites at high temperatures without possessing redox properties that combust hydrocarbons.⁵

Over the Na₂WO₄/SiO₂ catalyst, we identified that active components are alkali metal existing at the most outer surface, which forms peroxide



Figure 1. C₂ yield of OCM reaction as a function of CH₄ conversion with 5 wt% K₂WO₄/SiO₂ (filled circle) and 5 wt% Na₂WO₄/SiO₂ (open square) under different R: CH₄/O₂ ratio (0.8 g K₂WO₄/SiO₂ or 0.6 g Na₂WO₄/SiO₂, 850 °C, CH₄ 10 kPa, O₂ 0.83-10 kPa, H₂O 1.7 kPa, total pressure 101 kPa, Ar balance).

species in equilibrium with gas-phase oxygen, evident by the near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS).⁶ This surface peroxide is likely responsible for OH radical formation to selectively convert CH₄ to C₂, well consistent with the previous kinetic results.⁴

Although Na₂WO₄-based catalysts suffer from melting at the OCM operating condition, K₂WO₄-based catalysts maintain its crystal forms, which may have benefit for long-term durability.⁷ After optimization, we discovered that the similar maximum C₂ yields can be achieved using K₂WO₄/SiO₂ to those using Na₂WO₄/SiO₂, as shown in **Figure 1**.⁷ Very similar promotional effects of H₂O were identified by kinetic analysis, suggesting the OHradical mediated pathway as proposed in Scheme 1. The surface species in situ is indeed evident by NAP-XPS for the K₂WO₄/SiO₂, identifying Kperoxide or K-superoxide formation during the OCM condition.⁷ Common reaction pathway is thus proposed for Na-based, and K-based catalysts with H₂O effects.



Scheme 1. Schematic drawing of common surface reaction steps involved in OCM over alkali (Na, K) tungstate catalysts.

Reference

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