

2020年11月13日(金)

E会場

インターナショナル sess.

[2E01-03] インターナショナル sess. 5

司会:三浦 大樹(東京都立大学)

09:00 ~ 09:45 E会場 (3F・中会議室E1-2)

[2E01] ZSM-5担持 Rh二元機能触媒を用いた $n$ -ヘキサン接触  
分解の低温化

○藤埴 大裕<sup>1</sup>、山地 真愛<sup>1</sup>、多湖 輝興<sup>1</sup>（1. 東京工業大学物  
質理工学院）

09:00 ~ 09:15

[2E02] 高次な構造を有する Moおよび W酸化物触媒の合成  
と酸化触媒能

○下田 光祐<sup>1</sup>、宮沢 真維<sup>1</sup>、石川 理史<sup>1</sup>、上田 渉<sup>1</sup>（1. 神奈  
川大学工学部物質生命化学科）

09:15 ~ 09:30

[2E03] フェノキシ配位ハーフトタノセン触媒によるエチレ  
ン共重合：活性への配位子効果

○Kitphaitun Suphitchaya<sup>1</sup>、野村 琴広<sup>1</sup>（1. 東京都立大学  
理学研究科 化学専攻）

09:30 ~ 09:45

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インターナショナル sess.

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○藤墳 大裕<sup>1</sup>、山地 真愛<sup>1</sup>、多湖 輝興<sup>1</sup>（1. 東京工業大学物質理工学院）

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### [2E02] 高次な構造を有する Moおよび W酸化物触媒の合成と酸化触媒能

○下田 光祐<sup>1</sup>、宮沢 真維<sup>1</sup>、石川 理史<sup>1</sup>、上田 渉<sup>1</sup>（1. 神奈川大学工学部物質生命化学科）

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### [2E03] フェノキシ配位ハーフトタノセン触媒によるエチレン共重合：活性への配位子効果

○Kitphaitun Suphitchaya<sup>1</sup>、野村 琴広<sup>1</sup>（1. 東京都立大学 理学研究科 化学専攻）

09:30 ~ 09:45

# Low temperature catalytic cracking of *n*-hexane over bifunctional catalyst containing Rh and ZSM-5

(Tokyo Inst. Tech.) ○Hiroyasu Fujitsuka, Mai Yamaji, Teruoki Tago

## 1. Introduction

Light olefins, such as propylene and butenes, are important chemical feedstock in petrochemical industry. They are generally produced from naphtha (C5~C8 paraffins and isoparaffins) by thermal cracking at around 800 °C or catalytic cracking over solid acid catalysts at around 650 °C<sup>1</sup>. These processes consume enormous energy due to high temperature operation and therefore the development of low temperature conversion process is required for energy saving. We have reported that bifunctional catalyst consisting of metal and solid acid could effectively convert naphtha at 400 °C because paraffins in naphtha were converted to C5~C8 olefins over metal catalyst which were easily converted to light olefins over solid acid catalyst<sup>2</sup>. In this study, the effect of distance between metal and solid acid in catalyst bed on the *n*-hexane cracking was investigated to optimize the catalyst bed structure for low temperature cracking of naphtha.

## 2. Experiment

Rh@ZSM-5 (bifunctional catalyst), Rh@Silicalite-1 (metal catalyst), and ZSM-5 (solid acid catalyst) were prepared in water-in-oil microemulsion solution as reported in the literature<sup>3</sup>. Three types of catalyst beds with different distance between metal and solid acid sites, defined as “intimacy criterion”, were prepared (**Figure 1(a)**) and labeled as “layered”, “granular-mixed”, and “uniform” catalyst beds. In the layered catalyst bed, Rh@Silicalite-1 particle layer was placed onto ZSM-5 particle layer. The granular-mixed catalyst bed consisted of mixture particles of Rh@Silicalite-1 and ZSM-5. The uniform catalyst bed was prepared from Rh@ZSM-5. The amount of catalyst in bed was set at 0.2 g. Rh content and the Si/Al ratio in the catalyst bed were fixed at 0.3 wt% and 100, respectively.

The *n*-hexane conversion was performed at 400 °C using a fixed-bed flow

reactor. The catalyst was pretreated in 10 % H<sub>2</sub>/N<sub>2</sub> at 450 °C for 1 h. *n*-Hexane was supplied to the reactor accompanied by N<sub>2</sub> stream to adjust *W/F* value at 1.0 (kg-catalyst·h)/kg-*n*-hexane. The gas composition in the effluent of the reactor was analyzed by an on-line gas chromatograph.

## 3. Results and discussion

**Figure 1(b)** depicted the product yield of *n*-hexane cracking at 400 °C. All the catalyst beds showed larger conversion than that over ZSM 5 (less than 1 C-mol%), indicating that the combination of metal and solid acid promoted the *n*-hexane cracking at low temperature.

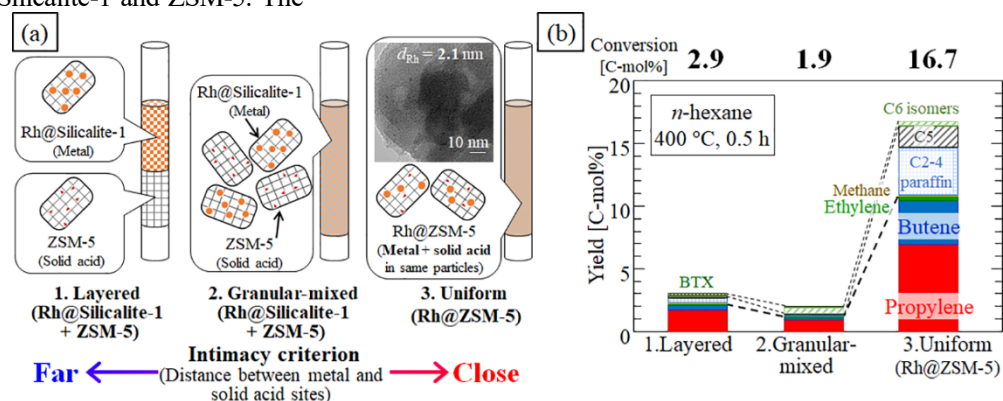
Among the catalyst beds tested, the uniform catalyst bed composed of Rh@ZSM-5 showed significantly higher conversion and olefin yield than the other catalyst beds tested. As shown in **Figure 1(a)**, metal and solid acid sites existed in the same zeolite particles for the uniform catalyst bed, and hence the intermediate olefins formed over metal was easily accessed the solid acid sites nearby. The synergetic effect of Rh metal and solid acid sites on *n*-hexane cracking was effectively obtained only when those sites were located close to each other (close intimacy).

**Acknowledgement:** This research is a part of technology development project conducted by JPEC commissioned by METI.

1) Sadrameli, S. M., *Fuel*, **173**, 285 (2016).

2) Yamaji, M. *et al.*, 49<sup>th</sup> Petroleum-Petrochemicals Symposium of JPI, Yamagata, 2019, P18.

3) Fujitsuka, H. *et al.*, *Catal. Today*, in press.



**Fig. 1** (a) Schematic image of catalyst beds with different distance between metal and solid acid (b) *n*-hexane conversion over the catalyst bed at 400 °C for 0.5 h

# Synthesis of High-Dimensionally structured Mo and W oxide and its oxidation properties

(Kanagawa University)○Kosuke Shimoda, Mai Miyasawa, Satoshi Ishikawa, Wataru Ueda.

## 1. Introduction

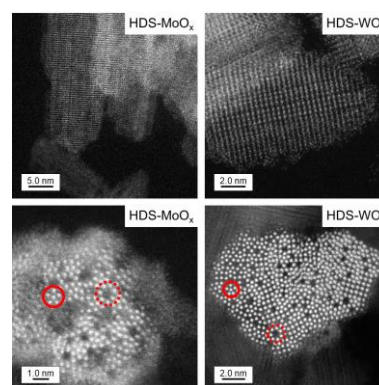
Crystalline Mo-V complex oxides (MoVO) are extremely active catalysts for selective oxidation of ethane and acrolein. MoVO is comprised of the structural arrangement based on pentagonal units  $\{\text{Mo}_6\text{O}_{21}\}^{6-}$  and octahedral ( $\{\text{MO}_6\}$ , M=Mo, V), forming a basal which is stacked for each other to form rod-shaped crystals. The complex arrangement of the pentagonal units constructs micropore channels, such as hexagonal and heptagonal channels in the cross-section. Among these channels, the heptagonal channel is reported to work as catalysis field for selective oxidations. We recently obtained Mo and W oxides constituted by the structural arrangement of pentagonal units and octahedra, forming complex texture containing heptagonal channels in a similar manner to MoVO. In the presentation, we demonstrate details of the physicochemical and catalytic properties of the above Mo and W oxides.

## 2. Experimental

High-dimensionally structured (HDS)- $\text{MoO}_x$  was synthesized by hydrothermal synthesis using the precursor solution prepared by methyl ammonium heptamolybdate  $(\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}$  (MAHM, Mo: 10 mmol) and molybdenum chloride  $\text{MoCl}_5$  (Mo: 2.5 mmol). High-dimensionally structured (HDS)- $\text{WO}_x$  was synthesized in a manner similar to HDS- $\text{MoO}_x$  using the precursor solution prepared by ammonium metatungstate  $(\text{NH}_4)_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$  (AMT, W : 10 mmol), tungsten chloride  $\text{WCl}_5$  (W : 2.5 mmol) and trimethyl ammonium chloride (30 mmol). Hydrothermal synthesis was carried out at 175 °C for 20 h.

## 3. Results and Discussion

HDS- $\text{MoO}_x$  and HDS- $\text{WO}_x$  were obtained by hydrothermal synthesis of the precursor solution prepared by using the mixture of  $\text{M}^{6+}$  and  $\text{M}^{5+}$  sources (M = Mo, W) with appropriate alkylammonium cations as structure directing agents. These materials showed XRD peaks at  $2\theta = 22^\circ$  and  $46^\circ$  attributable to the diffractions from (001) and (002) planes, indicating the periodic stacking of octahedral along the rod direction. We report that the materials showing the above two peaks belong to the family of HDS-oxides. Accordingly, we speculate that Mo and W oxides obtained here are the class of the HDS-materials. Figure 1 shows HAADF-STEM images of HDS- $\text{MoO}_x$  and HDS- $\text{WO}_x$ . These materials were rod-shaped crystals showing lattice



**Figure 1.** HAADF-STEM images of HDS- $\text{MoO}_x$  and HDS- $\text{WO}_x$  in side-section (upper) and cross-section (lower). Solid line, pentagonal unit; dotted line, heptagonal channel.

fridge with the distance of ca. 0.40 nm, which is consistent with the  $d$  values measured by XRD. Due to the arrangement of the pentagonal units, hexagonal and heptagonal channels are formed in the cross-section. Heat treatment of these oxides resulted in the formation of oxygen vacancies as evidenced by  $\text{O}_2$  pulse and TPO experiments. XPS and ORP experiments indicated that constituent elements were reduced with the formation of oxygen vacancies. If we assume that the elemental composition of HDS-(Mo or W) $\text{O}_x$  is (Mo or W) $\text{O}_3$ , these oxides retain the structure in the range of  $\text{MoO}_{2.65\sim3}$  and  $\text{WO}_{2.82\sim3}$ . These feature might bring about attractive oxidation abilities derived from the oxygen vacancy and low-valence Mo and W species in the structure<sup>1)</sup>. In order to investigate its oxidation ability, we carried out selective oxidation of isopropanol ( $\text{C}_3\text{H}_8\text{O}$ ) (Table 1). Conventional Mo oxides such as  $\alpha$ - $\text{MoO}_3$  and  $\beta$ - $\text{MoO}_3$  majorly afforded propylene ( $\text{C}_3\text{H}_6$ ) in this reaction as a result of acid type reaction. On the other hand, HDS- $\text{MoO}_x$  produced substantial amount of acetone ( $\text{C}_3\text{H}_6\text{O}$ ) as a oxidation product than the conventional oxide catalysts.

Table 1. Results of isopropanol oxidation

Sample	Conversion /%		Selectivity /%		
	$\text{C}_3\text{H}_8\text{O}$	$\text{O}_2$	$\text{C}_3\text{H}_6\text{O}$	$\text{C}_3\text{H}_6$	$\text{CO}_x$
HDS- $\text{MoO}_x^a$	99.7	9.2	23.7	76.2	0.1
$\alpha$ - $\text{MoO}_3^a$	99.4	4.4	1.0	98.9	0.1
$\beta$ - $\text{MoO}_3^b$	91.1	1.8	9.2	90.7	0.1

Reaction conditions. Catalyst amount(g). a; 0.05, b; 0.5, reaction gas; isopropanol/ $\text{O}_2/\text{N}_2 = 1.5/3.0/20.0$  mL/min, reaction temperature; 200 °C

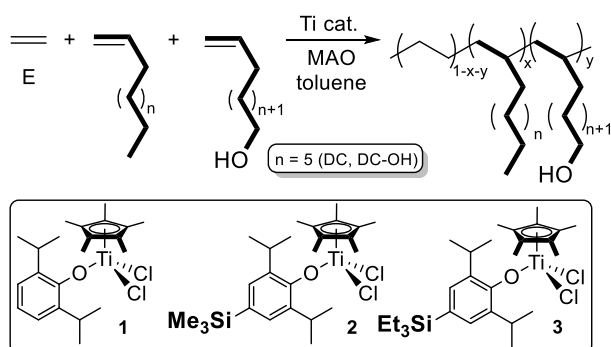
1) E. W. McFarland, H. Metiu, *Chem. Rev.* 113, 4391 (2013)

# Effect of *Para*-Substituent in Ethylene Copolymerizations Catalyzed by Phenoxy-Modified Half-Titanocene Catalysts

(都立大院理) ○Suphitchaya Kitphaitun, and Kotohiro Nomura\*

## 1. Introduction

Introduction of polar functionality into polyolefin has been an attractive target due to promising properties expected with improvement in the surface nature and compatibility with other polymers. Half-titanocenes containing anionic donor ligands,  $\text{Cp}^*\text{TiX}_2(\text{Y})$ , are known to be the efficient catalysts for synthesis of new polymers by ethylene copolymerization, and the ligand modification plays an important role.<sup>1,2</sup> We herein present our results for the synthesis of ethylene copolymers containing hydroxy group by incorporation of 9-decen-1-ol (DC-OH) in ethylene copolymerization with 1-decene (DC) using phenoxide-modified half-titanocenes  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{-4-R-C}_6\text{H}_2)$  [ $\text{R} = \text{H}$  (**1**),  $\text{SiMe}_3$  (**2**),  $\text{SiEt}_3$  (**3**)], in the presence of MAO (Scheme 1).<sup>3</sup>



Scheme 1

## 2. Experimental

All experiments were carried out under a nitrogen atmosphere in a drybox or using standard Schlenk technique. Ethylene copolymerizations were conducted in toluene in the presence of MAO white solid (d-MAO), prepared by removing toluene and  $\text{AlMe}_3$  in the commercially available sample [TMAO, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.]. Molecular weights and molecular weight distributions of the resultant polymers were analyzed by GPC and the microstructures were analyzed by NMR spectra.

## 3. Results and discussion

Selected results in ethylene/DC copolymerization in the presence of DC-OH by **1-3** (MAO cocatalyst) are summarized in Table 1. The results by linked

half-titanocene,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$  (**4**) are also placed for comparison. It turned out that the  $\text{SiMe}_3$  and the  $\text{SiEt}_3$  analogues (**2**, **3**) exhibited higher catalytic activities than **1** and **4** (even in the absence of DC-OH or DC), notably at high temperature (50 and 80 °C). These catalysts afforded high molecular weight copolymers containing OH group with unimodal molecular weight distributions. Note that the activity by **3** increased upon increasing the DC-OH concentration whereas the activities by the others decreased under the same conditions. Noteworthy, the apparent decrease in the  $M_n$  value was not observed with increasing the DC-OH content (2.5 mol%). The hydroxy group in the resultant copolymer was treated with  $\text{AlEt}_3$ , and the subsequent ring-opening polymerization of  $\epsilon$ -caprolactone afforded the grafting polymers with uniform molecular weight distributions. More details will be introduced in the symposium.

**Table 1.** Ethylene copolymerization with 1-decene (DC) and 9-decen-1-ol (DC-OH) by **1-4** – MAO catalysts.

cat. ( $\mu\text{mol}$ )	DC <sup>c</sup> / M	DC-OH <sup>c</sup> / M	activity <sup>d</sup>	$M_n^e$ $\times 10^{-4}$	DC <sup>f</sup> / mol%	DC-OH <sup>f</sup> / mol%
<b>1</b> (0.01)	0.79	0.093	31800	7.29	17.8	1.2
<b>2</b> (0.01)	0.79	0.093	183000	7.58	15.0	1.5
<b>3</b> (0.01)	0.79	0.093	47900	6.82	12.6	1.2
<b>3</b> (0.01)	0.70	0.190	73200	6.70	14.1	2.5
<b>3</b> (0.025) <sup>b</sup>	0.79	0.093	51800	2.65	14.1	0.8
<b>4</b> (0.01)	0.79	0.093	6700	-	-	-
<b>4</b> (0.01)	0.70	0.190	3100	-	-	-

<sup>a</sup>Conditions: total 30 mL, ethylene 6 atm, MAO 3.0 mmol, 50 °C, 10 min,  $\text{Al}^i\text{Bu}_3$  3.0 (DC 0.79 M) or 6.0 (DC 0.70 M). <sup>b</sup>At 80 °C, <sup>c</sup>Initial monomer concentration. <sup>d</sup>Activity in kg-polymer/mol-Ti·h. <sup>e</sup>GPC data in *o*-dichlorobenzene vs PS stds. <sup>f</sup>Comonomer content (mol%) estimated by <sup>1</sup>H NMR spectra.

## References

- (1) K. Nomura, *Dalton Trans.*, 8811 (2009).
- (2) K. Nomura, J. Liu, *Dalton Trans.*, **40**, 7666 (2011).
- (3) S. Kitphaitun, Q. Yan, K. Nomura, *Angew. Chem. Int. Ed.*, **59**, ASAP (2020).