

The Different Roles between Sodium and Potassium Ions in Ion Exchange of WO_3/SiO_2 Catalysts

K. Pipitthapan, S. Maksasithorn, P. Praserttham, J. Panpranot, K. Suriye, S. Kunjara Na Ayudhya

Abstract— WO_3/SiO_2 catalysts were modified by an ion exchange method with sodium hydroxide or potassium hydroxide solution. The performance of the modified catalysts was tested in the metathesis of ethylene and trans-2-butene to propylene. During ion exchange, sodium and potassium ions played different roles. Sodium modified catalysts revealed constant trans-2-butene conversion and propylene selectivity when the concentrations of sodium in the solution were varied. In contrast, potassium modified catalysts showed reduction of the conversion and increase of the selectivity. From these results, potassium hydroxide may affect the transformation of tungsten oxide active species, resulting in the decrease in conversion whereas sodium hydroxide did not. Moreover, the modification of catalysts by this method improved the catalyst stability by lowering the amount of coke deposited on the catalyst surface.

Keywords—Acid sites, alkali metals, isomerization, metathesis.

I. INTRODUCTION

PROPYLENE can be produced from many reactions such as steam cracking, fluid catalytic cracking, dehydrogenation of propane and metathesis etc. Metathesis reaction for propylene production was focused by many researchers. Typically, the catalysts that have been applied in a metathesis reaction are tungsten-based, molybdenum-based and rhenium-based catalysts [1]-[3].

Tungsten-based catalysts usually show higher stability compared to rhenium and molybdenum based catalysts. A main disadvantage on tungsten catalyst is the by-products formed by side reactions such as isomerization, which can be generated by acid sites of catalyst. Isomerization is formed via two pathways, Brønsted and Lewis mechanisms. Thus, some researchers have attempted to diminish catalyst acidity in order to reduce isomerization activity by the treatment with hexamethyldisilazane to poison the weakly Brønsted-acidic silanols [4]. Another way which was tested by [5] was the addition a small amount of alkali metal ion to catalyst. Maksasithorn S. et al. [6] also found that the modified WO_3/SiO_2 catalysts by ion exchange with low concentration of sodium hydroxide solution could reduce coke deposited on the catalyst surface.

Kritsada P. and Surasa M. are with the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand (e-mail: k.pipitthapan@hotmail.com).

Piyasan P. and Joongjai P. are with the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand (corresponding author to provide phone: +662 218 6861; e-mail: piyasan.p@chula.ac.th).

Kongkiat S. and Sirachaya K. are with the SCG Chemicals, Co., Ltd., 1 Siam Cement Road, Bangsue, Bangkok 10800, Thailand.

In the present work, the WO_3/SiO_2 catalysts were modified by ion exchange with sodium hydroxide and potassium hydroxide solution and their abilities to reduce isomerization activity were evaluated.

II. EXPERIMENTS

A. Catalyst Preparation

The 9% wt. WO_3/SiO_2 catalysts were prepared by incipient wetness impregnation. A silica gel which was used as the support was impregnated with an aqueous solution of ammonium metatungstate hydrate, and left at room temperature for 2 hrs and dried at 110°C for 12 hrs. The samples were calcined under air atmosphere for 8 hrs with a ramp rate $10^\circ\text{C}/\text{min}$. The catalysts were denoted as W.

B. Catalyst Modification

An alkali solution was prepared by dissolution of alkali metals (NaOH, KOH) into 200 ml of deionized water with appropriate concentration. The catalyst was added into the solution and then stirred for 2 hrs. The solid was separated from the mixture by filtration method and washed with deionized water for 3 times, and then dried at 110°C for 12 hrs. The modified catalysts were calcined under air atmosphere for 8 hrs with a ramp rate $10^\circ\text{C}/\text{min}$ and denoted as W-xNaOH and W-xKOH for sodium hydroxide and potassium hydroxide solutions, respectively. The letter x was referred to the mole ratio of the amount of alkali metal to acid sites of catalyst. The acid sites of the WO_3/SiO_2 catalysts were determined by titration for Brønsted acidity.

C. Catalytic Performance Testing

The catalyst performance in metathesis reaction was tested in a fixed bed reactor with 3 g of catalyst. The catalyst was pretreated under nitrogen flow 22 ml/min for an hour. Then the temperature was set to 450°C and kept constant for reaction time 12 hrs. A mixture of ethylene and trans-2-butene in nitrogen was used as feed gas to reactor. The experiments were tested at a reaction temperature 450°C , pressure 0.1 MPa and WHSV 1.127 hr^{-1} . The effluence gas was analyzed by a flame gas chromatography with ionization detector (GC-FID).

D. Catalyst Characterization

XRD was performed to determine the bulk phase of catalysts by SIEMENS D 5000. The experiments were carried out by using CuK_α radiation with Ni filter in the 2θ range of 10-80 degrees resolution 0.04° . The number of Brønsted acid sites was measured by using a method involving ion exchange between H^+ on the catalyst and Na^+ in NaCl solution [7]. The

0.2 g of catalyst was added to 10 ml of a 3.42 M aqueous solution of NaCl. The sample was stirred for 30 hours at room temperature then it was centrifuged. The separated liquid was titrated with a 0.05 M aqueous NaOH solution for the number of Brønsted acid site. The surface structure of catalysts was analyzed using Ultraviolet - Visible Spectroscopy in the wavelength range 200-800 nm. An absorbance at the different wavelength could apply to distinguish the tungsten species.

The amount of coke on catalyst surface was determined by temperature program oxidation method. The sample 0.5 g was packed into U-tube and set to Micromeritics ChemiSorb 2750 instrument. 1% O₂/He was fed to instrument with flow 15 ml/min and temperature was arose to 930°C with ramp rate 5°C/min. The vapor was tapped by liquid nitrogen. Then, the effluent gas was detected by thermal conductivity detector of gas chromatography (GC-TCD).

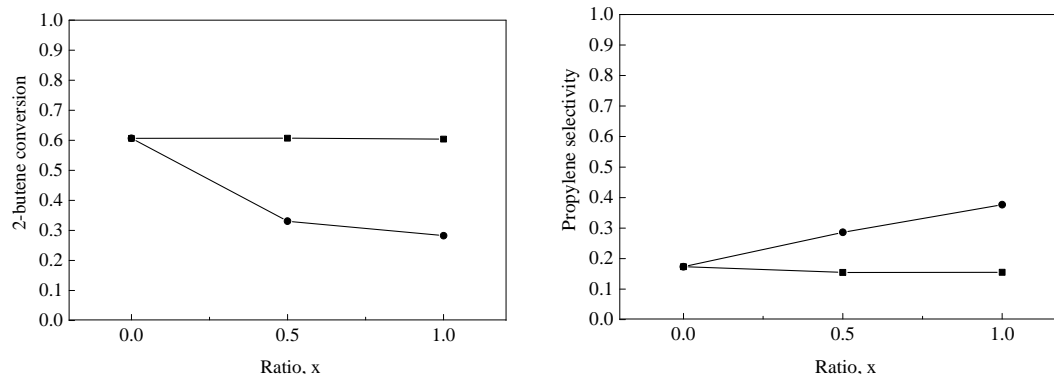


Fig. 1 The metathesis catalytic performance of modified catalysts by ion exchange (a) -■- W-NaOH (b) -●- W-KOH

III. RESULTS AND DISCUSSION

From Fig. 1, X-axis referred to the mole ratio of concentration of alkali solution to acid site of WO₃/SiO₂ catalyst as measured by titration method. With increasing ratio, the catalytic performance of the W-KOH catalysts, trans-2-butene conversion and propylene selectivity were decreased and increased respectively. For the W-NaOH catalysts, both conversion and selectivity were constant for all the ratios. It is implied that potassium and sodium exhibited different behaviors during ion exchange. Potassium ions influenced the change of active site species that caused the decrease in conversion. On the other hand, the conversion of the sodium modified catalysts was not changed, suggesting that sodium ions did not affect the active site species.

According to previous studies [8], tungsten tetrahedral and octahedral structures are active centers in metathesis reaction. To verify the above hypothesis, characterization by UV-visible spectroscopy was selected to prove the transformation of the active site species.

From the XRD patterns, the catalyst modification by ion exchange with NaOH and KOH made WO₃ crystalline species lost. With the increasing concentration of alkali metal solution, the disappearance of WO₃ crystalline species was observed, especially in the KOH solution. The activity of W-NaOH catalysts did not change, although some WO₃ species were lost. The results suggest that the lost WO₃ species was not active species.

The UV-Visible spectra could analyze the transformation of tungsten species on the modified catalysts. As shown in Fig. 3, there were three absorption bands at 230, 280 and 400 nm [8]. They can be assigned to isolated tetrahedral tungsten species, octahedral polytungstate species and tungsten oxide

crystallites species, respectively. In metathesis reaction, tetrahedral tungsten species and octahedral polytungstate species were active sites whereas tungsten oxide crystallites species was not. The spectra of potassium modified catalysts show the transformation of the signals whereas the spectra of sodium modified catalysts were slightly changed. Such results infer that potassium could induce tungsten active species to transform into inactive species, resulting in lower activity of the catalysts. To sum up, inducing ability of potassium hydroxide which used in the modification of WO₃/SiO₂ catalysts to tungsten active species was a cause of decreasing of the conversion of the modified catalysts by potassium hydroxide.

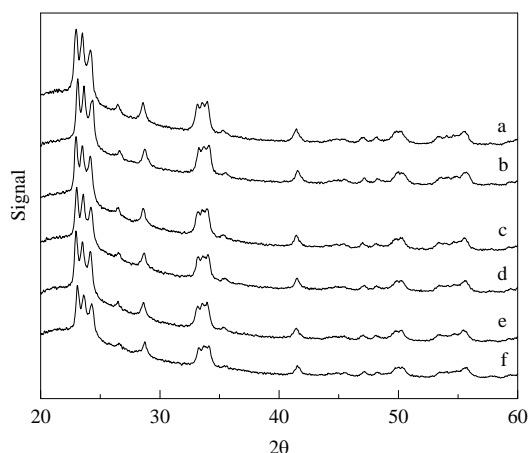


Fig. 2 X-ray diffraction pattern of modified catalysts (a) W (b) W-water (c) W-0.5NaOH (d) W-1.0NaOH (e) W-0.5KOH (f) W-1.0KOH

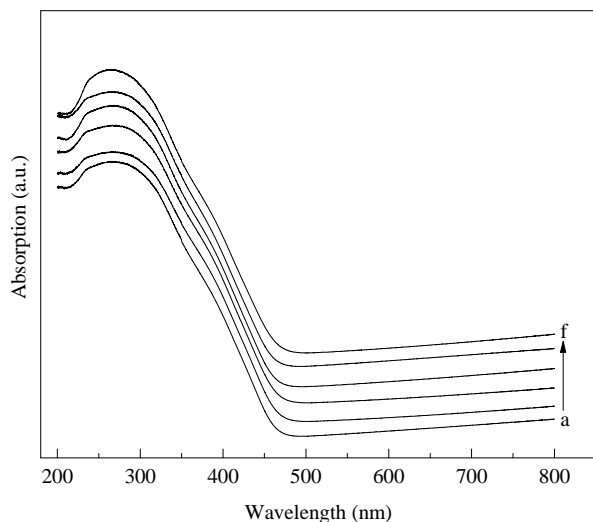


Fig. 3 UV-Visible spectra of modified catalysts (a) W (b) W-water (c) W-0.5NaOH (d) W-1.0NaOH (e) W-0.5KOH (f) W-1.0KOH

Figs. 4 and 5 show that the spent modified catalysts after 12 hrs reaction time had less amount of deposited coke than the WO_3/SiO_2 catalysts, especially the modified catalysts with potassium hydroxide. Generally, acidity of the catalysts influences coke formation and coke deposition [9]-[11]. From the TPO results, acidity of the catalysts could be diminished by ion exchange with alkali metal, as a consequence the amount of deposited coke of all the modified catalysts was lower.

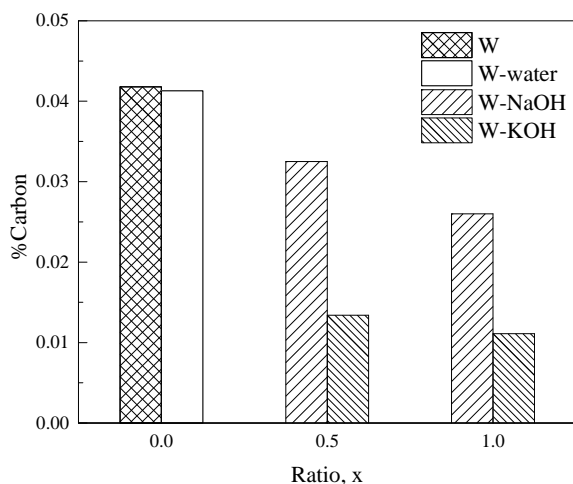


Fig. 4 TPO results of the spent catalysts

IV. CONCLUSION

During ion exchange, sodium hydroxide and potassium hydroxide played different roles although both sodium hydroxide and potassium hydroxide could leach WO_3 crystallite species from the WO_3/SiO_2 catalysts. Potassium hydroxide affected the transformation of tungsten active species whereas sodium hydroxide did not. It is likely that

potassium hydroxide could induce the transformation of tungsten oxides, which were the isomerization active species, resulting in decreased trans-2-butene conversion and increased propylene selectivity. Nevertheless, modification of the catalysts by ion exchange with sodium and potassium hydroxide solutions could decrease the amount of deposit coke on the catalyst surface.

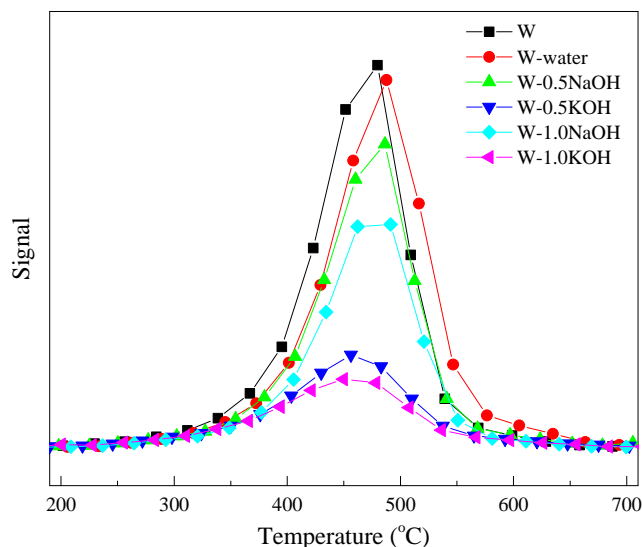


Fig. 5 TPO Profiles of the spent catalysts

ACKNOWLEDGMENT

This research has been supported by the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (RES560530086-AM) and National research University Project, Office of Higher Education Commission (WCU-029-AM-57). In addition, the authors would like to specially thank the SCG Chemicals Co., Ltd., Thailand for their financial supports.

REFERENCES

- [1] S. Lwin, I.E. Wachs, Olefin Metathesis by Supported Metal Oxide Catalysts, *ACS Catalysis*, vol. 4, pp. 2505-2520, 2014.
- [2] R.L. Banks, G.C. Bailey, Olefin Disproportionation. A New Catalytic Process, *I&EC Product Research and Development*, vol. 3, pp. 170-173, 1964.
- [3] L.F. Heckelsberg, R.L. Banks, G.C. Bailey, Tungsten Oxide on Silica Catalyst for Phillips' Triolefin Process, *I&EC Product Research and Development*, vol. 7, pp. 29-31, 1968.
- [4] A.J. Van Roosmalen, J.C. Mol, Active centers for the metathesis and isomerization of alkenes on tungsten-oxide/silica catalysts, *Journal of Catalysis*, vol. 78, pp. 17-23, 1982.
- [5] A. Spamer, T.I. Dube, D.J. Moodley, C. van Schalkwyk, J.M. Botha, The reduction of isomerisation activity on a WO_3/SiO_2 metathesis catalyst, *Applied Catalysis A: General*, vol. 255, pp. 153-167, 2003.
- [6] S. Maksasithorn, D.P. Debecker, P. Praserttham, J. Panpranot, K. Suriye, S.K.N. Ayudhya, NaOH modified WO_3/SiO_2 catalysts for propylene production from 2-butene and ethylene metathesis, *Chinese Journal of Catalysis*, vol. 35, pp. 232-241, 2014.
- [7] D.E. López, J.G. Goodwin Jr, D.A. Bruce, Transesterification of triacetin with methanol on Nafion® acid resins, *Journal of Catalysis*, vol. 245, pp. 381-391, 2007.

- [8] S. Huang, S. Liu, W. Xin, J. Bai, S. Xie, Q. Wang, L. Xu, Metathesis of ethene and 2-butene to propene on W/Al₂O₃-HY catalysts with different HY contents, *Journal of Molecular Catalysis A: Chemical*, vol. 226, pp. 61-68, 2005.
- [9] T. Horiuchi, K. Sakuma, T. Fukui, Y. Kubo, T. Osaki, T. Mori, Suppression of carbon deposition in the CO₂-reforming of CH₄ by adding basic metal oxides to a Ni/Al₂O₃ catalyst, *Applied Catalysis A: General*, vol. 144, pp. 111-120, 1996.
- [10] C.H. Bartholomew, Mechanisms of catalyst deactivation, *Applied Catalysis A: General*, vol. 212, pp. 17-60, 2001.
- [11] D.J. Moodley, C. van Schalkwyk, A. Spamer, J.M. Botha, A.K. Datye, Coke formation on WO₃/SiO₂ metathesis catalysts, *Applied Catalysis A: General*, vol. 318, pp. 155-159, 2007.