

Novel catalyst of mixed SiO₂-TiO₂ supported tungsten for metathesis of ethene and 2-butene

S. Chaemchuen¹, W. Limsangkass¹, B. Netiworaraksa¹, S. Phatanasri^{1*}, N. Sae-Ma¹, K. Suriye²

¹Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

²SCG Chemicals Co., Ltd. 1 Siam-cement Rd, Bang sue, Bangkok 10800, Thailand

Received March 8, 2011; Revised May 9, 2011

Mixed SiO₂-TiO₂ supported tungsten catalysts containing 8 wt.% tungsten were prepared by incipient wetness impregnation. The catalyst with 10% TiO₂ addition, designated as WO₃/SiO₂-10Ti, displayed improved conversion and propylene selectivity, 72 % and 48 %, respectively, toward metathesis of ethylene and 2-butene compared with conventional silica supported tungsten without TiO₂ addition. The better dispersion of tungsten achieved by TiO₂ addition and the tetrahedral tungsten oxide species of relatively high surface were believed to be responsible for the good metathesis activity of the catalyst for propylene formation.

Keyword: Metathesis, Silica-Titania, Mixed support, Tungsten

1. INTRODUCTION

Recently, there has been an ever increasing demand of polypropylene owing to the considerable growth of propylene production [1–2]. One of the pathways for propylene production is the metathesis reaction of ethene and 2-butene using suitable catalysts [3–4]. Supported WO₃ catalysts are known from several patents and publications where well dispersed low-loaded WO₃/SiO₂ catalysts have been claimed to have activity equal to that of catalysts of appreciable higher tungsten content. This points to the importance of obtaining a well dispersed catalyst [5–7].

Verpoort *et al.* [8–12] have made extensive studies on olefin metathesis catalysts relating to the catalytic activity of supported tungsten phenoxide complexes, activation and characteristics of a ‘molecular’ tungsten unit on silica and have found that the catalytic activity was related to the structure of the molecular entities on the surface of the precursor. Many researchers have tried to improve the catalyst performance by using composite supports, such as Al₂O₃-SiO₂ [13], Al₂O₃-B₂O₃ [14–15], and Al₂O₃-P₂O₅ [16]. Recently, SiO₂-TiO₂ mixed oxides were used as the support material for Pt [17–19], Er [20], Au [21], Ni [22], Fe-Pt [23] and Mo [24] metals in many reactions. It was found that the presence of a mixed oxide support has great effect on the dispersion of the active components

and their catalytic performances. Therefore, the objective of this work was to investigate the effect of mixed SiO₂-TiO₂ supported tungsten catalysts with 8 wt% metal loading on the catalytic performance in propylene production by metathesis.

2. EXPERIMENTAL

2.1 Catalysts Synthesis

SiO₂-TiO₂ mixed oxide supports were prepared by physical mixing of silica gel, Davisil grade 646 (pore volume: 1.15 cm³/g, supplied by Aldrich) and titania (Degussa P25). The catalysts were impregnated with an aqueous solution of metatungstate hydrate (Aldrich, 99.9%), to yield an 8 wt% loading on the mixed oxide support, then dried at 110 °C overnight. The catalysts were calcined at 550 °C for 8 h with a heating rate of 10 °C/min in an air atmosphere. These prepared catalysts are denoted as WO₃/SiO₂-xTi, where x indicates the wt. % of TiO₂ (5, 10, 30) in the SiO₂-TiO₂ support.

2.2 Catalyst Characterization

Surface areas of the samples were determined using a multipoint BET method. The catalyst samples were degassed at 300°C and 10⁻³ mm Hg for 3 h. Adsorption measurements were carried out using liquid nitrogen at -196°C with a Micromeritics ASAP 2020 device. The Raman spectra of the samples were collected by projecting a continuous wave YAG laser of Nd (810 nm)

* To whom all correspondence should be sent:

E-mail: s_phatanasri@yahoo.com

through the samples at room temperature. A scanning range of 200–1400 cm⁻¹ with a resolution of 2 cm⁻¹ was applied. Phase identification and investigation of the crystallite samples was performed by X-ray diffraction (Siemens D5000) using Ni filter Cu K α radiation from 10° to 60°.

2.3 Reaction Studies

The catalyst sample was placed at the center of a reactor with inner diameter (ID) of 7.5 mm. The catalyst was pretreated at 500 °C in nitrogen flow for 1 h before allowing the catalyst to cool down in an inert atmosphere to the reaction temperature 400 °C. The reaction conditions were as follows: pressure=0.1MPa, C₂H₄/trans-2-C₄H₈=2. The sampling was made at 8 h on stream, and sample analysis was performed on a Shimadzu GC 2014 equipment with a column of packed 10% silicone SE-30 (3.02 m with 0.53 mm ID) and a FID detector using helium as the carrier gas (5 ml/min).

3. RESULTS AND DISCUSSION

The catalysts performance on the metathesis activity of ethene and trans-2-butene is shown in Table 1. and Fig. 1. It was found that both conversion of 2-butene and propylene selectivity increased with TiO₂ addition and as high as 72% of conversion of 2-butene and 48% of propylene selectivity were obtained on a 10% TiO₂-containing catalyst designated as WO₃/SiO₂-10Ti. However, the side reaction of isomerization to 1-butene, cis-2-butene and butadiene became more competitive with the 30% TiO₂-containing catalyst, and almost no propylene formation was observed on the silica-free TiO₂ supported tungsten catalyst. According to XRD patterns of the relevant catalysts shown in Fig. 2, peaks characteristic to tungsten crystallites at 2 θ of 23.12, 23.60 and 24.38° were observed while silica is almost amorphous. It was noticed that lower peak intensities in this region corresponding to a lower amount of tungsten crystallites were discernible upon increasing the amount of TiO₂, and those peaks almost disappeared for the silica-free TiO₂ supported tungsten catalyst. This indicates the higher dispersion of tungsten species on the mixed SiO₂-TiO₂ support. Nevertheless, the intrinsic lower surface of TiO₂ seemed to result in a lower BET surface of the mixed SiO₂-TiO₂ supported tungsten catalysts with a high loading of TiO₂, as shown in Table 1. The marked increase in both conversion of 2-butene and propylene selectivity on WO₃/SiO₂-10Ti may be attributed to the higher dispersion of tungsten resulting from TiO₂ addition. However, the metathesis activity site for propylene formation on

the 30% TiO₂-containing catalyst, WO₃/SiO₂-30Ti, tends to be overshadowed by the TiO₂-related secondary reaction sites for 1-butene, cis-2-butene and butadiene formation.

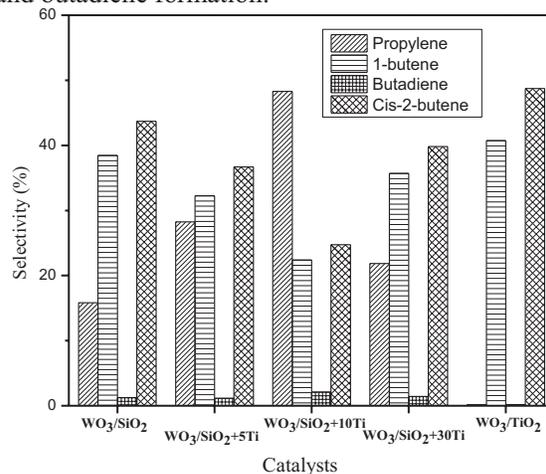


Fig.1. The product distribution of different catalysts after 8 h on stream.

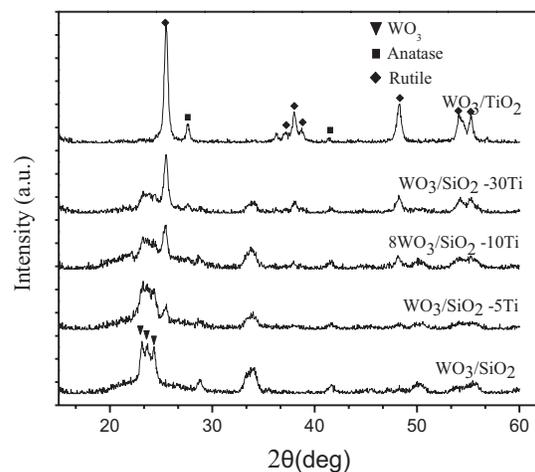


Fig.2. The XRD patterns of WO₃/SiO₂-xTi catalysts.

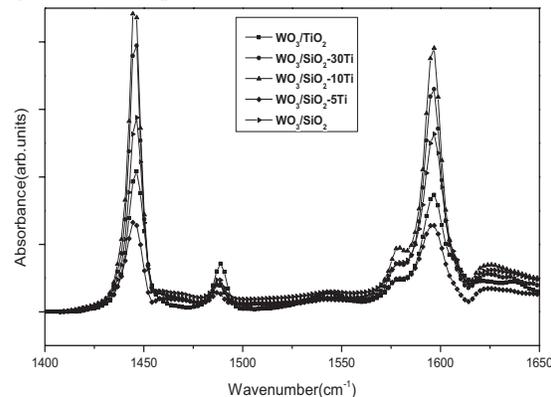


Fig3. The FT-IR spectra of pyridine adsorbed on various samples at 50°C.

Raman spectroscopy was adopted as a suitable tool for determination of the structure of tungsten

Table 1. The property and activity of catalysts with different TiO₂ content on mixed SiO₂-TiO₂ supported tungsten catalysts

Catalysts	TiO ₂ content (% wt)	Conversion (%)	BET Surface area (m ² g ⁻¹)	Raman ratio I_{970}/I_{805}
WO ₃ /SiO ₂	0	63	257	0.64
WO ₃ /SiO ₂ -5Ti	5	65	250	0.88
WO ₃ /SiO ₂ -10Ti	10	72	240	1.11
WO ₃ /SiO ₂ -30Ti	30	63	194	0.89
WO ₃ /TiO ₂	100	57	50	0.66

species present in supported catalysts. Huang *et al.* [25] proposed that the band at 970 cm⁻¹ was assigned to the surface tetrahedral tungsten oxide species which are the active species for metathesis reaction to propylene. According to the literature, the ratio of the relative intensities of Raman bands between 970 and 805 cm⁻¹ (I_{970}/I_{805}) was used to reflect the relative content of active sites for propylene formation. As shown in Table 1, the maximum ratio of I_{970}/I_{805} was achieved for WO₃/SiO₂-10Ti (10 wt% TiO₂ content).

The Lewis and Brønsted acidities were assessed by adopting the FT-IR technique for the desorption of pre-adsorbed pyridine at 50°C. As shown in Fig.3, the sharp peaks around 1595 and 1445 cm⁻¹ were assigned to Lewis acid sites and the less intense one around 1488 cm⁻¹ to the Brønsted acid site [26]. It was found that WO₃/SiO₂-10Ti displayed the highest number of total acid sites compared to the titania-free sample; however, the number of acid sites decreased with further addition of TiO₂ above 10%. Kim *et al.* [27] reported that the number of surface acid sites linearly increases with tungsten oxide surface density below tungsten oxide monolayer surface coverage. However, the number of exposed surface acid sites continuously decreases with tungsten oxide density at the above monolayer surface coverage because of the presence of WO₃ crystallites. The highest amount of acid sites found for WO₃/SiO₂-10Ti in this work should be attributed to the better dispersion of tungsten species to obtain tungsten oxide monolayer surface coverage. Nonetheless, with TiO₂ addition higher than 10%, the smaller support surface area influenced by the intrinsic low surface area of TiO₂ compared with SiO₂ may be not enough to obtain tungsten oxide monolayer surface coverage. As a consequence, the state of the above-monolayer surface coverage may be obtained for the catalysts with TiO₂ addition higher than 10%, causing a decrease in the number of acid sites. The H₂-TPR

Table 2. The relative amount of H₂ uptake and reduction temperature of catalysts with different TiO₂ content in mixed SiO₂-TiO₂ supported tungsten catalysts.

Catalysts	H ₂ uptake (a.u.)	Reduction Temperature (°C)
WO ₃ /SiO ₂	4.74	531, 800
WO ₃ /SiO ₂ -5TiO ₂	3.94	531, 807
WO ₃ /SiO ₂ -10TiO ₂	3.78	537, 817
WO ₃ /SiO ₂ -30TiO ₂	3.08	537, 824
WO ₃ /TiO ₂	1.80	601, 810

technique was used to investigate the interaction between tungsten species and the SiO₂-TiO₂ support. The H₂ uptake and the temperatures corresponding to the lower and higher reduction are summarized in Table 2. Ramirez *et al.* [28] ascribed the reduction peak at higher temperatures to the reduction of well-dispersed tungsten species rich in tetrahedral coordination. The variation in H₂ uptake as well as the shift of the reduction peak to higher temperature established for the samples with TiO₂ addition reflects the modification of surface tungsten oxide species as well as the stronger interaction between tungsten and the SiO₂-TiO₂ support. WO₃/SiO₂-10Ti should be a sample rich in surface tetrahedral tungsten oxide species, which contribute to the improvement in metathesis activity.

4. CONCLUSION

The improvement in catalytic performance by using a mixed support is a cheaper and more convenient approach, compared with changing the process conditions or the process system. The mixed SiO₂-TiO₂ supported tungsten catalyst containing 10% TiO₂ markedly improved both conversion of 2-butene and propylene selectivity for metathesis of ethene and trans-2-butene. Though the detailed mechanism is subject to further investigation, the preliminary characterization reveals that less tungsten crystallites are formed, which reflects the

better dispersion of tungsten as well as the achievement of relatively high surface tetrahedral tungsten oxide species, widely accepted as the metathesis active site for propylene formation. While TiO₂ addition seems to contribute to the better dispersion of tungsten, TiO₂ itself favors the secondary reaction of 1-butene, cis-2-butene and butadiene formation. WO₃/SiO₂-10Ti (10% TiO₂ content) represents a novel metathesis catalyst which displays good propylene selectivity not overshadowed by TiO₂-related secondary reaction sites.

Acknowledgements: The authors would like to express their deep appreciation to the Thailand Research Fund (TRF) and SCG Chemical Co., Ltd. for their financial support. Special thanks also go to the Office of Higher Education Commission for its support of the National Research University Program (CC557A).

REFERENCES

1. P.K. Ludwig, J.E. Asplin, G.F. Stuntz, W.A. Wachter, B.E. Henry, US Patent 6,069,287 (2000) (to Exxon Research and Engineering Corporation)
2. J.P. Dath, W. Vermeiren, K. Herrenbout, WO00/78894 (2000) (to Fina Oil and Chemical Corporation)
3. J.C. Mol, *J. Mol. Catal. A.*, **213**, 39 (2004).
4. R.M. Venner, S.I. Kantorowicz, *Technol. Q. Summer* 141 (2001).
5. D. Davazoglou, A. Moutsakis, V. Valamontes, V. Psycharis, *J. Electrochem. Soc.*, **144** (2), 595 (1997).
6. J. Hietala, EP Patent 0,524,522 A1 (1993), to Neste Oy.
7. J. Hietala, P. Knuutila, A. Kytökivi, US Patent 5,372,982 (1994), to Neste Oy.
8. F. Verpoort, A.R. Bossuyt, B. Coussens, L. Verdonck, *J. Mol. Catal. A.*, **115**, 207 (1997).
9. F. Verpoort, A.R. Bossuyt, B., L. Verdonck, *J. Electron Spectrosc. Relat. Phenom.*, **82**, 151 (1996)
10. F. Verpoort, A. Bossuyt, L. Verdonck, *J. Chem. Soc., Chem. Commun.*, 417 (1996).
11. F. Verpoort, A.R. Bossuyt, L. Verdonck, *J. Mol. Catal.* **95**, 75 (1995).
12. F. Verpoort, L. Fiermans, A.R. Bossuyt, L. Verdonck, *J. Mol. Catal.* **90**, 43 (1994).
13. M. Sibeijn, J.C. Mol, *Appl. Catal.*, **67**, 279 (1991).
14. X. Xu, C. Boelhouwer, J.I. Benecke, D. Vonk, J.C. Mol, *J. Chem. Soc. Faraday Trans.*, **82**, 1945 (1986).
15. F.C. Sheu, C.T. Hong, W.L. Hwang, C.J. Shih, J.C. Wu, C.T. Yeh, *Catal. Lett.* **14**, 297 (1992).
16. M. Sibeijn, R. Spronk, J.A.R. van Veen, J.C. Mol, *Catal. Lett.*, **8**, 201 (1991).
17. H.S. Hoffmann, P.B. Staudt, T.M.H. Costa, C.C. Moro, E.V. Benvenuti, *Surf. Interface Anal.*, **33**, 631 (2002).
18. B.K. Min, W.T. Wallace, D.W. Goodman, *J. Phys. Chem. B.*, **108**, 14609 (2004).
19. X. Zhang, H. Yang, F. Zhang, K.Y. Chan, *Mater. Lett.*, **61**, 2231 (2007).
20. Q. Fang, M. Meier, J.J. Yu, Z.M. Wang, J.Y. Zhang, J.X. Wu, A. Kenyon, P. Hoffmann, I.W. Boyd, *Mater. Sci. Eng. B.*, **105**, 209 (2003).
21. A.M. Venezia, F.L. Liotta, G. Pantaleo, A. Beck, A. Horváth, O. Geszti, A. Kocsonya, L. Gucci, *Appl. Catal. A.*, **310**, 114 (2006).
22. J.R. Grzechowiak, I. Szyszka, A. Masalska, *Catal. Today*, **137**, 433 (2008).
23. H. Tang, C.H. Yu, W. Oduoro, H. He, S.C. Tsang, *Langmuir*, **24**, 1587 (2008).
24. X. Gao, I.E. Wachs, *Catal. Today*, **5**, 233 (1999).
25. S. Huang, F. Chen, S. Liu, Q. Zhu, X. Zhu, W. Xin, Z. Feng, C. Li, Q.X. Wang, L. Xu, *J. Mol. Catal. A.*, **267**, 224 (2007).
26. X.L. Yang, R. Gao, *J. Phys. Chem. C.*, **112**, 3819 (2008).
27. T. Kim, A. Burrows, *J. Catal.*, **246**, 370 (2007).
28. J. Ramirez, A.G. Alejandre, *J. Catal.*, **170**, 108 (1997).

НОВ КАТАЛИЗАТОР ОТ ВОЛФРАМ ВЪРХУ SiO₂-TiO₂ ЗА МЕТАТЕЗА НА ЕТЕН И 2-БУТЕН

С. Чемчуен¹, У. Лимсангкас¹, В. Нетовораракса¹, С. Фатанасри¹, Н. Сасе-Ма¹, К. Сурие²

¹Център за върхови постижения по катализ и инженерство на каталитичните реакции, Департамент по инженерна химия, Инженерен факултет, Университет Чулалонгкорн, Бангкок 10330, Тайланд

²SCG Кемимълс Со., лимитед, 1 Сиам-цемент роуд, Банг сю, Бангкок 10800, Тайланд

Постъпила на 8 март, 2011 г.; коригирана на 9 май, 2011 г.

(Резюме)

Приготвени са волфрамови катализатори, нанесени върху смес от SiO₂-TiO₂, съдържаща 8 % тегл. волфрам чрез мокро импрегниране. Катализаторът с добавка от 10% TiO₂, определен като WO₃/SiO₂-10Ti, показва подобрена конверсия (72 %) и селективност спрямо пропилен (48 %) и съответно по отношение метатезата на етена и 2-бутена спрямо конвенционален катализатор от волфрам върху силициев диоксид без добавка на титанов диоксид. Предполага се, че добрата активност на катализатора спрямо образуването на пропилен се дължи на по-добрата дисперсия на волфрама при добавянето на титановия диоксид и на тетраедричния волфрамов оксид с голяма повърхност.