Korean J. Chem. Eng., 33(1), 140-146 (2016)
DOI: 10.1007/s11814-015-0126-7

pISSN: 0256-1115
eISSN: 1975-7220

Ethylene and mixed 2-butene cis/trans isomers metathesis: Influence of lanthanum as a second metal on the WO_3/SiO_2 catalysts

Narongrat Poovarawan*,*, Thidaya Thitiapichart*, Kongkiat Suriye**, Joongjai Panpranot*,
Wimonrat Limsangkass*, Francisco José Cadete Santos Aires***, and Piyasan Praserthdam*,†**

*Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering,
Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
**SCG Chemicals, Co., Ltd., 1 Siam Cement Road, Bangsue, Bangkok 10800, Thailand
***Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS/Université Lyon1,
2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

(*Received 20 April 2015 • accepted 12 June 2015*)

Abstract−Lanthanum (0.5, 0.6, 0.75, 0.9 and 1 wt%) was added as a second metal on the 9 wt% WO_3/SiO_2 catalysts by the incipient wetness impregnation method. The catalysts were tested in the metathesis reaction of ethylene and 2-butene using either pure 2% trans-2-butene and the mixture of 1% cis- and 1% trans-2-butene as the reaction feed and were characterized by X-ray diffraction (XRD), nitrogen physisorption (BET), inductively coupled plasma optical emission spectrometry (ICP-OES), scanning electron microscopy, ion-exchange titration, FT-Raman, ammonia temperature programmed desorption (NH_3-TPD) and reactant temperature programmed desorption (reactant-TPD). An optimum lanthanum loading at 0.5 wt% could improve dispersion of tungsten active phase and adsorption properties of the reactants on the catalysts. The adsorption of the mixed cis/trans-2-butene isomer was much improved on the La-WO_3/SiO_2 catalysts with 0.5 wt% La.

Keywords: Metathesis, Trans-2-butene, Cis-2-butene, Propylene, WO_3/SiO_2, Tungsten Dispersion

INTRODUCTION

The demand for propylene has increased every year because it is important for the production of petrochemical products such as polypropylene, alcohol, acrylic acid, and acrylonitrile [1]. Propylene can be produced from many routes such as fluid catalytic crackers [2], naphtha thermal crackers [3], Fischer-Tropsch synthesis [4], and propane dehydrogenation [5]. Metathesis reaction is an interesting way to produce propylene, especially metathesis of 2-butene and ethylene. The catalysts for metathesis reaction are W-, Re- and Mo-based catalysts. WO_3/SiO_2 [1,6-9] is generally employed for this reaction because it is durable for poisons and coke formation [6,10,11] and also has high stability. Zhao et al. [12], Spamer et al. [13], and Westhoff and Moulijn [14] investigated the influence of tungsten loading on the activity and selectivity of the WO_3/SiO_2 catalysts in the metathesis of ethylene and 2-butene using pure trans-2-butene feed and found that 8%wt of tungsten loading resulted in the highest conversion and the selectivity of propylene for metathesis reaction. Narongrat et al. [15] investigated the effect of 2-butene cis/trans isomers in the metathesis of ethylene and 2-butene over WO_3/SiO_2 catalysts and found that the isomer structure like cis/trans-2-butene isomers in the reactant affected the butene conversion and the yield of propylene. Using cis/trans-2-butene isomer as the reactants gave lower conversion and propylene yield than using pure trans-2-butene as the reactants. The effect of a second metal addition on WO_3 catalysts such as alkali-, alkali-earth, and thallium metal ions [6,13,16] has been reported. Atiporn et al. [17] show that the addition of a second metal can improve the catalytic activity and stability due to a better metal dispersion.

In this work, one of the SCG Chemicals's catalysts using lanthanum as the second metal doping in tungsten based catalyst (under patent pending) was used to study the effect of cis/trans isomer in the metathesis of ethylene and 2-butene. The dispersion of WO_3/SiO_2 catalysts was improved by adding lanthanum as a second metal. The metathesis reaction involved ethylene and cis/trans-2-butene isomer as reactants and was compared to the use of ethylene and pure trans-2-butene.

EXPERIMENTAL

1. Catalytic Preparation

The 9 wt% WO_3/SiO_2 catalysts were prepared by the incipient wetness impregnation method. Silica gel, Davisil grade 646, 35-60 mesh was used as the support (supplied by Aldrich). Ammonium metatungstate hydrate solution was added to the silica gel. The catalyst was dried at room temperature for 2 h and then 383 K for overnight. For the La-WO_3/SiO_2 catalysts, lanthanum (III) nitrate hexahydrate solution was added to the support with various lanthanum loadings 0.5, 0.6, 0.75, 0.9 and 1 wt%. Then, the prepared catalysts were left at room temperature for 2 h and dried overnight in an oven. Afterward, they were loaded with the ammonium metatungstate hydrate solution similar to that of 9 wt%WO_3/SiO_2 catalysts. Calci-

---

†To whom correspondence should be addressed.
E-mail: piyasan.p@chula.ac.th

nation was performed under air at temperature sufficiently removing the residue during the synthesis in a tubular furnace.

2. Reaction Studies

The catalytic tests were performed in a fixed bed reactor (316 Stainless Steel by Swagelok, diameter 19.05 millimeters) with 3 g of catalyst. The catalysts were activated at a temperature not greater than 873 K for 2 h under nitrogen, then cooled to reaction temperature at 673 K and at atmosphere. Two types of reactant feed, 2% trans-2-butene with excess ethylene (balancing with nitrogen) and) 1% trans-2-butene and 1% cis-2-butene with excess ethylene (balancing with nitrogen), were used in this study to investigate the effect of cis- and trans isomer on the catalytic performance of metathesis reaction (WHSVs is 0.04 hour^{-1}). After 10 hours, the reaction products were analyzed online by gas chromatography (GC Shimadzu 2014). The conversion selectivity and yield was calculated by

$$\text{Conversion} = \frac{\begin{array}{c}\text{amount of butene in feed}\\ -\text{amount of butene remained in products}\end{array}}{\text{amount of butene in feed}} \times 100$$

$$\text{Selectivity} = \frac{\text{amount of propylene}}{\begin{array}{c}\text{amount of butene in feed}\\ -\text{amount of butene remained in product}\end{array}} \times 100$$

$$\text{Yield} = \frac{\text{amount of propylene}}{\text{amount of butene in feed}} \times 100$$

3. Catalyst Characterization

The catalyst morphology, tungsten and lanthanum-distribution over the silica support were investigated by scanning electron microscopy (JEOL JSM-5800LV SEM equipped with a Pentafet LinK-Isis series) together with energy dispersive X-ray (EDX) spectroscopy. The actual compositions of tungsten and lanthanum metal on each catalyst after calcination was measured by ICP-OES on a Perkin Elmer Optima 2100DV. The crystallite phase and size were investigated by X-ray diffraction, XRD (Siemens D5000) using Ni filter Cu Ka radiation. Specific surface area (SBET) was determined from nitrogen adsorption studies by using Micromeritics Chemisorb 2750. Molecular structure of the tungsten oxide was determined by Raman spectroscopy. The Raman spectra were collected by projecting a continuous wave YAG laser of Nd (810 nm) through the samples at room temperature and recorded on a PerkinElmer Spectrum GX spectrometer. Acidity of catalyst was determined by ammonia temperature programmed desorption (NH_3-TPD) and ion exchange titration. For NH_3-TPD, 0.1 g of the catalyst was treated at the temperature not greater than 873 K in a flow of helium, then cooled to room temperature and saturated with 15% NH_3/He mixture. After purging with helium at room temperature for 1 h to remove weakly physisorbed NH_3, the sample was heated from room temperature to 773 K under helium flow. NH_3-TPD was performed by using a Micromeritics Chemisorb 2750 automated system equipped with ChemiSoft TPx software. Ammonia effluent was finally kept in a boric acid solution (20 g/dm^3) and titrated with a 0.01 M aqueous HCl solution. The number of Brønsted acid sites was also estimated by using a method involving an aqueous ion-exchange step of catalyst H^+ ions with Na^+ ions, followed by titration of the resulting solution [18].

Reactant-TPD was used to determine the adsorption behavior of the reactant. Then 1 g. of catalyst was packed in the middle of the quartz micro-reactor before placing the reactor in the furnace and treated at a temperature not greater than 873 K in a flow of nitrogen for 1 h.

The catalyst sample was saturated with the reactant. After purging with nitrogen at room temperature for 1 h to remove weakly physisorbed reactant, the catalyst was heated from room temperature to 673 K under a flow of nitrogen. The resulting gaseous desorption was sampled every 2 min and analyzed with an FID-Shimadzu 2014.

RESULTS AND DISCUSSION

1. Characteristics of WO_3/SiO_2 Catalysts with Different La Loadings as a Second Metal

The characterization of La-WO_3/SiO_2 catalysts containing various La loadings was investigated by BET, ICP, SEM-EDX, Raman, XRD and acidity measurements. The surface areas of the catalysts are shown in Table 1. When the silica support was impregnated with La and W, the surface area (~179-182 m^2/g) did not significantly change compared to the SiO_2 support (~185 m^2/g).

ICP and SEM-EDX were applied to determine the actual amount

Table 1. The specific surface area, relative intensities ratio of the Raman band between tetrahedral tungsten species and octahedral tungsten species (I_{970}/I_{805}) and the amount of lanthanum and tungsten from ICP and SEM-EDX of the catalysts and the SiO_2 support

Sample	Support	9 wt% WO_3/SiO_2	0.5 wt%La-WO_3/SiO_2	0.6 wt%La-WO_3/SiO_2	0.75 wt%La-WO_3/SiO_2	0.9 wt%La-WO_3/SiO_2	1.0 wt%La-WO_3/SiO_2
The surface area ($m^2 \cdot g^{-1}$) (BET)	185	182	180	180	179	179	179
I_{970}/I_{805} (Raman spectroscopy)	n.a.	0.34	0.40	0.38	0.34	0.33	0.32
The amount of Lanthanum on the surface of catalyst (%) (ICP)	n.a.	n.a.	0.51	0.58	0.77	0.88	1.03
The amount of tungsten on the surface of catalyst (%) (ICP)	n.a.	7.68	8.94	9.02	9.14	8.87	8.89
The amount of Lanthanum on the surface of catalyst (%) (SEM-EDX)	n.a.	n.a.	0.4	0.6	0.7	0.8	1.1
The amount of tungsten on the surface of catalyst (%) (SEM-EDX)	n.a.	8.3	8.2	8.4	8.2	7.9	8.1

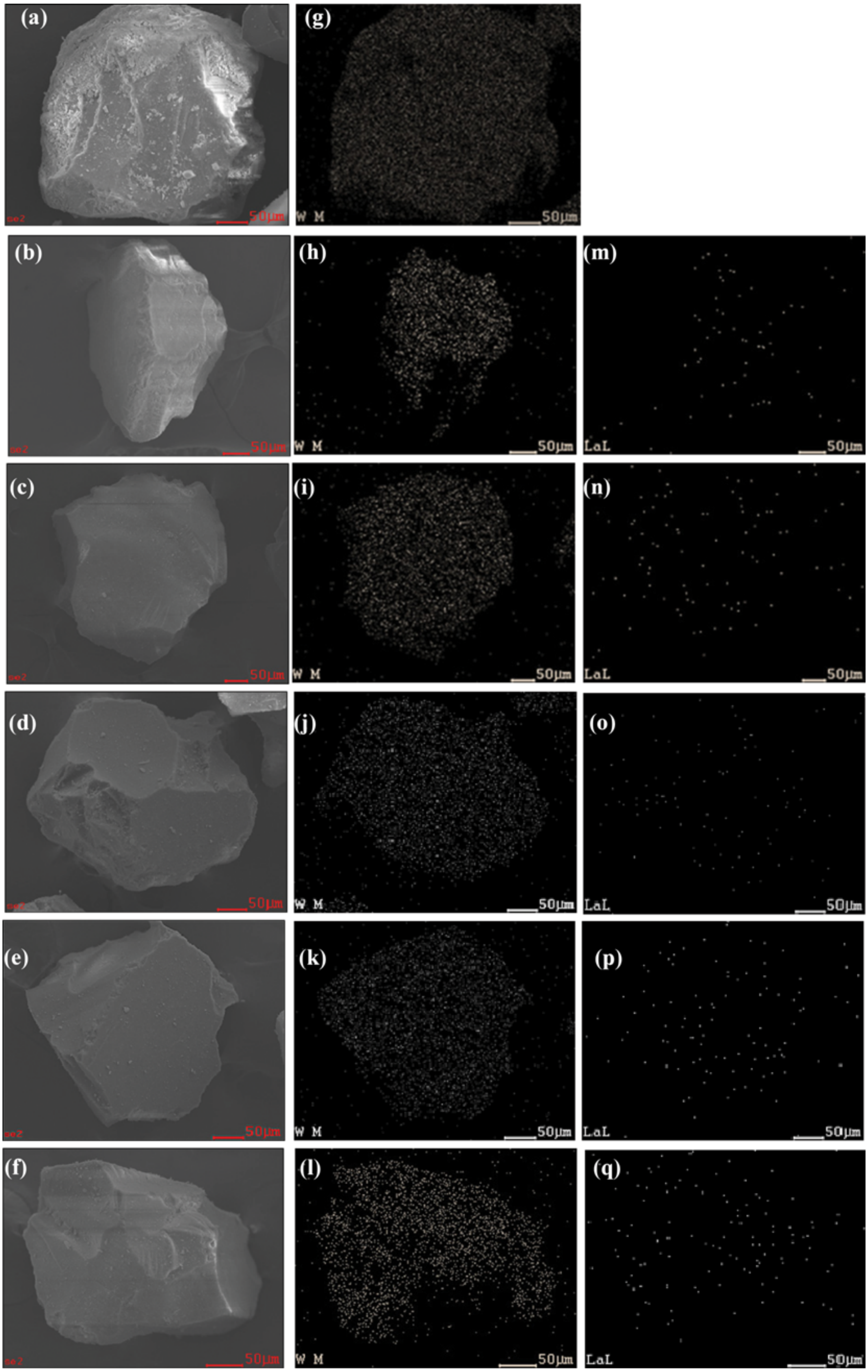

Fig. 1. SEM images of catalyst (a)-(f), corresponding EDX W-M line mapping (g)-(*l*) and corresponding EDX La-L line mapping (m)-(q) over the catalysts having various % Lanthanum oxide loadings: (a), (g) 9 wt% WO_3/SiO_2, (b), (h), (m) 0.5 wt%La-WO_3/SiO_2, (c), (i), (n) 0.6 wt%La-WO_3/SiO_2, (d), (j), (o) 0.75 wt%La-WO_3/SiO_2, (e), (k), (p) 0.9 wt%La-WO_3/SiO_2 and (f), (*l*), (q) 1 wt%La-WO_3/SiO_2.

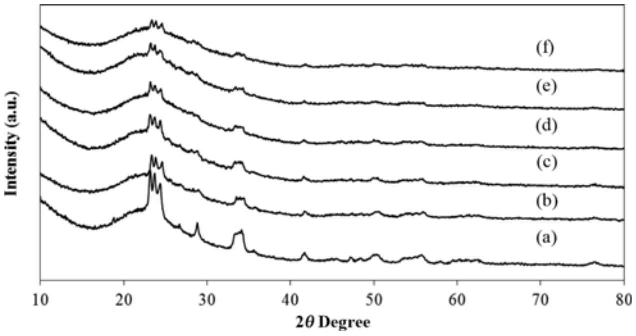

Fig. 2. XRD diffractograms of the catalyst with different lanthanum loadings: (a) 9 wt% WO_3/SiO_2, (b) 0.5 wt%La-WO_3/SiO_2, (c) 0.6 wt%La-WO_3/SiO_2, (d) 0.75 wt%La-WO_3/SiO_2, (e) 0.9 wt% La-WO_3/SiO_2 and (f) 1 wt%La-WO_3/SiO_2.

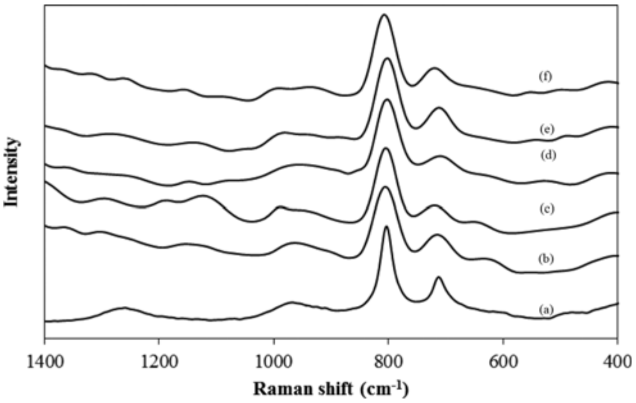

Fig. 3. FT-Raman spectra of the catalyst with different lanthanum loadings: (a) 9 wt% WO_3/SiO_2, (b) 0.5 wt%La-WO_3/SiO_2, (c) 0.6 wt%La-WO_3/SiO_2, (d) 0.75 wt%La-WO_3/SiO_2, (e) 0.9 wt% La-WO_3/SiO_2 and (f) 1 wt%La-WO_3/SiO_2.

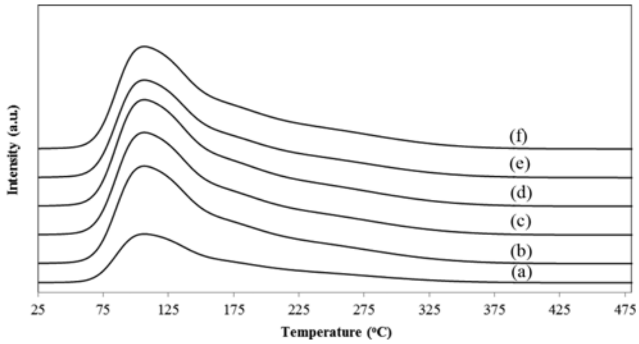

Fig. 4. NH_3-TPD profile for the catalysts with different lanthanum loadings: (a) 9 wt% WO_3/SiO_2, (b) 0.5 wt%La-WO_3/SiO_2, (c) 0.6 wt%La-WO_3/SiO_2, (d) 0.75 wt%La-WO_3/SiO_2, (e) 0.9 wt% La-WO_3/SiO_2 and (f) 1 wt%La-WO_3/SiO_2.

of tungsten and lanthanum on the catalysts and the results are shown in Table 1. The amount of tungsten loadings from both ICP and SEM-EDX was similar at ~9 wt% loadings and the amount of lanthanum loading from ICP and SEM-EDX was also in good agreement with the target amounts of lanthanum loading varying from 0.5-1 wt%. Typical SEM micrographs with EDX mapping of tungsten and lanthanum for the various La-WO_3/SiO_2 catalysts are shown in Fig. 1. The SEM figures show irregular shape of catalysts and the EDX results clearly show that tungsten was well dispersed over the catalyst surfaces. The dispersion of tungsten was slightly increased with increasing lanthanum loading as determined by SEM–EDX.

The XRD diffraction patterns of the catalysts are shown in Fig. 2. Without lanthanum, the peaks of WO_3 crystal were found at 2θ= 23.12°, 23.60°, and 24.38°, corresponding to crystalline tungsten oxide (orthorhombic WO_3) [19]. When the second metal lanthanum was added, no crystal peak of lanthanum species were found due to probably very small lanthanum crystallite size and/or the better dispersed tungsten species on the surface. Moreover, the XRD peak intensity of the crystalline phase of tungsten decreased with increasing lanthanum loading. It is indicated that the dispersion of tungsten species were improved with increasing lanthanum loading.

Raman spectroscopy is a tool for investigating the active species of WO_3-based the catalysts. In this work, the tetrahedral tungsten oxide species is the active site for the metathesis reaction of ethylene and 2-butene to produce propylene [20-23]. The active site precursor was monitored by the ratios of integrated intensities between the peaks at 970 and 805 cm^{-1} (I_{970}/I_{805}). The Raman bands at 960-980 cm^{-1} were assigned to the terminal W=O bonds of the isolated surface tetrahedral tungsten oxide species (i.e., at the crystal surface) [15,19-23]. The bands at 707-720 and 803-808 cm^{-1} were assigned to be O-W-O bending modes and W-O stretching modes, respectively [15,20-23].

The FT-Raman spectra of the La-WO_3/SiO_2 catalysts with various lanthanum loadings are shown in Fig. 3. The ratio of the relative intensities of the Raman bands at 970 and 805 cm^{-1} (I_{970}/I_{805}) was considered to reflect the relative content of metathesis-active sites on the metathesis catalysts. We found that the highest ratio of the relative intensities of FT-Raman band between 970 and 805 cm^{-1} was optimized at 0.5 wt% lanthanum loading.

Total acidity of the catalysts was determined by NH_3-TPD, and the boric acid back titration with 0.01 M aqueous HCl solution was employed to confirm the acidity from the NH_3-TPD. Moreover, Brønsted acidity of the catalysts was also determined by NaCl ion-exchange titration methods. The NH_3-TPD profiles are shown in Fig. 4 and amount of acid is summarized in Table 2. The NH_3-TPD peaks were found in the temperature range of 298-773 K. Compared to the WO_3/SiO_2 catalyst, the addition of lanthanum as a second metal did not significantly change the temperature of the NH_3-TPD, whereas the peak area was increased. It is suggested that adding a second metal lanthanum did not affect the acidic strength of the catalysts, but could have enlarged the amount of acidity. In addition, total Lewis acidity was increased with increasing lanthanum loading, while the total Brønsted acidity slightly increased.

2. Effect of 2-Butene Cis-trans Isomers in the Metathesis of Ethylene and 2-Butene over La-WO_3/SiO_2 Catalysts with Various Lanthanum Loadings

The gaseous phase metathesis reaction of ethylene and 2-butene was carried out in a fixed bed continuous flow reactor at 673 K under atmospheric pressure. The 2-butene reactants (with excess ethylene feed) were either pure 2% trans-2-butene (balanced with N_2) or the mixture of 1% cis- and 1% trans-2-butene (balanced with N_2).

Table 2. The amount of acidity estimated from NH_3-TPD and ion-exchange over the catalysts

Sample	9 wt% WO_3/SiO_2	0.5 wt%La-WO_3/SiO_2	0.6 wt%La-WO_3/SiO_2	0.75 wt%La-WO_3/SiO_2	0.9 wt%La-WO_3/SiO_2	1.0 wt%La-WO_3/SiO_2
Acidity from NH_3-TPD*						
(μmol NH_3/g-catatyst)	177	311	318	327	338	350
(mmol NH_3/g-tungsten)	2.2	3.9	4.0	4.1	4.2	4.4
Acidity from NH_3-TPD**						
(μmol NH_3/g-catatyst)	164	297	305	317	330	343
(mmol NH_3/g-tungsten)	2.1	3.7	3.8	4.0	4.1	4.3
Acidity from ion exchange						
(μmol H^+/g-catatyst)	95	110	115	119	123	125
(μmol H^+/g-tungsten)	1.2	1.4	1.4	1.5	1.5	1.6
Pseudo lewis acidity*						
(μmol H^+/g-catatyst)	82	201	203	208	215	225
(μmol H^+/g-tungsten)	1.0	2.5	2.5	2.6	2.7	2.8
Pseudo lewis acidity**						
(μmol H^+/g-catatyst)	69	187	190	198	207	218
(μmol H^+/g-tungsten)	0.9	2.3	2.4	2.5	2.6	2.7

*Acidity from area of NH_3 TPD

**Acidity from titration of H_3BO_3 with HCl

Pseudo lewis acidity=(Acidity from NH_3-TPD)−(Acidity from ion exchange)

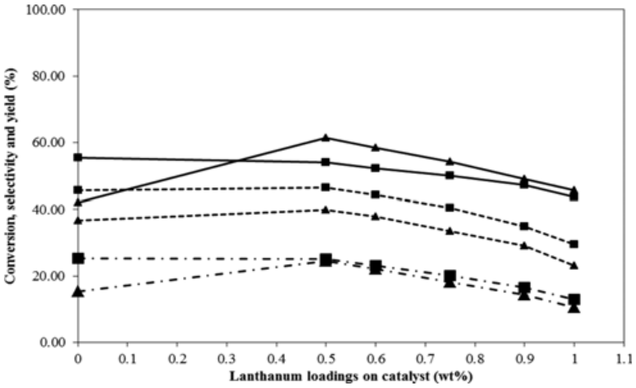

Fig. 5. 2-Butene conversion and propylene selectivity over the WO_3/SiO_2 catalyst: (–■–) conversion (--■--) selectivity (---■---) yield for the pure 2% trans-2-butene with excess ethylene feed and (–▲–) conversion (--▲--) selectivity (---▲---) yield for the mixture of 1% cis- and 1% trans-2-butene with excess ethylene feed.

The conversion of 2-butene and the propylene selectivity as a function of wt% lanthanum loading over the various La-WO_3/SiO_2 catalysts during 10 h time-on-stream are shown in Fig. 5.

In this work, 9 wt%WO_3/SiO_2 catalysts were used as the base catalyst. According to our previous work [15], it is the optimum tungsten loading catalyst for metathesis reaction.

The results in the present study show that conversion of 2-butene, propylene selectivity and propylene yield over the modified 9 wt% WO_3/SiO_2 catalysts with 0.5 wt% lanthanum did not change significantly from that of the original 9 wt%WO_3/SiO_2 when using the pure 2% trans-2-butene and excess ethylene as the reactant feed. However, when the amount of lanthanum adding exceeded 0.5%wt loading (up to 1 wt% lanthanum) the catalyst performance decreased, i.e., the conversion decreased from 54% to 43.7%, the propylene selectivity decreased from 46.48% to 29.52%, and the propylene yield decreased from 25.1% to12.9% as shown in Table 3 and Fig. 5.

In contrast, when the mixture of 1% cis- and 1%trans-2-butene

Table 3. 2-Butene conversion, propylene selectivity and yield on the WO_3/SiO_2 catalysts

Reactant	Trans-2-butene : Cis-2-butene (2 : 0)			Trans-2-butene : Cis-2-butene (1 : 1)			% Difference of yield
	Conversion	Selectivity	Yield^a	Conversion	Selectivity	Yield^b	
9 wt%WO_3/SiO_2	55.4	45.7	25.3	42.1	36.6	15.4	39.1
0.5 wt%La-WO_3/SiO_2	54.0	46.5	25.1	61.4	39.9	24.5	2.4
0.6 wt%La-WO_3/SiO_2	52.2	44.3	23.1	58.4	37.8	22.1	4.3
0.75 wt%La-WO_3/SiO_2	50.0	40.4	20.2	54.3	33.5	18.2	9.9
0.9 wt%La-WO_3/SiO_2	47.2	35.0	16.5	49.0	29.2	14.3	13.3
1.0 wt%La-WO_3/SiO_2	43.7	29.5	12.9	45.6	23.0	10.5	18.6

% Difference of yield$=\frac{(a-b)}{a}\times 100$

Table 4. Reactant-TPD result summarizing the amount of Ethylene, cis-2-butene and trans-2-butene adsorbed over the catalysts dosed with pure 2% trans-2-butene with excess ethylene feed and the mixture of 1% cis- and 1% trans-2-butene with excessethylene feed

	Tran-2-butene : Cis-2-butene (2 : 0)		Tran-2-butene : Cis-2-butene (1 : 1)			% Difference of reactant desorption from calculate
	Ethylene[a] (μmol/g cat)	Tran-2-butene[b] (μmol/g cat)	Ethylene[c] (μmol/g cat)	Tran-2-butene[d] (μmol/g cat)	Cis-2-butene[e] (μmol/g cat)	
9 wt%WO_3/SiO_2	39.54	229.21	27.63	82.6	48	41.12
0.5 wt%La-WO_3/SiO_2	34.69	225.31	30.69	140.44	70.4	7.10
0.6 wt%La-WO_3/SiO_2	31.11	217.04	32.12	122.59	65.77	11.15
0.75 wt%La-WO_3/SiO_2	32.14	205.43	34.47	115.16	54.19	14.21
0.9 wt%La-WO_3/SiO_2	30.25	190.79	33.71	106.43	44.81	16.33
1.0 wt%La-WO_3/SiO_2	30.64	181.50	30.64	92.58	41.85	22.19

$$\text{\% Difference of reactant desorption} = \frac{(a+b)-(c+d+e)}{(a+b)} \times 100$$

with excess ethylene feed was employed, 9 wt%WO_3/SiO_2 with 0.5 wt% lanthanum could enhance the conversion of 2-butene from 42.1% to 61.4%, the propylene selectivity from 36.58% to 39.9%, and the propylene yield from 15.4% to 24.5%. However, excess lanthanum loading more than 0.5 wt% lanthanum led to a decrease of the catalyst activities similar to those found when pure 2% trans-2-butene and excess ethylene were used as the reactant feed. The conversion, the propylene selectivity and the propylene yield declined from 61.4% to 45.6%, from 39.9% to 23.0% and from 24.5% to 10.5%, respectively.

The differences of the catalyst activities tested with the pure butene feed and the mixture of butene cis/trans isomers feed could be explained by the different adsorption behaviors of the reactants. The pure trans-2-butene and excess ethylene feed may be adsorbed better than the mixture of cis/trans-2-butene isomers as shown in Table 4. Our previous work [15] indicated that poor dispersion of tungsten oxide on silica support could obstruct the adsorption of the reactants, especially for the cis/trans isomers, so that they were more difficult to contact with the catalyst surface.

Adding 0.5 wt% lanthanum was found to improve the dispersion of active tungsten species. Therefore, the catalyst activities using the mixture of 2-butene cis/trans isomers feed could be boosted to be comparable to those using pure trans-2-butene feed (propylene yield ~25%). When adding more than 0.5 wt% lanthanum up to 1 wt% lanthanum, the dispersion of tungsten increased from the XRD result, but the active sites (I_{970}/I_{805}) of tungsten were decreased from 0.4 to 0.32. Additionally, the adsorption properties could be decreased with lanthanum loading higher than 0.5 wt% as shown in Table 4. It is presumed that lanthanum is able to modify the adsorption properties of the WO_3/SiO_2 catalysts. Excess lanthanum loading may lead to lower catalyst activities.

Comparing the use of different feed components for the catalysts with lanthanum loadings between 0.5 and 1 wt%, the propylene yield of the mixed 2-betene cis/trans isomers feed was lower than that obtained from the pure trans-2-butene feed. The relationship of the reactant adsorption properties and the propylene yield was demonstrated by plotting the percentages of the differences of the propylene yield between pure feed and mixed feed, and the percentages of the reactant adsorption as shown in Fig. 6. The percentage of the differences of the propylene yield between pure feed and mixed feed, and the percentage of reactant adsorption was linear, suggesting that tungsten dispersion has an effect on the cis/trans isomer reactant adsorption. Therefore, it is the key factor for improving the catalyst activity when using the cis/trans isomers feed as well as the pure trans-2-butene feed.

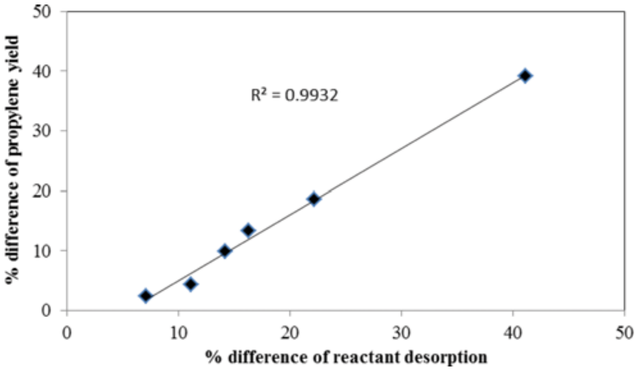

Fig. 6. Correlation between % difference of reactant desorption from the pure 2% trans-2-butene with excess ethylene feed and the mixture of 1% cis- and 1% trans-2-butene with excess ethylene feed and % difference of propylene yield from the pure 2% trans-2-butene with excess ethylene feed and the mixture of 1% cis- and 1% trans-2-butene with excess ethylene feed.

CONCLUSIONS

The effect of lanthanum loading as a second metal was investigated over 9 wt% WO_3/SiO_2 catalyst for metathesis reaction of ethylene and 2-butene using either pure trans-2-butene or the mixture of cis/trans 2-butene isomers as the reactants. The optimal lanthanum loading was found to be at about 0.5 wt%. The catalytic activity of La-WO_3/SiO_2 with 0.5 wt% lanthanum increased when using the mixture of 1% cis- and 1%trans-2-butene with excess ethylene as the reactant feed. Due to improved tungsten dispersion, the steric hindrance effect of cis/trans isomers on the adsorption of reactants over the 0.5 wt% La-WO_3/SiO_2 catalyst was less pronounced. Nevertheless, increasing lanthanum loading over 0.5 wt% could modify the surface structure of metathesis active sites and reactant adsorption properties so that the catalytic activity was diminished compared to those with 0.5 wt% lanthanum loading.

ACKNOWLEDGEMENTS

The financial support from the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (RES5605300086-AM) is gratefully acknowledged. The authors would also like to thank the Royal Golden Jubilee PhD Scholarship from the Thailand Research Fund and SCG Chemicals for N.P.

REFERENCES

1. J. C. Mol, *J. Mol. Catal. A.*, **213**, 39 (2004).
2. P. K. Ladwig, J. E. Asplin, G. F. Stuntz, W. A. Wachter, B. E. Henry and S. C. Fung, US Patent, 6,803,494B1 (2004).
3. J. Towfighi, A. Niaei, R. Karimzadeh and G. Saedi, *Korean J. Chem. Eng.*, **23**, 8 (2006).
4. K. Eisenacher and A. A. Adesina, *Korean J. Chem. Eng.*, **17**, 71 (2000).
5. Z. Nawaz, X. Tang, Q. Zhang, D. Wang and W. Fei, *Catal. Commun.*, **10**, 1925 (2009).
6. K. J. Ivin and J. C. Mol, *Olefin metathesis and metathesis polymerization*. Academic Press, San Diego (1997).
7. A. Spamer, T. I. Dube, D. J. Moodley, C. V. Schalkwyk and J. M. Botha, *Appl. Catal. A.*, **255**, 133 (2003).
8. R. C. Luckner and G. B. Wills, *J. Catal.*, **28**, 83 (1973).
9. A. J. Moffat, M. M. Johnson and A. Clark, *J. Catal.*, **18**, 345 (1970).
10. C. V. Schalkwyk, A. Spamer, D. J. Moodley, T. Dube, J. Reynhardt, J. M. Botha and H. C. M. Vosloo, *Appl. Catal. A.*, **255**, 143 (2003).
11. M. Zheng, S. L. Chen, J. H. Zhang, Y. Liu, L. Sang, J. You and X. D. Wang, *Petroleum. Sci.*, **10**(1), 112 (2013).
12. Q. Zhao, S. L. Chen, J. Gao and C. Xu, *Transit. Met. Chem.*, **34**, 621 (2009).
13. A. Spamer, T. I. Dube, D. J. Moodley, C. V. Schalkwyk and J. M. Botha, *Appl. Catal. A.*, **255**, 153 (2003).
14. R. Westhoff and J. A. Moulijn, *J. Catal.*, **46**, 414 (1977).
15. N. Poovarawan, K. Suriye, S. Kunjara Na Ayudhya, J. Panpranot, F. J. Cadete Santos Aires and P. Praserthdam, *Catal. Lett.*, **144**, 920 (2014).
16. R. L. Banks, *Appl. Ind. Catal.*, **4**, 215 (1984).
17. A. Chongterdtoonskul, J. W. Schwank and S. Chavadeja, *J. Mol. Catal. A. Chem.*, **372**, 175 (2013).
18. D. E. López, J. G. Goodwin Jr. and D. A. Bruce, *J. Catal.*, **245**, 381 (2007).
19. S. Huang, F. Chen, S. Liu, Q. Zhu, X. Zhu, W. Xin, Z. Feng, C. Li, Q. Wang and L. Xu, *J. Mol. Catal. A.*, **267**, 224 (2007).
20. A. Baserga, V. Russo, F. Di Fonzo, A. Bailini, D. Cattaneo, C. S. Casari, A. Li Bassi and C. E. Bottani, *Thin. Solid. Films.*, **515**, 6465 (2007).
21. W. Limsangkass, S. Phatanasri, P. Praserthdam, J. Panpranot, W. Jareewatchara, S. Kunjara Na Ayudhya and K. Suriye, *Catal. Lett.*, **143**, 919 (2013).
22. W. Limsangkass, P. Praserthdam, S. Phatanasri, J. Panpranot, N. Poovarawan, W. Jareewatchara, S. Kunjara Na Ayudhya and K. Suriye, *Catal. Lett.*, **144**, 1524 (2014).
23. W. Limsangkass, P. Praserthdam, S. Phatanasri, J. Panpranot, S. Chaemchuen, W. Jareewatchara, S. Kunjara Na Ayudhya and K. Suriye, *React. Kinet. Mech. Catal.*, **113**, 225 (2014).