Effect of 2-Butene *Cis/Trans* Isomers in the Metathesis of Ethylene and 2-Butene Over WO₃/SiO₂ Catalysts

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Received: 20 November 2013/Accepted: 26 February 2014/Published online: 19 March 2014 © Springer Science+Business Media New York 2014

Abstract Pure 2 % trans-2-butene and the mixture of 1 % cis- and 1 % trans-2-butene were used as feed to react with ethylene in metathesis reaction in order to produce propylene to study the effect of feed on WO₃/SiO₂ catalysts with various tungsten oxide loadings (5, 7, 9, and 11 wt%), which were prepared by incipient wetness impregnation. These catalysts were characterized by X-ray diffraction, nitrogen adsorption (BET), scanning electron microscopy, energy dispersive X-ray spectroscopy, ion-exchange titration, FT-Raman, ammonia temperature programmed desorption (NH₃-TPD) and reactant-TPD. At high tungsten oxide loading, when the mixture of cis- and trans-2butene was used as the reaction feed the conversion of 2-butene was lower than when pure trans-2-butene was used. However, the effect of cis-2-butene isomer on the conversion of 2-butene was less pronounced at low tungsten oxide loading. The dispersion of tungsten was a key factor to improve the activity of the tungsten catalysts when the mixture of cis- and trans-2-butene was used as a feed for metathesis reaction.

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K. Suriye · S. K. N. Ayudhya SCG Chemicals Co., Ltd., 1 Siam Cement Road, Bangsue, Bangkok 10800, Thailand **Keywords** Metathesis \cdot *Cis*-2-butene \cdot *Trans*-2-butene \cdot Propylene \cdot WO₃/SiO₂

1 Introduction

The demand for propylene is growing rapidly in the chemical industry. Propylene is mainly produced from naphtha steam crackers [1], fluid catalytic crackers [2], propane dehydrogenation [3], and Fischer-Tropsch chemistry [4]. It is used for making polypropylene, acrylonitrile, alcohol, acrylic acid, and other petrochemical products. Recently, metathesis reaction over WO₃/SiO₂ catalyst has received considerable attention by the industry to produce propylene [5]. The greatest advantage of WO₃/SiO₂ catalyst when compared to Re- and Mo-based metathesis catalysts, is that it is more robust [6–9], Westhoff and Moulijn [10], Zhao et al. [11], and Spamer et al. [12] investigated the influence of tungsten loading on the activity and selectivity of the WO₃/SiO₂ catalysts in the metathesis of ethylene and 2-butene using pure trans-2-butene feed. They found that the conversion and the selectivity reach a maximum at 8 % and higher tungsten oxide loadings and the catalysts with loadings lower than 8 % tungsten oxide loading have a faster deactivation.

The composition of reaction feed containing ethylene and *n*-butene used in the metathesis reaction for commercial-scale production of propylene has to be precisely controlled in order to obtain both propylene yield and long catalyst cycle time. The main problem resides in the fact that the composition of 2-butene in terms of *cis*- and *trans*ratio is generally poorly controlled. Engelhardt and Zsinka [13] found a higher rate of cross-metathesis between 1-butene and 2-butene in the feed containing *trans*-2butene reaction feed than that of the one containing *cis*-2butene. This was attributed to the fact that *cis*-2-butene converts easier to *trans*-2-butene than *trans*-2-butene converts to *cis*-2-butene; so *trans*-2-butene gives a higher rate of cross metathesis. However, the effect of *cis*- and *trans*-isomer ratio in the feed has not been understood yet. Therefore, an influence of *cis*- and *trans*-isomer in the feed mixture of 2-butene over the WO₃/SiO₂ catalyst having different tungsten oxide loading would be investigated in this study.

2 Experimental

2.1 Preparation of WO₃/SiO₂ Catalysts

Silica gel, Davisil grade 646 was used as the support (supplied by Aldrich). Catalysts with different tungsten oxide loadings (5, 7, 9, and 11 wt%) were prepared by incipient wetness impregnation of an aqueous solution of ammonium metatungstate hydrate (Aldrich, 99.9 %) over silica gel. The catalysts were dried at room temperature for 2 h and then 383 K for overnight. The calcination was performed under air at temperature sufficiently removing the residue during the synthesis in a tubular furnace.

2.2 Reaction Studies

Fixed bed reactor with 3 g of catalyst was used for performing the catalytic test. The catalysts were activated at the temperature not greater than 873 K for 2 h under nitrogen then cooled down to reaction temperature at 673 K. Two types of reactant feed which are (i) 2 % *trans*-2-butene with excess ethylene (balancing with nitrogen) and (ii) 1 % *trans*-2-butene and 1 % *cis*-2-butene with excess ethylene (balancing with nitrogen) were used in this study in order to investigate the effect of *cis*- and *trans*isomer on the catalytic performance of metathesis reaction. Gas product obtained from the reaction was analyzed by using FID-gas chromatography (Shimadzu 2014).

2.3 Catalyst Characterization

Crystallite phase and size were investigated by X-ray diffraction, XRD (Siemens D5000) using Ni filter Cu K α radiation. Specific surface area (S_{BET}) was determined from nitrogen adsorption studies by using Micrometrics Chemisorbs 2750.

The catalyst morphology and tungsten-distribution over the silica support were investigated by scanning electron microscopy (SEM) together with energy dispersive X-ray (EDX) spectroscopy (JEOL JSM-5800LV SEM equipped with a Pentafet LinK-Isis series 300 EDX spectrometer). Transmission electron microscopy (JEOL JEM 2010 TEM equipped with a LaB_6 gun and a Pentafet LinK-Isis EDX spectrometer) was also used as a local probe to visualize the morphology and distribution [14–18] of the tungsten particles on the silica support.

Molecular structure of the tungsten oxide was determined by using 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 were recorded using a PerkinElmer Spectrum GX spectrometer.

Acidity of catalyst was determined by ammonia temperature programmed desorption (NH₃-TPD) and ionexchange titration. For NH₃-TPD, 0.1 g of the catalyst was treated at the temperature not greater than 873 K in a flow of helium then cooled down to room temperature and saturated with 15 % NH₃/He mixture. After purging with helium at room temperature for 1 h in order to remove weakly physisorbed NH₃, the sample was heated from room temperature to 773 K under helium flow. NH₃-TPD was performed by using a Micrometrics Chemisorbs 2750 automated system equipped with ChemiSoft TPx software. Ammonia effluent was finally kept in a boric acid solution (20 g/dm³) and titrated with a 0.01 N aqueous HCl solution. The number of Brønsted acid sites was also estimated by using a method involving an aqueous ion-exchange step of catalyst's H⁺ ions with Na⁺ ions, followed by titration of the resulting solution [19].

Reactant-TPD was used to determine the adsorption behavior of the reactant. Catalyst sample was treated at the temperature not greater than 873 K in a flow of nitrogen for 1 h, then cooled down to room temperature and saturated with the reactant. After purging with nitrogen at room temperature for 1 h to remove weakly physisorbed reactant, the sample was heated from room temperature to 673 K under a flow of nitrogen (30 cm³/min). The resulting gaseous desorption was sampled every 2 min and analyzed by using a FID-Shimadzu 2014.

3 Results and Discussion

3.1 Characteristics of WO₃/SiO₂ with Various Tungsten Oxide Loadings

XRD diffractograms of the SiO₂ support and the WO₃/SiO₂ catalysts containing various amounts of tungsten are shown in Fig. 1. Only a broad peak at $2\theta = 22.5^{\circ}$ was observed for the SiO₂ support indicating the amorphous phase of silica [20]. The characteristic peaks at $2\theta = 23.12^{\circ}$, 23.60°, and 24.38° which corresponds to crystalline tungsten oxide (orthorhombic WO₃) [21] were observed for all WO₃/SiO₂ catalyst. The XRD peak intensity of the crystalline phase of tungsten increased with increasing tungsten oxide loading



Fig. 1 XRD diffractograms of the support and the WO_3/SiO_2 catalysts having various % tungsten oxide loadings: (*a*) SiO_2 support, (*b*) 5 wt% WO_3/SiO_2, (*c*) 7 wt% WO_3/SiO_2, (*d*) 9 wt% WO_3/SiO_2 and (*e*) 11 wt% WO_3/SiO_2

indirectly indicating that the dispersion of tungsten specie decreased with increasing tungsten oxide loading. The optimum tungsten loading and calcination temperature for catalyst preparation were determined to be 9 wt% and 773 K, respectively [12]. The results suggested that tungsten crystal species were very small crystal and well dispersed on the surface of silica support, which were invisible by XRD, for the catalyst sample with low tungsten oxide loading (5 wt%) [11] and the dispersion of tungsten decreased with increasing tungsten oxide loading (7, 9, and

11 wt%). Similar result was reported by Li and colleagues [22] that the XRD peaks of WO₃ crystalline phase in WO₃/ SiO₂ catalysts could be detected only when tungsten oxide loading was higher than 5 wt%.

TEM observation of the catalyst with 9 wt% (Fig. 2) clearly shows that the tungsten is dispersed on the surface of SiO₂ support as large agglomerates. A closer inspection by high resolution TEM of these agglomerates (Fig. 2c) reveals that their structure is an orthorhombic WO₃ which is consistent with the XRD results.

Figure 3 shows the typical SEM micrographs with the EDX mapping of tungsten for the various WO_3/SiO_2 catalysts. The EDX maps clearly show that tungsten is well dispersed all over the catalyst grains surfaces for all the samples. The dispersion of tungsten decreases with increasing tungsten oxide loading as determined by SEM–EDX.

The average amounts of tungsten on the catalyst grains as determined by SEM–EDX are shown in Table 1 and were found to be in good agreement with the targeted amount of tungsten oxide loading varying from 5 to 11 wt% (\pm 1 wt%). The surface areas of the SiO₂ support and the WO₃/SiO₂ containing various tungsten oxide loadings are given in Table 1. The surface areas of the WO₃/SiO₂ catalysts (~180–182 m²/g) were not significantly different comparing to the SiO₂ support (~185 m²/g).



Fig. 2 TEM images of the 9 wt% WO₃/SiO₂ catalyst: **a** general overview of the WO₃ particles on the SiO₂ support, **b** one single-crystalline particle, **c** high resolution detail of a particle in **b** where only showing $d_{(0\ 2\ 0)}$ interplane distances of orthorhombic WO₃ are

clearly detected, and **d** 2D-FFT of particle in **b** revealing $d_{(0\ 2\ 0)}$ interplane distances (*white circle*) as well as very faint $d_{(1\ 1\ 2)}$ interplane distances planes (*grey circle*) indicating that the particle is oriented in the [2 0 -1] direction

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Fig. 3 SEM images (a-d) and corresponding EDX *W-M line* mapping (e-h) over the WO₃/ SiO₂ catalysts having various % tungsten oxide loadings: a, e 5 wt% WO₃/SiO₂, b, f 7 wt% WO₃/SiO₂, c, g 9 wt% WO₃/ SiO₂, and d, h 11 wt% WO₃/ SiO₂



The structures of tungsten species on the surface of catalyst samples were investigated by FT-Raman as shown in Fig. 4. Raman bands at 707–720 and 803–808 cm⁻¹ were assigned to be O–W–O bending modes and W–O stretching modes, respectively [23]. These Raman bands

represented the tungsten octahedral of the bulk crystalline WO₃ [23]. The band at 960–980 cm⁻¹ was assigned to be terminal W=O bonds of the isolated surface tetrahedral tungsten oxide species (i.e., at the crystal surface) [21, 23]. Increasing of tungsten oxide loadings lead to the increase

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 tungsten on the catalyst's surface of the various WO₃/SiO₂ catalysts and the SiO₂ support

Samples	Support	5 wt% WO ₃ /	7 wt% WO ₃ /	9 wt% WO ₃ /	11 wt% WO ₃ /
		SiO ₂	SiO ₂	SiO ₂	SiO ₂
The surface area (BET, m ² /g)	184.6	182.2	181.0	180.0	179.7
<i>I</i> ₉₇₀ / <i>I</i> ₈₀₅ (Raman spectroscopy)	na	0.38	0.35	0.34	0.34
The amount of tungsten on the surface of catalyst (SEM– EDX, %)	na	4.03	5.77	7.54	10.96



Fig. 4 FT-Raman spectra of the SiO₂ support and the WO₃/SiO₂ catalyst having various % tungsten oxide loadings: (*a*) SiO₂ support, (*b*) 5 wt% WO₃/SiO₂, (*c*) 7 wt% WO₃/SiO₂, (*d*) 9 wt% WO₃/SiO₂ and (*e*) 11 wt% WO₃/SiO₂

of the intensities of peak at 804 and 710 cm^{-1} , obviously. Such a result was similar to that of Li and colleagues [22]. The FT-Raman results were in accordance to the XRD results that more crystalline WO3 was formed at higher tungsten oxide loading. According to Huang et al. [21], the tetrahedral tungsten oxide species are the active sites for the metathesis reaction of ethylene and 2-butene to produce propylene. The ratios of the relative intensities of the FT-Raman bands at 970 and 805 cm⁻¹ (I_{970}/I_{805}) reflect the relative contents of metathesis-active sites on the WO₃/ SiO₂ catalyst [24]. It was found that the ratios of the relative intensities of FT-Raman band between 970 and 805 cm^{-1} for all the catalysts were essentially the same. In other words, although the tungsten active sites increased with increasing tungsten oxide loading, the crystallite size of tungsten oxide being formed also increased as suggested by the XRD results, resulting in no changes in the relative content of active sites.



Fig. 5 NH₃-TPD profile of WO₃/SiO₂ catalyst having various % tungsten oxide loadings: (*a*) 5 wt% WO₃/SiO₂, (*b*) 7 wt% WO₃/SiO₂, (*c*) 9 wt% WO₃/SiO₂, and (*d*) 11 wt% WO₃/SiO₂

Table 2 The amount of acidity estimated from NH_3 -TPD and ionexchange over the various WO_3/SiO_2 catalysts

Samples	5 wt% WO ₃ /SiO ₂	7 wt% WO ₃ /SiO ₂	9 wt% WO ₃ /SiO ₂	11 wt% WO ₃ /SiO ₂
Acidity from NH ₃ -TPD ^a				
µmol NH ₃ /g catalyst	250	235	177	157
mmol NH ₃ /g tungsten	6.3	3.9	2.2	1.6
Acidity from NH ₃ -TPD ^b				
µmol NH ₃ /g catalyst	230	215	164	143
mmol NH ₃ /g tungsten	5.8	3.6	2.1	1.4
Acidity from ion exchange	ge			
µmol H ⁺ /g catalyst	65	80	95	98
mmol H ⁺ /g tungsten	1.6	1.3	1.2	1.0
Pseudo Lewis acidity ^a				
µmol H ⁺ /g catalyst	185	155	82	60
mmol H ⁺ /g tungsten	4.6	2.6	1.0	0.6
Pseudo Lewis acidity ^b				
µmol H ⁺ /g catalyst	165	135	69	46
mmol H ⁺ /g tungsten	4.1	2.3	0.9	0.5

^a Acidity from area of NH₃ TPD

^b Acidity from titration of H₃BO₃ with HCl

The catalysts acidity was determined by the NH₃-TPD and the ion-exchange titration methods. The total acidity was based on the NH₃-TPD results. The Brønsted acidity, which is typically attributed to the doubly bonded oxygen atom (W=O) on the surface of the crystalline WO_3 [25], was determined by ion-exchange titration. The Lewis acidity, which is generally attributed to two tungsten atoms bonded to an oxygen atom (W–O–W) within the crystalline WO₃ [26], was determined from the difference between the acidity deduced from NH₃-TPD and the acidity deduced from ion-exchange titration method. The NH₃-TPD profiles are shown in Fig. 5. All the WO_3/SiO_2 catalysts exhibited only one peak in the NH3-TPD profiles within the temperature range of 298-773 K. 11 wt% WO₃/SiO₂ catalyst showed a stronger acidity than the other WO₃/SiO₂ catalysts as shown by a shift of the desorption peak towards



Fig. 6 Correlation between 2-butene conversion and acidity from ion exchange over the WO₃/SiO₂ catalyst: *filled squares* conversion for the pure 2 % *trans*-2-butene with excess ethylene feed and *filled triangles* conversion for the mixture of 1 % *cis*- and 1 % *trans*-2-butene with excess ethylene feed



Fig. 7 Correlation between propylene selectivity and acidity from ion exchange over the WO₃/SiO₂ catalyst: *filled squares* conversion for the pure 2 % *trans*-2-butene with excess ethylene feed and *filled triangles* conversion for the mixture of 1 % *cis*- and 1 % *trans*-2butene with excess ethylene feed

higher temperature. Total acidity was calculated based on the integrated peak areas of the NH₃-TPD curves for each catalyst. In addition, titration with 0.01 M aqueous HCl solution was employed to confirm the acidity measured for each WO₃/SiO₂ catalyst. As summarized in Table 2, total Lewis acidity was found to decrease with increasing tungsten oxide loading whereas the total Brønsted acidity increased with increasing tungsten loading, according with the linear correlation between metathesis conversion and acidity sites as shown in Fig. 6. The slope of correlation of catalysts from pure 2 % trans-2-butene feed was steeper, indicating that conversion of ones from pure 2 % trans-2butene has been influenced by acidity sites more than that of catalysts from mixture feed. In addition, the similar trend of linear correlation between propylene selectivity as shown in Fig. 7 was also observed for all catalysts.



Fig. 8 2-Butene conversion and propylene selectivity over the WO₃/SiO₂ catalyst having various % tungsten oxide loadings: *filled triangles with continuous line* conversion, *filled triangles with dotted line* selectivity for the pure 2 % *trans*-2-butene with excess ethylene feed and *filled squares with continuous line* conversion, *filled squares with dotted line* selectivity for the mixture of 1 % *cis*- and 1 % *trans*-2-butene with excess ethylene feed

3.2 Effect of 2-Butene *Cis–Trans* Isomers in the Metathesis of Ethylene and 2-Butene Over WO₃/SiO₂ Catalysts

A gas 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 n-butene reactants used were either pure 2 % trans-2-butene (balancing with N₂) or the mixture of 1 % cis- and 1 % trans-2-butene (balancing with N₂). Conversions of 2-butene and propylene selectivity as a function of % tungsten oxide loading over the various WO₃/SiO₂ catalysts after 10 h time-on-stream are shown in Fig. 8. At higher % tungsten oxide loading from 5 to 11 wt%, the conversion of 2-butene increased from 12.50 to 70.00 % for the metathesis testing with pure 2 % trans-2butene and excess ethylene feed whereas it increased from 12.00 to 40.00 % for those testing with the mixture of 1 % cis- and 1 % trans-2-butene with excess ethylene. Both cases show that there were no significant improvements in term of 2-butene conversion when % tungsten oxide loading was increased from 9 to 11 wt%. A similar trend was reported by Zhao et al. [11] in which the conversion of 2-butene reached an optimum point at 9 wt% tungsten oxide loading. This is attributed to the presence of a pseudo-amorphous surface phase, which would have a minor contribution compared to the crystalline WO₃ phase, for loadings higher than 9 wt%. Moreover, at this tungsten oxide loading, tetrahedral tungsten oxide species (i.e., at the crystal surface) reached their maximum level.

The 2-butene conversion and propylene yield of 5 wt% WO_3/SiO_2 catalysts were rather similar over both of feeds, which are pure 2 % *trans*-2-butene with excess ethylene

Reactants	Trans-2-butene: cis-2-butene (2:0)			Trans-2-butene: cis-2-butene (1:1)			A % difference	A % difference
	Conversion ^a	Selectivity	Yield ^c	Conversion ^b	Selectivity	Yield ^d	of conversion ^e	of yield ¹
5 wt% WO ₃ /SiO ₂	12.50	69.00	8.63	12.00	71.70	8.60	4.00	0.24
7 wt% WO3/SiO2	45.00	50.00	22.50	34.00	66.00	22.44	24.44	0.27
9 wt% WO3/SiO2	65.00	49.00	31.85	40.00	62.00	24.80	38.46	22.14
11 wt% WO ₃ /SiO ₂	70.00	51.00	35.70	40.00	61.00	24.40	42.86	31.65

Table 3 2-Butene conversion, propylene selectivity, yield, and % difference over the various WO₃/SiO₂ catalysts tested with pure 2 % trans-2butene with excess ethylene feed and the mixture of 1 % cis- and 1 % trans-2-butene with excess ethylene feed

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

amount of propylene

Selectivity = $\frac{\text{amount of propylene}}{\text{amount of butene in feed-amount of butene remained in products}} \times 100$

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

^e % Difference of conversion $= \frac{a-b}{a} \times 100$

^f % Difference of yield $= \frac{c-d}{c} \times 100$

Table 4 Reactant-TPD result summarizing the amount of ethylene, cis-2-butene and trans-2-butene adsorbed over various WO₃/SiO₂ catalysts dosed with pure 2 % trans-2-butene with excess ethylene feed and the mixture of 1 % cis- and 1 % trans-2-butene with excess ethylene feed

	Trans-2-butene: cis-2-butene (2:0)		Trans-2-butene	% Difference		
	Ethylene ^a (μmol/g cat)	<i>Trans</i> -2-butene ^b (μmol/g cat)	Ethylene ^c (μmol/g cat)	<i>Trans</i> -2-butene ^d (μmol/g cat)	<i>Cis</i> -2-butene ^e (µmol/g cat)	of reactant desorption
5 wt% WO ₃ /SiO ₂	9.16	110.06	8.45	73.33	37.00	0.37
7 wt% WO ₃ /SiO ₂	26.70	175.04	19.40	78.40	44.20	29.61
9 wt% WO3/SiO2	39.54	229.21	27.63	82.60	48.00	41.13
11 wt% WO ₃ /SiO ₂	47.45	275.05	34.40	85.92	50.30	47.10

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

feed and mixture of 1 % cis-, 1 % trans-2-butene with excess ethylene feed. Differences in 2-butene conversion and propylene yield were seen when tungsten oxide loading increased to 7 wt% and higher loading. For tungsten oxide loading >7 wt%, the use of the pure 2 % trans-2-butene with excess ethylene feed resulted in higher 2-butene conversion than those of use of the mixture of 1 % cis- and 1 % trans-2-butene with excess ethylene feed. Table 3 summarizes % difference of conversion between the use of pure 2 % trans-2-butene with excess ethylene feed and the use of the mixture of 1 % cis- and 1 % trans-2-butene with excess ethylene feed. The % differences increased with increasing tungsten oxide loading. In the other words, for metathesis reaction, when the dispersion of tungsten over the SiO₂ support was fairly low, the presence of the mixture between cis- and trans-2-butene isomers had a strong effect on 2-butene conversion. Such effect was not markedly observed when the catalyst contained low tungsten oxide loading (i.e., 5 wt% WO₃/SiO₂). Propylene yield for the metathesis testing with pure 2 % trans-2butene with excess ethylene feed was higher than the

testing with the mixture of cis/trans-2-butene feed especially 9 and 11 wt% loading.

The temperature programmed desorption of the reactants (reactant-TPD) was performed in order to elucidate the adsorption/desorption behavior of pure 2 % trans-2-butene and excess ethylene as well as the mixture of 1 % cis- and 1 % trans-2-butene with excess ethylene over the WO₃/SiO₂ catalyst. The amounts of ethylene, trans-2-butene, and cis-2butene adsorbed in the WO₃/SiO₂ catalyst that were estimated by the means of reactant-TPD are summarized in Table 4. It was found that the adsorption of the reactants increased with increasing tungsten oxide loading. The linear correlation between reactant desorption and acid sites is shown in Fig. 9, agreed with correlation between metathesis activity and acidity sites as mentioned above.

In the case of higher tungsten dispersion over SiO₂ support (5 % WO₃/SiO₂ catalyst), there was no significant difference of the total amount of the adsorbed reactants between the pure 2 % trans-2-butene with excess ethylene and the mixture of 1 % cis- and 1 % trans-2-butene with excess ethylene. However, the difference was more



Fig. 9 Correlation between temperature programmed desorption of the reactants (reactant-TPD) and acidity from ion exchange over the WO₃/SiO₂ catalyst: *filled squares* reactant-TPD for the pure 2 % *trans*-2-butene with excess ethylene feed and *filled triangles* reactant-TPD for the mixture of 1 % *cis*- and 1 % *trans*-2-butene with excess ethylene feed

pronounced over the WO_3/SiO_2 catalyst sample having higher tungsten oxide loadings which means lower tungsten dispersion over SiO_2 support. This is in a good agreement with the metathesis testing results.

Both cis- and trans-2-butene adsorb on metathesis active sites, however, the results in this study showed much lower conversion of 2-butene when the mixture of cis/trans-2butene were used as the feed. The reactant-TPD records that the presence of cis-2-butene led to lower amount of reactant adsorb. At higher loading (tungsten oxide loading more than 7 wt%), the lower dispersion led to agglomeration of tungsten as seen from TEM in Fig. 2. According to the lower tungsten dispersion, the active sites positions were close to each other and this obstructed cis/trans-2butene absorption. Cis/trans-2-butene could access to the active sites difficultly, leading to the lower conversion. The effect of 2-butene cis/trans isomers became less pronounced at lower tungsten oxide loading (better tungsten dispersion) because the active sites positions were faraway. Therefore, it was proposed here that tungsten dispersion affected the reactant adsorption and catalyst activities.

4 Conclusions

Effect of 2-butene *cis/trans* isomers on the metathesis reaction of ethylene and 2-butene to propylene over WO₃/ SiO₂ catalysts having various % tungsten oxide loadings was investigated in this study. With higher % tungsten oxide loading, the relative content of metathesis-active sites on the WO₃/SiO₂ catalyst was still maintained while the dispersion of tungsten was lower. It was discovered that the *cis/trans* isomers could obstruct each other accessing to the metathesis-active site, especially when the dispersion of tungsten is low. This is in a good agreement with reactant-TPD in the result of lower propylene yield over higher %tungsten oxide loading of WO₃/SiO₂ catalyst.

Acknowledgments The financial supports from the Thailand Research Fund (TRF) and the Office of Higher Education Commission are gratefully acknowledged. The authors would like to thank the Royal Golden Jubilee PhD Scholarship from TRF and SCG Chemicals for Narongrat Poovarawan.

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