

Metathesis of ethene and 2-butene to propene on W/Al₂O₃–HY catalysts with different HY contents

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Abstract

Catalysts containing 10 wt.% W were prepared using Al₂O₃–HY mixed supports with various HY contents. The catalytic performance of these catalysts for the metathesis of ethene and 2-butene to propene was determined in a fixed-bed flow reactor at 180 °C under 0.1 MPa. The 2-butene conversion of these catalysts increases remarkably with the HY content in the range of 0–30 wt.%. Between 30 and 70 wt.% of HY content, the conversion reaches a plateau of 60–63%, which is very close to the thermodynamic equilibrium value of ~64%. After that, the 2-butene conversion decreases substantially. The propene selectivity shows the similar trends. The maximum propene selectivity goes up to 88%. By the studies of NH₃-TPD, H₂-TPR and UV–vis, the role of HY zeolite in the 10W/Al₂O₃–xHY is explained in two following aspects: (i) changing the Brønsted acidity of catalysts, which may affect the formation of initial carbene species; (ii) modifying the interaction between W species and support for the formation of active centers with intermediate oxidation number (W⁴⁺, W⁵⁺, W^{(6-y)+} (0 < y < 1)). Based on this information, the optimal HY content for 10W/Al₂O₃–xHY catalysts is about 50–70%.

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1. Introduction

The metathesis of propene has known for long time since the pioneering work from British Petroleum and from Philips. The reason why this process attracts much interest is its adaptability to the desired alkenes according to the demand. In the past 40 years, most of attention has been put to the metathesis of propene because of the increase in the ethene output. However, with the increasing need of the propene, the reverse of the reaction, i.e. the metathesis of ethene and 2-butene to propene, attracts more and more interest [1,2]. For this rea-

son, we carried out the research of the metathesis between ethene and 2-butene.

A wide variety of transition metal compounds catalyze the alkene metathesis and the most successful are based on W, Mo and Re. The heterogeneous catalysts are general aforementioned transition metal oxides supported on high surface area silica or alumina. Conventionally, the supported tungsten oxide catalysts are less active for metathesis than their rhenium and molybdenum counterparts. In order to achieve acceptable metathesis activity, much higher reaction temperatures (250–500 °C) have to be used for the tungsten-based catalysts [3,4]. However, the tungsten-based catalysts still have a high potential for practical applications in metathesis, mainly due to their low sensitivity to trace amounts of impurities. Recently, ABB Lummus has reported a WO₃/SiO₂ catalyst for

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the metathesis of ethene and 2-butene, which shows 2-butene conversion 65–70% and selectivity above 90% at 250–300 °C [2]. For metathesis of long chain alkenes, such as 1-octene and 1-heptene, WO₃/SiO₂ catalyzes the reaction with 88% conversion and an online lifetime of 700 h at 460 °C [5].

The catalytic performance of Re₂O₇/Al₂O₃ has been tried to improve by the addition of other oxides to the alumina support, e.g. SiO₂–Al₂O₃ [6,7], Al₂O₃–B₂O₃ [8,9] or Al₂O₃–P₂O₅ [10]. The resulting improved catalytic performances were partly attributed to the higher Brønsted acidity of SiO₂–Al₂O₃ or Al₂O₃–B₂O₃ than that of commonly used Al₂O₃ or SiO₂ support. It was also claimed that the modified support better stabilizes the Re species in the favorable oxidation state for the formation of the initial rhenium carbene species [9]. Since many zeolites have notable Brønsted acidity, the use of alumina–zeolite supports seems to be another good alternative to improve the Brønsted acidity of the catalysts.

In this paper we investigated the influence of HY content on the metathesis between ethene and 2-butene over 10 wt.% W/Al₂O₃–*x*HY catalysts. We found a very active catalyst, 10 wt.% W/(30 wt.% Al₂O₃–70 wt.% HY), which promotes the reaction with 2-butene conversion ca. 60% and propene selectivity ca. 88% at 180 °C. Then 10 wt.% W/Al₂O₃–*x*HY catalysts were characterized by Py-FTIR, H₂-TPR, and UV–vis and other techniques. Efforts are put to correlate the metathesis catalytic performances with the physico-chemical properties of the catalysts, in particular, with the acidity of catalysts and interaction between W species and supports as the function of HY content in the 10W/Al₂O₃–*x*HY.

2. Experimental

2.1. Catalyst preparation and its evaluation

The Al₂O₃–HY support was prepared by extruding a mixture of γ-Al₂O₃ powder and HY zeolite (WenZhou Zeolite Manufacture of China, Si/Al₂ = 10, Na₂O < 0.2 wt.%) at desirable weight percent into strips with a diameter of about 2 mm. The drawn extrudate was left at room temperature for a few hours and placed in an oven at 120 °C for 12 h. Subsequently, the dried extrudate was calcined at 500 °C for 2 h and then grinded into 16–32 mesh.

Catalysts containing 10 wt.% tungsten were prepared by impregnating the Al₂O₃–HY support with ammonium metatungstate solution according to the incipient wetness method. The impregnated samples were dried at 120 °C for 5 h, and then calcined at 600 °C for 2 h. These prepared catalysts are denoted as 10W/Al₂O₃–*x*HY, where *x* indicates the weight percent of HY zeolite in the Al₂O₃–HY support.

The catalysts were tested in a fixed-bed flow microreactor of 10 mm inner diameter, and 3 g of catalyst with an average particle size of 0.56–1.3 mm was loaded. A EU-2 type thermocouple was fixed in the middle position of the catalyst bed

at the outside of the steel reactor to measure the temperature of the electric furnace, which was taken as the reaction temperature. After the catalyst was pretreated in situ at 500 °C for 1 h under high purity N₂ (0.1 MPa, 30 ml/min), it was cooled to the reaction temperature in flowing N₂. The catalyst was then used for the metathesis reaction between ethene and 2-butene to propene. The reaction conditions are as follows: temperature = 180 °C, pressure = 0.1 MPa, N₂/C₂H₄ = 1.5, C₂H₄/2-C₄H₈ = 1, WHSV(C₂H₄ + 2-C₄H₈) = 1.5 h⁻¹, and catalyst = 3.0 g. The reaction products are analyzed by a gas chromatograph with a FID detector. The 2-butene conversion and propene selectivity are calculated as follows:

$$S_{\text{propene}} = \frac{[C_3^-]_m}{[C_3^-]_m + [1 - C_4^-]_m + [C_5]_m + [C_6]_m + [C_6^+]_m} \quad (1)$$

$$S_{\text{propene}} = \frac{[C_3^-]_m}{[C_3^-]_m + [1 - C_4^-]_m + [C_5]_m + [C_5^+]_m} \quad (2)$$

where $[C_3^-]_n$, $[1 - C_4^-]_n$ are the molar percent of each component in effluent gas and $[C_3^-]_m$, $[1 - C_4^-]_m$ are the weight percent of each component in effluent gas.

And the weight percent of other products are estimated as done to propene. In our experiments for the metathesis on the 10W/Al₂O₃–*x*HY catalysts, the ethene conversion increases synchronously with that of 2-butene, thus we use the 2-butene conversion as the catalytic activity.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were made with a Rigaku D/Max Diffractometer using Cu Kα radiation, operating at 40 kV and 50 mA. Patterns were recorded from 3° to 70° (2θ).

Under flowing 10% H₂/Ar flow (20 ml/min), H₂-TPR profiles were obtained in the range of ambient to 800 °C at a programmed temperature rate of 14 °C/min after the samples had been pretreated in an Ar flow at 500 °C for 30 min.

NH₃-TPD measurements were performed in a conventional flow apparatus using a U-shaped microreactor (4 mm i.d.) made of stainless steel, with helium (He) as the carrier gas. The NH₃-TPD process was monitored by a gas chromatograph with a TCD detector. A catalyst sample of 0.14 g was pretreated at 600 °C for 0.5 h in a He stream with a flow rate of 25 ml/min and was cooled to 150 °C. Then, it was exposed to an NH₃-containing He stream for 10 min. The sample was purged with a pure He stream for a certain period of time until a constant baseline was attained. NH₃-TPD was carried out in the range of 150–700 °C at a heating rate of 18.8 °C/min. The acid amount of sample was calculated according to reference [11].

Pyridine adsorption measurement was performed on a Thermo Nicolet Nexus 470 instrument. Prior to pyridine sorp-

tion, the wafers were outgassed at 550 °C for 2 h under vacuum. The sample was then cooled to room temperature and the IR spectrum was recorded as the background spectrum. Subsequently, dry pyridine (equilibrium vapor at 0 °C) was admitted in the sample chamber for about 0.5 h. The sample was then evacuated at 180 °C for about 0.5 h. After cooled down to room temperature, the IR spectrum was recorded. All IR spectra of adsorbed species are obtained by subtracting the background spectra. The IR adsorption bands at around 1540 and 1450 cm⁻¹ were used to determine Brönsted or Lewis acids, respectively [12]. The ratio of Brönsted to Lewis acid sites was obtained by using correlations developed by Emeis for Porous aluminosilicates [13]. On the basis of this correlation, the ratio of Brönsted acid to Lewis acid can be estimated as following equation:

$$\frac{C_B}{C_L} = \left(\frac{1.88}{1.42} \right) \frac{IA(B)}{IA(L)} \quad (3)$$

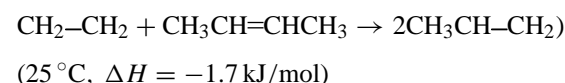
where C is the concentration and IA (B or L) the integrated absorbance of Brönsted or Lewis band.

UV–vis spectra were recorded with a JASCO 500 spectrophotometer equipped with a diffuse reflectance attachment. The samples were studied in the form of 12 mm diameter, 2 mm thick pellets prepared as self-supporting waters. The spectra were recorded under air-exposed conditions in the range 200–800 nm and the scan speed was 120 nm/min.

3. Results and discussion

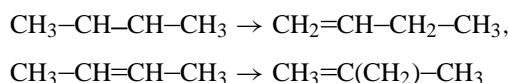
3.1. Catalytic performance of 10W/Al₂O₃-xHY catalysts

The metathesis between ethene and 2-butene is an equilibrium reaction, which is slightly exothermic:

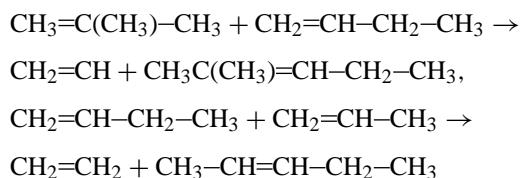


Besides the metathesis reaction, side reactions such as isomerization, subsequent secondary metathesis, oligomerization may occur:

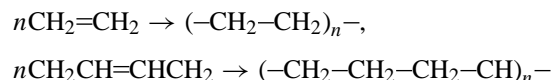
- *isomerization:*



- *secondary metathesis:*



- *Oligomerization:*



Therefore, it is difficult to make a comprehensive list of all the side products. For a simple treatment, we divide these side products into three categories: $1 - C_4^-$, C_5 and C_5^+ . Among them, $1 - C_4^-$ originates from the double bond isomerization or skeletal isomerization of 2-butene feed. C_5 represents substances bearing five carbon atoms, which are mainly produced from secondary metathesis, and C_5^+ is used to denote the products in the C_6 – C_{10} range.

Table 1 shows the activity and selectivity of 10W/Al₂O₃-xHY catalysts as a function of HY zeolite content. The catalytic performance of catalysts depends on the HY content in the support. 10W/Al₂O₃ proceeds the metathesis reaction with 23.6% 2-butene conversion at 180 °C. This is in fair agreement with reference results, which always report a low activity for WO₃/γ-Al₂O₃ at relatively mild conditions [4]. A remarkable increase in 2-butene conversion from 23.6% to 59.4% is observed with increasing HY content up to 30 wt.%. Then the 2-butene conversion does not change much at ca.60% in the range of 30–70 wt.% HY. Further increment of HY content results in the sharp decrease in 2-butene conversion. Similar trend can be observed for the propene selectivity. The maximum 2-butene conversion is obtained at 10W/Al₂O₃-70HY, whose 2-butene conversion of 62.6% is near the thermodynamic equilibrium value (~64%). The maximum propene selectivity, 88.2%, also belongs to 10W/Al₂O₃-70HY. As shown in Table 1, $1 - C_4^-$ and C_5 are the major side products for all catalysts. Their weight percents vary inversely as propene selectivity. On the 10W/Al₂O₃-50HY and 10W/Al₂O₃-70HY catalysts, the weight percent of C_5^+ is only 1.2%, indicating that the isomerization and secondary metathesis are the major side reactions for the active catalysts. In contrast, the 10W/HY shows the poorest performance, which shows only 16.6% 2-butene conversion and 36.2% propene selectivity. The weight percent of $1 - C_4^-$ and C_5^+ is very high as

Table 1
Catalytic performance of 10W/Al₂O₃-HY with different HY zeolite contents

Catalyst	2- C_4^- conversion (%)	Selectivity (%)			
		C_3^-	$1 - C_4^-$	C_5	C_5^+
10W/Al ₂ O ₃	23.6	64.0	22.6	6.7	6.7
10W/Al ₂ O ₃ -10HY	26.9	65.2	20.7	7.1	7.1
10W/Al ₂ O ₃ -30HY	59.4	83.3	9.7	5.4	1.6
10W/Al ₂ O ₃ -50HY	60.6	88.1	6.3	4.4	1.2
10W/Al ₂ O ₃ -70HY	62.6	88.2	6.1	4.5	1.2
10W/Al ₂ O ₃ -90HY	52.7	83.8	8.7	6.1	1.4
10W/HY	16.6	36.2	46.7	6.8	10.3

Reaction condition: $T = 180$ °C; $P = 0.1$ MPa; WHSV = 1.5 h⁻¹; ethene/2-butene = 1 (mol ratio); time on stream = 1 h.

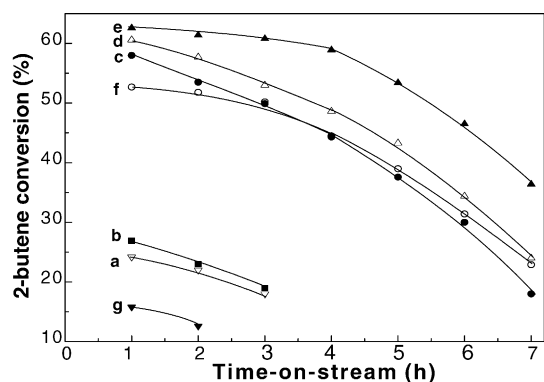


Fig. 1. Catalytic performance of 10W/Al₂O₃-xHY as a function of the process time. (a) 10W/ γ -Al₂O₃; (b) 10W/Al₂O₃-10HY; (c) 10W/Al₂O₃-30HY; (d) 10W/Al₂O₃-50HY; (e) 10W/Al₂O₃-70HY; (f) 10W/Al₂O₃-90HY; (g) 10W/HY. Reaction condition: $T=180\text{ }^{\circ}\text{C}$; $P=0.1\text{ MPa}$; $\text{WHSV}=1.5\text{ h}^{-1}$; ethene/2-butene = 1 (mol ratio).

46.7% and 10.3%, respectively, implying the isomerization reactions predominate over the metathesis process.

Not only the activity and selectivity but also the stability changes with the HY content in the Al₂O₃-xHY support. As shown in Fig. 1, besides the rather low activity and selectivity, the 10W/Al₂O₃, 10W/Al₂O₃-10HY and 10W/HY catalysts also show poor stability. The most active catalyst 10W/Al₂O₃-70HY is also the most stable one among all 10W/Al₂O₃-xHY catalysts. For the 10W/Al₂O₃-30HY and 10W/Al₂O₃-50HY catalysts, the 2-butene conversion decreases almost linearly as a function of time. Despite its lower initial 2-butene conversion than that of 10W/Al₂O₃-30HY or 10W/Al₂O₃-50HY, the 10W/Al₂O₃-90HY shows a slower deactivation rate, whose trend resembles that of 10W/Al₂O₃-70HY.

From the results of Table 1 and Fig. 1, we can conclude that the combination of Al₂O₃ and HY is prerequisite for the active catalysts, and only the catalysts with appropriate HY content (30–70 wt.%) give good catalytic performance. Catalysts with either too low (<10 wt.%) or too high HY (>90 wt.%) content show rather poor catalytic performance.

3.2. Characterization of 10W/Al₂O₃-xHY catalysts

XRD patterns of 10W/Al₂O₃-xHY samples calcined at 600 °C are shown in Fig. 2. No diffraction patterns of any W phase were detected in the different samples and the only peaks present in the patterns correspond to the γ -Al₂O₃ or HY phase. This indicates that the W phases were well dispersed on the different supports forming either an amorphous phase or microcrystallites that cannot be detected at this measuring scale. The intensities of sharp HY characteristic peaks increase with the increment of HY content in the Al₂O₃-HY support. The coexistence of broad γ -Al₂O₃ ($2\theta=37.39, 45.95, \text{ and } 67.06$) and sharp HY characteristic peaks is shown in samples with HY content below 70 wt.%. Only HY characteristic peaks, except their difference in intensity, appear as the HY content is higher than 70 wt.%, due

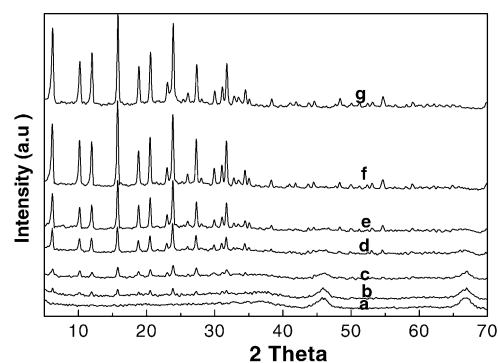


Fig. 2. XRD patterns of 10W/Al₂O₃-xHY catalysts. (a) 10W/ γ -Al₂O₃; (b) 10W/Al₂O₃-10HY; (c) 10W/Al₂O₃-30HY; (d) 10W/Al₂O₃-50HY; (e) 10W/Al₂O₃-70HY; (f) 10W/Al₂O₃-90HY; (g) 10W/HY.

to the spontaneous dispersion of γ -Al₂O₃ onto the HY zeolite surface to form a monolayer or submonolayer [14].

Fig. 3 shows infrared spectra of adsorbed pyridine on the catalyst. The characteristic infrared bands near 1540 cm⁻¹ are attributed to pyridinium ions on Brönsted (B) acid sites and those near 1450 cm⁻¹ are corresponding to pyridine coordinatively bonded to Lewis (L) acid centers [12]. As shown in Fig. 3, no evidence is found for a band at 1540 cm⁻¹ on the 10W/Al₂O₃ sample, indicating that there is no Brönsted acid site on the surface strong enough to react with the pyridine. Only the band at 1450 cm⁻¹ appears on the 10W/Al₂O₃, suggesting there are only Lewis acid sites on WO₃/Al₂O₃ [12]. The 10W/HY sample shows bands both at 1540 and 1450 cm⁻¹, indicating that there are both Brönsted and Lewis acid sites on the 10W/HY sample. With the increment of HY content in the Al₂O₃-HY support, the intensity of band at 1540 cm⁻¹ become stronger and that at 1450 cm⁻¹ does not change obviously. On the other hand, the bands at about 1490 cm⁻¹, contributed by both the Brönsted and Lewis acid sites [12], become stronger with the increment of HY content. The relative distribution of acid sites (expressed as C_B/C_L ratios) as a function of HY content in Al₂O₃-HY was estimated according to Eq. (3). As shown in Fig. 4, the C_B/C_L value increases from 0 to 2.8 with the HY content changing from 0 to 100 wt.% in the Al₂O₃-HY support. The total acid

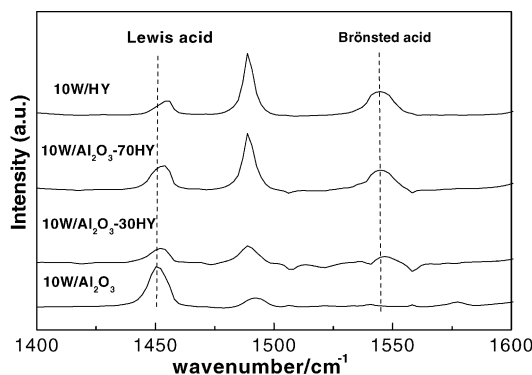


Fig. 3. FTIR spectra of chemisorbed pyridine on 10W/Al₂O₃-xHY catalysts with different HY contents.

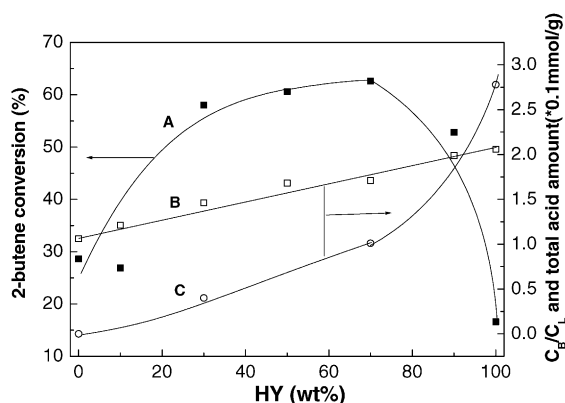


Fig. 4. Correlation between 2-butene conversion and acid character of supported WO_3 catalysts. (A) 2-Butene conversion (■); (B) total acid amount (□); (C) C_B/C_L (○).

amount of catalyst was determined by NH_3 -TPD. The minimum value is 0.106 mmol/g for 10W/ Al_2O_3 and the maximum one is 0.206 mmol/g for 10W/HY. The amount of acid increases almost linearly with the increment of HY content. Correlating the results of Py-FTIR with those of NH_3 -TPD, we can conclude that the increment of HY content in the 10W/ Al_2O_3 -xHY samples results in an increase in total acid sites, and a progressive increase in Brönsted acid sites.

The interaction between W species and the Al_2O_3 -HY support was investigated by the H_2 -TPR technique, as shown in Fig. 5. The Al_2O_3 -HY support has no H_2 reduction peak (not shown) in the range of our reduction temperature (<800 °C). Three peaks are observed at about 420, 550 and 800 °C on the 10W/HY sample, which are denoted as *l*, *m* and *h*, respectively. The *l* and *m* peaks are assigned to the reduction of W species in octahedral coordination [15,17], which are reduced at relative low temperature. The broad *h* peak at 800 °C is assigned to the reduction of the surface amorphous tungsten oxide species or the WO_3 microcrystallites to the W metal [15–17]. With the decrement of HY content in Al_2O_3 -HY, the intensities of these three peaks decrease obviously and the *h* reduction peak shifts to higher temperature. In fact, almost no reduction peaks appear below

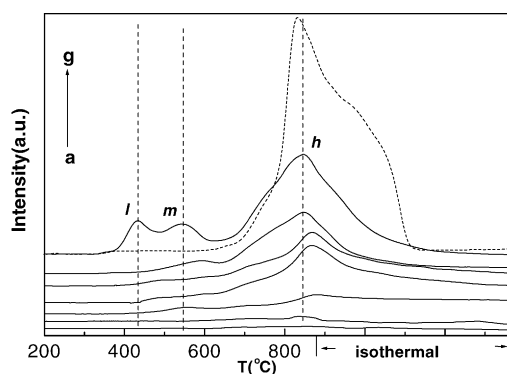


Fig. 5. TPR profiles of 10W/ Al_2O_3 -xHY catalysts. (a) 10W/ γ - Al_2O_3 ; (b) 10W/ Al_2O_3 -10HY; (c) 10W/ Al_2O_3 -30HY; (d) 10W/ Al_2O_3 -50HY; (e) 10W/ Al_2O_3 -70HY; (f) 10W/ Al_2O_3 -90HY; (g) 10W/HY.

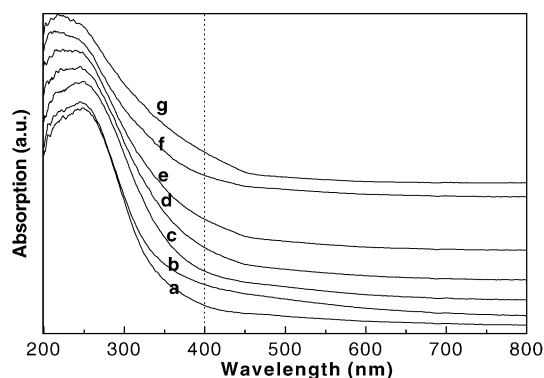


Fig. 6. UV-vis spectra of 10W/ Al_2O_3 -xHY catalysts with different HY contents. (a) 10W/ γ - Al_2O_3 ; (b) 10W/ Al_2O_3 -10HY; (c) 10W/ Al_2O_3 -30HY; (d) 10W/ Al_2O_3 -50HY; (e) 10W/ Al_2O_3 -70HY; (f) 10W/ Al_2O_3 -90HY; (g) 10W/HY.

800 °C for the 10W/ Al_2O_3 . Moulijn and co-workers have reported that the reduction of WO_3 / Al_2O_3 with similar tungsten loading (10%) as this work shows no reduction peaks below 800 °C due to the strong interaction of alumina support with tungsten oxide [18]. The dash TPR profile is for the mechanical mixture of WO_3 and HY with the same W content as those 10W/ Al_2O_3 -xHY catalysts, which reveals a complete reduction of bulk WO_3 to metal W at this reduction condition. Compared with the profile of bulk WO_3 , the area of *h* peak for supported 10W/HY catalysts are obvious diminished. This indicates that the some W species have interaction with the HY supports, which requires a higher reduction temperature for them. The diminishment of *h* peak area becomes more remarkable with the decrement of HY content in support, which suggests more and more W species require higher reduction temperature. Until for 10W/ Al_2O_3 catalysts, this *h* peak vanishes completely. Based on the above results, we conclude that the W species interact much more strongly with Al_2O_3 than do with HY. As a result, the interaction between W species and Al_2O_3 -xHY become diminished with the increment of HY content in supports.

The UV-vis spectra are sensitive to the structure change of catalysts. As shown in Fig. 6, all fresh catalysts show two bands: one at about 215 nm and another at about 250 nm. According to the literature [19], 215 nm band corresponds to the normal tetrahedral WO_4^{2-} . And the band at 250 nm can be attributed to distorted tetrahedral WO_4^{2-} species due to the strong interaction between W species and Al_2O_3 support [19], or to the octahedral W species [20]. On the 10W/ Al_2O_3 -xHY catalysts, we propose that the adsorption of 250 nm band is the combination of distorted tetrahedral and octahedral W species. With the increment of the HY content, the intensity of band at 250 nm decreases, while that of band at 215 nm increases. This reveals that the increment of HY content in the 10W/ Al_2O_3 -xHY support results in the reduction of distorted WO_4^{2-} species or the presence of some octahedral W species, whose bands normally are much less intense than tetrahedral ones [21]. The reduction of distorted tetrahedral WO_4^{2-} species is an indirect reflection of

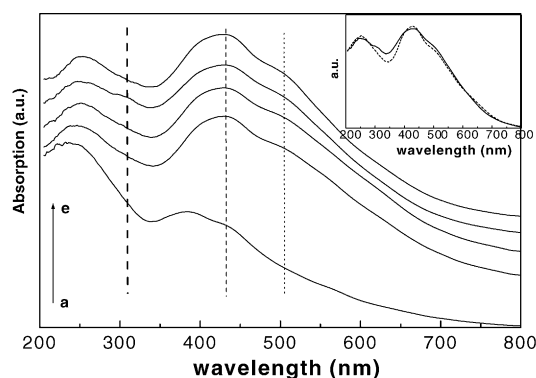


Fig. 7. The UV-vis spectra of spent catalysts (1 h) with different HY contents. (a) 10W/Al₂O₃; (b) 10W/Al₂O₃-30HY; (c) 10W/Al₂O₃-50HY; (d) 10W/Al₂O₃-70HY; (e) 10W/HY. Inset spectra (—) 10W/Al₂O₃-70HY (1 h); (---) 10W/Al₂O₃-70HY (7 h).

diminished interaction between W species and Al₂O₃-HY support, which is consistent with the results of TPR. In accord with our results, Ramírez and Gutiérrez-Alejandre [21] have reported the geometry of W species change from tetrahedral coordination to octahedral coordination and a diminished interaction between tungsten species and Al₂O₃-TiO₂ support with the increment of TiO₂ content in WO₃/Al₂O₃-TiO₂, which was evidenced by the TPR, UV-vis and FT-Raman spectra.

Further, the spent 10W/Al₂O₃-xHY catalysts were also characterized by UV-vis technique to investigate the oxidation state of W species after reaction. It has been reported for molybdenum species that the adsorption band between 400 and 800 nm is due to the reduced Mo ions such as Mo⁴⁺ and Mo⁵⁺ [22]. Since supported WO₃ and MoO₃ catalysts are comparable in chemistry, it is reasonable to attribute the adsorption between 400 and 800 nm to the reduced W ions such as W⁴⁺ and W⁵⁺. On the other hand, bands at 215 and 250 nm have been attributed to W⁶⁺ species in the preceding section. In addition, we observed bands between 250 and 400 nm, which are tentatively assigned to the W species charged between +5 and +6. As discussed above, all fresh samples show two intensive bands at 215 and 250 nm besides a minor band at above 400 nm, which means the predominant tungsten species of the fresh W/Al₂O₃-xHY catalysts is W⁶⁺ and the amount of W⁴⁺ and W⁵⁺ is minor. After 1 h reaction time, the spectra of spent catalysts become different from those of fresh ones. As shown in Fig. 7, two new bands at ca. 380 and 450 nm are observed in the 10W/Al₂O₃, whose intensities are lower than those of bands at 215 and 250 nm. The increment of HY content in the 10W/Al₂O₃-xHY results in the higher intensities of bands at 420 and 500 nm, while that of band at 250 nm become lower. For the spent 10W/HY sample, the band at 215 nm vanishes completely, and bands at 420 and 500 nm predominate in adsorption. The UV-vis spectra of spent catalyst imply that after reaction part of W⁶⁺ species are reduced to W⁴⁺ and W⁵⁺ species, whose amount increases with the HY content in the Al₂O₃-HY support.

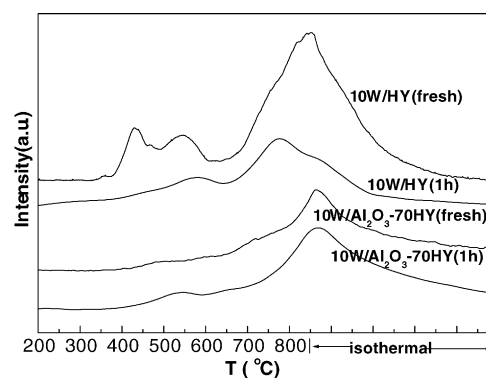


Fig. 8. Comparison of reducibility between fresh and spent catalysts.

3.3. Correlation between catalytic performance and characterization results of 10W/Al₂O₃-xHY catalysts

The Al₂O₃-HY support surely plays an important role in the activity of supported WO₃ catalysts from above results. As the study on the metathesis activity of several SiO₂-Al₂O₃ supported Re₂O₇ catalysts by Sibeijn and Mol [23], an improvement in activity with the increasing Brønsted acidity of the support was observed [23,24]. For the Al₂O₃-HY supported catalysts, the catalytic activity is also positively correlated with Brønsted acidity as the HY content increasing from 0 to 70 wt.%, due to the notable Brønsted acidic hydroxyl groups of HY zeolite. This promoting effect of Brønsted acid could be realized as Laverty and Xiaoding's suggestions that the Brønsted acid sites can improve the metathesis activity by reacting with the reduced transitional metal ion or by protonizing the adsorbed alkene molecules [25,26].

However, for the 10W/Al₂O₃-xHY with higher than 70 wt.% HY, the catalytic activity and selectivity begins to decrease, which implies that besides the catalyst Brønsted acidity some others factors influences the catalytic performance. The interaction between W species and support may play an important role in the metathesis reaction. From the TPR profiles of fresh catalysts (Fig. 5), it can be concluded that the interaction between W species and support becomes diminished with the increasing HY content, which is applicable to reveal their resistance to the reductive alkene feed. Furthermore, Fig. 8 shows the comparison of TPR spectra between fresh and spent catalyst for 1 h in the reaction stream. There is almost no change for the profiles of the 10W/Al₂O₃ before and after reactions (not shown). While for the 10W/HY catalyst, the intensities of three peaks after 1 h reaction time become obviously diminished. It is understandable that there is a slightly change in the intensities of three peaks for the 10W/Al₂O₃-70HY catalyst.

In addition, the UV-vis spectra of spent 10W/Al₂O₃-xHY catalysts reveal the relative amount of reduced W species after 1 h reaction time. For 10W/Al₂O₃, the obvious low intensities of bands beyond 250 nm indicate most of W species is still kept in +6 oxidation state. The intensities of those bands beyond 250 nm become higher with the increment of

HY content in the $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ support, symbolizing an increasing amount of reduced W species. The largest amount of reduced W species on spent 10W/HY reflects the weakest interaction between W species and HY.

According to the these results of TPR and UV–vis, W species supported on Al_2O_3 is hard to be reduced by reductive feed alkene, while those species on 10W/HY can be reduced easily in the reactant feed. W species supported on the $\text{Al}_2\text{O}_3\text{-HY}$ with a suitable HY contents of 30–70 wt.% have suitable resistance to the reductive alkene feed, which is beneficial for the catalytic performance. Under the reaction conditions, the high valence W species (W^{6+}) in the 10W/ $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ catalysts are reduced to lower and suitable oxidation state, acting as the active centers for the metathesis.

As shown by the UV–vis spectra of spent catalysts (Fig. 7), the active centers of the 10W/ $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ catalysts for the metathesis of ethene and butene may be W^{4+} , W^{5+} and W species charged between +5 and +6. The increment of HY content in the $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ support results in more amount of active sites and enhances the activity of catalysts. Although the spent W/HY sample possesses quite a number of W^{4+} and W^{5+} species, it still shows rather poor catalytic performance with the 2 h online time. The reason may be that the deep reduced species (such as W^{2+} , W^{3+} , $\text{W}^{(0)}$) on the spent 10W/HY causes the loss of catalyst activity. Our preliminary results have also proved that the 10W/ $\text{Al}_2\text{O}_3\text{-}70\text{HY}$ catalyst pretreated by H_2 atmosphere shows rather poor activity and quick deactivation for the metathesis.

An interesting phenomenon is that the active catalysts show a minor band at 310 nm, corresponding to one of W species charged in between +5 and +6, which is tentatively denoted as $\text{W}^{(6-y)+}$ ($0 < y < 1$). The intensity of this band is most strong for the most active 10W/ $\text{Al}_2\text{O}_3\text{-}70\text{HY}$, indicating the $\text{W}^{(6-y)+}$ species may be the most active species for the metathesis. From the inset spectra in Fig. 7, it is clear that the band at 310 nm band vanishes completely on the 10W/ $\text{Al}_2\text{O}_3\text{-}70\text{HY}$ sample with reaction time to 7 h, while the other two adsorption bands change very slightly. At that time, the 2-butene conversion is down to only 36.4%. Therefore, the $\text{W}^{(6-y)+}$ ($0 < y < 1$) species are really related with the high active centers, as Choung et al. have shown some intermediate nonstoichiometric tungsten oxide to be the most active for propene metathesis [27]. The improvement of HY zeolite to the 10W/ Al_2O_3 activity as well as the stability may be resulted from the promotion effect of HY for the formation of $\text{W}^{(6-y)+}$, W^{5+} and W^{4+} species.

The influence of HY content in the 10W/ $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ catalysts on the metathesis activity is the integrative results of change in Brønsted acidity and that in interaction between W and $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ support. Lower HY content will result in inadequate amount of Brønsted acid sites and too strong interaction between W and the support, leading to a relative lower catalytic activity. While higher HY content, especially than 90 wt.%, can produce enough Brønsted acid sites, but much weaker interaction between W species and support will still

cause the loss of catalytic activity. Only those catalysts with suitable HY content, e.g. about 50–70 wt.%, have both adequate amount of Brønsted acid sites and a just interaction between W and support for the formation of active reduced W species, which are favorable for the production of propene by the metathesis between ethene and 2-butene.

4. Conclusion

The HY content in the 10W/ $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ support can make an influence on the Brønsted acidity of catalyst and the interaction between W species and support simultaneously, both of which play their important roles in the metathesis reaction of ethene and 2-butene to propene. Inadequate Brønsted acid sites and too strong interaction lead to the inferior activity of the 10W/ $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ catalysts with low HY content. The higher HY content in support promotes the Brønsted acidity of catalyst and the reduction of W species, therefore improves the catalytic performance. However, much too weak interaction between W species and support, caused by excessive HY content, leads to the deep reduction of W species and the loss of metathesis activity. That is to say the combination of $\gamma\text{-Al}_2\text{O}_3$ with proper weight percent HY can provide suitable interaction between W species and supports, which is favorable for the formation of active centers with intermediate oxidation number (W^{4+} , W^{5+} , $\text{W}^{(6-y)+}$ ($0 < y < 1$)). Generally, an optimal HY content is quite necessary for active 10W/ $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ catalysts. Especially, over 10W/ $\text{Al}_2\text{O}_3\text{-}x\text{HY}$ catalysts with 50–70 wt.% HY content, 60–63% 2-butene conversion can be achieved at 180 °C.

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