[Article]

doi: 10.3866/PKU.WHXB201503032

www.whxb.pku.edu.cn

钨含量对W/SiO₂/Al₂O₃催化剂上1-丁烯自歧化反应的影响柳 娜^{1,*} 张 辉¹ 薛念华² 丁维平²(¹西安科技大学化学与化工学院, 西安 710054; ²南京大学化学与化工学院, 介观化学教育部重点实验室, 南京 210093)

摘要: 采用浸渍法制备了一系列钨负载量不同的W/SiO₂/Al₂O₃催化剂. 采用X射线衍射(XRD)、激光拉曼(Raman)光谱、紫外-可见(UV-Vis)光谱、氢气程序升温还原(H₂-TPR)和氨程序升温脱附(NH₃-TPD)等技术对催化剂进行了表征. 实验结果表明: 钨的负载量对催化剂上氧化钨物种的分散程度、还原性以及催化剂的酸性有非常重要的影响. 对该类催化剂上1-丁烯自歧化反应进行了详细考察, 结果表明: 当钨的质量分数为6.0%时, W/SiO₂/Al₂O₃催化剂表现出最佳的歧化活性和稳定性. 原因在于6.0%的钨负载量可以使催化剂上氧化钨物种具有中等程度的分散性、合适的还原性, 并且使催化剂具有一定程度的酸性, 这些因素有利于在催化剂上形成烯烃歧化活性位.

关键词: 1-丁烯; 丙烯; 歧化; 钨负载量; 催化活性

中图分类号: O643

Influence of Tungsten Loadings on the 1-Butene Metathesis Reaction over W/SiO₂/Al₂O₃ CatalystsLIU Na^{1,*} ZHANG Hui¹ XUE Nian-Hua² DING Wei-Ping²¹College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an 710054, P. R. China;²Key Laboratory of Mesoscopic Chemistry of MOE, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China)

Abstract: A series of W/SiO₂/Al₂O₃ catalysts with various tungsten loadings were synthesized via the impregnation method. The as-synthesized catalysts were characterized by X-ray diffraction (XRD), Raman spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, H₂ temperature-programmed reduction (H₂-TPR), and NH₃ temperature-programmed desorption (NH₃-TPD). The results reveal that the tungsten loadings were crucial to the dispersion and reducibility of the tungsten oxide species and the acidity of catalysts. The catalytic performances were also investigated during the metathesis of 1-butene to propene. Amongst these catalysts, W/SiO₂/Al₂O₃ with a tungsten mass fraction of 6.0% gave the highest activity and stability during the 1-butene metathesis reaction. The excellent catalytic performance of the catalyst containing a tungsten mass fraction of 6.0% is attributed to its moderate dispersion, suitable reducibility of the WO_x species and suitable acidity. We speculate that these factors are favorable for the formation of active centers for olefin metathesis.

Key Words: 1-Butene; Propene; Metathesis; Tungsten loading; Catalytic activity

1 Introduction

The propene demand is expected to grow faster than the supply, the technologies for propene production, such as propane dehy-

drogenation, metathesis, and methanol to olefins conversion, have received much attention recently.¹⁻³ Among them, the cross-metathesis of ethylene and 2-butenes has already been com-

Received: December 30, 2014; Revised: February 17, 2015; Published on Web: March 3, 2015.

*Corresponding author. Email: liuna307@126.com; Tel: +86-29-85583183.

The project was supported by the National Natural Science Foundation of China (21403164) and National Innovation Experiment Program for University Students, China (S14024).

国家自然科学基金(21403164)和国家大学生创新创业训练项目(S14024)资助

© Editorial office of *Acta Physico-Chimica Sinica*

mercialized as an economical means to produce propene.^{4–6} Auto-metathesis of butene is another promising way since it negates the loss of the valuable ethene in the production of propene.^{7–9} Now the catalysts used for the olefin metathesis include Rhenium-Based catalyst,¹⁰ Molybdenum-Based catalyst,¹¹ and Tungsten-Based catalyst.¹² For olefin metathesis reaction, supported tungsten oxide catalyst is less active than Re and Mo oxide. However, it is attractive for industry because it is tolerant to various poisons in the industrial feed stream.¹³ The activity of tungsten catalyst is influenced by many factors, among which the tungsten loading on supports is a very important factor due to its influence on the structures and properties of supported tungsten oxide species and the acid of catalysts. Some studies have been devoted to explore the influence of the structure of tungsten species and the acid of catalysts on metathesis of 1-butene.^{9,14–17} Huang *et al.*⁹ thought that WO_3 supported catalysts were composed of surface amorphous compound and crystalline trioxide depending on the surface concentration, WO_3 crystals were not active in metathesis and the catalytic sites should be contained in the amorphous surface compound. Wang *et al.*¹⁴ have reported highly efficient tungsten-substituted mesoporous SBA-15 catalysts for 1-butene metathesis, which showed excellent catalytic performance. Such outstanding catalytic performance should be attributed to the proper content of tungsten species and its high dispersion. Chen *et al.*¹⁵ have used $\text{WO}_3/\text{MTS-9}$ catalyst for metathesis of butene, they speculated that the tetrahedral and the octahedral polytungstate species may be the active sites rather than crystalline WO_3 . Spamer *et al.*¹⁶ found that metathesis activity was not related to Brønsted acidity as metathesis activity does not increase with increasing the WO_3 loading while Brønsted acidity does, Lewis acidity was necessary for metathesis activity, proper acidity of catalysts would suitable for metathesis activity. Praserthdam *et al.*¹⁷ used NaOH to mitigate the acidity of the catalysts, they indicated that NaOH treatment was a good way to tune the selectivity of WO_3/SiO_2 catalysts to give a little more propene yield without affecting their metathesis activity, the acidity of the catalysts was crucial to metathesis products.

We have reported recently that the tungsten oxide loaded on silica modified γ -alumina exhibited high activity for the metathesis of 1-butene, with 1-butene conversion (molar fraction) up to 71% and propene yield up to 21% at 453 K and 0.1 MPa.¹⁸ In the previous work, the excellent catalytic activity was related to the suitable dispersion of tungsten species and acidity of support. The tungsten loading on supports has important effect on the structures and properties of supported tungsten oxide species and the acid of catalysts. Thus, it is necessary to prepare the catalysts with appropriate tungsten loadings, which can improve the metathesis activity and stability of catalysts. In this study, the influence of tungsten loadings on the activity of $\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst is investigated for metathesis of 1-butene to propene at 453 K and 0.1 MPa. In addition, XRD, N_2 adsorption techniques, Raman scattering, UV-Vis spectroscopy, H_2 -TPR, and NH_3 -TPD are used for characterizing the catalysts to investigate the relationship between

the activity and the dispersion, reducibility of supported tungsten oxide species and the acid of catalysts.

2 Experimental

2.1 Preparation of the catalysts

2.1.1 Silica modified γ - Al_2O_3

γ - Al_2O_3 powder was obtained from Fu Shun Research Institute of Petroleum and Petrochemicals. The silica modified γ - Al_2O_3 was prepared according to the procedure reported elsewhere.¹⁸ Typically, the samples of silica modified γ - Al_2O_3 were prepared by immersing 1 g of γ - Al_2O_3 into an ethanol solution (20 mL) containing a certain amount of 3-aminopropyl-triethoxysilane (Aldrich, 99.9%) under stirring for 2 h at room temperature. The slurry was dried at 373 K for 12 h and calcined at 823 K for 8 h in air. The silica mass fraction was fixed at 20%. The resulted modified γ - Al_2O_3 supports were designated as $\text{SiO}_2/\text{Al}_2\text{O}_3$.

2.1.2 Supported tungsten oxide

The supported tungsten catalysts were prepared by impregnation method. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ support was immersed in the solution of ammonia metatungstate and stirred at 298 K for 6 h. The resulted slurry was then dried at 373 K and calcined at 823 K for 8 h in air. Tungsten supported on $\text{SiO}_2/\text{Al}_2\text{O}_3$ was denoted as $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$, where $x\%$ indicated the loading of W (mass fraction) supported on $\text{SiO}_2/\text{Al}_2\text{O}_3$. The mass fractions of W in the catalyst were 2.0%, 4.0%, 6.0%, 8.0%, and 12.0%.

2.2 Catalyst characterization

2.2.1 X-ray diffraction

X-ray diffraction (XRD) patterns of catalysts were recorded in the 2θ region of 20° – 80° on a Rigaku D/Max-3c (Rigaku Company, Japan) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The scan speed was set at $10^\circ \cdot \text{min}^{-1}$ with a step size of 0.02° .

2.2.2 Surface area

The specific surface areas were measured by means of the nitrogen adsorption at 77 K on a Micrometrics ASAP 2020 instrument (Micrometrics company, USA). Before N_2 adsorption, the sample was outgassed under vacuum at 573 K for 3 h. The specific surface area of the catalyst was calculated using the Brunauer-Emmett-Teller (BET) method.

2.2.3 Raman and UV-Vis characterization

Raman spectra were recorded with a Renishaw inVia system equipped with a confocal microscope (Renishaw company, England). A 514.5 nm exciting line was focused using a $50\times$ objective lens. UV-Vis spectra were recorded with a Thermo Scientific Evolution 220 spectrometer (Thermo company, USA) at room temperature. The spectra were recorded under air-exposed conditions in the range of 200–800 nm and the scan speed was $120 \text{ nm} \cdot \text{min}^{-1}$.

2.2.4 Temperature-programmed desorption and reaction

NH_3 -TPD profiles were obtained by using a Xianquan Auto-Chem TP-5080 apparatus (Xianquan Company, China) with a thermal conductivity detector. The samples were pretreated at 823 K for 1 h in He stream ($30 \text{ mL} \cdot \text{min}^{-1}$) and were then cooled to 373 K. The pretreated sample was exposed to NH_3 stream for 30

min, and then purged with a pure He stream for a certain period of time until a constant baseline was obtained. NH₃-TPD was carried out in the range of 373–823 K at a heating rate of 20 K·min⁻¹. H₂-TPR profiles were obtained by using a Xianquan AutoChem TP-5080 apparatus (Xianquan Company, China) with a thermal conductivity detector. Under flowing 10% H₂/Ar flow (30 mL·min⁻¹), H₂-TPR profiles were obtained in the range of 293–1073 K at a programmed temperature rate of 10 K·min⁻¹ after the samples had been pretreated in an He flow at 823 K for 1 h.

2.3 Catalytic test

The 1-butene metathesis reaction was carried out in a continuous-flow, fixed-bed system. A 0.2 g catalyst sample was placed into a quartz wool plug located in a quartz U-tube. After the catalyst was pretreated *in situ* at 873 K for 1 h under an Argon flow (99.99% purity, 60 mL·min⁻¹), it was cooled to the reaction temperature in the Argon flow. Then the Ar was switched to 1-butene (99.5%). The reaction conditions were as following: temperature 453 K, pressure 0.1 MPa. The weight hourly space velocity (WHSV) of 1-butene was 2.4 h⁻¹. The reaction products were analyzed online by gas chromatography (GC) with a 50 m fused silica chrompack PLOT Al₂O₃/Na₂SO₄ capillary column and a flame ionization detector. The reaction pathway was illustrated in Scheme 1 in detail.¹⁹ The 1-butene conversion was determined by the mass percentage in the exhaust gas and the molar yield of products was calculated by the following equation:

$$Y(C_n) = X \times \frac{W(C_n)}{n} \div \left[\frac{W(C_2)}{2} + \frac{W(C_3)}{3} + \frac{W(C_4)}{4} + \frac{W(C_5)}{5} + \frac{W(C_6)}{6} + \frac{W(C_7)}{7} \right] \quad (1)$$

where $Y(C_n)$ is the molar yield of alkene with carbon number n , X is the 1-butene conversion and $W(C_n)$ is the mass fraction of alkene with different carbon number n .

3 Results and discussion

3.1 Characterization of the catalysts

Fig. 1 shows the powder XRD patterns of WO₃, SiO₂/Al₂O₃, and x W/SiO₂/Al₂O₃ catalysts. When the mass fraction of tungsten was lower than 8.0%, no peaks corresponding to the phase of WO₃ crystallites were observed and only the diffraction peak of support (SiO₂/Al₂O₃) was presented, suggesting the presence of well dispersed surface tungsten oxide species or amorphous WO₃ or very small crystallites, which were undetectable by XRD. However, a slight diffraction peak of WO₃ microcrystal was observed ($2\theta=23.6^\circ$) when tungsten content was 12.0%, the other peaks presenting in the patterns were diffraction lines of support. The surface areas of all samples with various tungsten loadings (2.0%, 4.0%, 6.0%, 8.0%, 12.0%) are listed as 157, 148, 140, 132, 125 m²·g⁻¹. In terms of x W/SiO₂/Al₂O₃, surface area decreased with increasing the tungsten loading. The loss in surface area must be ascribed to the adsorption of tungsten species on the support surface.

The Raman spectra of catalysts with 2.0%, 4.0%, 6.0%, 8.0%,

Fig.1 XRD patterns of WO₃, SiO₂/Al₂O₃, and x W/SiO₂/Al₂O₃

Fig.2 Raman spectra of WO_3 and $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$

and 12.0% tungsten on $\text{SiO}_2/\text{Al}_2\text{O}_3$ support are shown in Fig.2, which can help us to understand better the nature of the surface tungsten species present in supported $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts. The Raman spectral peaks of crystalline WO_3 at 804, 712, 270 cm^{-1} were assigned to the symmetric stretching mode of $\text{W}-\text{O}$, bending mode of $\text{W}-\text{O}$, and deformation mode of $\text{W}-\text{O}-\text{W}$, respectively.^{15,20,21} For catalysts with different tungsten loadings, very strong bands at 712 and 804 cm^{-1} and weak bands at 270 and 970 cm^{-1} were observed. The band at 970 cm^{-1} was attributed to the symmetric $\text{W}=\text{O}$ stretching of tetrahedrally coordinated WO_x species, a part of which is in dimeric form.²² For the $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ samples, the intensities of bands at 712 and 804 cm^{-1} increased and the intensity of band at 270 and 970 cm^{-1} decreased with increasing the loadings of tungsten, which indicating that high loadings of tungsten species may result in the agglomeration of WO_x species and the decreasing of dispersion of WO_x species on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ surface.

The UV-Vis is a good way for determining the dispersion of tungsten species with different tungsten loadings. Fig.3 gives the diffuse reflectance UV-visible spectra of all samples; three absorption bands appeared at 216, 250, and 280 nm. According to the literature,^{23–25} these absorption bands could be assigned as follows: 216 nm band to tetrahedral monomeric tungstate species; 250 nm one to tetrahedral species with other linkage mode; 280 nm band to octahedral polytungstate species. The intensity of band at 216 nm decreased and the intensity of the two bands at 250 and 280 nm increased significantly with increasing the loading of

Fig.3 Diffuse reflectance UV-Vis spectra of $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$

tungsten. It could be concluded that the dispersion of surface tungsten species decreased with increasing the loading of tungsten. These results were consistent with the evidence provided by XRD and Raman spectroscopy.

The dispersion and the reducibility of the tungsten oxide species on $\text{SiO}_2/\text{Al}_2\text{O}_3$ are characterized by H_2 -TPR technique. The H_2 -TPR curves of all the catalysts are shown in Fig.4. Two reductive peaks were observed at 600–750 K and higher than 988 K on $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst with tungsten loading beyond 6.0%, the peak at 600–750 K was assigned to reduction of octahedrally coordinated WO_x species, and the reduction peak higher than 988 K was attributed to the reduction of surface amorphous tungsten oxide species or WO_3 micro crystallites to W metal,^{25–28} the intensities of these two peaks increased and the peak at higher than 988 K shifted to lower temperature with increasing the tungsten loadings. For the 8.0W/ $\text{SiO}_2/\text{Al}_2\text{O}_3$ and 12.0W/ $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts, the H_2 -TPR curves exhibited a broad peak at 800–988 K in addition to the peaks at 600–750 K and higher than 988 K, which was attributed to the reduction of polytungstate species,^{27,28} the intensities of all peaks increased and all the peaks shifted to the lower reduction temperature with increasing the tungsten loadings compared to the $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts with tungsten loading beyond 6.0%, reflecting an improved reducibility of dispersed WO_x species. As a result, the interactions between WO_x species and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ support became weakened and the dispersion of WO_x species on the support decreased with increasing tungsten loading in catalysts, especially when the tungsten loading was higher than 6.0%.

The NH_3 -TPD curves display the influence of tungsten loadings on the acidity of the catalysts in Fig.5. Values in parentheses represented the density ($\mu\text{mol} \cdot \text{g}^{-1}$) of desorbed NH_3 in sample surface from 373 to 800 K after steady adsorption. The broad desorption peak centering at about 473 K was observed for the neat support corresponding to weak acid peak. After WO_3 supported on $\text{SiO}_2/\text{Al}_2\text{O}_3$ with tungsten loading beyond 6.0%, the area of desorption peak became larger, indicating that the density of acid sites increased remarkably with increasing tungsten loading. For the 8.0W/ $\text{SiO}_2/\text{Al}_2\text{O}_3$ and 12.0W/ $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts, two desorption peaks of ammonia were found at 473 and 550 K corresponding to weak acid peak and mild strong acidity peak

Fig.4 H_2 -TPR patterns of $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$

Fig.5 NH₃-TPD patterns of $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$

(Fig.5), indicating that new acid sites formed and the acid strengths increased. The total amount of the acid sites from NH₃-TPD of the catalysts decreased in the following sequence: 12.0W/SiO₂/Al₂O₃ > 8.0W/SiO₂/Al₂O₃ > 6.0W/SiO₂/Al₂O₃ > 4.0W/SiO₂/Al₂O₃ > 2.0W/SiO₂/Al₂O₃ > SiO₂/Al₂O₃.

3.2 Catalytic performance of $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts

The reactions of 1-butene over $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts may include isomerization, self-metathesis, cross-metathesis, reaction and possible olefin oligomerization as shown in Scheme 1. GC results indicate that ethene, propene, pentene, hexene, 2-butene, and polymerization alkene are the major products. In the present work, C₅⁺ represents the alkene bearing five carbon atoms and C₆⁺ for the alkene with six carbon atoms, C₇⁺ is used to denote all the polymerization alkene (C₇⁺–C₁₀⁺). The tungsten loading is an important factor that influences the performance of catalysts. The effect of tungsten loading on metathesis reactivity of 1-butene at 453 K over $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst is listed in Table 1. Due to the acidity of the SiO₂/Al₂O₃ support, conversion of 1-butene to 2-butene (isomerization reaction) was observed, however, the support was inactive in the metathesis of 1-butene at 453 K. The other tungsten oxide supported on SiO₂/Al₂O₃ catalysts exhibited good performance for 1-butene metathesis. The conversion of 1-butene and the yields of 1-butene metathesis products including ethene, propene, pentene, and hexene increased with increasing tungsten loading and they reached maximum values over the sample with 6.0% tungsten loading. Subsequently, the catalytic activity of samples in 1-butene metathesis decreased with increasing the loading amount of tungsten. The yields of 2-butene and polymerization alkene (C₇⁺) increased with increasing the tungsten loading in $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts.

The difference in catalytic performance of the catalysts in 1-butene metathesis is strongly dependent on the dispersion of WO_x and the acidity of catalysts at the same pretreatment and reaction conditions. We recently reported that over 6.0W/SiO₂/Al₂O₃ exhibited excellent activity for metathesis 1-butene to propene, due to the moderate dispersion of tungsten oxide and the suitable acidity of the support by tuning the surface property of γ -Al₂O₃ using deposited silica.¹⁸ Different tungsten loadings could also lead to the changes of the dispersion of tungsten species, the reducibility of the catalyst, and the acidity of catalysts. Combining the

Table 1 Catalytic performance of all catalysts with different tungsten loadings for 1-butene metathesis

Catalysts	Conversion/%	Yield of products/%					
		C ₂ ⁺	C ₃ ⁺	C ₄ ⁺	C ₅ ⁺	2-C ₄ ⁺	C ₇ ⁺
SiO ₂ /Al ₂ O ₃	26.8	0	0	0	0	25.8	1.0
2.0W/SiO ₂ /Al ₂ O ₃	52.6	0.8	13.8	8.6	2.1	26.3	1.0
4.0W/SiO ₂ /Al ₂ O ₃	60.7	1.2	16.3	11.7	2.9	27.5	1.1
6.0W/SiO ₂ /Al ₂ O ₃	71.7	1.4	20.9	15.2	3.5	29.6	1.1
8.0W/SiO ₂ /Al ₂ O ₃	67.4	1.3	16.9	12.1	3.2	32.6	1.3
12.0W/SiO ₂ /Al ₂ O ₃	54.4	0.5	7.2	3.8	1.8	39.5	1.6

catalyst mass: 0.2 g; temperature: 453 K; pressure: 0.1 MPa;
WHSV: 2.4 h⁻¹; and time on stream: 1 h

results from XRD, Raman, UV-Vis, H₂-TPR, and the metathesis of 1-butene, the dispersion of WO_x species on the support decreased with increasing the tungsten loading in catalysts and the highest metathesis activity of supported WO_x catalysts was achieved when the loading of tungsten species was in the moderate dispersion, not in bulky crystalline WO₃. Generally, the partially reduced WO_x was beneficial to form W-carbene species by contacting with olefins. The stoichiometric composition of the supported tungsten oxide on SiO₂ with high activity has been demonstrated between WO₃ and WO_{2.95}; and inactive sites would be produced for the over-reduced tungsten species.²⁶ From the H₂-TPR profiles of catalysts (Fig.4), it could be concluded that the reducibility of WO_x species dispersed on the support increased with increasing the tungsten loading in $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts. The catalyst 12.0W/SiO₂/Al₂O₃ was the least active for 1-butene metathesis. The over-reduced W species of the bulky crystalline WO₃ on SiO₂/Al₂O₃ caused the decreasing of metathesis activity. The 2.0W/SiO₂/Al₂O₃ was also less active for the 1-butene metathesis because of the strong interaction of WO_x species with SiO₂/Al₂O₃, which were less easy to be reduced by alkene to active W sites at 453 K or the form of less active center. The moderate dispersed tungsten oxide on the 6.0W/SiO₂/Al₂O₃ with a suitable reducibility generated the most active sites, which were responsible for the fairly good performance for the metathesis reaction. The acid sites in the $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts also influenced the metathesis activity of 1-butene. Debecker *et al.*¹² has reported that WO₃-SiO₂-Al₂O₃ exhibited excellent activity for metathesis of ethene and 2-butene to propene, because of the generation of acidic matrices of catalyst by aerosol route to produce nano-structured WO₃-SiO₂-Al₂O₃ catalyst. Praserttham *et al.*¹⁷ used NaOH to mitigate the acidity of WO₃/SiO₂ catalyst to tune metathesis activity. According to characterization results by NH₃-TPD (Fig.5), the increase of tungsten loadings enhanced the total acidity and acid strength of catalysts proportionally. As shown in Table 1, the initial propene yield increased stepwise with tungsten loadings within 6.0% range. However, catalysts with further higher tungsten loading, especially 12.0W/SiO₂/Al₂O₃, underwent dramatic decrease in metathesis activity despite the steadily enhanced acidity. This suggested that less acidity or more acidity was bad for metathesis activity, the adequate acidity of catalysts was favorable for the production of metathesis products. The bi-

functional sites in $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts are responsible for the isomerization and metathesis simultaneously. Combining the results of Raman, UV-Vis, H_2 -TPR, and NH_3 -TPD with the metathesis activity of 1-butene, it was concluded that the metathesis reaction was complicated. The dispersion, reducibility, and acidity of the prepared supported tungsten catalysts were both contributed to the catalytic activity.

The metathesis activities of $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts with different tungsten loadings as a function of time are compared in Fig.6. As shown in Fig.6(a-d), for all the catalysts, the yields of ethene and $\text{C}_6^=$ were stable with the time on stream. However, the yields of propene and $\text{C}_5^=$ increased with the time in the initial 3 h, indicating the possible presence of "induction period" during which metathesis active intermediates were generated *in situ* under olefin atmosphere, and decreased with reaction running

time. This was common to WO_3/SiO_2 catalysts used in 1-butene metathesis.²⁹ It should be pointed out that the induction period was about 3 h for $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts with different tungsten loadings. However, the amount of tungsten in $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts influenced the metathesis activity of 1-butene and the stability of catalyst (Table 1 and Fig.6). The yields of propene and $\text{C}_5^=$ on the $12.0\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ increased in the initial 3 h and sharply decreased after 5 h running time and only 1% yield could be obtained at 8 h time on stream. As a comparison, the catalysts with lower tungsten loadings, e.g., 6.0% showed better stability. The stability of catalyst also firstly increased with the surface coverage of tungsten, then reached maximum over the sample with 6.0% tungsten loadings. Subsequently, the stability of catalyst decreased with increasing the loading amount of tungsten. Since propene and $\text{C}_5^=$ are from the cross-metathesis between 1-

Fig.6 1-Butene metathesis reaction as a function of time on stream

(a) ethene yield; (b) propene yield; (c) $\text{C}_5^=$ yield; (d) $\text{C}_6^=$ yield; (e) 2-butene yield; and (f) conversion of 1-butene; catalyst mass: 0.2 g; temperature: 453 K; pressure: 0.1 MPa; WHSV: 2.4 h^{-1}

Scheme 2 1-Butene metathesis reaction on $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts at 453 K

butene and 2-butene, the yield of 2-butene and the conversion of 1-butene as a function of time on stream for the $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts are also presented (Fig.6e and Fig.6f). The yield of 2-butene increased while the conversion of 1-butene decreased with extended reaction time for all the catalysts, indicating that more 1-butene converted to 2-butene on these catalysts. The decreased 1-butene yield could be due to deactivation for the coke deposition on the acid site of catalysts. As for 12.0W/SiO₂/Al₂O₃ catalyst, the conversion of 1-butene decreased rapidly with time on stream, suggesting a fast deactivation on the catalyst. Spamer *et al.*¹⁶ reported that at high WO₃ loadings the formation of crystalline material also protected the active tungsten surface compound from deactivation by being the preferred species for over-reduction. From the results of Raman, UV-Vis, H₂-TPR, and NH₃-TPD, the increased amount of tungsten loadings resulted in larger size of WO_x species and more acidity of catalysts. However, the stability of catalysts increased with tungsten loadings increasing from 2.0% to 6.0%, reached the maximum at 6.0% tungsten loading, and then decreased when the tungsten loadings was higher than 8.0%. Considering above catalytic properties, it suggests that the moderate dispersion, suitable reducibility of WO_x species, and the amount of acid of catalysts are very important for not only the metathesis activity but also the metathesis stability, which is schematically shown in Scheme 2.

4 Conclusions

The tungsten loadings of $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts have an influence on the dispersion of tungsten species, the reducibility of the catalyst, and the acidity of catalysts simultaneously, which played the important roles in the metathesis reaction of 1-butene. The high dispersion of WO_x species which were difficult to be reduction and inadequate acid sites lead to the inferior activity and stability of the $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts with low tungsten loadings. The increasing of tungsten loadings in support promoted the reduction of WO_x species and the acidity of catalyst, therefore improved the catalytic performance. However, excessive tungsten loadings lead to lower dispersion of WO_x species, deeper reduction of W species, more acid sites, and less metathesis activity and stability of catalysts. Considering the above catalytic properties, it also suggested that the $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts with proper tungsten loadings could provide the moderate dispersion, suitable reducibility of WO_x species and the amount of acid sites of catalysts, which were favorable for the formation of active centers

for olefins metathesis. Generally, an optimal tungsten loading was quite necessary for metathesis activity and stability of $x\text{W}/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts.

References

- (1) Lu, H. Q.; Shi, L.; He, C.; Weng, W. Z.; Huang, C. J.; Wan, H. L. *Acta Phys. -Chim. Sin.* **2012**, *28*, 2697. [鲁怀乾, 石磊, 何冲, 翁维正, 黄传敬, 万惠霖. 物理化学学报, **2012**, *28*, 2697.] doi: 10.3866/PKU.WHXB201207091
- (2) Zhu, X. X.; Li, X. J.; Xie, S. J.; Liu, S. L.; Xu, G. L.; Xin, W. J.; Huang, S. J.; Xu, L. Y. *Catal. Surv. Asia* **2009**, *13*, 1. doi: 10.1007/s10563-008-9055-3
- (3) Wang, F.; Yan, S. J.; Yong, X. J.; Luo, C. T.; Zhang, Q.; Wen, P. Y.; Gong, Y. J.; Dou, T. *Acta Phys. -Chim. Sin.* **2013**, *29*, 358. [王峰, 颜蜀雋, 雍晓静, 罗春桃, 张卿, 温鹏宇, 巩雁军, 窦涛. 物理化学学报, **2013**, *29*, 358.] doi: 10.3866/PKU.WHXB201211143
- (4) Hu, B.; Liu, H.; Tao, K.; Xiong, C. R.; Zhou, S. H. *J. Phys. Chem. C* **2013**, *117*, 26385. doi: 10.1021/jp4098028
- (5) Bouchmella, K.; Stoyanova, M.; Rodemerck, U.; Debecker, D. P.; HubertMutina, P. *Catal. Commun.* **2015**, *58*, 183. doi: 10.1016/j.catcom.2014.09.024
- (6) Mazoyer, E.; Szeto, K. C.; Merle, N.; Norsic, S.; Boyron, O.; Basset, J. M.; Taoufik, M.; Nicholas, C. P. *J. Catal.* **2013**, *301*, 1. doi: 10.1016/j.jcat.2013.01.016
- (7) Xuan, D.; Liu, S.; Dong, J.; Wang, Y. D. *Nat. Gas Chem. Ind.* **2014**, *39*, 29. [宣东, 刘苏, 董静, 王仰东. 天然气化工, **2014**, *39*, 29.]
- (8) Cui, Y. M.; Liu, N.; Xia, Y. F.; Lü, J. G.; Zheng, S. J.; Xue, N. H.; Peng, L. M.; Guo, X. F.; Ding, W. P. *J. Mol. Catal. A: Chem.* **2014**, *394*, 1. doi: 10.1016/j.molcata.2014.06.027
- (9) Liu, H. J.; Zhang, L.; Li, X. J.; Huang, S. J.; Liu, S. L.; Xin, W. J.; Xie, S. J.; Xu, L. Y. *J. Nat. Gas Chem.* **2009**, *18*, 331. doi: 10.1016/S1003-9953(08)60113-9
- (10) Li, R.; Yuan, G. M.; Chen, S. L.; Hua, D. R.; Zhou, Z.; Sang, L.; Chen, A. C. *J. Fuel Chem. Technol.* **2012**, *40*, 855. [李睿, 袁桂梅, 陈胜利, 华德润, 周政, 桑磊, 陈爱城. 燃料化学学报, **2012**, *40*, 855.]
- (11) Amakawa, K.; Wrabetz, S.; Kröhnert, J.; Tzolova-Müller, G.; Schlögl, R.; Trunschke, A. *J. Am. Chem. Soc.* **2012**, *134*, 11462. doi: 10.1021/ja3011989

- (12) Debecker, D. P.; Stoyanova, M.; Rodemerck, U.; Colbeau-Justin, F.; Boissère, C.; Chaumonnot, A.; Bonduelle, A.; Sanchez, C. *Appl. Catal. A* **2014**, *470*, 458. doi: 10.1016/j.apcata.2013.06.041
- (13) Xu, F.; Jiang, W. L.; Li, P. D.; Zhou, G. L.; Zhou, H. J. *Chem. Ind. Eng. Prog.* **2014**, *33*, 3253. [徐 峰, 姜伟丽, 李沛东, 周广林, 周红军. 化工进展 **2014**, *33*, 3253.]
- (14) Hu, J. C.; Wang, Y. D.; Chen, L. F.; Richards, R.; Yang, W. M.; Liu, Z. C.; Xu, W. *Microporous Mesoporous Mat.* **2006**, *93*, 158. doi: 10.1016/j.micromeso.2006.02.019
- (15) Hua, D. R.; Chen, S. L.; Yuan, G. M.; Wang, Y. L.; Zhao, Q. F.; Wang, X. L.; Fu, B. *Microporous Mesoporous Mat.* **2011**, *143*, 320. doi: 10.1016/j.micromeso.2011.03.012
- (16) Spamer, A.; Dube, T. I.; Moodley, D. J.; van Schalkwyk, C.; Botha, J. M. *Appl. Catal. A* **2003**, *255*, 153. doi: 10.1016/S0926-860X(03)00537-4
- (17) Maksasithorn, S.; Debecker, D. P.; Praserttham, P.; Panpranot, J.; Suriye, K.; Ayudhya, S. K. N. *Chin. J. Catal.* **2014**, *35*, 232. doi: 10.1016/S1872-2067(12)60760-8
- (18) Liu, N.; Ding, S. L.; Cui, Y. M.; Xue, N. H.; Peng, L. M.; Guo, X. F.; Ding, W. P. *Chem. Eng. Res. Des.* **2013**, *91*, 573. doi: 10.1016/j.cherd.2012.08.008
- (19) Huang, S. J.; Liu, H. J.; Zhang, L.; Liu, S. L.; Xin, W. J.; Li, X. J.; Xie, S. J.; Xu, L. Y. *Appl. Catal. A* **2011**, *404*, 113. doi: 10.1016/j.apcata.2011.07.020
- (20) Benitez, V. M.; Figoli, N. S. *Catal. Commun.* **2002**, *3*, 487. doi: 10.1016/S1566-7367(02)00192-9
- (21) Huang, S. J.; Chen, F. C.; Liu, S. L.; Zhu, Q. J.; Zhu, X. X.; Xin, W. J.; Feng, Z. C.; Li, C.; Wang, Q. X.; Xu, L. Y. *J. Mol. Catal. A: Chem.* **2007**, *267*, 224. doi: 10.1016/j.molcata.2006.11.048
- (22) Horsley, J. A.; Wachs, I. E.; Brown, J. M.; Via, G. H.; Hardcastle, F. D. *J. Phys. Chem.* **1987**, *91*, 4014. doi: 10.1021/j100299a018
- (23) Ross-Medgaarden, E. I.; Wachs, I. E. *J. Phys. Chem. C* **2007**, *111*, 15089. doi: 10.1021/jp074219c
- (24) Ramírez, J.; Gutiérrez-Alejandre, A. *J. Catal.* **1997**, *170* (1), 108. doi: 10.1006/jcat.1997.1713
- (25) Zhao, Q. F.; Chen, S. L.; Gao, J. S.; Xu, C. M. *Transition Met. Chem.* **2009**, *34*, 621. doi: 10.1007/s11243-009-9239-3
- (26) Spamer, A.; Dube, T. I.; Moodley, D. J.; van Schalkwyk, C.; Botha, J. M. *Appl. Catal. A* **2003**, *255*, 133. doi: 10.1016/S0926-860X(03)00535-0
- (27) Westhoff, R.; Moulijn, J. A. *J. Catal.* **1977**, *46*, 414. doi: 10.1016/0021-9517(77)90225-1
- (28) Vermaire, D. C.; Vanberge, P. C. *J. Catal.* **1989**, *116*, 309. doi: 10.1016/0021-9517(89)90098-5
- (29) Wang, Y. D.; Chen, Q. L.; Yang, W. M.; Xie, Z. K.; Xu, W.; Huang, D. Y. *Appl. Catal. A* **2003**, *250*, 25. doi: 10.1016/S0926-860X(03)00186-8