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Enhanced Catalytic Performance for Metathesis Reactions over Ordered Tungsten and Aluminum Co-doped Mesoporous KIT-6 Catalysts

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Abstract

Ordered tungsten and aluminum co-doped mesoporous KIT-6 catalysts (W-Al-KIT-6) with different Si/Al molar ratios were successfully synthesized by a one-pot synthesis method. The obtained W-Al-KIT-6 catalysts were tested for catalytic conversion of 1-butene and ethene to propene via isomerization of 1-butene to 2-butene and subsequent cross metathesis of 2-butene and ethene. Various characterization techniques, such as ICP-OES, XRD, BET, TEM, Raman, XPS and NH_3-TPD, were used to characterize the catalysts. The introduction of Al did not change the mesoporous structure of KIT-6, when the nominal Si/Al was 10, 20 or 30. Besides, the sample demonstrated a larger amount of acidic sites. The W-Al-KIT-6 catalysts with suitable Si/Al ratios illustrated a superior catalytic performance to W-KIT-6 catalyst. The origin of catalytic performance enhancement over W-Al-KIT-6 catalysts was preliminarily discussed, and ascribed to highly dispersed W species and a large amount of acidic sites. The acidic sites were formed by introduction of a suitable amount of Al in the W-KIT-6 framework, which accelerated the isomerization of 1-butene to 2-butene and promoted the cross metathesis of 2-butene and ethene to propene.

Key Words: aluminum doping; metathesis; mesoporous; KIT-6; propene

1. Introduction

With the increasing demand of propene, cross-metathesis of butene and ethene to propene has attracted more and more attentions in recent years.[1] Supported WO_3 catalysts showing a moderate activity, outstanding stability, anti-poisoning property,

as well as low price, were highly desirable for industrial metathesis.[2, 3]

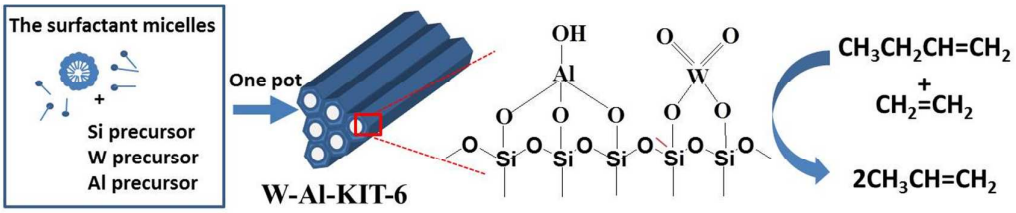
The catalytic performance of supported tungsten oxides for olefin metathesis is determined by many factors, of which the supports have a significant influence on the physico-chemical properties of catalysts, such as structures and dispersion of tungsten oxide species, and thus significantly influence the catalytic performance.[4] Conventional support materials for metathesis catalysts include commercially available silica gel, γ-Al_2O_3, α-Al_2O_3, and mixed oxides such as SiO_2-Al_2O_3,[5] and zeolite-Al_2O_3.[6] Compared with these traditional supports, mesoporous materials show uniform pores, large BET surface areas and pore volumes, which are beneficial for dispersion of active species and providing rapid transportation channels for reactants and products. Thus, great efforts are made to develop highly efficient mesoporous catalysts for various reactions [7, 8] during the last decades. So far, many mesoporous materials have been explored in olefin metathesis,[9] such as HMS,[10] SBA-15,[11, 12] MCM-41,[13] and FDU-12.[14] Generally, mesoporous catalysts showed much higher catalytic activity than conventional SiO_2 or Al_2O_3 supported catalysts due to the high dispersed active species on the mesoporous supports.

On the other hand, it has been demonstrated that the Brønsted acidity of the supports would be beneficial for olefin metathesis.[6] Literature has revealed that alumina supported tungsten oxides exhibits strong acid sites and tungsten-support interaction, but too strong acid sites could induce by-reactions such as cracking and isomerization.[15] In contrast, silica supported tungsten oxides were barely acidic and could suppress the by-reactions.[16] However, the weak interaction between W species

and silica could result in poor dispersion of tungsten oxide species, causing a poor catalytic performance. Mixed silica-alumina materials with moderate acidity and interaction between metal and support are promising as catalyst supports for olefin metathesis reactions. Xu et al.[6] reported that WO_3/HY-Al_2O_3 catalysts exhibited higher activity than WO_3/Al_2O_3 with HY content in the range of 0–30 wt%. The improved catalytic performance over WO_3/HY-Al_2O_3 was ascribed to the moderate acidity of the supports and the suitable interaction between W species and support. The same phenomenon was also found in supported Mo or Re catalysts. Literature has reported that MoO_3/Al_2O_3-SiO_2 and Re_2O_7/Al_2O_3-SiO_2 catalysts were more active than alumina or silica supported catalysts due to high dispersion of active species and moderate acidity.[17-19]

Here, we first report one-pot synthesis of ordered tungsten and aluminum co-doped mesoporous KIT-6 materials (W-Al-KIT-6) for metathesis of 1-butene and ethene to propene. KIT-6, a mesoporous silica with 3D interconnected large mesopores, has been shown to be an advanced support for many reactions.[20, 21] In our previous work, we successfully synthesized tungsten doped KIT-6 catalysts (W-KIT-6), and the obtained W-KIT-6 exhibited excellent catalytic performance for metathesis reactions.[22, 23] In this work, Al and W were co-doped into the KIT-6 framework simultaneously by a one-pot method. The schematic demonstration of synthesis of tungsten and aluminum co-doped W-Al-KIT-6 is shown in Scheme 1. Al is introduced to form the acid center and improve the performance of catalysts. The influence of Si/Al ratio on physico-chemical properties was systematically

investigated with various characterization techniques, and the catalytic performance for metathesis of 1-butene and ethene to propene over W-Al-KIT-6 with different Si/Al ratios was also studied.



Scheme 1. The schematic demonstration of synthesis of ordered tungsten and aluminum co-doped mesoporous KIT-6 materials.

2. Experimental section

2.1. Chemicals

Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123, M_w=5800, EO20PO70EO20) was purchased from Aldrich as the structure directing agents. Tetraethyl orthosilicate (TEOS, AR) as the silica source was purchased from Aladdin. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, AR), hydrochloric acid (HCl, AR), and n-butanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.. Aluminum-isopropoxide as the Al source was purchased from Chengdu Gray West Chemistry Technology Company. Ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$) was obtained from Kunshan Xingbang W&M Technology Company. All chemicals were used as received without further purification.

2.2. Catalyst preparation

2.2.1 Synthesis of W-KIT-6

W-KIT-6 catalysts with a Si/W ratio of 40/1 was prepared according to our previous study.[22] Typically, 3.0 g of P123 was dissolved in 108.5 g of deionized water, and 3.0 g of 1-butanol and 5.9 g of HCl (35 wt%) were added into the above solution. The mixture was vigorously stirred at 35 ^{o}C for 1 h and then 6.45 g of TEOS was slowly added into the solution. After that, the mixture was vigorously stirred at 35 ^{o}C for 1 h, and 0.25 g of sodium tungstate dissolved in 6 mL of water (Si/W=40/1) was dropwise added into the above solution, and the obtained mixture was further stirred for another 24 h. The resultant mixture was transferred to a Teflon-lined autoclave and heated at 100 ^{o}C for 24 h. The solid products were collected by filtering, washing thoroughly with deionized water and drying at 100 ^{o}C overnight. Finally, the powders were calcined in a muffle furnace at 550 °C for 4 h with a heating rate of 1.0 ^{o}C/min to remove P123 surfactants. KIT-6 was also synthesized using the same procedure as that of W-KIT-6 without adding sodium tungstate.

2.2.2 One-pot synthesis of W-Al-KIT-6

The incorporation of Al in W-KIT-6 was carried out by a one-pot synthesis method using aluminum-isopropoxide as Al source. In a typical synthesis for W-Al-KIT-6 with a Si/Al ratio of 10/1, 0.63 g of aluminum-isopropoxide were dissolved in a solution containing 108.5 g of deionized water and 5.9 g of HCl (35 wt%). The solution was vigorously stirred at 35 ^{o}C for at least 1 h, and then 3.0 g of P123 and 3.0 g of 1-butanol were added into the above solution. The mixture was vigorously stirred at 35 ^{o}C for 1 h, and then 6.45 g of TEOS (Si/Al=10/1) was slowly added into the solution. After that, the mixture was vigorously stirred at 35 ^{o}C for 1 h.

A solution containing 0.25 g of sodium tungstate dihydrate and 6 mL of water (Si/W=40) was dropwise added into the above solution, and the resultant mixture was stirred for another 24 h. W-Al-KIT-6 was obtained after the same hydrothermal treatment, collecting procedures and calcination process as those of W-KIT-6. The W-Al-KIT-6 with other Si/Al ratios were synthesized by the same procedures except that the amount of aluminum-isopropoxide was changed according to the desired nominal Si/Al ratios. The W-Al-KIT-6 materials with Si/Al ratios of 1/1, 10/1, 20/1 and 30/1 were denoted as W-Al-KIT-6-1, W-Al-KIT-6-10, W-Al-KIT-6-20 and W-Al-KIT-6-30, respectively.

2.2.3 Preparation of control WO_3/SiO_2 catalyst

A control WO_3/SiO_2 catalyst was prepared by impregnating a commercial silica gel (BET surface area: 399.0 m^2/g, Qingdao Haiyang Chemical Co. Ltd.) with an aqueous solution of ammonium metatungstate. The impregnated sample was dried at 100 ^oC overnight and subjected to an identical calcination procedure to W-KIT-6 catalyst. The loading of W was fixed identical to that of W-KIT-6.

2.3. Catalyst characterization.

Elements analysis was conducted by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using Perkin-Elmer OPTIMA 2100 DV optical emission spectrometer. Brunauer−Emmett−Teller (BET) surface area, pore volume, and pore size was obtained using a Micromeritics ASAP 2020M adsorption apparatus. Prior to measurement, the sample was degassed under vacuum at 200 ^oC for 3 h. Small angle and wide angle X-ray diffraction patterns (XRD) were recorded on a

Bruker D8 Advance X-Ray diffractometer using Cu Kα radiation. Raman spectra were obtained using a Renishaw Raman spectrometer equipped with a microscope (laser wavelength of 532 nm). Transmission electron microscopy (TEM) image was obtained on a JEOL 2100 transmission electron microscope operated at 200kV. The sample was dispersed in ethanol by sonication and dropped onto a carbon-coated copper grid followed by evaporating naturally. X-ray photoelectron spectroscopy (XPS) experiments were performed on an AXIS ULTRA DLD multifunctional X-ray photoelectron spectroscopy with an Al source. Temperature-programmed desorption of ammonia (NH_3-TPD) was carried out in a quartz microreactor. The as-prepared sample (50.0 mg) was pretreated in N_2 at 600 ^oC for 0.5 h prior to NH_3-TPD measurement, and then a stream of 10/90 (v/v) NH_3/N_2 was introduced for adsorption at room temperatures for 0.5 h. The sample was further purged by N_2 for 2 h to remove the physically absorbed NH_3. Temperature-programmed desorption of ammonia was carried out from 50 ^oC to 800 ^oC with a ramping rate of 10 ^oC/min, and the amount of desorbed NH_3 was monitored by a thermal conductivity detector (TCD).

2.4 Catalytic conversion of 1-butene and ethene to propene

Catalytic conversion of 1-butene and ethene to propene was carried out in a fixed-bed stainless steel microreactor (i.d. 10 mm). In each run, 1.0 g of catalyst (20-40 mesh) was placed in the center of reactor, and the catalyst layer was below and upper supported by an inert SiO_2 bead layer. The catalysts were pretreated by pure N_2 at 550 ^oC for 4 hours (0.1 MPa, 30 mL/min). After cooling down to the reaction

temperatures, C_2H_4 and 1-C_4H_8 (98 %, Dalian special gas company) were directly delivered to the reactor from cylinders. The gas flow rates of C_2H_4 and 1-C_4H_8 were controlled to by two mass flow controllers (MFC) to keep the molar ratio of C_2H_4/1-C_4H_8 equal to 2/1. The metathesis reactions were carried out at ambient pressure, reaction temperature from 400 to 500 ^{o}C, and gas hourly space velocity (WHSV) of 0.8 h^{-1}. All products were analyzed online using a gas chromatograph equipped with a flame ionization detector (FID). The 1-butene conversion and product selectivity were calculated by following formulas:

$$x_{1-butene} = \frac{[C_3^{=}]_n + 2[2-C_4^{=}]_n}{[C_3^{=}]_n + 2[1-C_4^{=}]_n + 2[2-C_4^{=}]_n + 2[\text{iso-}C_4^{=}]_\text{n}} \quad (1)$$

$$s_{propene} = \frac{[C_3^{=}]_m}{[C_3^{=}]_m + [2-C_4^{=}]_m + [\text{iso-}C_4^{=}]_\text{m}} \quad (2)$$

$$s_{2-butene} = \frac{[2-C_4^{=}]_m}{[C_3^{=}]_m + [2-C_4^{=}]_m + [\text{iso-}C_4^{=}]_\text{m}} \quad (3)$$

Where $[C_3^{=}]_n$, $[1\text{-}C_4^{=}]_n$, $[2\text{-}C_4^{=}]_n$ and $[\text{iso-}C_4^{=}]_n$ are the molar fraction of each component in effluent gas, and $[C_3^{=}]_m$, $[1\text{-}C_4^{=}]_m$, and $[\text{iso-}C_4^{=}]_m$ are the mass fraction of each component in effluent gas.

3. Results and discussion

3.1 Characterization of catalysts

3.1.1 Elemental analysis

ICP-OES analysis is performed to determine the real content of Na, W and Al in the final products. The result suggested that only trace amount of Na (below 0.1 wt %) was left in the catalyst, since the sample was washed thoroughly before calcination. Table 1 summarized the real loading of W and Al in final catalysts. Approximately

67-80 % of W species in the initial synthesis gel was introduced in the final W-Al-KIT-6, and this tendency was consistent with literature.[22] In contrast, approximately 21 % of Al species in the initial synthesis gel was introduced in the final W-Al-KIT-6 at the Si/Al ratios ranging from 10/1 to 30/1 while ~40 % of Al species in the initial synthesis gel was introduced in the final products at the Si/Al ratio of 1/1. A limited amount of Al doped in the final product was also reported by literatures.[24, 25] In the acidic medium, most of Al species were in cationic forms rather than oxo forms (necessary for formation of Si–O–Al linkages), restricting the amount of Al species in the final products.

Table 1. Elemental analysis of various catalysts by ICP-OES.

Catalysts	Si/W (molar)		Si/Al (molar)		Product	
	Gel	Product	Gel	Product	W (wt %)	Al (wt %)
KIT-6	N/A	N/A	N/A	N/A	N/A	N/A
WO_3/SiO_2	40/1	N/A	N/A	N/A	4.85	N/A
W-KIT-6	40/1	58/1	N/A	N/A	5.01	N/A
W-Al-KIT-6-30	40/1	55/1	30/1	138/1	5.26	0.30
W-Al-KIT-6-20	40/1	51/1	20/1	94/1	5.51	0.44
W-Al-KIT-6-10	40/1	53/1	10/1	47/1	5.06	0.88
W-Al-KIT-6-1	40/1	59/1	1/1	2.5/1	3.49	12.93

3.1.2 Transmission electron microscope

TEM images of various samples are illustrated in Figure 1. As shown in Figure 1a, KIT-6 exhibited a three dimensional (3D) ordered mesoporous structure, which

was consistent with literatures.[26, 27] The W doped KIT-6 samples (W-KIT-6) in Figure 1b also showed a well-ordered mesoporous structure, except for few irregular domains at the peripheries of the materials. The introduction of Al did not change the structure/texture/appearance of the sample (when Si/Al in 10, 20 or 30) as shown in Figure 1c, d and e. However, for the W-Al-KIT-6-1 (Figure 1f) at the highest ratio of Al/Si, the ordered mesoporous structures disappeared, showing disordered structures. It is suggested that the introduction of a proper amount of Al is beneficial for maintenance of mesoporous structures and excess Al introduction cause the collapse of mesoporous structure.

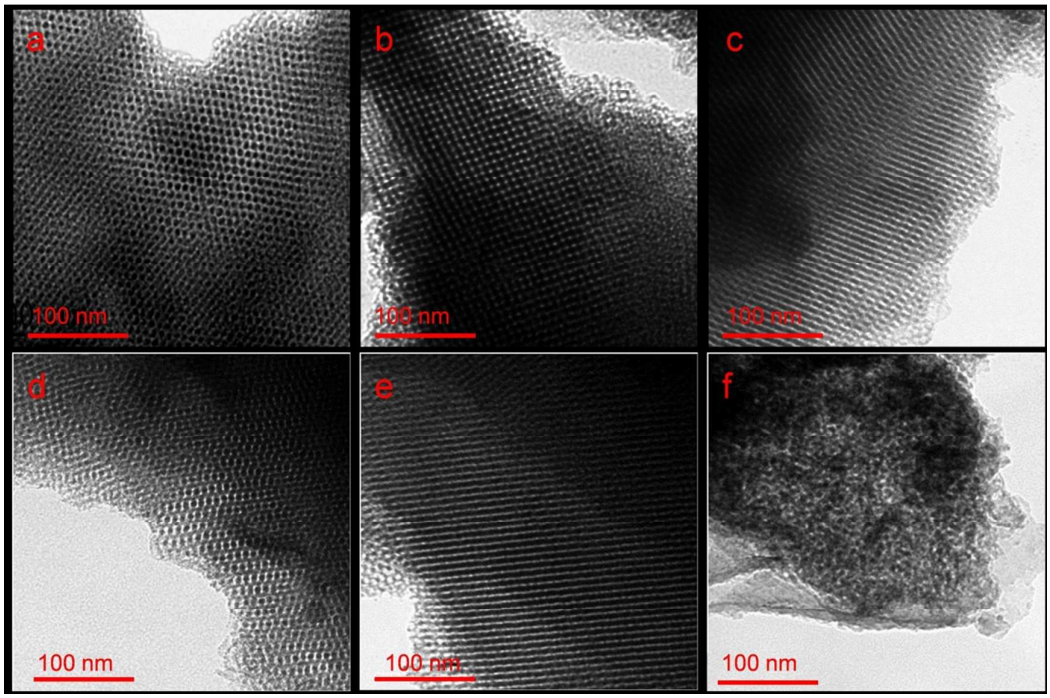


Figure 1. TEM images showing a), KIT-6; b), W-KIT-6; c), W-Al-KIT-6-30; d), W-Al-KIT-6-20; e), W-Al-KIT-6-10; f), W-Al-KIT-6-1. Scale bars are 100 nm.

3.1.3 Nitrogen physisorption

The N_2 adsorption isotherms and BJH pore size distributions of KIT-6, W-KIT-6

and W-Al-KIT-6 materials are shown in Figure 2. Except for W-Al-KIT-6-1, all samples showed type IV isotherms with H1 hysteresis loops, which revealed that all samples had ordered mesoporous channels.[28] The sharp capillary condensation feature at relative pressure of 0.6-0.8 (P/P_0) indicating the existence of uniform pores in all samples. It is clearly observed that all samples except W-Al-KIT-6-1 show narrow pore-size distributions. An increase of the Si/Al ratio typically resulted in a small increase in the average pore size, so the pore diameter showed a slight shift. For W-Al-KIT-6-1, the isotherm and pore size distribution was significantly different from that of W-KIT-6 and W-Al-KIT-6 catalyst with Si/Al of 10, 20 or 30. It is indicated that the ordered mesoporous structure of KIT-6 is disappeared as confirmed by TEM observation (Figure 1f).

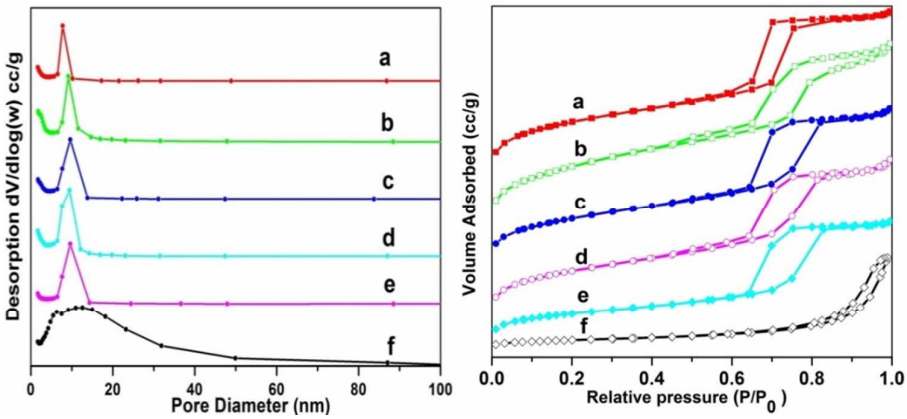


Figure 2. N_2 adsorption−desorption isotherms (left panel) and pore size distributions (right panel) showing a), KIT-6; b), W-KIT-6; c), W-Al-KIT-6-30; d), W-Al-KIT-6-20; e), W-Al-KIT-6-10 and f), W-Al-KIT-6-1.

Table 2 summarizes the BET surface areas, pore volumes and mean pore sizes of different samples. The reduction of BET surface areas and pore volumes are observed for W-KIT-6, as compared with these of KIT-6. However, after the introduction of an

appropriate amount of Al, W-Al-KIT-6-30, W-Al-KIT-6-20 or W-Al-KIT-6-10 showed slightly improved BET surface area, pore volume and pore size as compared with that of W-KIT-6, which suggested that the incorporation of a suitable amount of Al did not disturb the mesoporous structure. In contrast, the W-Al-KIT-6-1 sample with the highest Al/Si ratio exhibited a drastic reduction of BET surface areas due to the collapse of mesoporous structures and blocking of pores caused by excess aluminum.

Table 2. BET surface areas, pore volumes, and pore sizes of various catalysts.

Catalysts	a_0[a] (nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)	Acidity amount (umol/g)
KIT-6	19.6	835	0.98	4.6	68.1
W-KIT-6	21.0	721	0.81	4.6	126.3
W-Al-KIT-6-30	20.6	764	0.93	5.1	191.6
W-Al-KIT-6-20	20.6	758	0.94	5.1	207.6
W-Al-KIT-6-10	20.8	754	1.1	6.2	232.8
W-Al-KIT-6-1	N/A	265	1.0	15.7	274.6

[a] Unit cell parameter calculated from the formula $a_0 = 6^{1/2} d_{211}$

3.1.4 X-ray diffraction

Small angle XRD measurement is used to study the mesoporosity of various samples, and the results are presented in Figure 3. A well-resolved diffraction peak in the 1.0-1.1° range was observed for KIT-6, which could be indexed as the (211) reflection in the bicontinuous cubic Ia3d symmetry reported for KIT-6.[29] Besides, the existence of a broad shoulder corresponding to (220) reflection further indicated

ordered mesoporous structures. Except for the W-Al-KIT-6-1 sample at the highest ratio of Al/Si (Figure 3f), all samples exhibited the well resolved diffraction patterns similar to KIT-6, confirming that the ordered mesoporous structure of KIT-6 was maintained after the incorporation of W and Al with suitable Si/Al ratios (10/1, 20/1 or 30/1). For W-Al-KIT-6-1, the absence of diffraction peaks in small angles suggested the collapse of mesoporous structures. In addition, cubic unit cell parameters (a_0) of samples are also calculated and presented in Table 2. It is found that the unit cell parameter a_0 increased after introducing of W and Al atoms in the framework of KIT-6, accompanied by the shift of (211) reflections to lower angles in Figure 3. This phenomenon may be caused by the doping of tungsten with larger atomic radius compared to that of Si^{4+}.[30, 31]

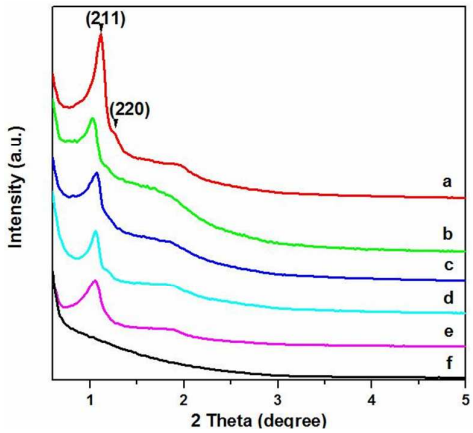


Figure 3. Small-angle XRD patterns of various samples showing a), KIT-6; b), W-KIT-6; c), W-Al-KIT-6-30; d), W-Al-KIT-6-20; e), W-Al-KIT-6-10; f), W-Al-KIT-6-1.

Wide-angle XRD profiles of various samples are shown in Figure 4. KIT-6 showed a broad peak in the 2θ range from 15 to 30 ^{o}C, which are the characteristic

diffractions of amorphous silica. Obvious crystalline WO_3 diffractions (JCPDS 00-043-1035) are observed for W-KIT-6 in Figure 4b, which is due to the formation of WO_3 extraframework at a high W loading.[22] In contrast, no WO_3 diffractions are observed for all W-Al-KIT-6 samples (Figure 4c-f), indicating that the W species are highly dispersed in W-Al-KIT-6 samples. It is concluded that the introduction of Al in W-KIT-6 by the current one-pot synthesis method could enhance the dispersion of W species, which may further enhance the catalytic performance for metathesis of 1-butene and ethene to propene.

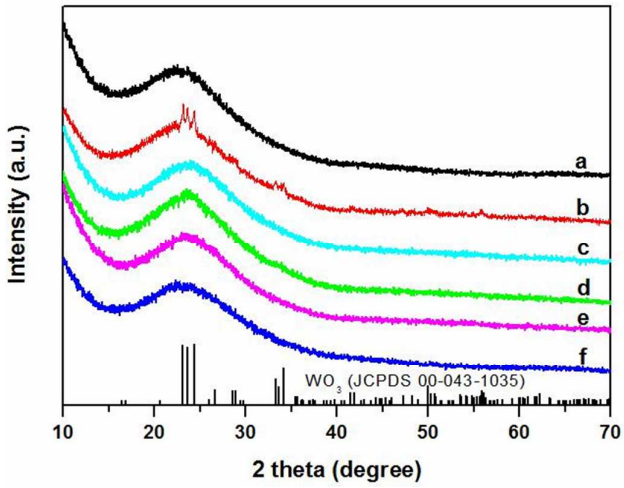


Figure 4. Wide-angle XRD patterns of various samples showing a), KIT-6; b), W-KIT-6; c), W-Al-KIT-6-30; d), W-Al-KIT-6-20; e), W-Al-KIT-6-10; f), W-Al-KIT-6-1. Vertical lines indicating the diffractions of crystalline WO_3 (JCPDS 00-043-1035).

3.1.5 X-ray *photoelectron spectroscopy*

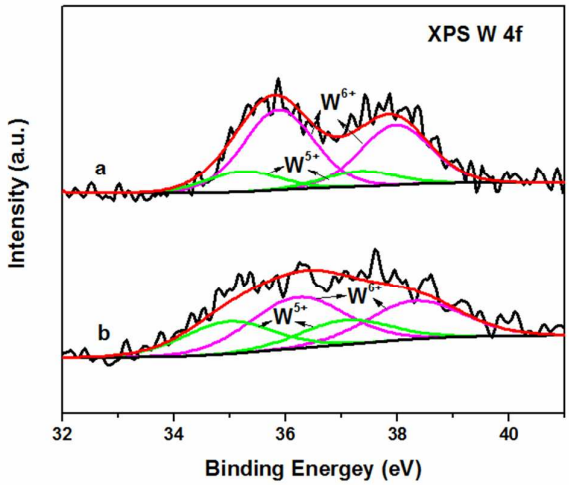


Figure 5. XPS spectra showing a), W-KIT-6; and b), W-Al-KIT-6-10.

XPS experiments were carried out to investigate the effect of Al doping on the oxidation states of tungsten. Figure 5 shows the XPS spectra of the W-KIT-6 and W-Al-KIT-6-10 samples. The XPS curves were fitted according to the theory of Doniach and Sunjic.[32] The binding energies of 35.9-36.2 eV and 38.0-38.3 eV were attributed to $4f_{7/2}$ and $4f_{5/2}$ of W^{6+} species while the binding energies of 37.0-37.3 and 34.9-35.2 eV were assigned to $4f_{5/2}$ and $4f_{7/2}$ of W^{5+} species.[33-35] The presence of W^{5+} species in W-KIT-6 sample was consistent with our previous work.[22] W^{5+} species was also observed in the W-Al-KIT-6 sample. Table S1 summarizes the molar percentage of W^{6+} and W^{5+} species in W-KIT-6 and W-Al-KIT-6-10 samples. The molar percentage of W^{5+} species in W-KIT-6 was 20.6 % while the molar percentage of W^{5+} in W-Al-KIT-6-10 samples increased to 37.5 %. The presence of high concentration of W^{5+} species could favor olefin metathesis, as suggested by the previous studies.[6, 22]

3.1.6 NH_3-Temperature programmed desorption

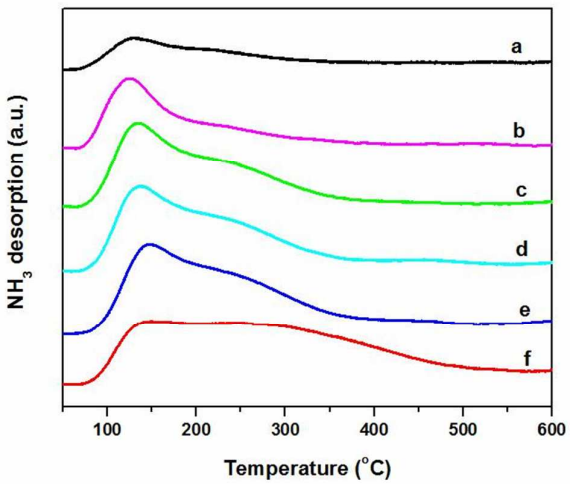


Figure 6. NH_3-TPD profiles of different samples showing a), KIT-6; b), W-KIT-6; c), W-Al-KIT-6-30; d), W-Al-KIT-6-20; e), W-Al-KIT-6-10; and f), W-Al-KIT-6-1.

NH_3-TPD technique is used to study the effect of aluminum doping on the acidity of catalysts, and the results are shown in Figure 6. KIT-6 showed a weak desorption peak centered at 130 ^{o}C. In contrast, the W-KIT-6 exhibited an intense desorption peak at 125 ^{o}C, indicating more acid sites in W doped KIT-6 materials. For W-Al-KIT-6 catalysts at the Si/Al ratios of 30/1, 20/1 and 10/1, the main ammonia desorption peaks around 130-148 ^{o}C with a broad shoulder in the range of 200-500 ^{o}C range were observed, corresponding to weak and medium acid sites, respectively.[13, 36] Moreover, with the aluminum content increasing, the ammonia desorption peaks became more intense and the peaks shifted to higher temperature range, revealing that the total amount of acid sites and the strength of acid increased with the aluminum content increasing. Especially for W-Al-KIT-6-1, the NH_3-TPD profiles showed a drastic increase of peak intensity over the 350-500 ^{o}C, indicating the drastic increase of medium acid sites amount under the same acid strength. The total acidity is calculated based on desorbed NH_3 from 50 to 550 ^{o}C after steady adsorption and the

data are presented in Table 2. Among these materials, the total amount of the acid sites increased in the following sequence: KIT-6<W-KIT-6<W-Al-KIT-6-30<W-Al-KIT-6-20<W-Al-KIT-6-10<W-Al-KIT-6-1.

3.1.7 Raman spectra

Raman spectra of various samples are shown in Figure 6. Three peaks at 804, 716 and 272 cm^{-1} were observed for W-KIT-6 and for W-Al-KIT-6-30, assigning to symmetric stretching mode of W-O, bending mode of W-O, and deformation mode of W-O-W in the crystalline WO_3,[37, 38] respectively. Compared with W-KIT-6, W-Al-KIT-6-30 showed broader Raman bands, suggesting that the dispersion of W species in W-Al-KIT-6-30 were better than that of W-KIT-6. With further increasing the aluminum contents, the W-Al-KIT-6 samples showed very weak Raman peaks of crystalline WO_3, strongly suggesting that the introduction of Al could enhance the dispersion of W species in the W-Al-KIT-6.

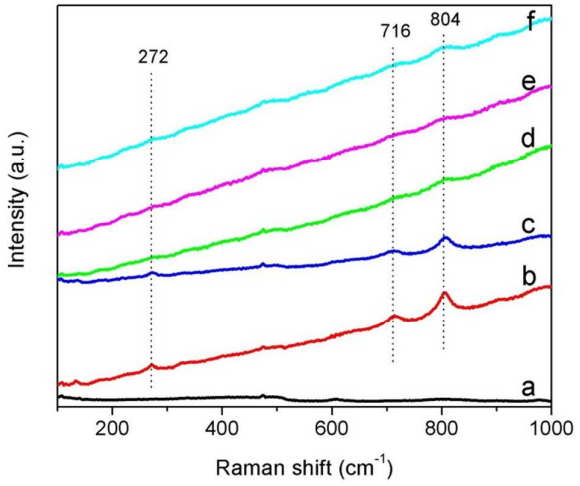
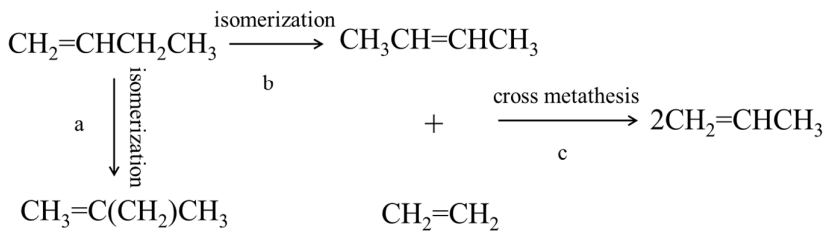


Figure 7. Raman spectra of different samples showing a), KIT-6; b), W-KIT-6; c), W-Al-KIT-6-30; d), W-Al-KIT-6-20; e), W-Al-KIT-6-10; f), W-Al-KIT-6-1.

3.2 Catalytic conversion of 1-butene and ethene to propene

3.2.1 Effects of mesoporosity and Si/Al ratio



Scheme 2. The main reaction pathways of catalytic conversion of ethene and 1-butene.

WO_3/SiO_2, W-KIT-6 and W-Al-KIT-6 catalysts are evaluated in catalytic conversion of 1-butene and ethene to propene. Possible reaction pathways are shown in Scheme 2. According to the well-established mechanism[39, 40] of olefin metathesis, propene was mainly produced by the cross metathesis of 2-butene and ethene (Scheme 2a). Therefore, 1-butene was needed to be first isomerized to 2-butene during the reaction (Scheme 2b). In our previous work[22] MgO was used as isomerization catalysts and the catalytic reactions were conducted at 350 ^{o}C. In this work, no MgO was added, and consequently the reactions were carried out at relative higher temperatures in the range from 400 to 500 ^{o}C.

The catalytic performances of WO_3/SiO_2, W-KIT-6 and W-Al-KIT-6 catalysts are compared in Figure 8 and the detailed data are summarized in Table 4. WO_3/SiO_2 showed a low 1-butene conversion of 36.6% and propene selectivity of 11.0%. For mesoporous W-KIT-6, the conversion of 1-butene and selectivity of propene were 55.1 % and 67.1 %, respectively, which were much better than these of conventional non-mesoporous WO_3/SiO_2 catalyst as expected. The incorporation of a suitable amount of Al into W-KIT-6 resulted in an increase of 1-butene conversion and

propene selectivity. When the Al/Si ratios increased from 1/30 to 1/10, the 1-butene conversion/propene selectivity increased from 59.5 %/68.8 % to 78.2 %/82.4 %, respectively. Moreover, at the range of Al/Si ratios from 1/30 to 1/10, the catalytic performance over W-Al-KIT-6 was quite stable. When introduction of an excess amount of Al into W-KIT-6, the 1-butene conversions and propene selectivity over W-Al-KIT-6-1 decreased, and the catalysts deactivated quickly during the first four hours of reactions.

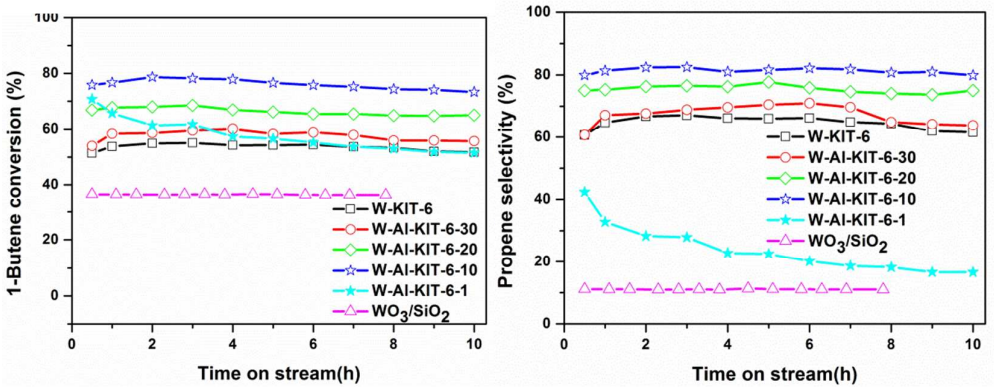


Figure 8. 1-butene conversion (left panel) and propene selectivity (right panel) of various catalysts. Reaction conditions: catalyst weight-1.0 g; T=450 °C; P=0.1 MPa; WHSV=0.8 h^{-1}; C_2H_4/1-C_4H_8=2.

It was suggested that highly dispersed surface tetrahedral tungsten species were active while bulk WO_3 were non-active for olefin metathesis.[2] Besides, the acidity of the support was also beneficial for olefin metathesis.[6] In the present work, W-KIT-6 showed a mediate catalytic performance. The doping of an appropriate amount of Al leaded to an increased amount of acid sites without changing the mesoporous structure of KIT-6 for W-Al-KIT-6 samples (Si/Al=30/1, 20/1 and 10/1), resulting in enhanced catalytic performances. However, for W-Al-KIT-6-1 at the highest Al/Si

ratio of 1/1, the collapse of mesoporous structures and an excess amount of acid sites induced by the introduction of an excess amount of Al into the framework resulted in a poor catalytic performance for metathesis of 1-butene and ethene to propene. As shown in Table 3, the high acidity of W-Al-KIT-6-1 caused severe by-reactions, as evidenced by 34.1 % of selectivity of isobutene. The high acidity would induce 1-butene skeletal isomerization to isobutene, as reported in literature (Scheme 2a). [41]

Table 3. Effect of Si/Al ratios on conversion of 1-butene and product selectivity over W-KIT-6 and various W-Al-KIT-6 catalysts.

Catalysts	1-butene conversion (%)	Selectivity (%)		
		Propene	2-butene	Isobutene
WO_3/SiO_2	36.6	89.0	11.0	0.0
W-KIT-6	55.1	67.1	32.9	0.0
W-Al-KIT-6-30	59.5	68.8	29.4	1.8
W-Al-KIT-6-20	68.5	76.6	21.0	2.4
W-Al-KIT-6-10	78.2	82.4	12.4	5.2
W-Al-KIT-6-1	61.6	27.9	38.0	34.1

Reaction conditions: catalyst weight-1.0 g; temperature-450 °C; pressure-0.1 MPa; WHSV=0.8 h^{-1}; C_2H_4/1-C_4H_8=2/1; data collected after 3.0 hours of reactions.

It is indicated that the amount of Al plays a crucial role in catalytic conversion of 1-butene and ethene. At higher Si/Al ratio, the W-Al-KIT-6 (Si/Al ratio of 10, 20 or 30) showed ordered mesoporous structure with moderate acidity. The moderate acidity could promote the conversion of 1-butene to 2-butene, and consequently the

catalyst showed higher 1-butene conversion and propene selectivity. At low Si/Al ratio, the W-Al-KIT-6-1 catalyst exhibited high acidity and deteriorated structure. The poor texture resulted in low 1-butene conversion and the high acidity stimulated the unwanted side-reaction such as, isomerization or oligomerization reactions, resulting low propene selectivity and bad stability. W-Al-KIT-6-10 catalyst with optimum amount of Al showed best catalytic performance due to the highly dispersed W species and suitable acidity.

3.2.1 Effects of reaction temperature

Table 4. Effect of reaction temperatures on catalytic performance over W-Al-KIT-6-10.

Temperature	1-butene	Selectivity (%)		
(^{o}C)	conversion (%)	Propene	2-butene	Isobutene
400	44.3	37.5	58.0	4.5
450	78.2	82.4	12.4	5.2
500	83.5	86.1	9.0	4.9

Reaction conditions: catalyst weight-1.0 g (W-Al-KIT-6-10); pressure-0.1 MPa; WHSV=0.8 h^{-1}; C_2H_4/1-C_4H_8=2/1

The influence of reaction temperatures on catalytic performance of W-Al-KIT-6-10 catalysts was summarized in Table 4. At 400 ^{o}C, the catalyst showed 44.4 % of 1-butene conversion and 37.5 % of propene selectivity. When the reaction temperature increased to 450 ^{o}C, the 1-butene conversion and propene selectivity increased dramatically. Further increasing the temperature resulted in slightly improved

catalytic performance.

To investigate the stability of catalyst, a longer time on stream reaction over W-Al-KIT-6-10 catalyst is conducted and the result is presented in Figure S1. The catalyst showed slight loss of activity after 24 h of reaction. The morphology of spent catalyst is observed by TEM. The TEM image (Figure S2) of post-reaction W-Al-KIT-6-10 catalyst suggested that mesoporous structure was well retained although some domains became non-ordered. The result indicated that the catalyst showed good stability.

4. Conclusions

Ordered tungsten and aluminum co-doped mesoporous KIT-6 materials were successfully synthesized by a one-pot method, and their catalytic performances for catalytic conversion of 1-butene and ethene to propene were investigated. Characterization results revealed that the doping of an appropriate amount of Al in W-KIT-6 did not change the mesoporous structure. Besides, the incorporation of Al could increase the amount of acid sites and favor the dispersion of W species. When Al/Si ratios ranged from 1/30 to 1/10, W-Al-KIT-6 catalysts showed enhanced catalytic performance. The introduction of excessive Al resulted in the collapse of mesoporous structures of KIT-6 and a poor catalytic performance. The improvement of catalytic activtiyt was ascribed to the retained mesoporous structure, the increased amount of acid sites and the better dispersion of W species facilitated by Al incorporation. The introduction of excess Al resulted in collapse of mesoporous structure and poor catalytic performance. The findings in this study are helpful to

design more efficient metathesis catalysts for propene production, and could be extended to other olefin metathesis reactions.

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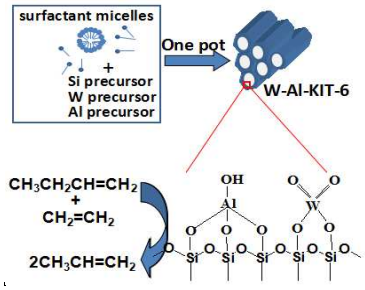

W-Al-KIT-6 (Si/Al=10) with high dispersion of active W species and moderate acidity, shows highest activity and selectivity to propene.