Enhanced catalytic activity for butane isomerization with alumina-promoted tungstated mesoporous zirconia

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Abstract

Mesoporous zirconia, synthesized from surfactant templating, was used to disperse alumina and tungstate as a catalyst (denoted as AW/m-ZrO₂) for the isomerization of *n*-butane. At a relatively low temperature of calcination (700 °C), the catalyst (AW/m-700) performed exceptionally well, both in maximum rate and stability, at a temperature of 250 °C. This was lower than the temperature needed by other tungstated zirconia-based catalysts reported so far. This lower temperature of calcination leads to the presence of more Brønsted acid sites with higher acid strength. In comparison with the normal dense phase zirconia catalyst, AW/m-ZrO₂ catalyst showed higher *n*-butane isomerization activity than the corresponding AW/d-ZrO₂ catalyst, which has about the same surface area. The difference in catalytic activity was attributed to the higher degree of dispersion of tungstate on the surface of m-ZrO₂.

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1. Introduction

Acid catalyzed skeletal isomerization reactions of *n*-alkanes are important in the chemical industry. However, under the worldwide trend for safer and cleaner processes, the conventional catalysts such as corrosive liquid acids and metal halides have to be replaced by the more environmental friendly halide-free solid acid catalysts. Zirconia-based solid acids, sulfated zirconia and tungstated zirconia, have thus received increasing attention recently.

Tungstated zirconia is in a class of solid acid catalyst that show promising prospects in the isomerization of normal alkanes [1–4]. Although tungstated zirconia is structurally more stable than sulfated zirconia, thus giving more steady performance in catalysis, it is also less active. This leads to higher reaction temperatures, usually above 300 °C for the

isomerization of butane for example. High reaction temperatures are thermodynamically less favorable for the branched isomers. Thus, improving the catalytic activity of tungstated zirconia catalyst so that the reaction can be operated at lower temperatures is the goal of this work. In this research, two methods for increasing the catalytic activity of tungstated zirconia are employed: (a) using mesoporous zirconia [5] to increase the surface area and textural properties of the catalyst and (b) using alumina as the promoter of the catalyst, so that catalytic activities are not only promoted but also stabilized. Previously, we reported on the promotional effect of Al and Ga on butane isomerization over tungstated zirconia catalyst [6–8]. The improved activity of alumina promoted tungstated zirconia (AWZ) for *n*-butane isomerization was related to the prevention of crystalline WO₃ phase [7] and to the increased acid sites [6] created by the Al promoter. However, the origin of the promoted activity is still not completely understood.

First, we briefly describe the preparation and characterization of alumina-promoted tungstated mesoporous zirconia (AW/m-ZrO₂) catalyst. Then, *n*-butane isomerization was used as the test reaction for the catalysis system. The mesoporous

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zirconia was made from cationic surfactant ($C_{16}TAB$) templated sol–gel process [5,9]. The acidity of these catalysts was characterized by NH_3 -TPD, in situ DRIFT spectroscopic analysis of chemisorbed NH_3 and XPS analysis tungstate species. We are able to resolve the acid sites into Lewis and Brønsted components. The composition of the acid sites on AW/m- ZrO_2 catalysts calcined at different temperatures was correlated to their catalytic performances. Besides the AW/m- ZrO_2 catalyst, we also synthesized the normal kind of dense phase zirconia (d- ZrO_2) without $C_{16}TAB$, to make the dense phase alumina-tungstated zirconia (AW/d- ZrO_2). We compared the two different catalysts of their activities. We found that the catalytic activity for mesoporous AW/m- ZrO_2 catalyst is a lot higher than that of dense phase AW/d- ZrO_2 . We then discuss the origin of the difference by comparison of the textural and acidity characterizations.

2. Experimental

2.1. Preparation of the catalysts

Mesoporous zirconia was made using the cationic surfactant hexadecyl trimethyl ammonium bromide ($C_{16}TAB$)-templated sol–gel process according to the method outlined by Ciesla et al. [5] (designated as m- ZrO_2). The details are in our previous report on sulfated mesoporous zirconia [9]. Alumina-promoted catalyst, AW/m- ZrO_2 , was prepared by simultaneous impregnation of the uncalcined m- ZrO_2 precursor with the required amount of ammonium tungstate and aluminum nitrate in H_2O/C_2H_5OH solvent. Samples were dried at 100 °C, and then calcined at one of several temperatures (from 630 °C to 850 °C) in static air for 3 h. For the purpose of comparison, a conventional dense phase catalyst (AW/d- ZrO_2) [10] was also prepared with similar loadings of Al and W but without the template. In the case of AW/d- ZrO_2 , amorphous zirconium hydroxide was used instead of the uncalcined m- ZrO_2 precursor. Here, d- ZrO_2 represents dense-phase zirconia (without the template).

2.2. Characterization techniques

Elemental analysis was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Jarrel-Ash ICAP 9000 instrument. Carbon analysis was done with a Heraeus VarioEL-III instrument. Powdered X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO diffractometer using $Cu K\alpha$ radiation operating at 45 kV and 40 mA. N_2 adsorption–desorption isotherm, BET surface area, and porosity data were determined at 77 K on a Micromeritics ASAP 2010 instrument. Ultraviolet–visible (UV–vis) absorption spectra were taken on a Hitachi U-3310 spectrophotometer.

NH_3 temperature-programmed desorption (NH_3 -TPD) of samples was carried out on Micromeritics AutoChem 2910 instrument. Before NH_3 adsorption, 0.2 g calcined sample was pretreated at 400 °C in flowing He for 1 h. The NH_3 adsorption was carried out at 100 °C and the desorption of NH_3 was started

at 100 °C and continued until 800 °C at 10 °C/min. The desorption process was monitored by a Quadruple Mass Spectrometer (Thermo ONIX ProLab) using the mass number 16 (NH_2^+) to obtain NH_3 -TPD profiles. In situ diffuse-reflectance infrared Fourier-transformed (DRIFT) spectra of ammonia chemisorbed on catalyst were taken with a Thermo Nicolet 380 FT-IR spectrometer. The sample was first dried at 400 °C for at least 1 h prior to ammonia adsorption. The adsorption of ammonia was done by flowing 5% NH_3/N_2 mixture through the catalyst at 120 °C for 5 min; the system was then flushed with dry N_2 for 15 min. The catalyst with adsorbed ammonia was then subjected to a desorption process at increasing temperatures. Spectra were recorded after the catalyst's temperature was held for 15 min at each temperature. X-ray photoelectron spectroscopic (XPS) analysis was performed using a Thermo VG Scientific ESCALAB 250 instrument with a monochromatic Al $K\alpha$ radiation (1486.8 eV) and under a residual pressure of $\sim 5 \times 10^{-10}$ Torr. The pyridine-adsorbed sample was first degassed ex situ under vacuum at about 120 °C for 0.5 h. The pretreated sample was then transferred into the XPS instrument and spectra were collected in the N 1s region. Charge effects were compensated by electron flux from a flooding gun and the Zr 3d_{5/2} binding energy was set at 182.2 eV. The spectral profiles were deconvoluted into peaks by using XPSPEAK software from RCSMS lab.

The W-L_{III}-edge extended X-ray absorption fine structure (EXAFS) study was performed at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The electron storage ring was operated at about 1.5 GeV with a ring current of about 200 mA.

2.3. Catalytic study

Each catalytic reaction was carried out in a fixed bed continuous flow quartz reactor at atmospheric pressure. The catalyst (usually 1.0 g) was first pressed into 40–60 mesh (0.8–1.0 mm diameter) particles and mixed with quartz sand. It was then pretreated under air flow at 450 °C for 3 h, and then reduced with H_2 at 300 °C for 1 h. After flushing the system with N_2 at the reaction temperature for 0.5 h, the reaction was started by introducing a mixture of *n*-butane and H_2 ($n-C_4H_{10}:H_2 = 1:10$, v/v) at a total inlet flow rate of 15.5 ml min⁻¹. The reaction product was analyzed by an on-lined Agilent 6890N gas chromatograph equipped with a flame ionization detector and a 60 m DB-1 column.

3. Results

3.1. Structure study

Before we advance onto the catalytic properties of AW/m- ZrO_2 catalysts, we should have a clear idea about their textural properties. More importantly, we would like to examine the effect of calcination temperature on the stability of these catalysts. The effect of doped species on the thermal phase transformation of zirconia, however, has been studied. Dopants

Fig. 1. XRD patterns of m-ZrO₂ and AW/m-ZrO₂ catalysts calcined at different temperatures. *Sample of AW/d-ZrO₂.

such as aluminum [9] and tungsten [11] can retard the transformation from tetragonal to monoclinic phase of zirconia. The tetragonal phase of zirconia is thought to play a vital role in *n*-butane isomerization reaction [12]. In this study, we found that AW not only retards the phase transformation of m-ZrO₂ but also leads to an increase of its average pore size.

Fig. 1 shows the XRD patterns of m-ZrO₂ and AW/m-ZrO₂ calcined at different temperatures. In our study, 630 °C is the minimum calcination temperature required to generate the tetragonal phase of m-ZrO₂ in AW/m-ZrO₂, which is crucial for the *n*-butane isomerization reaction. At 630 °C, only the tetragonal phase of zirconia (peaks denoted as T) is prominent in AW/m-ZrO₂ while the monoclinic phase of zirconia (peaks denoted as M) is also present in the case of pure m-ZrO₂.

Obviously, the presence of AW on m-ZrO₂ surface retards its transformation from tetragonal phase to monoclinic phase. This phenomenon was also observed in alumina-promoted sulfated m-ZrO₂ (AS/m-ZrO₂) [9]. Its tetragonal phase of zirconia also becomes better developed. On the other hand, mixed tetragonal and monoclinic dense-phases were obtained in the case of pure m-ZrO₂.

The AW/m-630 and AW/m-700 catalysts exhibited a single peak at 0.9–1.0 that is due to the mesostructure. Previously, we have examined the mesostructure of the support m-ZrO₂ and found that the mesopores are of worm-like structure [9]. When the calcination temperature was increased above 750 °C, the XRD peak in the low angle region almost vanished, which implies collapse of the mesostructure. For alumina-doped AW/m-ZrO₂, the monoclinic phase of zirconia only starts to develop after it was calcined at 800 °C, which is near its structural collapse point.

Interestingly, we also found that the average pore sizes of m-ZrO₂ and AW/m-ZrO₂ catalysts can be expanded by increasing the calcination temperature. Fig. 2 shows the N₂ adsorption–desorption isotherms and the corresponding pore size distribution for these calcined samples. At 630 °C, the hysteresis originally seen in m-ZrO₂ diminished after AW was loaded onto it. Besides, the total volume of N₂ adsorbed also decreased in AW/m-ZrO₂. Apparently, some of the loaded AW must have diffused into the channels of this catalyst. We have tried to use HR-TEM to directly locate Al and W in AW/m-ZrO₂. Because of the high absorption of electron by W, however, the TEM images are too dark to identify the position of W on m-ZrO₂. Table 1 summarizes the results of the textural properties of these samples.

The two samples m-ZrO₂ and AW/m-ZrO₂ behaved differently as the calcination temperature was increased to

Fig. 2. N₂ adsorption–desorption isotherms of m-ZrO₂ (left), AW/m-ZrO₂ (middle), and pore size distribution of AW/m-ZrO₂ (right) catalysts calcined at different temperatures.

Table 1
The textural and catalytic properties of catalysts

Catalyst	W ^a (wt.%)	Al ^a (wt.%)	Surface area ^b (m ² g ⁻¹)	Pore size (nm)	Pore volume (ml g ⁻¹)	W surface density (atom nm ⁻²)	TON ^c (μmol g ⁻¹ s ⁻¹)
AW/m-630	7.91	1.34	134	3.1	0.08	2.1	0.0973
AW/m-700	8.69	1.52	103	3.7	0.12	3.1	0.1860
AW/m-750	6.87	1.48	68	5.0	0.10	3.3	0.0315
AW/m-800	6.67	1.32	51	8.0	0.09	4.2	0.0019
AW/d-700	10.4	0.93	103	3.9	0.14	3.3	0.0007
m-700	–	–	33	3.5	0.03	–	0.0002
AS/m-630	–	1.45	121	3.1	0.09	–	0.6220

^a Determined from ICP-AES.

^b Determined from N₂ adsorption–desorption isotherm at 77 K.

^c Turnover number, which is the number of micromoles of *n*-butane converted per gram of catalyst per second. Reaction data were taken after 6 h on stream.

700 °C. In the case of pure m-ZrO₂, a great loss of the volume of N₂ adsorbed occurred, indicating a collapse of its mesoporous structure. Conversely, the volume of N₂ adsorbed increased slightly in AW/m-ZrO₂ and a hysteresis loop appeared concurrently. This hysteresis loop later shifted to higher *P*/*P*₀ values. The average pore sizes were enlarged as AW/m-ZrO₂ was calcined at higher temperatures. As the pore size is enlarged, the surface area decreased due to increased wall thickness (Table 1). The pore volume increased for the same reason. At 750 °C, the pore volume decreases again and this signifies the beginning of structural collapse. This observed temperature of structural instability is quite consistent with the XRD result for monoclinic zirconia formation at 800 °C. On the other hand, similar temperature treatment for pure m-ZrO₂ caused its pore structure to collapse rapidly, so the dense-phase zirconia, with very low surface area, is formed at 700 °C. For AW/m-ZrO₂, the W surface density increased as the calcination temperature increased. The W atom surface density of AW/d-700 is 3.3 nm⁻², nearly equals to the densities of AW/m-700 and AW/m-750. This surface density is nearly equal to the monolayer coverage of tungsten oxide on zirconia, which is 3.5 nm⁻². Recently, we have shown for dense phase zirconia that such loading of W is close to optimum catalytic activity for pentane isomerization [10].

In summary, 700 °C seems to be the optimum calcination temperature for obtaining maximum loadings of W and Al shown in Table 1 for the AW/m-ZrO₂ catalyst; a fully developed tetragonal phase m-ZrO₂ of high porosity can be obtained. The porosity properties of the sample calcined at 630 °C are poor even though the same tetragonal phase of m-ZrO₂ can be obtained. Therefore, the choice of calcination temperature is very important for this system. The improved textural property of the catalyst at 700 °C should have a positive effect on AW/m-700 catalytic performance in *n*-butane isomerization reactions (see Section 3.4).

3.2. Acidity of the catalysts

In *n*-butane isomerization, the Brønsted acid sites play a very important role. They are responsible for the protonation of butene formed from the dehydrogenation of *n*-butane, and this reaction leads further to the formation of carbene intermediates

for the isomerization reaction [13]. The Brønsted acidity thus has a direct influence on the isomerization rate and coke formation of AW/m-ZrO₂ catalyst in this reaction.

To research the acidity of our catalysts, we employed TPD and in situ DRIFT techniques to study their surface acidity. For both AW/m-ZrO₂ and AW/d-ZrO₂ catalysts, we employed temperature programmed ammonia desorption (NH₃-TPD) to study the amount and strength of acid sites on solid acid catalysts. We first investigated the total acid sites and acid strength of AW/m-630, AW/m-700, and AW/d-700, as shown in Fig. 3. The desorption temperature (appearing at ~260 °C) for the dense phase catalyst AW/d-700 is lower than those of AW/m-630 and AW/m-700 (~295 °C). The integrated NH₃ desorption profiles are calculated as the relative total acid sites. The total acid sites of AW/d-700 are the lowest among the

Fig. 3. NH₃-TPD profiles of (a) AW/m-630, (b) AW/m-700, and (c) AW/d-700.

samples. The mesoporous structured zirconia seems to favor the formation of stronger acid sites and enhanced the total acid sites at the same time.

The DRIFT results of chemisorbed ammonia are compared on AW/m-630, AW/m-700, and AW/m-750 (Fig. 4). The band at 1417 cm^{-1} (denoted as B) and a small shoulder at about 1670 cm^{-1} (denoted as L) correspond to NH_4^+ on Brönsted acid sites [6]. The band due to NH_3 coordinated to Lewis acid sites, appears at 1606 cm^{-1} (L). All the bands decrease in intensity with increasing desorption temperatures, indicating the loss of NH_3 adsorbed on Brönsted and Lewis acid sites. However, it seems that a Brönsted acid site corresponding to the 1417 cm^{-1} peak is stronger than Lewis acid sites since it still retains a significant amount of NH_3 at 400°C , whereas the NH_3 adsorbed on Lewis acid sites is almost completely desorbed. With respect to the calcination temperature, the lower the calcination temperature, the more Brönsted acid sites there are, in the order of $\text{AW/m-630} > \text{AW/m-700} > \text{AW/m-750}$. The AW/m-630 sample retained more chemisorbed ammonia as the catalyst was heated to 400°C than the other catalysts did. In other words, AW/m-630 has more strong Brönsted acid sites than AW/m-700 and than AW/m-750. Also the strength of the Brönsted acid sites in AW/m-750 is the weakest. Among the three catalysts, the Brönsted acid strength in AW/m-700 is intermediate.

Previously, we have employed the XPS of the N 1s peak of adsorbed pyridine to investigate the types and strengths of acid sites displayed by sulfated zirconia catalysts by resolving the spectra position and intensity [9]. We found the N 1s peaks were rather broad and we de-convoluted the peaks into a distribution of three different acidic sites of a range of acid strength [9]. In our case here, the fraction of strong Brönsted acid sites in the total Brönsted acidity (or overall acidity) is the highest in AW/m-630 but moderate in AW/m-700 (figure not shown), which is in agreement with the DRIFT results. Relatively, the fraction of Lewis acid is increased as the temperature of calcination is increased.

Fig. 4. DRIFT spectra for the desorption of chemisorbed ammonia on AW/m-630, AW/m-700, and AW/m-750. These spectra were normalized to the same intensity of the m- ZrO_2 lattice band at about 1342 cm^{-1} .

3.3. The dispersion of tungstate

It is known the catalytic activity of tungstated zirconia depends crucially on the degree of dispersion of WO_x on the surface of zirconia [14]. We here employ three techniques to investigate the dispersion of tungstate. UV-vis spectra are sensitive to the dispersion of tungstate. EXAFS analysis can help us to reveal the radial distribution function (RDF) of various scatters around the central X-ray absorbing atom. X-ray photoelectron spectroscopy (XPS) on the other hand can give the relative surface composition of W versus Zr.

Comparing the dispersion of WO_x species on d- ZrO_2 and m- ZrO_2 by XRD and UV-vis techniques, the XRD peaks characteristic of WO_3 crystallites ($2\theta = 23.3^\circ$, 23.8° , and 24.5°) were not detected in AW/d-700 and AW/m-700 samples (Fig. 1). In Fig. 5, the UV-vis spectra of three catalysts are compared. The AW/m-630 sample shows a shoulder absorption band near 430 nm, which is due to WO_3 . As the calcination temperature was increased from 630°C to 700°C , the characteristic absorption edge ($\sim 430\text{ nm}$) of crystalline WO_3 disappeared and we have a fully dispersed AW/m-700 catalyst.

Fig. 6 compares the Fourier-transformed W-LIII-edge EXAFS spectra of AW/d-700, AW/m-700, and AW/m-630 catalysts. The data were recorded ex situ at room temperature after a H_2 pretreatment at 300°C . These RDFs are not corrected for phase shifts. The assignment of peaks was made according to the published work of Wong et al. on zirconia-supported tungsten oxide system [6]. The peaks between $R = 0.80$ and $R = 1.99\text{ Å}$ in the RDF plots are due to W–O bond distances. The distribution of W–O distance is rather broad, indicating a much disordered WO_x octahedral polytungstate structure on zirconia. One notes that the W–O bond distance of AW/m-700 and AW/m-630 (1.24 Å) is significantly shorter than that of AW/d-700 (1.35 Å), indicating that the terminal H atom bound to the W–O may be eliminated more easily in the mesoporous system than that in the dense phase system. In addition, we can

Fig. 5. UV-vis absorption spectra of AW/d-700, AW/m-630, and AW/m-700 catalysts.

Fig. 6. W-L_{III}-edge EXAFS radial distribution functions of AW/d-700, AW/m-700, and AW/m-630 catalysts.

see that the W–O–W peak at 3.46 Å in AW/d-700 is similar to that of bulk WO₃ [10]. However, W–O–W and W–O–Zr peaks in the RDF spectra of AW/m-700 collapse into a broad peak, indicating highly dispersed disordered tungstate clusters on the surface of zirconia. We propose that this is because the mesoporous zirconia itself can provide more continuous surface area for WO_x species to disperse better. From Fig. 6, AW/m-630 seems to disperse less well than the AW/m-700 catalyst.

The XPS spectra of W 4f and Zr 4p (left) and Zr 3d (right) of AW/d-700 and AW/m-700 are shown in Fig. 7. For the W 4f energy region in the range of 32.3–39.5 eV, the complex features were deconvoluted into two doublets corresponding to W⁵⁺ and W⁶⁺. The characteristics first peaks of W⁵⁺ and W⁶⁺ are at 34.7 eV and 35.6 eV, respectively. The ratios of the two species were found to be W⁵⁺/W⁶⁺ = 0.64 for AW/d-700 and 0.77 for AW/m-700. The surface W/Zr ratios of samples can be determined from the ratio of the integrated area of W 4f XPS peaks to the integrated area of Zr 3d XPS peaks with

Table 2
W 4f XPS fitting results

Sample	BE (eV)	Assignment	W (%)	W/Zr
AW/d-700	35.6	W ⁶⁺	61	0.155
	34.7	W ⁵⁺	39	
AW/m-700	35.7	W ⁶⁺	56	0.088
	34.9	W ⁵⁺	44	

consideration of the atomic sensitivity factors of W and Zr. The fitting results of the XPS are compiled in Table 2.

The surface W/Zr ratio is a good measure of the degree of dispersion of W on the surface. One could have the same loading of W per unit area while giving different surface W/Zr ratios because of different degrees of aggregation of WO_x. Multilayer structures for WO_x would give a higher value of W/Zr compared to monolayer ones. In our catalyst, surface ratios are determined to be W/Zr = 0.155 for AW/d-700 and 0.088 for AW/m-700. The results show that the dispersion of WO_x on the surface of zirconia is better on mesoporous zirconia than on the dense phase zirconia.

The relative richness of W(V) can also be checked by the W-L_{III}-edge XANES spectra of the catalysts. Fig. 8 shows the W-L_{III}-near edge white line of the three samples. The mesoporous catalysts AW/m-630 and AW/m-700 possess a peak that is shifted by 1.8 eV to lower photon energy. This indicates a lower valence of W for the mesoporous sample, in agreement with the conclusion reached by XPS analysis.

3.4. Catalytic properties of AW/m-ZrO₂ catalysts

As AW/m-ZrO₂ has more acid sites and stronger acid strength than AW/d-ZrO₂, it is interesting to look at its performance in catalytic reactions. We choose a well-studied reaction system, the *n*-butane isomerization reaction, which can be catalyzed by highly dispersed WO_x species on the zirconia surface.

Fig. 7. W 4f and Zr 4p XPS spectra (left) and Zr 3d XPS spectra (right) of AW/d-700 and AW/m-700. (Samples were treated with H₂ at 300 °C for 1 h.)

Fig. 8. W-L_{III}-edge XANES spectra of AW/d-700, AW/m-700, and AW/m-630 catalysts.

Fig. 9 compares the catalytic activities of some selected W/m-ZrO₂, and AW/m-ZrO₂, AW/d-ZrO₂ catalysts, and that of un-doped m-ZrO₂ support in *n*-butane isomerization reaction at 250 °C. Especially, we studied the effect of calcination temperature. Indeed, one can see that AW/m-ZrO₂ catalyst has much higher activity than the dense phase AW/d-ZrO₂ catalyst due to the enhanced acid sites and acid strength. If we compare the initial activities, we do see a higher activity for the catalyst calcined at lower temperature. This is in agreement with the higher amount of observed Brønsted acid sites for the AW/m-630 sample. After 1 h or so, however, the catalytic activity of AW/m-630 drops rapidly due to coking. Then the steady state activity of AW/m-700 becomes higher than that of AW/m-630 and its activity profile is also more stable. For catalyst calcined at 750 °C, the steady state activity is even lower. It seems the framework structure of m-ZrO₂ starts to collapse in the catalyst AW/m-750 as shown by the decrease in both its surface area and pore volume, whereas the tetragonal phase of zirconia is not yet well-developed in AW/m-630. Therefore, 700 °C seems to be the optimal calcination temperature for this system and the high

Fig. 9. Catalytic profiles of W/m-ZrO₂, AW/m-ZrO₂, AW/d-ZrO₂, and m-ZrO₂ catalysts in *n*-butane isomerization reaction at 250 °C.

porosity and moderate acidity made AW/m-700 an active and stable catalyst. For the purpose of background check, we also measure the activity for the starting materials m-ZrO₂, i.e. the mesoporous zirconia without any loadings of Al or W. As expected, it exhibits a very low activity as shown in Fig. 9.

4. Discussion

Our catalyst AW/m-700 performed exceptionally well at a low temperature of 250 °C compared to other tungstated zirconia-based catalyst reported so far which generally required a reaction temperature higher than 300 °C [6,7,10,15].

The promotion of catalytic activity by Al may be through two different effects: (a) the formation of more strong acid sites [6], (b) the increased redox activity of W where butane molecules are activated by dehydrogenation on well-dispersed polyoxotungstate via a redox process [16]. Both processes may be important for the catalytic isomerization of alkanes.

Recent investigations indicate that both of the above effects are controlled by WO_x surface density (at. W nm⁻²) [14,17,18]. The nearly monolayer regime (corresponding to our sample) is characterized by distorted WO_x species that are well dispersed on the ZrO₂ surface [19]. In order to achieve a better dispersion of WO_x on the surface, we need a zirconia support with high surface area, porosity, and thermal stability. These requirements are all met by mesoporous zirconia, m-ZrO₂. The variations of activity for AW/m-ZrO₂ catalysts calcined at different temperatures may be correlated to the surface density values of tungstate, as shown in Table 1. The optimum W surface density for catalysis, at 3.1 W nm⁻², is a little below the monolayer density.

We note that in our samples a higher temperature of calcination leads to pore expansion and lower surface area. Comparing AW/m-630, AW/m-700, and AW/m-750 in Table 1, one would expect lower dispersion of the WO_x species on zirconia at higher temperature of calcinations, which in turn would lead to lower acidity and redox capability. However, catalytic activities cannot simply be explained by the surface area effect alone, since d-ZrO₂ and m-ZrO₂ possess about the same surface area. We have to consider the dispersion effect on the distribution of acidity and correlate with the catalytic performance of AW/m-ZrO₂ catalysts. In addition to surface density, one is thus also concerned with the degree of dispersion. The more extensive the W/Zr contact is, the more active the catalyst will be. In other words, the bulk WO₃ phase is inactive. In this paper, we measure the degree dispersion by surface W/Zr ratio determined by XPS (Fig. 7). Previously, Di Gregorio and Keller [19], using the same XPS technique, have shown a non-linear increase of W/Zr with respect to W% loading. Near monolayer the ratio W/Zr is about 0.08 and it increases with W loading up to about 0.25 in their tungstated zirconia catalyst. In our catalysts, it is interesting to compare the two samples of AWZ/d-700 and AWZ/m-700. They have the same surface area, but the mesoporous zirconia sample AWZ/m-700 has much better dispersion (lower W/Zr value). This correlates well with the higher amount of surface acidity detected in AWZ/m-ZrO₂. This may partially explain

why we observe a better catalytic activity in AWZ/d-700. It seems the continuous channel wall of mesoporous zirconia with surfactant in it provides one a better surface to disperse uniformly the polytungstate species. UV–vis, EXAFS and XPS studies all indicate higher degrees of dispersion of the tungstate on the mesoporous zirconia surfaces.

The degrees of dispersion of tungstates affect both the redox and acidic properties of the WZ catalyst [18–20]. For characterizing the redox tendency of AWZ, we measured the relative ratio of the two species W^{5+}/W^{6+} . Our investigation by XPS technique found that the addition of Al did help the dispersion of tungstates on zirconia and did lead to the more active W^{5+} species [10]. Since the Al-loading in mesoporous supported AW/m-ZrO₂ is higher than that in dense phase supported catalyst AW/d-ZrO₂, the pentavalent W^{5+} species is higher in the mesoporous catalyst AW/m-ZrO₂. Recently, Kuba et al. have associated the initiation of C–H bond breaking and dehydrogenation with the reducibility of surface W species [21]. The butane molecules are activated by dehydrogenation on well-dispersed polyoxotungstate via a redox process. Then the resulting alkenes are protonated on the acidic sites. Since we found the W^{5+}/W^{6+} ratio to be higher for the mesoporous sample, the improved redox pair of W^{5+}/W^{6+} in promoted mesoporous WZ is accompanied by the easier activation of alkanes.

We would like to put emphasis on the much lower calcination temperature of 700 °C of our catalyst, which leads to the presence of more Brönsted acid sites while calcination at higher temperature would convert some Brönsted acid to Lewis acid. In the reported works on tungstated zirconia catalysts, the calcination temperature was always higher than 800 °C [7,14,21–25], which would lead to less surface Brönsted sites while giving too many Lewis acid sites. It seems that the relative concentration of Brönsted acid sites in the catalyst should be moderate for a good performing catalyst, as in the case of AW/m-700. Too many strong Brönsted acid sites would lead to coking and thus rapid decay of the catalytic activity. Although a high relative concentration of strong Brönsted acid sites in AW/m-630 can protonate butene rapidly (high initial activity), they are also more susceptible to coke formation (thus a fast decay rate). Indeed, the amount of coke in the spent catalyst of AW/m-630 (0.38 wt.%) is higher than in AW/m-700 (not detected). On the other hand, too low a concentration of the Brönsted acid sites is also not effective for the reaction. It seems the effective acidic sites result from polytungstate species. Highly dispersed monomeric species do not seem to be effective in the acidic catalysis [14]. In fact, recently Lebarbier et al. [26] have shown that the surface density of W on WZ needs to be above a certain threshold to be effective in acid catalysis. The activity thresholds are 1.3 at. W nm^{−2} for propanol dehydration and 2.3 at. W nm^{−2} for hexane isomerization [26]. The surface W densities of our catalysts are above 2.1 at. W nm^{−2}.

Also, we would like to emphasize that the hydrogen adsorbed on the surface of tungstated zirconia would also contribute to acidity. It is known that the Brönsted acid sites form on WO_x domains due to the delocalized electrons from H atoms. In fact, Pt

promoted tungstated zirconia under hydrogen is much more active for catalysis than without hydrogen [27]. Barton et al. [18] suggested catalysts with crystal WO₃ presented on the surface of ZrO₂ are less active because crystal WO₃ decreases the ability of accepting electrons from H atoms to form the Brönsted acids and some H atoms are accommodated inside the crystal WO₃ where they are inaccessible to reactant molecules. The highly dispersed WO_x species can form Brönsted acid sites more easily under hydrogen environment.

In summary, the extensive continuous surface of m-ZrO₂ seems to favor better dispersion and better reducibility of the surface tungstate species. Alumina also helps in the dispersion. This good dispersion of W leads to more and stronger acid sites. The reducibility of W helps in two ways in catalysis: it favors electron transfer-induced C–H bond activation and thus the initiation of the reaction chain; then the hydrogen would decompose on the surface to generate the proton species, which also increases acidity. However, further researches into the details of catalytic sites in tungstated zirconia solid acid would certainly be welcome.

5. Conclusion

In this research, we successfully synthesized AW/m-ZrO₂ catalyst with mesoporous structure. In comparison to AW/d-ZrO₂, synthesized without template, AW/m-ZrO₂ has a higher activity for *n*-butane isomerization at a lower calcination temperature of 700 °C and at a lower reaction temperature of 250 °C. The increased activity, which reaches nearly 30% of that for alumina-promoted sulfated zirconia (AS/m-630), is dependent on the promotion of Al and the mesostructure ZrO₂. As a result, we obtained a well-dispersed tungstate on zirconia while the mesostructure ZrO₂ favors the formation of stronger acid sites and enhanced the total acid sites.

A notable characteristic of AW/m-ZrO₂ catalysts is that they are composed of mixed oxides without noble metal, which would make it more tolerant to sulfur contents in the feed gas. More importantly, tungstated zirconia catalyst is much more stable than the sulfated zirconia catalyst which would lose sulfur during long-term reactions. The high activity and stability of this catalyst at low temperature make it a new kind of halogen-free solid acid catalyst that is friendly to the environment.

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