Comparison of the promotion effects on sulfated mesoporous zirconia catalysts achieved by alumina and gallium

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ABSTRACT

Mesoporous zirconia, hydrothermally synthesized from surfactant templating, was directly impregnated with aluminum sulfate or gallium sulfate to give the solid acids, Al- and Ga-promoted sulfated mesoporous zirconia catalysts (AS/MP-ZrO₂ and GS/MP-ZrO₂). The promotional effects achieved by these two catalysts for the *n*-butane isomerization were compared to clarify the differences in mechanism in catalytic activities in butane isomerization. The catalysis was found to be strongly promoted by the addition of a proper amount of alumina or gallium. The activities of Ga-promoted catalysts were higher than those of Al-promoted catalysts. Diffuse-reflectance infrared Fourier-transformed (DRIFT) spectra and temperature programmed desorption mass (TPD-MS) analyses were employed to identify and quantify properties of the acid sites on catalyst surfaces. The 3AS/MP-ZrO₂ catalyst shows a slightly higher acidity in strength and amount than that of 3GS/MP-ZrO₂, but much higher than that of the unpromoted 3S/MP-ZrO₂ catalyst. All three catalysts were further compared in their redox properties, with the H₂-temperature programmed reduction (TPR) analysis showing totally different tendencies (redox ability: 3GS > 3S > 3AS/MP-ZrO₂). A small concentration of olefins accompanied with water formation were observed by in situ DRIFT spectra and quantified by the Baeyer test. The results show that this occurs via oxidative dehydrogenation of butane by the sulfate groups to form butene, which leads to butyl carbenium species for skeleton isomerization. The catalytic promotion effect of alumina on sulfated zirconia is mainly due to a balanced increase of acid sites; on the other hand, gallium promotes sulfated zirconia through enhancing both the surface acidity and its redox properties on the surface.

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1. Introduction

Skeletal isomerization of normal alkane to branched alkanes by using solid acid catalysts is one of the important technologies for RON improvement in oil refining [1,2]. Traditionally, the solid acids employed are either chlorided alumina or Pt–mordenite catalysts. For chlorided alumina, constant addition of chloride is necessary and its disposal is often environmentally damaging. For Pt-enhanced zeolites, the disadvantage is the relatively high operating temperature which leads to poor RON results. Since the discovery of its strong acidity, sulfated zirconia (SZ) has attracted much attention as a promising isomerization catalyst thanks to its high activity and environmental friendliness. However, promoters are needed for a steady and high activity. It is generally accepted that the noble metal Pt is an adequate promoter in the sulfated zirconia catalyst (SZ) for the skeleton

isomerization of *n*-alkane [1]. The addition of Pt/H₂ improved the stability of SO₄^{2−}/ZrO₂ catalyst and reduced coke formation. Currently Pt/SZ is the basis of commercial C5–C6 naphtha isomerization processes like the Par-Isom (UOP). However, the high cost of Pt and its high sensitivity to sulfur in the feed gas make searching for alternative promoters desirable. Lately, the promotion effect of main group metals (alumina or gallium) [2,3] on SZ in the isomerization reaction of *n*-alkanes has received much attention, for it simultaneously promoted and stabilized activity without the use of Pt [4–9]. The promotion and stabilization effects of Al or Ga on sulfated zirconia in *n*-alkane isomerization without using the expensive Pt are technologically very attractive.

An interesting observation is that, although Al and Ga belong to the same group in the periodic table and both exhibit excellent promoting effects in the catalysis of *n*-alkane isomerization, their promoting mechanisms may be quite different [8]. Gao and co-workers [10] attributed the catalytic promotion effect of Al on SZ to an increase of acid sites. We previously reported that the remarkable activity and stability of Al-promoted SZ catalysts are due to the balanced distribution of acid site strengths with an enhanced amount of weak Brønsted acid sites [11]. On the other

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hand, Ga-containing zeolite is known to catalyze the oxidative dehydrogenation reaction of alkanes [12]. Ga-promoted SZ catalyst shows an enhancement of its redox properties [8].

For a long time, the main active sites of SZ for the catalytic isomerization of *n*-alkane have been considered to be its acid sites, and indeed a balanced distribution of acid sites strength was proven to be crucial to enhance activity and stability of the Al-promoted SZ catalyst [11]. However, this concept should be further modified according to recent studies of the redox properties of sulfated zirconia. SZ catalyst not only plays the role of solid acid, but it was also shown to initiate the catalytic cycle by dehydrogenation to an olefin, which then forms a carbenium ion for the chain initiation [13,14]. So, in view of the recent deeper understanding of the redox property of SZ, we would like to investigate the roles of promoters especially in the promotion of redox reaction. In a recent study, we found that the doping of alumina onto sulfated zirconia increases the extent of sulfur retention on the surface of zirconia, which then promotes the oxidative dehydrogenation of butane to butene and the initiation of skeleton isomerization [15]. By analyzing the distribution of products, we also proposed a detailed mechanism to clarify the multiple roles of Al in Al-promoted SZ.

Based on these new understandings, it would be interesting to compare the promotional effects of Al and Ga on SZ catalyst. In a previous report, it was shown that the activity of Ga-promoted SZ catalyst gave a higher value than that of Al-promoted catalyst [8]. It was also concluded that Ga promotes SZ in a different way from Al promotion of SZ catalyst. However, there was no detailed understanding of the origins of the promotional effects.

In this paper, we would like to compare in details the promotional effects of Ga and Al on the SZ catalysis in butane isomerization. For the purpose of gaining larger surface area, we primarily use a special form of zirconia–mesoporous zirconia (named as MP-ZrO₂) which is synthesized by templating micelles of CTAB [11,16]. We are going to focus on the Ga-promoted sulfated mesoporous zirconia catalyst (denoted as GS/MP-ZrO₂) and compare it with the promoting effects of Al on sulfated mesoporous zirconia (AS/MP-ZrO₂) in the isomerization of *n*-butane. The two catalysts differ only in the precursor of promoters while the solid acid used is the same, e.g. sulfated mesoporous zirconia. Ga₂(SO₄)₃ was replaced by nearly the same amount of Al₂(SO₄)₃ (in mol%). In addition to the information about identification and relative quantification of acid sites on catalyst surfaces after chemisorption of probe molecules, other characterization techniques, such as TPR, in situ DRIFTS, and Baeyer tests of olefin were used to investigate these two different promoters in SZ catalyst.

2. Experimental

2.1. Catalyst preparation

The mesoporous ZrO₂ (named as MP-ZrO₂) was synthesized by the surfactant-assisted route, as in the previous report [16]. An ordered mesoporous ZrO₂ material loaded with aluminum sulfate (AS/MP-ZrO₂, Hayashi, Osaka), gallium sulfate (GS/MP-ZrO₂, Acrös), and ammonium sulfate (S/MP-ZrO₂, Acrös) was prepared via incipient wetness impregnation: the required quantity of each source dissolved in 75% (vol.%) alcohol solution was impregnated by the as-synthesized mesoporous zirconia-containing surfactant. The slurry was stirred for 5 h and oven-dried at 100 °C overnight. All the catalysts were calcined at 400 °C for 5 h to eliminate the template and then at 630 °C for 5 h to obtain the tetragonal phase of zirconia (in static air with a heating ramp of 3 °C/min). For the purpose of comparison, a conventional dense-phase catalyst (GS/Z-NP) was also prepared with similar loadings of Ga and S but

without the template. In the case of GS/Z-NP, amorphous zirconium hydroxide was used instead of the uncalcined MP-ZrO₂ precursor. Here, Z-NP represents dense-phase zirconia nanoparticles.

2.2. Characterization techniques

Elemental analysis was conducted 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.

In situ diffuse-reflectance infrared Fourier-transformed (DRIFT) spectra of ammonia chemisorbed on catalyst were taken with a Thermo Nicolet 380 FTIR spectrometer. The sample was first dried at 400 °C for at least 1 h prior to butane adsorption. The adsorption process was done by flowing butane gas ($\geq 99.9\%$, San-Fu) through the catalyst at 50 °C for 5 min and the system was then flushed with dry N₂ for 10 min. The catalyst with adsorbed butane molecules was then subjected to a desorption process at increasing temperatures. Spectra were recorded after the catalyst's temperature was held for 10 min at each temperature.

The Baeyer test was adopted to check for certain unsaturated olefin species produced during the *n*-butane isomerization. The reaction gases exiting the reactor were passed through a potassium permanganate aqueous solution with 5 ml of 0.5 μ M and the time-dependent UV–vis experiment was monitored with a Hitachi U-3310 spectrophotometer.

2.3. Catalytic study

Catalytic reaction was carried out in a fixed bed continuous flow quartz reactor at atmospheric pressure. Each catalyst (usually 1.0 g) was first pressed into 10–20 mesh size pellets and mixed with quartz sand. It was then pretreated under an air flow at 450 °C for 3 h, and then pre-reduced with H₂ at 300 °C for 1 h. After flushing the system with N₂ at the reaction temperature for 0.5 h, the reaction was started by introducing a mixture of *n*-butane and H₂ (*n*-C₄:H₂ = 1:10, v/v) at a total inlet flow rate of 15.5 ml min^{−1}. The reaction product was analyzed using an on-lined Agilent 6890N gas chromatograph equipped with a flame ionization detector and a 60 m DB-1 column.

3. Results and discussion

3.1. Texture properties of the catalysts

Textural properties of various sulfated mesoporous zirconia catalysts, including alumina or gallium or without any promoters, were characterized by X-ray diffraction and N₂ adsorption–desorption isotherm. X-ray diffraction patterns (not shown here) for the mesoporous zirconia catalysts generally exhibited a single broad peak at $\sim 1.0^\circ$ due to their disordered mesostructure, while the angle peaks show the tetragonal structure of zirconia. It has been shown that surface area and mesoporosity do matter in the catalytic activity of SZ [17]. Thus we use mesoporous zirconia as templated by CTAB [11,15]. This leads to high surface area and many mesopores, which are advantageous to transport of reactants. In Table 1, one can see that the nanoparticle form of Al-promoted SZ catalyst has a surface area of 73 m²/g which is normal compared to other reported results [18]. All the mesoporous samples in Table 1 show about twice the surface area compared with that of 3AS/Z-NP. This leads to a higher loading of sulfur (Table 1).

The calcination temperature was also shown to be important for higher catalytic activity [19]. Previously, we used mesoporous sulfated zirconia catalysts calcined at 630 °C to give the optimum

Table 1
Elemental analyses, texture properties, and catalytic results of catalysts.

Catalyst ^a	Surface area (m ² /g) ^b	Pore volume (cm ³ /g)	Pore diameter (Å)	Loading (wt%) ^c		
				Ga	Al	S
3GS/MP-ZrO ₂	148.0	0.10	29.9	3.40	–	3.95
2GS/MP-ZrO ₂	137.4	0.08	30.7	2.30	–	2.95
1GS/MP-ZrO ₂	139.1	0.09	30.2	0.90	–	1.79
3AS/MP-ZrO ₂	151.2	0.11	31.3	–	2.20	3.83
2AS/MP-ZrO ₂	150.8	0.10	31.0	–	1.45	2.89
3S/MP-ZrO ₂	121.6	0.08	29.3	–	–	0.29
MP-ZrO ₂	144.0	0.12	32.1	–	–	–
3AS/Z-NP	73.0	–	–	–	2.11	3.61

^a All catalysts above were calcined at 630 °C for 5 h.

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

^c Determined from ICP-AES and EA.

catalytic activity in the *n*-butane isomerization reaction [15]. When one compared the effects on surface area and pore sizes, the loadings of Al and Ga give similar results. A finding in our elemental analysis study is that the amount of Ga or Al loaded onto the catalyst has a direct influence on the amount of sulfur in the catalyst. From the sulfur content in Table 1, one can see that both Al and Ga increase the sulfur loading in a roughly similar fashion. Thus, we conclude that the effects of Al and Ga are quite similar in affecting the textural properties and the loadings of sulfur. Both increase the surface area and the retention of sulfur in a similar fashion.

3.2. Catalyst properties and catalytic performance

To obtain some idea on the catalytic performance of various sulfated zirconia catalysts, we turned to *n*-butane isomerization reaction as the test reaction for the sulfated zirconia catalyst system. Under our standard reaction conditions (see Section 2), the main product in *n*-butane isomerization was isobutane (selectivity > 85% at 250 °C, *n*-butane/H₂ = 1/10 (v/v), and 0.62 h^{−1} WHSV). The selectivity for isobutane was higher if the reaction temperature was lowered to 200 °C, even to 100 °C.

Fig. 1 compares the catalytic activities of some selected GS/MP-ZrO₂, AS/MP-ZrO₂, and 3AS/Z-NP, and that of un-doped MP-ZrO₂ support in *n*-butane isomerization reaction at 250 °C. The effects of Ga and Al promoters on the catalytic performance were investigated by varying their loading. For most catalysts, the activity decays (but not too seriously) during the initial 120 min of reaction and then reaches a steady state. One can see that the

Fig. 1. The catalytic conversion of a series of sulfated zirconia catalysts calcined at 630 °C. Reaction conditions: reaction temperature = 250 °C, *n*-butane/H₂ = 1/10 and WHSV = 0.62 h^{−1}.

butane conversion of 3GS/MP-ZrO₂ is nearly twice that of 3AS/MP-ZrO₂ (best Al promoted catalyst) and much higher than that of unpromoted sulfated mesoporous zirconia catalyst (3S/MP-ZrO₂).

In addition, the influence of catalyst support on the catalytic activity was also checked by comparing sulfated zirconia with both mesoporous and dense-phase nanoparticle supports (denoted by “Z-NP”). Since the effective gallium active sites are directly proportional to the surface area of the support, the catalytic performances of catalysts with MP-ZrO₂ structure are higher than that with Z-NP, as expected.

3.3. Surface acidity

In our previous work, we had shown that the Brønsted acid sites played a very important role in the *n*-butane isomerization reaction [11,15]. As these sites are involved directly in the formation of carbenium ion, which is an important intermediate in allowing the following oligomerization processes to proceed, the sites have a direct influence on the initial activity and coke formation of GS/MP-ZrO₂ catalyst in butane isomerization. Therefore, an understanding of the acidity of these catalysts is of primary importance.

In order to study the Brønsted acidity of GS/MP-ZrO₂ catalysts and to compare the results with the corresponding previously studied alumina-promoted catalysts (AS/MP-ZrO₂), we adopted TPD-MS and in situ DRIFT techniques that are commonly used in such work. Ammonia was chosen as the probe molecule for the distribution of acid sites on these catalysts.

We first compared the amount and strength of the acid sites in 3GS/MP-ZrO₂, 3AS/MP-ZrO₂, and 3S/MP-ZrO₂ samples by mass spectra detection of temperature programmed desorption of ammonia (NH₃-TPD-MS) (Fig. 2). The ammonia TPD pattern appears to be similar to those reported before by other researchers [18]. The TPD peak at very high temperature (above 700 °C) is due to ammonia-induced decomposition of sulfate group. The TPD peaks at lower temperature can be used for qualitative investigation of the strength of the acid sites. Two desorption maxima are observed: (a) a broad peak at 200–400 °C due to weak acidic sites of wide distribution of strengths and (b) a shoulder near 500 °C due to stronger acidic sites. The two catalysts, 3GS/MP-ZrO₂ and 3AS/MP-ZrO₂ catalysts, show similar acidity in both strengths and amounts (the integrated intensity of the NH₃ desorption profiles in 3GS/MP-ZrO₂ is actually a little lower than that of 3AS/MP-ZrO₂). On the other hand, unpromoted 3S/MP-ZrO₂ catalyst has much less surface acidity. In particular, the shoulder at 500 °C due to stronger acidic sites almost disappeared.

The important feature is the relatively strong NH₃ desorption peak centered at 490 °C which falls within the temperature range of strong acid catalysts such as in zeolites. Previously, we have shown that the strong Brønsted acid sites in our AS/MP-ZrO₂

Fig. 2. NH_3 -TPD profiles of 3AS/MP- ZrO_2 , 3GS/MP- ZrO_2 , and 3S/MP- ZrO_2 catalysts.

catalysts are due to isomorphous substitution of the framework Zr^{4+} by Al^{3+} in our catalyst system [15]. Recently, Pereira et al. found that isomorphous substitution of the framework Zr^{4+} by Fe^{3+} gives strong acidity in Fe-promoted sulfated zirconia [20]. We believe that Ga^{3+} ions play similar roles in substitution of Zr^{4+} ions in GS/MP- ZrO_2 . In the profile of 3GS/MP- ZrO_2 , this peak is somewhat less prominent, which may be due to the larger size of Ga^{3+} with respect to Al^{3+} making it less efficient in undergoing such substitution processes.

The in situ DRIFT technique was employed for obtaining further information on the relative strengths of the Brønsted and Lewis acid sites on these catalysts. Fig. 3 shows the DRIFT spectra of these catalysts after the desorption of surface-adsorbed NH_3 at different temperatures. Two types of acid sites were found on these catalysts: namely, the Brønsted acid sites (B) and the Lewis acid sites (L). The assignment of IR bands was made according to the published works [15,21]. The band at 1609 cm^{-1} corresponds to the asymmetric N–H deformation mode (δ_{as}) of NH_3 coordinated to the Lewis acid sites. Another intense band at 1428 cm^{-1} and the weak band at 1675 cm^{-1} correspond to the δ_{s} and δ_{as} of NH_4^+ formed on the Brønsted acid sites, respectively. The bands in the region below 1373 cm^{-1} are mainly due to the lattice vibrations of

m- ZrO_2 . One can see there are more Brønsted acid sites in 3AS/MP- ZrO_2 than in the other two catalysts, judging from the peak intensity. Besides, it also retained more chemisorbed ammonia as the catalyst was heated to $400\text{ }^\circ\text{C}$ than the other catalysts. In other words, 3AS/MP- ZrO_2 has more strong Brønsted acid sites than either 3GS/MP- ZrO_2 or 3S/MP- ZrO_2 .

Upon desorption at $400\text{ }^\circ\text{C}$, NH_4^+ is the main species remaining. Indeed, the strength of the Brønsted acid sites in 3AS/MP- ZrO_2 and 3GS/MP- ZrO_2 catalysts is higher than that of the Lewis acid sites. It follows that 3AS/MP- ZrO_2 has more strong Brønsted acid sites than 3GS/MP- ZrO_2 and 3S/MP- ZrO_2 do. Certainly, sulfated mesoporous zirconia catalyst promoted by aluminum brings even greater contributions to the acidity of the catalyst than that by gallium under the present metal loadings.

It is worth mentioning that 3GS/MP- ZrO_2 catalyst has relatively higher catalytic activity than 3AS/MP- ZrO_2 notwithstanding the fact that it has lower surface acidity as revealed by TPD and DRIFT analysis. Focusing only on the acidity enhancement by alumina or gallium promoters seems to be contradictory to the results of catalysis in isomerization reaction. Thus in next section, we examine the redox properties of 3GS/MP- ZrO_2 catalyst and correlate them with its catalytic performance.

3.4. Redox measurements

Previously, the redox properties of sulfated zirconia had been correlated to the activation of *n*-alkane [13,14]. A bifunctional catalysis mechanism (initiation by redox processes followed by acid catalysis) was proposed and used to explain the differences in catalytic activity between sulfated zirconia and Fe–Mn promoted sulfated zirconia [22]. For studies of the effect of Ga on the redox properties of sulfated mesoporous zirconia, H_2 -TPR technique was used. The redox characteristics of 3GS/MP- ZrO_2 were evaluated and compared to those of the 3AS/MP- ZrO_2 and 3S/MP- ZrO_2 samples.

A TPR instrument equipped with a quadrupole mass spectrometer was employed to investigate the effects of gallium and alumina promoters on the redox properties of sulfated mesoporous zirconia catalysts. TPR profiles in the temperature range from 100 to $850\text{ }^\circ\text{C}$ and the relevant mass analyses are shown in Fig. 4. The 3S/MP- ZrO_2 sample (Fig. 4(c)) displays a reduction peak with a maximum centered at $\sim 665\text{ }^\circ\text{C}$. The Al-promoted catalysts 3AS/MP- ZrO_2 show a reduction peak (Fig. 4(b)), a little higher than that of 3S/MP- ZrO_2 , with its maximum at $\sim 704\text{ }^\circ\text{C}$. The higher reduction temperature of 3AS/MP- ZrO_2 catalyst relative to 3S/MP- ZrO_2

Fig. 3. DRIFT spectra of the adsorption of NH_3 at $120\text{ }^\circ\text{C}$ on 3S/MP- ZrO_2 , 3AS/MP- ZrO_2 , and 3GS/MP- ZrO_2 catalysts, followed by desorption at 250, 350, $400\text{ }^\circ\text{C}$ (B: Brønsted acid sites and L: Lewis acid sites).

Fig. 4. H_2 -TPR analysis and mass spectra of the gases evolved during the TPR process.

seems to indicate strong interactions between Al and S, as we have suggested before based on elemental analysis results. However, much different from the two catalysts above, the Ga-promoted catalyst 3GS/MP-ZrO₂ exhibits a strong reduction peak shifted to lower temperature with two maxima of different intensity, centered at 500 and 590 °C, respectively.

The TPR experiments show that the doublet reduction peaks corresponding to the reductions of S⁶⁺ species (SO₄²⁻) to S⁴⁺ (SO₂) and to S²⁻ (H₂S) species respectively. In the above cases, most of the SO₄²⁻ species were reduced to SO₂ (detected at both *m/e* = 64 and 48); however, except for the 3GS/MP-ZrO₂ catalyst, no obvious formation of H₂S (*m/e* 34) were detected in the cases of 3S/MP-ZrO₂ and 3AS/MP-ZrO₂, which suggests a much greater enhancement of sulfate reduction by Ga. In addition, the mass spectra peak at *m/e* 18 indicates H₂O desorbing from the surfaces of catalysts during the H₂-TPR process. Sauer and co-workers [13] have successfully shown that butene, water, and sulfur dioxide species were formed during *n*-butane isomerization on sulfated zirconia catalysts through oxidative dehydrogenation of *n*-butane. In our case, the formation of water (*m/e* 18) shows that the amount of surface water produced by oxidative dehydrogenation of *n*-butane decreased in the order of 3GS/MP-ZrO₂ > 3AS/MP-ZrO₂ > 3S/MP-ZrO₂. This phenomenon suggests that gallium is likely to play more the role of a redox promoter rather than an acid promoter like aluminum.

Fig. 5 illustrates in situ DRIFT spectra of the calcined 3GS/MP-ZrO₂ catalyst, before and after activation, and upon adsorption and desorption of butane at various temperatures. Before activation, the spectra are typical of hydrated surfaces with adsorbed water peaks over the 1600–1700 cm⁻¹ range. Activation process in a dry air flow results in strong reduction of this broad band, consistent with dehydration, and the spectrum of the activated sample exhibits an distinctive band at 1390 cm⁻¹ (Fig. 5(b)), which is assigned to the stretching vibration of the S=O bond in an adsorbed SO₃ molecule [23]. The band at 2850–3010 cm⁻¹ (Fig. 5(a)) after butane adsorption corresponds to butane adsorbed on 3GS/MP-ZrO₂ surface [24]. In the initial process of desorption, the IR bands correspond to the butane molecules appeared

strongly at low temperatures (50 °C) due to a large amount of physisorption. Even so, they decrease much at 100 °C and nearly vanish above 150 °C. Apparently, there is some conversion of butane already on 3GS/MP-ZrO₂ at a low temperature between 50 and 100 °C. Previously, Klose et al. studied DRIFT spectra of butane adsorption on sulfated zirconia (SZ) and Fe- and Mn-promoted SZ (FeSZ and MnSZ). They found no reaction of butane for SZ until 200 °C. In contrast, FeSZ and MnSZ show reactions at 100 °C [24]. Our Ga-promoted MP-ZrO₂ is more reactive at a lower temperature.

Another interesting feature in Fig. 5 is that 3GS/MP-ZrO₂ catalyst with its stretching vibration of the S=O bond located at 1390 cm⁻¹ shifted downward to 1370 cm⁻¹ when exposed to butane molecules. As the desorption temperature increased, the vibration band shifted upward in the range of 1370–1384 cm⁻¹. This phenomenon suggests that there are certain kinds of interaction between butane molecules and the sulfate sites on 3GS/MP-ZrO₂ catalyst during the isomerization reaction. It is reasonable for us to suggest that, on a 3GS/MP-ZrO₂ catalyst, a labile SO₃ surface species is likely to be the active site involved in the butane isomerization reaction. At the same time, the formation of water during desorption process is shown by the increasing intensity of the deformation band of water at 1600 cm⁻¹ (Fig. 5(b)) with the disappearance of the adsorbed butane molecules (Fig. 5(a)). The gradual formation of water on 3GS/MP-ZrO₂ catalyst also indicates that the butane molecules were initiated via oxidative dehydrogenation by SO₃ groups, as we proposed previously in Al-promoted SZ [15]. Such SO₃ species react with butane to give butene, which is the starting species for the rest of acid-catalyzed isomerization reactions:

Similar methods were applied to the other two samples: 3AS/MP-ZrO₂ and 3S/MP-ZrO₂ [15]. The amount of produced water detected on these three catalysts versus the desorption temperatures is plotted in Fig. 6. This shows that the amount of surface water produced by oxidative dehydrogenation on catalytic surfaces

Fig. 5. In situ DRIFT spectra of 3GS/MP-ZrO₂ catalyst recorded before and after activation and followed by desorption at the range from 100 to 250 °C after the adsorption of *n*-butane at 50 °C on the activated catalyst. Finally, the catalyst was regenerated with an air flow at 400 °C.

Fig. 6. Correlation between the oxidative dehydrogenation abilities of 3AS/MP-ZrO₂, 3GS/MP-ZrO₂, and 3S/MP-ZrO₂ samples and the concentration of water observed by in situ DRIFT during the period of butane desorption.

decreased in the order of 3GS/MP-ZrO₂ > 3AS/MP-ZrO₂ > 3S/MP-ZrO₂. The correlation between the intensity of the deformation band of water and the increase of catalytic activity of butane isomerization indicates that the catalytic performance increases in direct proportion with the amount of butane oxidized to butene.

Finally, as previously done in Ref. [15] for Al-promoted SZ, we employed the Baeyer test – a simple method to check for the presence of alkenes with aqueous potassium permanganate (KMnO₄) – to explore whether certain unsaturated olefin species were produced upon interacting butane with our catalysts in the initiating step of butane isomerization. Since MnO₄[−] is purple and MnO₂ is light brown, this color change can be easily used to assay for the presence of alkenes. Fig. 7 manifests the corresponding evolution of UV–vis spectra of KMnO₄ aqueous solution at room temperature upon reacting with the effluent of butane passing through the catalyst. Potassium permanganate is a powerful oxidant and we can attribute the formation of MnO₂ to the direct redox reaction between olefin species and KMnO₄. With the elapsed reaction time, it can be easily seen that three peaks at about 315, 525, and 545 nm, which originated from KMnO₄, gradually disappeared with the concurrence of a new peak shifted to 370 nm, which indicated the formation of MnO₂ aqueous solution. One notes that the spectra corresponding to KMnO₄ reduction to MnO₂ by the species generated from the 3GS/MP-ZrO₂ catalyst change much more than that for the other catalyst 3AS/MP-ZrO₂ at the same condition. The difference shows that sulfated mesoporous zirconia promoted by gallium possesses higher redox ability resulting in more butene species, the crucial intermediate during *n*-butane isomerization, than those from alumina-promoted catalyst.

Fig. 7. Time-dependent UV–vis spectra of KMnO₄ aqueous solution used to check certain unsaturated olefin species produced by 3AS/MP-ZrO₂ and 3GS/MP-ZrO₂ samples during the *n*-butane isomerization.

promotional effect of Al. Let us first summarize the effect of Ga and Al loadings on the structure and composition of the catalyst. From Table 1, one can see that both Ga and Al increase the sulfur loading. The increased sulfate groups have four consequences: (1) stabilizing the active tetragonal crystalline phase of zirconia, (2) increasing the total surface area, (3) enhancing the Brønsted acidity, and (4) increasing the oxidative dehydrogenation [15]. The first two effects ((1) and (2)) have been extensively discussed before, so we will not deal with them here. The last two factors, acidity and redox properties, are in fact more important because they are directly related to the reaction mechanism. For the purpose of discussion here, let us now examine a simplified mechanism shown below [25]. The first step (1) is the dehydrogenation step to form butene. Then step (2) follows on an acid site to produce the carbenium ion. Step (3), the isomerization chain reaction, is rather complex. It requires surface acidity. We ignore details in the isomerization chain reaction, either monomolecular or bimolecular. But a linear chain reaction is involved in step (3) which generates another butane to start at step (2) again. The final hydride transfer (step (4)) gives iso-butane.

4. Discussions

In this section, we would like to discuss the origin of the excellent promotional effect of Ga and Al on sulfated zirconia in the isomerization of butane. Since we have just investigated recently in great detail the case of Al-promotion [15], the discussions here will be mainly focused on the case of Ga as compared with the

In principle, one could have infinite chain length and 100% selectivity; that is, for every isobutene formed, another olefinic species may be formed to continue the chain. Then, step (1) would not be very important. In reality, continuous generation of olefinic species is important for sustained activity because of finite chain length and of coke formation blocking some active sites. From kinetic considerations, a steady rate of isomerization is the result of

balancing the rates of dehydrogenation step (1) and acid-catalyzed isomerization step (3). For a steady activity, a high rate of dehydrogenation demands a matching high rate of isomerization. If the rate of dehydrogenation is higher than the isomerization/desorption rate initially, coke will form, leading to deactivation. On the other hand, if the dehydrogenation rate is too low, the surface acid sites are under-used.

With the above analysis, we can then try to understand the differences in catalytic activities between Ga and Al promoted sulfated zirconia. Specifically, when one compares the two catalysts 3GS/MP-ZrO₂ and 3AS/MP-ZrO₂, one finds that they have almost identical sulfur content and surface area. As a consequence, the two catalysts, 3GS/MP-ZrO₂ and 3AS/MP-ZrO₂ catalysts, show very similar acidity in both strengths and amount. Then it is clear that the reason 3GS/MP-ZrO₂ gives higher activity must be due to higher production of butene from the dehydrogenation step. For the above two catalysts, the comparisons of the redox properties by TPR, Bayer's tests of olefin production and DRIFT studies of evolved water upon oxidative dehydrogenation all indicate the higher initiation rate in step (1) in Ga-promoted SZ catalyst. Gallium oxide has been known to promote activation of C–H bond in hydrocarbons [26]. Compared with Al-promoted SZ, the extra acid reservoir in SZ apparently could be further used when Ga-promotion leads to more production of butene and thus to carbenium intermediates.

In the past, other promoters for sulfated zirconia have been used, including Fe, Mn and Pt. However, Fe and Mn promoted SZ catalysts usually start with high initial rate but then deactivate quickly. It is known that Fe and Mn do not increase the surface acidity while promoting dehydrogenation [24,27]. This probably leads to relative over-production of surface olefin species, which then leads to coke formation. On the other hand, Ga and Al promotion of SZ appear to be both active in the oxidative dehydrogenation and also in the increase of surface acidity. Both steps (1) and (3) have to be increased to result in an increase of the steady rate of isomerization. Another often used promoter for SZ catalyst in isomerization is Pt/H₂ [28,29]. The Pt metal has been proposed to be bifunctional in providing both the dehydrogenation–hydrogenation function and in hydrogen spill-over to increase acidity [29]. However, in most of the reported studies, Pt/H₂ probably served more in hydrogenation rather than dehydrogenation as hydrogen served to depress the reaction rate [30].

Furthermore, Al and Ga have been found not only to increase the total amount of surface acidic sites but also to change the balance of the types of surface acidity. In our previous study of the acidity of Al-promoted sulfated zirconia [11], we have identified by XPS measurement of adsorbed pyridine three kinds of acid sites: one Lewis acid (L), one strong Brønsted (SB) and one weak Brønsted (WB) site. It was found that too much of SB often gives a high initial rate but the material quickly deactivates. A larger number of SB sites promote the initial rate of reaction. However, this will also promote coke formation. In order to sustain the reaction through the later stages of reaction, there must be many WB sites which are less susceptible to deactivation by coke formation. WB sites played an important role in the steady stages of reaction. Apparently, the optimum amount of Al or Ga loading would give the optimum distribution of the type of acid sites.

5. Conclusions

In conclusion, we have investigated the promotional effect of alumina and gallium to mesoporous SZ on the butane isomeriza-

tion. There are two mechanisms of metal promotion of catalytic activities. First, in the promoted acidity, Al is a slightly better promoter than Ga, giving more acidity in mesoporous sulfated zirconia. On the other hand, both metals also promoted the redox properties in mesoporous sulfated zirconia. The doping of alumina or gallium to SZ increased the extent of sulfur retention on the surface of zirconia, which then promotes the oxidative dehydrogenation to butene and consequently the skeleton isomerization. Ga turns out to be a much stronger promoter of the redox property of SZ, giving more butene than Al-promotion. Overall, Ga-promoted sulfated mesoporous zirconia gives better catalytic activity in butane isomerization than the corresponding Al-promoted sulfated mesoporous zirconia. It is important to achieve an optimum balance in the initial rate of butene formation by oxidative dehydrogenation and the subsequent rate of acid-catalyzed isomerization. Apparently, Ga-promoted sulfated zirconia is the best catalyst in achieving such a fine balancing act. The GSZ catalyzed isomerization reaction also does not need any Pt to stabilize its long term activity. The Pt-free catalyst is attractive as a practical industrial catalyst.

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