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n-Pentane isomerization over promoted SZ/MCM-41 catalysts

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Abstract

With metal sulfate as the precursor, the catalysts of sulfated zirconia on MCM-41, Al- and Ga-promoted sulfated zirconia on MCM-41 (named as SZ/MCM-41, ASZ/MCM-41 and GSZ/MCM-41, respectively) were prepared by direct dispersion in the as-synthesized MCM-41 materials, followed by thermal decomposition. The catalysts were characterized with various techniques such as XRD, FTIR, N_2 adsorption, NH_3-TPD, DRIFT, and TPR-MS. The ordered porous structure was still maintained in the catalysts. The addition of promoters helps to retard the phase transformation of ZrO_2 from tetragonal phase to monoclinic phase. Isomerization of *n*-pentane was investigated over the catalysts. In comparison to SZ/MCM-41, both promoted catalysts showed much improved catalytic activity and selectivity for isomerization of *n*-pentane. Moreover, the catalytical activities of both promoted catalysts for pentane isomerization remained steady over the period of 180 min while the activities of the unpromoted catalyst decreased in <120 min. Characterization of acidity showed no significant difference in strength distributions of the acid sites over the catalysts. The nature of acid sites in SZ/MCM-41 was affected by the presence of aluminum, but not affected by the presence of gallium. On the other hand, TPR study shows sulfur on GSZ/MCM-41 is much easier to reduce than SZ/MCM-41 and ASZ/MCM-41. The presence of gallium improved the redox capability provided by the sulfate ions in GSZ/MCM-41 catalyst. The causes for the promotion effects of Ga and Al are discussed.
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1. Introduction

The trend of existing and forthcoming regulations on gasoline has highlighted the need for ''clean'' high-octane molecules in the gasoline pool. To increase the octane number of the gasoline pool, the light straight run (LSR) gasoline fraction of oil need to be isomerized and in this way its research octane number (RON) increases from ∼64 to ∼80. This increase is achieved by isomerizing *n*-pentane and *n*-hexane, which are the main components of LSR. Isomerization of *n*-pentane and *n*-hexane has the right combination of RON/MON properties and compliance with environmental regulations. The commercial catalysts used for carrying out this isomerization are Pt on chlorinated alumina and Pt/H-mordenite. However, a major drawback of the former is the sensitivity to water and sulfur even in concentrations as low as 10 ppm. On the other hand, the latter requires higher reaction temperature (250 °C) with the corresponding 2-point RON penalty. The environmental problems with the regeneration of these catalysts have also revived interest in halogen-free isomerization catalysts.

Solid acid catalysts are required for the isomerizations of alkanes and a renewed interest in their use is noticeable in the last few years. Among them, sulfated zirconia is attractive since it offers a nice alternative to the corrosive halogen-containing solid acids in the skeletal isomerization of light linear alkanes at low temperature. Much work has been devoted to sulfated zirconia and discussed in several reviews [1–7]. These catalysts exhibit high initial activity that may decline rapidly unless certain metals are present. In

fact, incorporation of Pt leads to a SZ catalyst that retains its activity for a much longer period of operation than the metal-free SZ [8–13]. In the case of *n*-pentane isomerization, the de-activation was more severe if no Pt metal is added to the catalyst. However, even with platinum insertion the catalytic activity is still relatively low. Similarly, some transition metals, such as Fe, Mn [14–17], incorporations have been reported capable of enhancing *n*-alkane conversion activity. However, after an induction period during which a maximum activity is obtained, the performance of these metal-promoted SZ catalysts tends to decline with time also [18].

An important factor affecting the performance of the solid acid catalyst is its texture porosity. Typically, surface areas for active SZ is about $100 \, \text{m}^2/\text{g}$ in the tetragonal crystalline phase. However, recently Risch and Wolf reported mesoporous sulfated zirconia catalyst with surface area $269 \, \text{m}^2/\text{g}$ and obtained significantly higher activity for isomerization of butane and pentane [19]. Therefore, it is desirable to design a sulfated zirconia catalyst system with both mesoporosity and metal promoter simultaneously to gain both high activity and stability. Several papers have been published on the preparation and applications of SZ supported on various mesoporous silica [20–23].

Recently, we have reported elsewhere that the addition of small amounts of main group metals, such as Al [24,25] and Ga [26] to the sulfated zirconia on mesoporous MCM-41 gives rise to the catalysts much more active than the corresponding unpromoted sulfated zirconia on MCM-41 for *n*-butane isomerization at $250 \, °\text{C}$ in the presence of H_2. The results suggest that the same catalysts might be useful for isomerization of other light alkanes. In the present work, isomerization of *n*-pentane was investigated over SZ/MCM-41, ASZ/MCM-41, and GSZ/MCM-41 catalysts. The activities of promoted catalysts for *n*-pentane isomerization with changing reaction temperature were studied. Addition of Al and Ga prevented the rapid deactivation of the catalyst. The catalysts were characterized by XRD, FTIR, N_2 adsorption, NH_3-TPD, DRIFT, and TPR-MS. The reasons for the improvement on activity and stability of the catalysts in *n*-pentane isomerization by the addition of promoters are discussed.

2. Experimental

2.1. Catalysts preparation

As-synthesized pure siliceous MCM-41 was synthesized with the delayed neutralization process [27]. The as-synthesized mesoporous material was impregnated with a desired amount of $Zr(SO_4)_2$ in methanol and stirred for 15 h at room temperature. The resulting sample was dried at $80 \, °\text{C}$. Finally, it was calcined at $660 \, °\text{C}$ for 3 h in air. Ga- and Al-promoted samples were prepared in the same way

with the desired amount of zirconium sulfate and gallium sulfate or aluminum sulfate mixture. ZrO_2 content was kept at 50 wt.% on each sample.

2.2. Catalysts characterization

XRD patterns of the samples were obtained on a Bruker D8 Advance instrument with Cu Kα radiation at 40 kV and 30 mA. FTIR absorption spectra were recorded on a Nicolet 550 spectrometer using a KBr pellet. About 1 mg of sample was mixed with 300 mg of dried KBr and then pressed. The surface area and pore size distribution measurements were carried out on a Micromeritics ASAP 2010 automatic adsorption instrument using N_2 gas. Sulfur content in the catalysts was detected by a chemical method. The sulfate was turned into $BaSO_4$ and determined by gravimetric method. The TPR and NH_3-TPD were carried out on a Micromeritics AutoChem 2910 instrument. In NH_3-TPD experiment, about 100 mg of dried sample was pre-treated at $500 \, °\text{C}$ under ultra-high pure helium (50 ml/min) for 1 h and then cooled to $120 \, °\text{C}$. After introducing 3% NH_3 in He at $120 \, °\text{C}$ for 0.5 h, the sample was flushed with helium for 1.5 h. The TPD profile of ammonia was obtained from 120 to $720 \, °\text{C}$ at a heating rate of $10 \, °\text{C/min}$. In TPR experiment, about 80 mg of dried sample was pre-treated at $500 \, °\text{C}$ under air (40 ml/min) for 1 h and then cooled to $120 \, °\text{C}$. The TPR profile was recorded in 10% H_2/Ar of 40 ml/min from 120 to $800 \, °\text{C}$ at $15 \, °\text{C/min}$. The desorption process was monitored by a Quadruple Mass Spectrometer (Thermo ONIX, ProLab) connected on-line through a heated capillary interface. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of the samples were recorded using a BOMEM MB155 FT-IR/Raman spectrometer. The equipment was furnished with an in situ sample cell (Harrick). The sample was pre-heated at $300 \, °\text{C}$ for 3 h under 10^{-6} mbar vacuum before pyridine vapor was introduced at room temperature, followed by evacuation for 1 h.

2.3. Catalytic tests

The isomerization of *n*-pentane was performed in a fixed-bed continuous flow reactor. The catalyst samples were palletized and sized to 20/60 mesh. Approximately 0.7 g of the catalyst was loaded into the steel reactor and then pre-treated at $450 \, °\text{C}$ in flowing dry air (20 ml/min) for 3 h at atmospheric pressure. The reactor temperature was then lowered to the desired reaction temperature, mostly $180 \, °\text{C}$ or other desired temperature. After thermal equilibrium was established, the unit was pressurized with hydrogen to 2.0 MPa. *n*-Pentane was fed into the reactor using a high-pressure pump. Hydrogen and *n*-pentane flow rates were adjusted to give a 5 H_2/*n*-C5 mole ratio. The *n*-pentane weight hourly space velocity (WHSV) is $3.0 \, \text{h}^{-1}$. An on-line gas chromatograph equipped with FID was used to analyze the reaction products.

3. Results

3.1. Crystalline structure of catalysts

Fig. 1 shows the powder XRD patterns of the SZ/MCM-41 and the promoted catalysts. As can be seen, all samples show a diffraction peak due to the (1 0 0) reflection of MCM-41 at low 2θ ranges, which is usually used to characterize the ordered porous structure. The XRD results show that the structure of the mesoporous molecular sieve is still well-maintained after the loading of the catalyst. Fig. 1 also gives very weak and broad reflections in the higher 2θ range (above 30°). This suggests that very small sulfated zirconia particles were formed. When the XRD patterns at higher ranges are magnified ten times, it can be seen that a small amount of monoclinic ZrO_2 phase, which is less active than tetragonal $ZrO2$ phase, is presented in SZ/MCM-41 along with the tetragonal ZrO_2 phase. For the promoted catalysts only the tetragonal phase can be observed. It is reported that the dispersion threshold of zirconium sulfate is ca. 0.26 g/100 m^2 on silica [28]. Monoclinic ZrO_2 phase was observed when the $Zr(SO_4)_2$ loading was above the dispersion threshold. In our experiment, zirconium sulfate content was kept at 0.268 g/100 m^2 on each support, which is slightly above the dispersion threshold of zirconium sulfate on MCM-41. These results indicate that the transformation from the metastable tetragonal phase to the monoclinic phase is retarded in the presence of promoters.

To confirm further the retardation of the phase transformation of ZrO_2 from tetragonal phase to monoclinic phase for the promoted catalysts, a systematic study using IR technique was undertaken. The MCM-41 calcined at 660 °C was used for comparison. Fig. 2 shows the FTIR spectrum of the catalysts. The spectrum of SZ/MCM-41 presents one band due to Zr–O bond vibrations. It is situated at 750 cm^{-1} and assigned to m-$ZrO2$ [29]. However, it disappeared with the addition of promoters. It indicates that the tetragonal
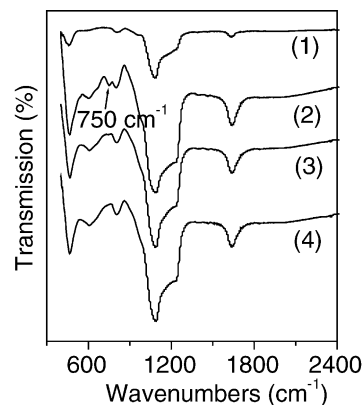
Fig. 2. FTIR spectra of (1) MCM-41, (2) SZ/MCM-41, (3) ASZ/MCM-41, (4) GSZ/MCM-41.

phase of ZrO_2 may have been stabilized by the addition of promoters.

3.2. Physico-chemical properties of samples

The N_2 adsorption/desorption isotherms were measured and pore size distributions of SZ/MCM-41 were calculated. These samples show type IV isotherms as they are expected for mesoporous systems. Table 1 shows the sulfur content, BET surface area, pore volume, and pore diameter of the catalysts. Data of the parent MCM-41 carrier is also given in Table 1 for comparison. The surface areas of samples were decreased with the deposition of sulfated zirconia modified samples in comparison to that of parent MCM-41, and the pore volume values were also decreased at the same time. The pore diameter of SZ/MCM-41 is less than that of the siliceous MCM-41 support. These results indicate that the supported sulfated zirconia has been well-dispersed into the mesopores of MCM-41. However, the surface area of the catalysts is still over 300 m^2/g, which is larger than that of the traditional sulfated zirconia, typically below 100 m^2/g [30]. The sulfur content increases with the incorporation of promoter. There is a very small difference between ASZ/MCM-41 and GSZ/MCM-41 catalysts as far as its effect on sulfur loading is concerned. It may be explained that promotion with Ga and Al had a favorable effect on sulfate retention with respect to SZ/MCM-41 catalyst during calcinations of the catalysts.

3.3. Surface acidity studies of the catalysts

Two methods were used to characterize the acidic properties of the samples: the NH_3-TPD was used to characterize the acid strength distribution of the catalysts. DRIFT spectroscopy was carried out in order to distinguish between Lewis and Brønsted acid sites.

The NH_3-TPD spectra of the catalysts are shown in Fig. 3. These catalysts are characterized by similar broad desorption patterns peaked at 215 °C, spanning in the range
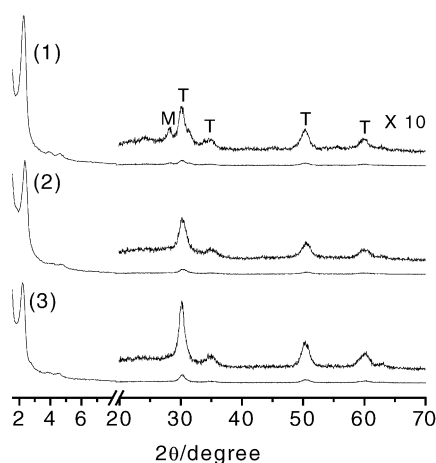
Fig. 1. X-ray diffraction patterns of the catalysts calcined at 660 °C. (1) SZ/MCM-41, (2) ASZ/MCM-41, (3) GSZ/MCM-41. T, tetragonal phase; M, monoclinic phase.

Table 1
Physico-chemical properties of the supported catalysts and the support

Sample	Sulfur content (wt.%)	BET S.A. (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SZ/MCM-41	1.01	407	0.262	2.17
ASZ/MCM-41	1.45	320	0.239	2.07
GSZ/MCM-41	1.46	318	0.231	2.17
MCM-41	–	857	0.703	2.33

150–550 °C and asymmetric on the high temperature side. This feature suggests the presence of sites with wide range of different acid strength. It is also found that there is no significant overall difference in the strength of acid sites with the addition of the promoters.

Fig. 4 shows the DRIFT spectra of the pyridine adsorbed samples at different temperature. Inspection of the spectra clearly shows that both Brønsted acid sites and Lewis acid sites are present on ASZ/MCM-41. When the promoter Al_2O_3 was introduced, the band at 1540 cm^{-1} corresponding to pyridine adsorbed on Brønsted acid sites appeared. However, the infrared spectra of both GSZ/MCM-41 and SZ/MCM-41 show that Lewis acid sites were dominant. The peak at 1540 cm^{-1} was not observed. Clearly, the nature of acid sites presents on SZ/MCM-41 is affected by the presence of aluminum, but not affected by the presence of gallium.

3.4. Temperature-programmed reduction (TPR) analysis of the catalysts

TPR profiles of the catalysts were measured in the temperature range 120–800 °C. Here the gallium-promoted SZ/MCM-41 becomes the odd one. The TPR patterns for SZ/MCM-41 and ASZ/MCM-41 look very similar. There is only one large peak, starting near 570 °C and reaching maximum at 650–670 °C. These results indicated that there was no difference of sulfate reduction with the addition of Al. However, the reduction of GSZ/MCM-41 occurs at

temperatures much lower than that of SZ/MCM-41; the onset temperature for sulfate reduction in GSZ/MCM-41 is between 400 and 420 °C. These results showed an enhancement of sulfate reduction by Ga. On-line mass spectrometric analysis during the TPR runs with the catalysts confirmed the identity of the reduction products in the gas phase. Fig. 5 shows that H_2S is the only product (Fig. 5a), except water. And the H_2 consumption curves (Fig. 5b) match that of H_2S evolution. The reduction profile of GSZ/MCM-41 exhibits a shift of the hydrogen consumption peak of about 120 °C towards lower temperatures, compared to the SZ/MCM-41 catalyst. The temperature for maximum hydrogen uptake of ASZ/MCM-41 is similar to that for SZ/MCM-41 catalyst. The addition of Al does not produce a significant effect over sulfate temperature reduction.

3.5. Activity in n-pentane isomerization

In the presence of the three catalysts, the predominant product was isopentane, formed with small amounts of methane, ethane, propane, butane, and isobutane. The conversion–time curves and selectivity–time curves obtained at 180 °C over the catalysts are compared in Fig. 6. Initial conversion obtained on SZ/MCM-41 is about 40% but then the catalyst quickly deactivate to a much lower conversion with time on stream. Both the promoted catalysts exhibited higher conversions and stability than SZ/MCM-41. The GSZ/MCM-41 catalyst deactivates more slowly than the ASZ/MCM-41 catalyst. The initial conversion of the promoted catalysts is similar. In the n-butane isomerization reaction, the Al-promoted catalyst is appreciably less active than the Ga-promoted catalyst [26]. Here for pentane isomerization, the steady-state conversion of GSZ/MCM-41 at 77% is just slightly higher than that of ASZ/MCM-41. The steady-time selectivity to isopentane of the promoted catalysts is about 95%. In the case of GSZ/MCM-41, the selectivity to isopentane remains constant with time on stream for the duration of the 180 min test and level off
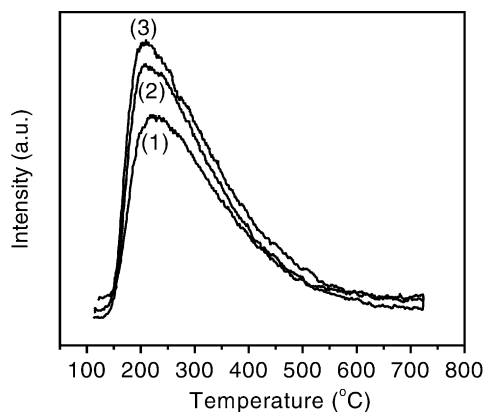

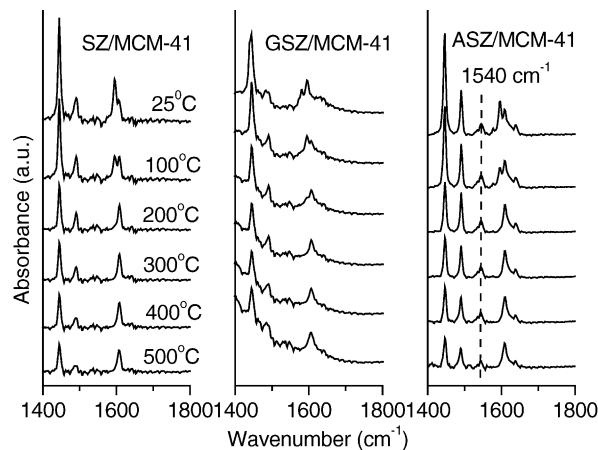Fig. 3. NH$_3$-TPD curves obtained on (1) SZ/MCM-41, (2) ASZ/MCM-41, (3) GSZ/MCM-41.

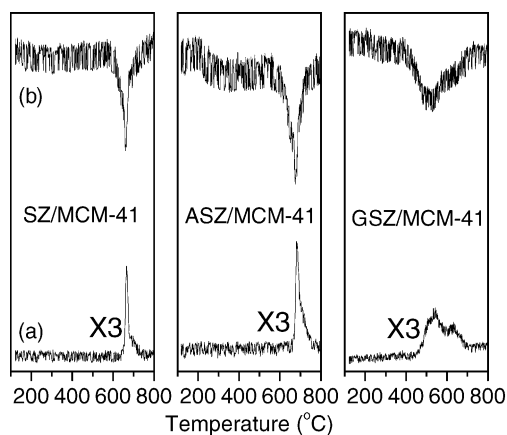Fig. 4. DRIFT spectra of samples after adsorption of pyridine and evacuation at different temperature.

Fig. 5. Mass spectrometric detection of hydrogen consumption and evolution of H_2S during TPR of the catalysts: (a) H_2S evolution, (b) H_2 consumption.

Fig. 7. Effect of reaction temperature on the conversion of *n*-pentane and selectivity to isopentane after 20 min reaction and at steady regime over ASZ/MCM-41 (A) and GSZ/MCM-41 (B), respectively.

at approximately 95%. In the case of ASZ/MCM-41, the initial selectivity is lower than that of GSZ/MCM-41.

There are a few recent reports on the isomerization of pentane by promoted sulfated zirconia [19,30]. Without promoters, the catalytic activity always decays rapidly with time. With Pt addition, the rapid initial deactivation is not detected but the initial activity is lower [19]. In Occelli work, copper was used as promoter with sulfated zirconia, the initial conversion at 15 min and 150 °C is about 53%. But, they did not report on the stability of the catalyst. The catalytic activities and selectivity towards isopentane in our Al- and Ga-promoted catalysts appears to be very high.

The effect of reaction temperature on the promoted catalysts was investigated. The variation of the conversion and the corresponding selectivities at 20 and 180 min for Al- and Ga-promoted SZ/MCM-41 catalysts are given in Fig. 7A and B. For the Ga-promoted catalyst, when the reaction temperature is increased to 180 °C, it is observed that higher reaction temperature gave higher initial activity though the selectivity slightly decreases. The initial and steady-time selectivity at reaction temperature of 180 °C is above 94%.
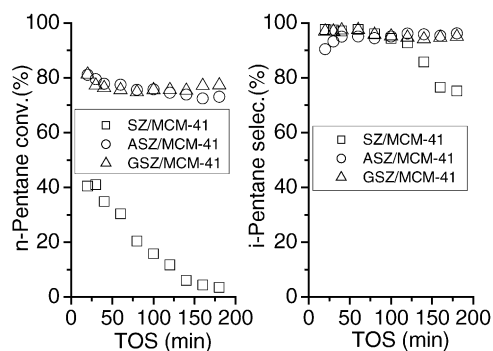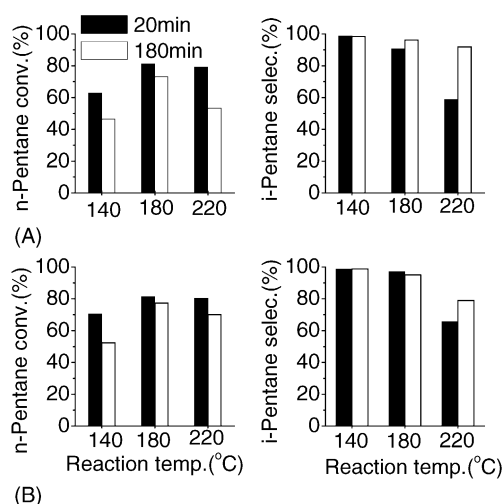

Fig. 6. Conversion of *n*-pentane and selectivity to isopentane vs. time on stream on SZ/MCM-41, ASZ/MCM-41, and GSZ/MCM-41 catalysts at 180 °C.

When the reaction temperature is increased to 220 °C, the initial conversion at reaction temperature of 220 °C is equal to that of 180 °C, however, the initial selectivity at reaction temperature of 220 °C decreases to about 60%. For the Al-promoted catalyst, the *n*-pentane conversion is similar to that of GSZ/MCM-41. When the reaction was run at or below 180 °C, isopentane was a major product. When the reaction temperature is increased to 220 °C, the initial selectivity decreases to about 60%.

4. Discussions

We have investigated the promotion effects of main group metals Al and Ga on SZ/MCM-41 catalyst on the isomerization of pentane. The presence of promoters on SZ/MCM-41 is important to achieve good activity and stability during *n*-pentane isomerization. The rapid initial deactivation is not detected on the promoted catalysts. The *n*-pentane conversion over the two promoted catalysts is similar and the differences appear only slight after 120 min. The selectivity towards isopentane is very high (>95%) in all promoted catalysts, and it decays somewhat for the unpromoted SZ/MCM-41. In this section we discuss the possible causes of the promoting effect of Al and Ga. The role of the promoters in the presence of hydrogen is still a controversial issue. In the literature, the catalytic results over unpromoted and promoted sulfated zirconia have been discussed in terms of crystalline phase, sulfate content, and acidity [31,32]. First, both aluminum and gallium help the retardation of the phase transformation of ZrO_2 from tetragonal to monoclinic. This contributes partly towards the catalytic activities. However, this does not explain the high stability in the promoted catalysis.

In our experiments, if one takes all the above characterization results into consideration, the causes for

the promotion effect of Al and Ga are unexpectedly different. The improvement of activity by Al in ASZ/MCM-41 is not difficult to understand. In the Al case, DRIFT spectra provide evidence for the promotion of Brønsted acid sites. The high catalytic activity and stability of ASZ/MCM-41 is thus probably mainly caused by the simultaneous presence of Brønsted and Lewis acid sites. On the other hand, acidity characterization of the samples showed no significant difference in nature and strength of the acid sites between SZ/MCM-41 and GSZ/MCM-41 catalysts. TPR profiles, however, indicate that Ga enhances the sulfate reduction. These results suggest that the nature and strength of the intrinsic acid sites are not sufficient to account for the higher activity of GSZ/MCM-41 catalyst. The reason for the higher activity of the GSZ/MCM-41 is probably related to the higher oxidization ability of Ga(III) in GSZ/MCM-41 catalyst.

There are two mechanisms for the isomerization of pentane: monomolecular and bimolecular as depicted in Eqs. (1) and (2), respectively [33]. In both, the reaction starts with the formation of carbenium ion on acid sites,

$$C_5H_{12} + H^+ \rightarrow C_5H_{11}^+ H_2$$
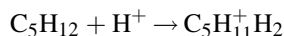
and in the monomolecular mechanism, the rearrangement of the pentyl cation into isopentyl action is followed by hydride transfer leading to isopentane.

$$C_5H_{11}^+ \leftrightarrow C-C-C \overset{C^+}{-\!\!-\!\!-\!\!-}C \rightarrow i\ C_5H_{11}^+$$
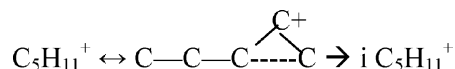
The bimolecular mechanism requires the equilibrium formation of pentene (Eq. (2)) followed by the reaction between pentene and pentyl cation to form dimeric C_{10}^+ species.

$$C_5H_{11}^+ \leftrightarrow C_5H_{10} + H^+ \tag{2}$$

The dimeric species can re-arrange and scission to form isopentane. However, it is also known to produce C_3–C_5 species and cyclic olefins and thus coking [34]. The fact that we have little decay of catalytic activity and almost single product of isopentane in both Al- and Ga-promoted SZ indicates that only monomolecular mechanism operates in our catalysis reaction. This can be expected in ASZ/MCM-41 since its stronger Brønsted acidity shifts the equilibrium in Eq. (2) towards pentyl cation and thus promotes monomolecular reaction (1). C_3–C_5 species and coking are then avoided.

For Ga-promoted SZ, the enhanced acidity does not come directly from framework substitution by Ga itself. However, we have seen Ga(III) can help the uptake of hydrogen to form hydrogen sulfide. It is known that hydrogen can be converted into acid sites [33]. We propose that Ga(III) indeed helps the formation of acid site by the redox reaction;

$$Ga(III) + H_2 \rightarrow Ga(I) + 2H^+(ad) \tag{3}$$
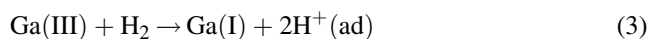
This increased acidity also shifts the equilibrium in Eq. (2) towards pentyl cation and thus to monomolecular mechanism leading to simple isomerization. Although a much higher temperature (500 °C) than the reaction temperature

is needed for hydrogen sulfide desorption from SZ, the acidity production in Eq. (3) is probably operating at a much lower temperature.

The promoting and stabilizing effect of Al and Ga on sulfated zirconia in pentane isomerization without the use of expensive Pt is technologically very encouraging. We may thus be able to develop a new generation of catalyst for alkane isomerization. In fact, recently we have found GSZ catalyzes excellently and very stably the isomerization of hexane. Almost all the conversions were isomers of hexane. Cracking products of C_1–C_5 were negligible [35]. Further studies to understand the detailed reasons for the excellent catalytic behavior in Al- and Ga-promoted sulfated zirconia for alkane isomerization is desirable.

Acknowledgements

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