The role of H₂ in n-butane isomerization over Al-promoted sulfated zirconia catalyst

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ABSTRACT

C, H, N-elemental analyzer, and NH₃-TPD, FTIR, XPS and reactor system are used to investigate the function of hydrogen in n-butane isomerization over the Al-promoted (3 mol% as Al₂O₃) sulfated zirconia catalyst (Al/SZ). Findings show relatively stable Al/SZ catalyst activity at 250 °C with H₂ introduction; however it decreases very quickly when N₂ replaces H₂. Deactivation is attributed to coke formation. The main components of coke are graphite and polymeric hydrocarbons. Activity can be recovered about 70% when H₂ is admitted again. Conversely, catalytic activity is lower but more stable in the presence of H₂ than in that of N₂ at 150 °C. Findings also show that activity cannot be restored if n-butane conversion is down to zero (i.e., the catalyst is completely deactivated). This study infers that H₂ reacts with coke at 250 °C, but inhibits isobutane formation and cannot react with coke at 150 °C. Catalytic activity restoration is via the reaction between coke and adsorbed hydrogen on the Brønsted acid sites. Although many researchers report that decayed sulfated zirconia regenerates by burning coke off with oxygen, this work finds that the fouled catalyst regenerates, though not completely, by hydrogen, provided it is not fully deactivated.

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1. Introduction

Alkylate products, produced from alkylation of C₃–C₅ alkenes with isobutane, improve octane number and gasoline quality, and replace aromatics and methyl tertiary butyl ether (MTBE). Their quality improvement is currently becoming an important subject in petroleum refineries. Isobutane can be produced by n-butane isomerization. Both liquid and solid acid catalysts can be used, but the commercial process changes to solid acid catalysts due to environmental considerations. Sulfated zirconia (SZ) and other sulfated metal oxides exhibit a strong acidity, allowing them to catalyze butane isomerization at low temperature [1].

Rapid deactivation seriously disadvantages sulfated zirconia, so many researchers attempt to elucidate the cause of deactivation and prevent it. Several factors may cause SZ catalyst deactivation: (1) coke deposit formation on the catalyst surface [2,3], (2) reducing Zr₄⁺ to Zr₃⁺ by hydrocarbon reaction [4], (3) sulfate group attenuation owing to reduction by hydrogen [5], (4) change of sulfur charge [6], (5) change of zirconia phase from tetragonal to monoclinic [7], and (6) poisoning by water [8]. Coke deposition is the main cause of catalyst deactivation, so coke deposition control and/or the reduction of coke deposition rate prolongs catalytic life.

Two kinds of reaction pathways are proposed for isomerization over solid acid, one is monomolecular, and the other is bimolecular [9,10]. The bimolecular mechanism involves C₈⁺ carbenium ion formation, followed by cracking and subsequent hydride transfer/desorption steps [9,11]. Hydrocarbons of larger molecules adsorbed on the catalyst surface do not desorb easily at the reaction temperature and accumulate as coke or coke precursors [11]. In other words, catalyst decay prevails more with a bimolecular reaction mechanism than with a monomolecular mechanism [12].

SZ promoted with small amounts of Al (Al/SZ) significantly enhances catalyst activity and stability for n-butane isomerization at 250 °C in the presence of H₂ [13,14]. The optimum Al₂O₃ content is 3 mol%. Moreover, the catalyst activity of Al/SZ is higher than Pt/SZ for n-butane isomerization in the presence of H₂ [15]. Canton et al. [16] further studies the influence of a small addition of alumina onto zirconia structure and microstructure. Recently, Sun et al. [17] reports that Al-promoted mesoporous sulfated zirconia increases steady state conversion compared with unsupported SZ and catalytic activity is highest with 3 mol% Al₂O₃ contents. Catalytic activity and stability improvement attributing to Al₂O₃ helps stabilize the sulfate complex on oxides and enhances the number of acid sites with intermediate strength [18]. The promoting mechanism of the main group element Al is different from that of transition metals. Mou and co-workers [19,20] reports that Al-promoted SZ retards phase transformation from tetragonal to monoclinic and balances distribution of acid site strength with an

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enhanced amount of weak Brønsted acid sites, so catalytic activity and stability improve. However, the hydrogen role in Al-promoted SZ has not been investigated.

This study prepares aluminum-promoted sulfated zirconia and designs testing methods for investigating the role of hydrogen in the n-butane isomerization reaction. The current work examines catalyst characteristics by several characterization techniques for elucidating the cause of catalyst deactivation.

2. Experimental

2.1. Catalyst preparation

The methods for preparing SZ are already described elsewhere [19,21]. Hexadecyl trimethyl ammonium bromide (2.5 g, Aldrich) is dissolved in a solution of 115 g water and 22.4 g HCl (37 wt%), followed by 5.99 g of 70 wt% $Zr(O-nPr)_4$ in added 1-propanol. After stirring for 30 min, $(NH_4)_2SO_4$ in 23.0 g water is introduced to the solution (the molar ratio of SO_4/Zr is about 0.7). The solution is stirred for 1 h at room temperature, then transferred into a polypropylene bottle and heated at 100 °C for 3 days. The precipitate is filtered and washed with de-ionized water, ethanol, and de-ionized water consecutively, finally drying at 100 °C for 12 h. Aqueous alumina sulfate is introduced into the uncalcined sulfated-ZrO_2 via the incipient wetness impregnation technique to obtain the Al-promoted SZ with nominal 3 mol% Al_2O_3, calculated on the weight basis of ZrO_2. The slurry is stirred for 1 h and oven-dried at 100 °C for 12 h. Solid particles are then calcined for 5 h at 650 °C in static air, thus obtaining the Al/SZ catalyst.

2.2. Characterization

The surface area and pore size distribution of catalysts are determined by nitrogen desorption at −196 °C with a Mircomeritics TriStar 3000 instrument. For determining catalyst acidity, NH_3-TPD is performed in a flow apparatus. A sample 0.1 g is activated in helium at 400 °C for 1 h. The system is then cooled under helium to 100 °C. At 100 °C, NH_3 is adsorbed till saturation. Then the sample is heated to 820 °C at a heating rate of 7 °C/min to desorb NH_3. Aluminum and sulfur contents are determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a PerkinElmer ICP 4300 instrument.

The types of coke deposited on the used catalyst are analyzed using an X-ray photoelectron spectroscope (Thermo VG Scientific, ESCALAB 250) fitted with a monochromatic Al Kα radiation (1486.8 eV) X-ray source, under a residual pressure of ∼1 × 10⁻⁹ Torr. Binding energy is calibrated to Zr in ZrO_2, BE = 182.7 eV because of electrostatic charging.

This work adopts the method described by Föttinger et al. [22] for characterizing acidic sites in both fresh and used catalysts. The infrared spectra are recorded with a BIO-RAD Digilab FTS-40V FT-IR spectrometer. Coke content of the used catalyst is determined by the Elementar Vario EL C, H, N-elemental analyzer.

2.3. Catalytic reaction

The isomerization of n-butane to isobutane is carried out in a fixed-bed reactor and operated at atmospheric pressure. 1.0 g of the catalyst is loaded into the reactor and then pretreated in dry air for 3 h at 450 °C. Thereafter, the catalyst is cooled to 250 °C (or 150 °C). Subsequently, the reaction is performed with three different modes (Table 1).

In mode I, the reaction starts with 250 °C using hydrogen as a carrier gas (step I). The carrier gas is shifted to nitrogen (step II) when conversion is nearly unchanged. Then, the carrier gas changes back to hydrogen (step III). Mode II is similar to mode I except that step

Table 1
Operation mode.

Mode	Operating temperature (°C)	Carrier gas			
		Step I	Step II	Step III	Step IV
I	250	H_2	N_2	H_2	–
II	250	H_2	N_2[a]	H_2	–
III	150	H_2	N_2	H_2	N_2

[a] In this step, reaction proceeded until catalyst was fully decayed.

II proceeds until complete catalyst decay. The operating procedure in mode III is the same as that in mode I except the reaction is carried out at 150 °C and an additional step in which the carrier gas is shifted to nitrogen (step IV).

The weight hourly space velocity (WHSV) of n-butane is set at 0.62 h⁻¹ and n-butane/H_2 ratio is 1/10 (v/v). Effluent gas analysis uses a gas chromatograph (Varian 3800) equipped with a 50-m plot AL/M column and FID.

3. Results and discussion

3.1. Catalyst characterization

The surface area, composition, and acidity characteristics of the fresh catalyst are listed in Table 2. Note that the higher measuring temperature is the larger ratio of Lewis acid to Brønsted acid (L/B) because the number of Brønsted acid sites reduces with raising measuring temperature [23]. In order to obtain the actual ratio of L/B in isomerization reaction, the measuring temperature for the used catalysts is the same as the reaction temperature.

The XRD results show that the Al/SZ catalysts are mainly tetragonal phase. No change is detected by XRD in the crystalline phase for used catalysts.

3.2. n-Butane isomerization at 250 °C

In elucidating the fact that the Al/SZ catalyst for n-butane isomerization is more active and stable in the presence of hydrogen than other gases, this reaction uses operating mode I and mode II at 250 °C and analyzes the coke content of used catalysts at the end of each step.

3.2.1. Catalytic activity and selectivity

Fig. 1 shows the mode I result. Conversion at step I is about 50% at the very beginning of the run, declining gradually and slightly to a relatively stable level of about 44% after 5 h. However, when the carrier gas changes from hydrogen to nitrogen (step II), conversion decreases very quickly because of catalyst decay. These conversion variations are similar to those reported previously [24]. When hydrogen is admitted again (step III), conversion suddenly drops from 4.7% to 1.7% due to competitive adsorption of hydrogen with n-C_4 onto active sites, increasing gradually to 29%, and stabilizing thereafter. The conversion does not completely recover to the step I level, but is much higher than that at the end of step II.
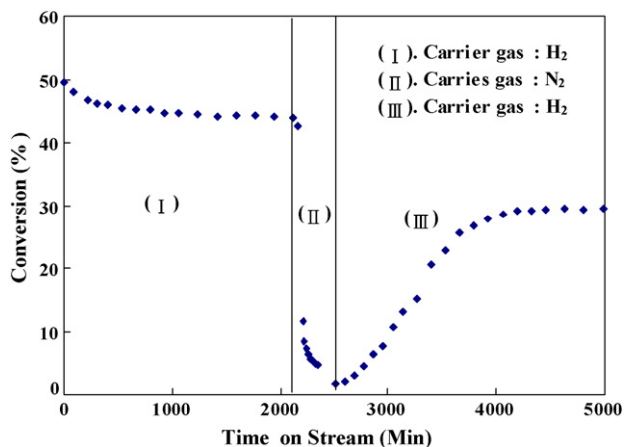
Table 2
Characteristics of the fresh catalyst.

Item	Value
BET S.A. (m^2/g)	101
Sulfur (wt%)	1.3
Al (wt%)	1.3
L/B[a] at 150 °C	1.75
L/B[a] at 200 °C	2.01
L/B[a] at 250 °C	2.14

[a] Ratio of Lewis acid sites to Brønsted acid sites.

Table 3
Product composition (mol%) and selectivity (%) in step II and step III in operating mode I.

Conversion (%)	Step	C$_2$	C$_3$	Iso-C$_4$	n-C$_4$	Iso-C$_5$	n-C$_5$	Selectivity	C$_3$/C$_5$
12.3	II	0.00	0.82	11.08	87.37	0.55	0.18	87.7	1.1
12.3	III	0.32	0.38	11.60	87.40	0.20	0.08	92.1	1.4
6.1	II	0.00	0.37	5.74	93.60	0.22	0.07	89.6	1.3
6.1	III	0.17	0.16	5.99	93.57	0.10	0.00	93.2	1.7

Fig. 1. Variation of n-butane conversion with different carrier gases at 250°C (operating mode I).

Fig. 2. Variation of n-butane conversion at 250°C with different carrier gases (operating mode II. Note the completely decayed catalyst in step II).

Product compositions at the same conversion level in step II and step III of operating mode I are shown in Table 3. The selectivity of iso-C$_4$ product in step III is higher than that in step II using nitrogen as the carrier gas. The ratio of C$_3$/C$_5$ clearly reaches to 1.7 in step III, and is larger than that at step II. The amount of C$_3$ is much larger than C$_5$ at step III, but the amount of C$_3$ is a little larger than C$_5$ with no C$_2$ generated at step II. Bimolecular reaction produces more propane and pentane, both generated from C$_8$ intermediate, and additional propane formed by cracking or hydrogenolysis of n-C$_4$ [25]. Pentane reduces obviously in step III, therefore the isomerization reaction might mainly proceed via the monomolecular mechanism in the presence of hydrogen and generates much more C$_2$ and C$_3$, about 2–4 times of C$_5$. Garin et al. [26] reports that the monomolecular mechanism prevails when isomerization reaction proceeds on SZ at 250°C in the presence of hydrogen, and C$_1$–C$_3$ components are about 5–10 times those of C$_5$ components. Different reaction mechanisms also result in different selectivities for iso-C$_4$ [9]. The monomolecular reaction offers a higher selectivity for iso-C$_4$ than the bimolecular reaction and irreversible disproportionation, giving higher selectivity at lower conversion [9].

Fig. 2 shows the result of applying operating mode II. Note that carrier gas changes from nitrogen to hydrogen when catalytic activity decays completely at step II and catalyst activity cannot be restored in step III with hydrogen introduction.

3.2.2. Coke content analysis

Table 4 lists the coke content of the used catalyst at each step measured by the C, H, N-elemental analyzer. Although step II operating time is much shorter than step I, the coke content in step II is much higher than that in step I. In step II, the coke deposits quickly and its amount increases from 0.04 wt% to 0.15 wt% within 186 min. However, coke content reduces when the reaction proceeds from step II to step III, a little higher than that at step I.

The coke content of the completely decayed catalyst at the end of step II is 0.61 wt%, much higher than at the end of step II in mode I. Coke contents of the fully decayed catalysts are quite different for different kinds of SZ catalysts. Vera et al. [4] demonstrate that coke content of the used SZ catalyst is about 1–1.2 wt%, while Föttinger et
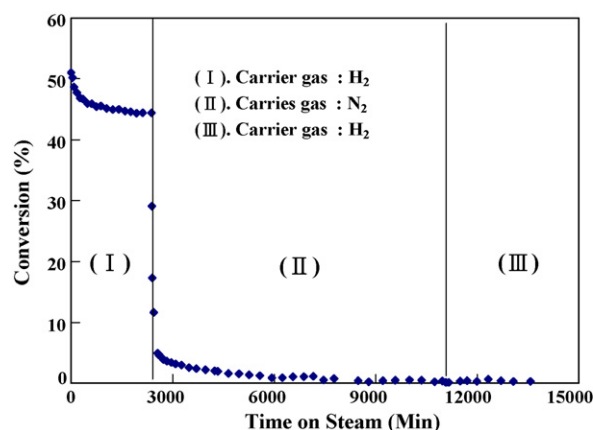
al. [27] investigate isomerization of n-heptane at 200°C in He and observe the inactivated catalyst due to coke formation after a short on-stream time. They find coke contents at 0.6 wt% and 0.8 wt% in decayed SZ and Pt/SZ catalysts, respectively.

The catalyst tolerates 6–10 wt% coke without much activity loss when coke deposition occurs mainly on the support surface and not directly on active sites [28]. Coke contents (0.15 wt% and 0.61 wt% at the end of step II in mode I and mode II, respectively) are much lower than 6–10 wt%, hence coke deposition might occur on active sites rather than on the support surface.

3.2.3. Types of coke

This study carries out X-ray photoelectron spectroscopy analysis for elucidating types of coke deposited on used catalysts. The intensity and distribution of components in the C 1s peak is shown in Fig. 3. Major components of coke on the fresh catalyst are graphite and polymeric hydrocarbons (C$_x$H$_y$) formed during catalyst preparation. This finding is in agreement with that reported in the literature [29]. The polymeric C$_x$H$_y$ and graphite in the coke at the end of Step I are 61% and 39%, respectively.

Coke content increases from 0.04 wt% to 0.15 wt% in step II of mode I, and the coke has two additional types other than polymeric C$_x$H$_y$ and graphite. The highest binding energy (BE) component (ca. 287.4 eV) is assigned to carbonylic or quinonic C=O groups [30], and the lowest BE (ca. 282 eV) reveals small amounts of carbidic species [31]. Paál et al. [30] finds Pt carbide in the used Pt-black catalyst for

Table 4
Coke contents and ratios of Lewis acid to Brønsted acid (L/B) of fresh and spent catalysts at different steps in operating mode I and mode II.

Catalyst	Coke (wt%)	L/B (at 250°C)
Fresh	–	2.14
Used, at step I[a]	0.04	2.16
Used, at step II[a]	0.15	3.82
Used, at step III[a]	0.06	3.02
Completely decayed[b]	0.61	7.51

[a] Steps in the operating mode I.
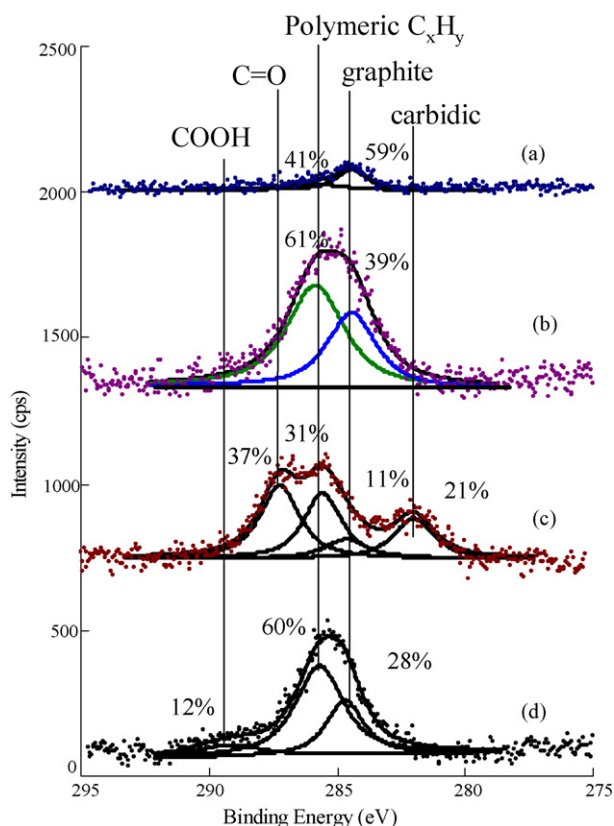
[b] At the end of step II in the operating mode II.

Fig. 3. XPS spectra in C 1s region of catalysts at different steps of mode I. (a) Fresh catalyst; (b) used catalyst at step I; (c) used catalyst, at step II; (d) used catalyst, at step III.

Fig. 4. IR spectra of fresh and used Al/MSZ catalysts. (a) Completely decayed catalyst; (b) used catalyst, at step III of mode I; (c) used catalyst, at step II of mode I; (d) fresh catalyst.

the n-hexane reaction. Carbidic species probably are hydrocarbon fragments consisting of one or more C atoms attached by chemical bonds to Zr or Al rather than a contiguous zirconium carbide or aluminum carbide phase [30]. Carbidic species can mainly hydrogenate to methane even below 500 K [32] or remove with O_2–H_2 treatment at 600 K [30].

This work eliminates carbidic species after the end of step III of mode I, recovering the ratio of graphite and polymeric C_xH_y. Unfortunately approximately 11% of COOH groups exist, heavily oxidized residues, generated at ca. 289.2 eV [29]. This is probably one of the reasons why catalyst activity of step III could not recover to step I. Coke rapidly forms in step II, similar to the unstable soft coke in the hydrotreating process [33–35]. This investigation detects four different types of coke, including carbonaceous species containing heavier carbonylic groups and carbidic species, most of which are removable under a suitable environment because coke content reduces in step III (Table 4). Coke containing C=O groups are heavier carbonaceous species; some cannot be removed in step III, but might change to COOH groups [30].

3.2.4. Types of acid sites and acidity at different reaction steps

The current work studies types of acid sites present with FTIR spectroscopy of chemisorbed pyridine and records IR spectra of adsorbed pyridine on different used Al/SZ samples after the same pretreatment conditions. Table 4 shows reduced Brønsted acid sites and predominant Lewis acid sites on used catalysts (Fig. 4). The higher the catalyst activity is, the lower L/B ratio will be. Compared with coke content data, the used catalysts with higher coke contents have more Lewis acid sites [27]. In operation mode I, the value of L/B on the used catalyst at step II is larger than that at step III. In other words, the number of Brønsted acid sites recovered and the L/B ratio reduce [2,27] after coke removal in step III. The Brønsted acid
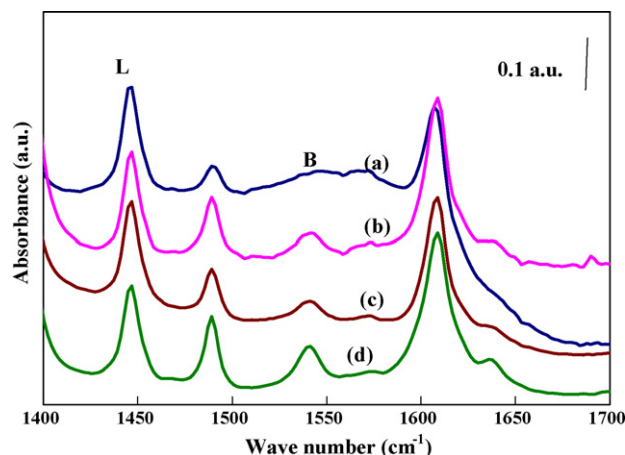
sites almost disappear at 250 °C when catalyst activity completely decays, but Lewis acid site intensity almost does not change (Fig. 4). It is obvious that the coke deposit mainly on Brønsted acid sites, and Brønsted acid sites play crucial roles in n-C_4 isomerization.

Li et al. [36] uses water to wash sulfated zirconia for investigating acid sites, finding all Brønsted acid sites removed and the amount of Lewis acid sites increased, but the water-washed sample is inactive for n-butane skeletal isomerization. They conclude that Brønsted acid sites are necessary and Lewis acid sites do not directly participate in n-butane isomerization. The acid site role on n-butane isomerization has been investigated intensively but without a consensus conclusion until now. Pinna et al. [37] show that Lewis acid sites are crucial in n-butane isomerization. They introduce CO during the reaction and observe catalytic activity dropping to almost (nearly) zero, but recovering back to steady state with CO interruption. Chen et al. [38] reports both strong Lewis and Brønsted acid site involvement for n-butane isomerization. Yaluris et al. [39] report the importance of Lewis acid sites in generating initial activity and those Brønsted acid sites are indispensable for extending catalytic activity for n-butane isomerization.

In this study, the NH_3-TPD patterns of fresh and used catalysts are compiled in Fig. 5. Acid sites corresponding to peaks in the range between 130 °C and 350 °C are Brønsted and Lewis acid sites, and both are useful for isomerization reaction. Coke deposition on catalysts (including completely decayed catalyst) slightly inhibits NH_3 adsorption on this kind of acid site [2,27], because both Lewis and
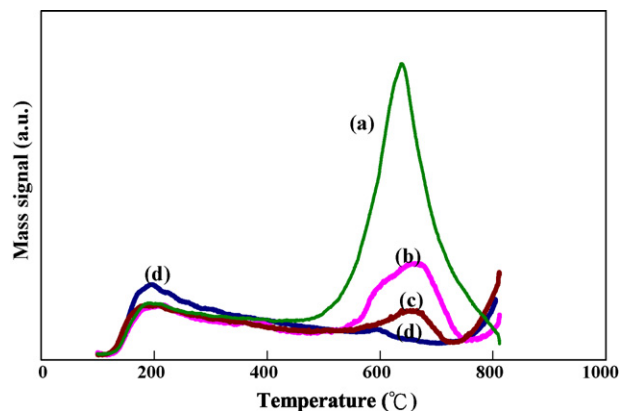

Fig. 5. NH_3-TPD of: (a) completely decayed catalyst; (b) used catalyst, at step III of mode I; (c) used catalyst, at step II of mode I; (d) fresh catalyst.
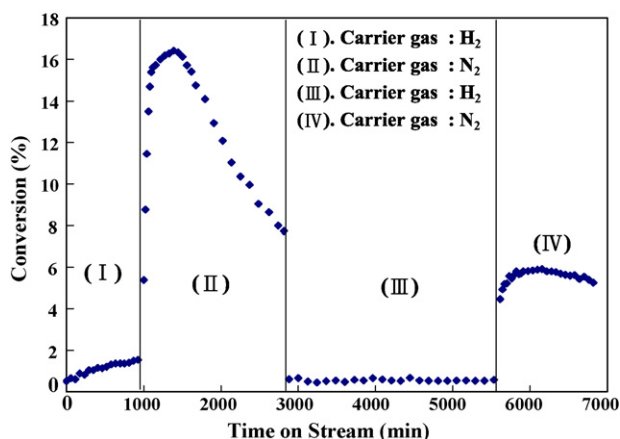
Fig. 6. Variation of n-butane conversion with different carrier gas at 150 °C (operating mode III).

Brønsted acid sites have the ability to adsorb NH_3. A peak appears in each of the used SZ catalysts in the range of 570–770 °C. The peak in this temperature range should be owing to functional group decomposition in the catalysts, because GC–MS detects SO_2 and CO_2, but not NH_3 in the desorbed gas. Rising temperature above 570 °C under nitrogen or He for the used catalyst causes oxygen atoms of the sulfate group to react with deposited carbon atoms on active sites to form CO_2, resulting in immediate evolution of SO_2 [40]. Increasing peak area caused by used catalyst coke content reflects coke deposition on the used catalyst.

A small fraction of total sulfate in the SZ catalyst is responsible for catalytically active sulfate sites. Marcus et al. [41] use a TGA/FTIR technique and finds that the number of catalytically active sulfate sites never exceeds 14% of total sulfate loading. Li et al. [2] study regeneration of the decayed SZ catalyst with nitrogen at 500 °C, finding the catalyst totally inactive; however total acidity is only 11% lower than that of the fresh catalyst. This observation concludes that the number of catalytically active sites and Brønsted acid sites for n-butane isomerization is rather small. That is why NH_3-TPD pattern intensity reduces only slightly when catalyst activity reduces or almost fully decays.

When n-butane isomerization proceeds with bimolecular mechanism, alkenes react with carbenium ions to form C_8^+ intermediate or hydrocarbons of longer carbon chains. As pointed above, hydrocarbons of larger molecules adsorbed on the catalyst accumulate as coke or coke precursors at reaction temperature because they cannot desorb easily [11], therefore coke deposited very rapidly in step II (Table 4) causes fast catalyst decay. If hydrogen only functions as a coke inhibitor, conversion remains stable and does not tend to increase after changing from nitrogen to hydrogen from step II to step III. However, coke on used catalysts reduces, hence the Brønsted acid sites and catalyst activity recover gradually though not completely (Fig. 1 and Table 4). Therefore, this study concludes that hydrogen also reacts with coke deposited on the Al/SZ during n-butane isomerization.

3.3. n-Butane isomerization at 150 °C (operating mode III)

Fig. 6 shows the effect of hydrogen and nitrogen on n-butane isomerization at 150 °C. Hydrogen is first introduced as a carrier gas (step I), nitrogen is admitted after nearly stable conversion (step II). Note that catalytic activity is higher in the presence of nitrogen than in hydrogen, however, the catalyst decays more rapidly in nitrogen than in hydrogen. Subsequently, the carrier gas changes back to hydrogen (step III). The conversion in step III is lower than that at step I. The amounts of coke in the used catalysts at the end of these

Table 5
Coke contents of spent catalysts at the end of each step in operating mode III (at 150 °C).

Catalyst	Coke (wt%)
Used, at step I	0.04
Used, at step II	0.06
Used, at step III	0.07
Used, at step IV	0.09

steps are summarized in Table 5. The amount of coke at the end of step III is a little higher than that at the end of step II. When catalyst activity is nearly stable at step III, carrier gas changes to nitrogen (step IV). Catalyst activity at this step is still higher than that at step III, but lower than step II. Reaction temperature of 150 °C is too low to remove coke by hydrogen, and even reaction time is over 2500 min in step III. As a result, deposited coke cannot be removed and catalyst activity decayed continuously whether in the presence of hydrogen or nitrogen.

Bimolecular mechanism occurs instead of monomolecular when isomerization reaction carries out at 150 °C (the operating mode III), because monomolecular isomerization of a butyl carbenium ion requires formation of a primary carbenium ion, characterized by a high-energy barrier. Conquering this barrier requires a superacid or higher reaction temperature [9]. Findings show that adding butene to the reactant stream leads to enhanced reaction rate for n-butane isomerization over SZ at 150 °C [42]. Catalyst activity of Pt/SZ or SZ inhibits in the presence of hydrogen at 150 °C, but not in nitrogen [43]. The use of Al/SZ in this study also gives the same result.

3.4. Mechanisms for coke removal

The above results and discussion indicate that coke is clearly removable by reacting with hydrogen at 250 °C. This work now proposes two mechanisms for coke removal. In mechanism A, as shown in Fig. 7, hydrogen is adsorbed on coke surface, and reacts with coke directly, while in mechanism B, hydrogen is first adsorbed on the surface of active sites and then reacts with nearby coke. Coke reaction by hydrogen proceeds whether active sites exist on the catalyst surface or not if removal reaction follows mechanism A. However, free active sites must exist on the catalyst surface if the reaction follows mechanism B. Actually, as pointed above, catalyst
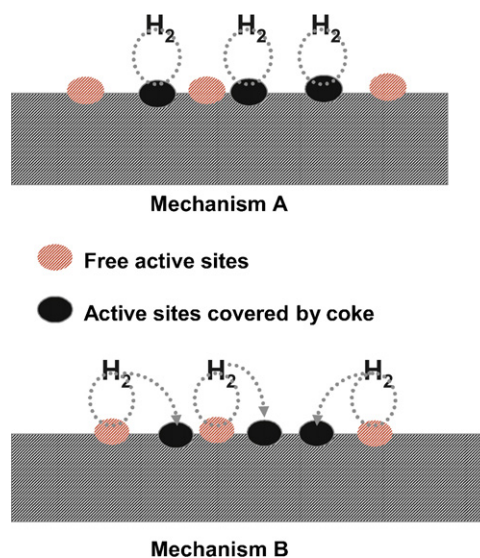

Fig. 7. Reaction mechanism of coke with hydrogen. Mechanism A: hydrogen is adsorbed on the coke surface and reacts with coke directly. Mechanism B: hydrogen is adsorbed on active sites first and then reacts with nearby coke.

activity cannot recover when catalyst activity fully decays in operation mode II, so coke removal reaction must follow mechanism B.

4. Conclusions

When n-butane isomerization is catalyzed by Al/SZ catalyst at 250 °C, it mainly proceeds via monomolecular mechanisms. The deposited coke on catalyst can be removed by reacting with hydrogen. Therefore, catalytic activity is higher and more stable in the presence of hydrogen than in the presence of nitrogen. Catalyst activity decays quickly in the absence of hydrogen due to coke deposition on Brønsted acid sites, though total acidity by NH_3-TPD measurement decreases only slightly. In the presence of H_2 coke deposited takes the form of graphite and polymeric C_xH_y, however, as described above, that formed in the presence of N_2 also has C=O groups and carbidic groups. Heavier coke, such as C=O groups, cannot completely react with hydrogen at 250 °C.

On the other hand, isomerization reaction at 150 °C proceeds mainly via bimolecular mechanism in the presence of hydrogen. However, hydrogen cannot react with coke deposited at this low temperature, so catalyst activity decays gradually. Brønsted acid sites on the Al/SZ catalyst play a crucial role in n-butane isomerization, as the catalyst is no longer active when those sites are covered by coke. Decayed catalyst activity can be partly restored by admitting hydrogen. Hydrogen must adsorb on Brønsted acid sites before reacting with nearby coke. When Brønsted acid sites are completely covered by coke, catalyst activity cannot be recovered by hydrogen at 250 °C.

Acknowledgement

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