

Hydrogen Effect on *n*-Butane Isomerization over Sulfated Zirconia-Based Catalysts

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Iron- and manganese-promoted sulfated zirconia (SFMZ) has been tested as an *n*-butane isomerization catalyst in the temperature range of 35 to 180°C. The catalytic activity exhibits an induction period whose length is dependent on the reaction conditions. The presence of H₂ in the feed stream strongly suppresses *n*-butane conversion over unpromoted sulfated zirconia (SZ) and over Pt-containing SFMZ (PtSFMZ). However, hydrogen had no effect on *n*-butane isomerization over SFMZ. These findings were interpreted on the basis of a bimolecular mechanism where unsaturated intermediates (carbenium ions and/or butene) are formed during the break-in period. The role of promoters (Fe and Mn) is not only facilitating the formation of hydrogen-deficient intermediates and their accumulation on the catalyst surface, but also enhancing their stability. The negative effect of hydrogen over PtSFMZ is attributed to the occurrence of atomic hydrogen via the dissociative adsorption of H₂ on Pt.

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INTRODUCTION

Sulfated zirconia-based materials are strong, noncorrosive solid acid catalysts targeted by many research groups as potentially viable substitutes for currently used HF, H₂SO₄, and chlorinated alumina catalysts. Recent progress in this area has been reviewed (1, 2). Hsu *et al.* (3) found that at low temperature, sulfated zirconia promoted with Fe and Mn (referred to as SFMZ) is about three orders of magnitude more active in *n*-butane isomerization than the unpromoted sulfated zirconia (SZ) catalyst. Using temperature-programmed desorption (TPD) of benzene, Lin and Hsu (4) reported that SFMZ has more and stronger acid sites than SZ which has long been considered as a superacid (5). The remarkable catalytic activity of SFMZ in *n*-butane isomerization was later confirmed by several authors (6–10). However, the validity of using TPD to characterize the acid strength of SZ-based catalysts has been questioned because of the oxidative decomposition of adsorbed probe

molecules (e.g., benzene, acetonitrile, ammonia, pyridine) during heating (6, 7, 11–13). By means of Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies of adsorbed bases, Adeeva *et al.* (7) found that both SZ and SFMZ are not superacids, and they have similar acid strengths. This conclusion was also reached by several other authors (8, 9, 12). It is important to mention that earlier UV-visible data have already indicated that SZ is not a superacid (14).

Adeeva *et al.* (7) explained the remarkable activity difference between SZ and SFMZ catalysts on the basis of mechanistic considerations. These authors argued that the acidity of a catalyst is not the only factor that governs its activity in acid-catalyzed reactions. The catalyst activity can also be dependent on the nature of the intermediates and the energetics associated with the reaction pathway. To explain the occurrence of disproportionation products from *n*-butane isomerization over H-mordenite at about 350°C, Guisnet *et al.* (15–17) proposed that the reaction proceeds via an intermolecular mechanism with the intermediacy of a C₈ species. The same mechanism was also suggested by Gates and co-workers (18, 19) for *n*-butane isomerization over SFMZ at 40–225°C. Reaction studies by Adeeva *et al.* (20–22) using double ¹³C-labeled butane indicated that at low temperature, *n*-butane isomerization over SFMZ, SZ, and PtSZ catalysts proceeds predominantly via a bimolecular mechanism involving (i) the formation of C₄ carbenium ion and butene, (ii) reaction of the carbenium ion with butene to form a C₈ intermediate, and (iii) rearrangement and β -scission of the C₈ intermediate to isobutane. This reaction pathway is energetically more favorable compared to a monomolecular *n*-butane isomerization mechanism (23).

The function of the promoters is still unclear. There is a broad consensus now that Fe and Mn promoters, and possibly others such as Ni and Cr, do not increase the acid strength of Brønsted and Lewis acid sites on the surface of the catalyst. Tábara and Davis (8) found not only that SZ and SFMZ catalysts exhibit similar FTIR spectra of sulfate groups, adsorbed CO, and adsorbed pyridine, but, also that EXAFS data indicate that the addition of promoters does not alter the surface properties and the crystallographic

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phase of SZ. Furthermore since Ni (9) and Cr/Mn (24) exhibit similar promoting effects as Fe/Mn, it is inferred that they play the same role as Fe/Mn. Adeeva *et al.* (7, 20, 21) suggested that the role of Fe and Mn promoters is to facilitate the reaction path by enhancing the formation of the unsaturated intermediates (butenes or carbenium ions) or increasing their stability. Furthermore, Coelho *et al.* (9, 10) stated that in addition to generating olefins, transition metal promoters enhance the surface concentration of hydrogen-deficient reaction intermediates. Several authors suggested the occurrence of two (8) or even three (12) different active sites for *n*-butane isomerization over SFMZ. Wan *et al.* (12) proposed that at 30°C, SFMZ has a dual catalytic function for *n*-butane isomerization, i.e., the promoters are redox-active and responsible for the oxidative dehydrogenation of *n*-butane to butene which is then protonated over the acid sites, forming a carbenium ion. The isomerization proceeds further through the formation, rearrangement, and β -scission of a C₈ intermediate.

According to the bimolecular mechanism, the presence of hydrogen in the feedstock is expected to affect *n*-butane conversion adversely since it inhibits the formation of hydrogen-deficient intermediate species (C₄ carbenium ions and/or butenes). However, as reported briefly in a previous paper (24), we did not observe any effect of hydrogen on *n*-butane isomerization over SFMZ. We proposed that this is most likely due to the strong stabilization of C₄ carbenium ions by the promoters. The main objective of this work is to shed further light on the role of the promoters by investigating the hydrogen effect over different SZ-based catalysts.

EXPERIMENTAL

Zr(OH)₄ was prepared as described earlier (24–26) by hydrolyzing a ZrOCl₂ · 8H₂O (98%, Aldrich) solution by dropwise addition of aqueous ammonia (28 wt% NH₃, Anachemia) under vigorous stirring at room temperature to pH 8. The precipitate was filtered and washed with deionized water until no chloride ions were detected by the AgNO₃ test. Then the solid was dried overnight at 110°C and crushed to below 100 mesh. SZ, SFZ, and SFMZ were prepared using the procedure of Jatia *et al.* (6); 0.15 M Mn(NO₃)₂, 0.30 M Fe(NO₃)₃, and 3 wt% SO₄²⁻ solutions were prepared by dissolving the appropriate amounts of Mn(NO₃)₂ · 6H₂O (98%, Aldrich), Fe(NO₃)₃ · 9H₂O (98%, Aldrich), and (NH₄)₂SO₄ (99%, Aldrich). Manganese, iron, and sulfate were impregnated one at a time, in this order, onto dried Zr(OH)₄ by stirring a mixture of 1.5 ml per gram of solid for 1 min and soaking for 14 min. After each impregnation, the solid was separated from the solution by filtration without washing and dried for several hours at 110°C. A PtSFMZ catalyst with 0.4 wt% Pt was prepared by incipient wetness using 1 ml of 1 wt% H₂PtCl₆ solu-

tion per gram of SFMZ catalyst. The resulting mixture was stirred at room temperature for 1 h and then dried at 110°C for several hours.

n-Butane isomerization was carried out in a fixed bed downflow quartz reactor (10 mm i.d.) under atmospheric pressure. The dried fresh catalyst (0.4–1.0 g) was loaded in the reactor, and unless otherwise stated, it was pretreated in dry air (30 ml/min) at 650°C for 3 h, and then cooled to reaction temperature (35–180°C) in flowing He (30 ml/min). The gas mixture consisted of *n*-butane and helium flowing either at 0.5 and 30 ml/min, or at 1 and 4 ml/min, respectively. In some runs, helium was replaced by hydrogen. *n*-Butane (CP grade), He (UHP), H₂ (UHP), and compressed air (industrial) used in this work were purchased from Air Products, Inc.

The reaction products were analyzed on-line using a HP-5890 II gas chromatograph (GC) equipped with a capillary column (crosslinked methyl silicone gum, 50 m × 0.32 mm × 0.52 mm) and a flame ionization detector. In experiments carried out at 100°C over SFMZ, the first analysis of the reactor effluent was undertaken after 2 min on stream, and subsequent injections were made at 1-min intervals because of the rapid deactivation of the catalyst. Consequently, by-products (i.e., propane and pentane) were most often not detected. In some runs, these by-products were measured, and their combined selectivity was found to be less than 5%. For reactions carried out at temperature below 50°C, the first GC analysis was made after 5 min on stream, and subsequent injections were made every 5 min.

RESULTS

Figure 1 shows *n*-butane conversion versus time on stream at different reaction temperatures. It is seen that increasing the reaction temperature in the range of 35–100°C leads to a shorter induction period, a faster rate of deactivation, and a higher maximum rate of *n*-butane conversion. An apparent activation energy of 12.7 kcal/mol was determined from an Arrhenius plot based on the maximum *n*-butane conversion over the temperature range 35–100°C (Fig. 1, insert). This value is in good agreement with the 11.4 and 10.5 kcal/mol reported by Hsu *et al.* (3) and Wan *et al.* (12), respectively.

To investigate the contention that Fe and Mn promoters enhance the surface concentration of butene (10), we undertook the following set of experiments. The first experiment was carried out at 35°C using a short residence time over the same SFMZ catalyst as in Fig. 1 (*n*-butane = 0.5 ml/min, He = 30 ml/min, SFMZ = 1 g). As shown in Fig. 2 (curve A), under these conditions, the conversion of *n*-butane was very low. In the second experiment, a longer residence time was used (*n*-butane = 1 ml/min, He = 4 ml/min, SFMZ = 1 g), and a much higher *n*-butane conversion was

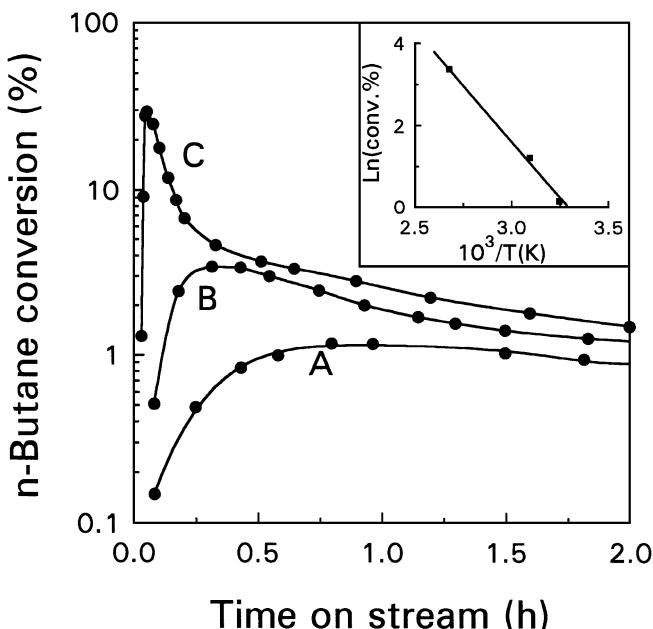


FIG. 1. *n*-Butane conversion over regenerated SFMZ vs time on stream at different reaction temperatures. Reaction conditions: 1 g of catalyst; $n\text{-C}_4 = 0.5 \text{ ml/min}$; He = 30 ml/min; reaction temperature: (A) 35°C, (B) 50°C, (C) 100°C. Insert: Arrhenius plot.

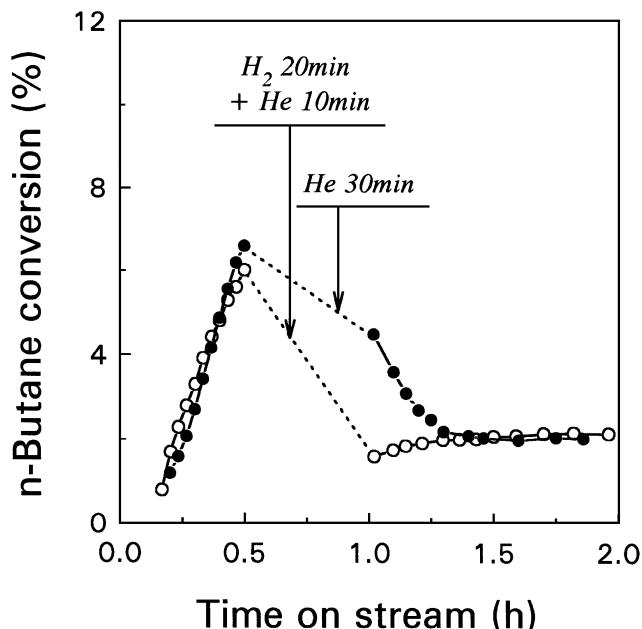


FIG. 3. *n*-Butane conversion over SFMZ vs time on stream at 35°C. During the first 0.5 h on stream, the reaction conditions were the same as in Fig. 2, curve B. The catalyst was purged by He (30 ml/min) for 0.5 h (●) or by H_2 (30 ml/min) for 20 min followed by He (30 ml/min) for 10 min (○). Then the reaction was resumed under the same conditions as in Fig. 2, curve A.

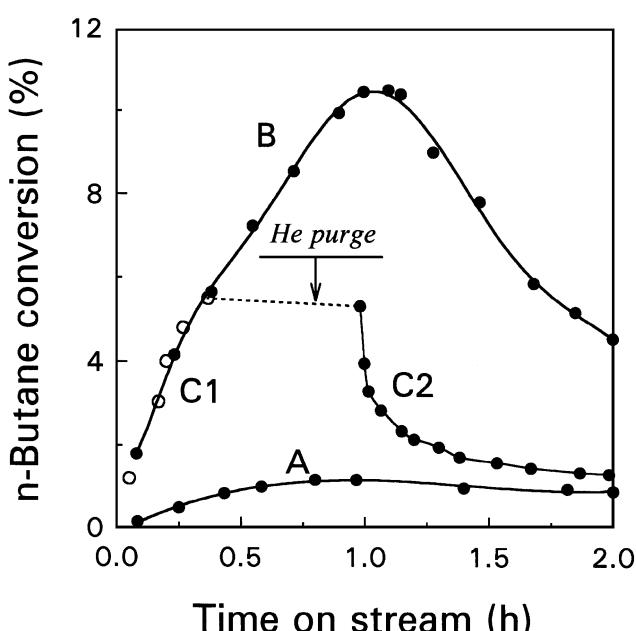


FIG. 2. *n*-Butane conversion over SFMZ vs time on stream at 35°C. Reaction conditions: 1 g of catalyst; (A) $n\text{-C}_4 = 0.5 \text{ ml/min}$, He = 30 ml/min; (B) $n\text{-C}_4 = 1 \text{ ml/min}$, He = 4 ml/min. (C) During the first 0.4 h on stream (curve C1), the reaction conditions were the same as for curve (B). At 0.4 h on stream the catalyst was purged by He (30 ml/min) for 0.5 h. Then the reaction was resumed (curve C2) under the same conditions as for curve A.

observed (Fig. 2, curve B). In the third experiment (Fig. 2, curves C1 and C2), the reaction was started under the same conditions as for curve B. The *n*-butane conversion thus obtained versus time on stream is shown by open circles in Fig. 2 (curve C1). At 0.4 h on stream, the reaction was stopped and the catalyst was purged with helium (30 ml/min) for 0.5 h. Then the reaction was resumed under the same conditions as for curve A. In this case, higher *n*-butane conversions (curve C2) than those shown in curve A were obtained.

Figure 3 summarizes two comparative experiments carried out on a different batch of SFMZ catalyst and a different experimental set-up. Data (full circles) were obtained under the same pretreatment and reaction conditions as those in Fig. 2, curves C1 and C2. The slight decrease in the activity after the helium purge is probably related to analysis timing during rapid deactivation. The other data (Fig. 3, open circles) were obtained under identical conditions except that the purge took place under flowing H_2 (30 ml/min for 20 min) followed by He (30 ml/min for 10 min).

Figure 4 shows the effect of hydrogen on *n*-butane isomerization over the SZ catalyst. Similar pretreatment and reaction conditions as those reported by Adeeva *et al.* (21) were used. The catalyst (1.5 g) was first calcined *ex situ* in static air (620°C, 3 h), and then pretreated *in situ* in air (30 ml/min) at 450°C for 2 h and cooled to the reaction temperature (180°C) under flowing He. The feed stream

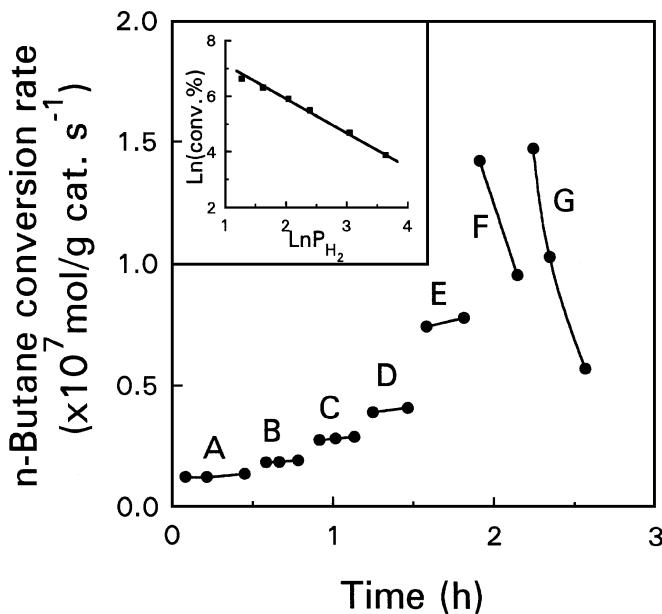


FIG. 4. *n*-Butane conversion rate over SZ vs time at different $\text{H}_2/\text{n-C}_4$ ratio. Reaction conditions: 1.5 g of catalyst; reaction temperature, 180°C. $\text{H}_2/\text{n-C}_4$ (mol/mol): (A) 60, (B) 45, (C) 30, (D) 20, (E) 9, (F) 4, (G) 0. Insert: Dependence of *n*-butane conversion on hydrogen partial pressure.

(120 ml/min) consisted of *n*-C₄ (0.75 ml/min), hydrogen, and helium. The flow rates of H₂ and He were adjusted according to the desired H₂/He ratio. As seen in Fig. 4, at high H₂/n-C₄ ratios, the catalyst activity was stable and the conversion rate increased as more hydrogen was replaced by helium. As the H₂/n-C₄ ratio reached 4 and then 0, the deactivation rate increased dramatically so that data had to be collected immediately after changing the feed composition in order to measure the initial (or intrinsic) activity of the catalyst. It is shown clearly in Fig. 4 that the rate of *n*-butane conversion increases significantly (from ca. 2×10^{-8} to 1.5×10^{-7} mol/g cat. s $^{-1}$) with decreasing partial pressure of hydrogen (from H₂/n-C₄ = 60 to 0). Kinetic analysis of the hydrogen effect (Fig. 4, insert) shows that the reaction order in H₂ as calculated from the slope of the straight line ln(conv. %) vs hydrogen pressure is -1.2. This result is in excellent agreement with that reported recently (-1.1 to -1.3) by Liu *et al.* (22).

Figures 5–7 depict the effect of hydrogen on *n*-butane isomerization over three different catalysts (SZ, SFZ, and SFMZ) under the same reaction conditions (0.4 g of catalyst; 0.5 ml/min of *n*-butane; 30 ml/min of He or H₂; at 100°C). Again, a strong negative effect of hydrogen was observed over SZ (Fig. 5). In addition, isomerization of butane in helium exhibits an induction period followed by deactivation. When Fe was added to SZ, the hydrogen effect became very weak (Fig. 6). Further, when both Fe and Mn promoters were present on SZ, the hydrogen effect disappeared (Fig. 7).

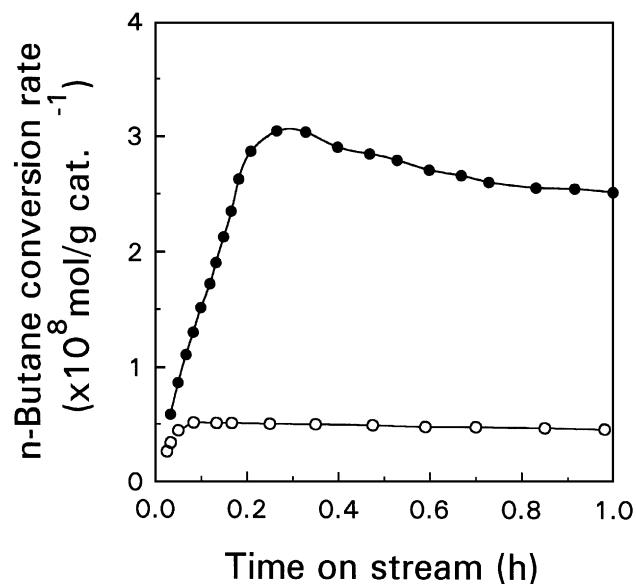


FIG. 5. *n*-Butane conversion rate over SZ vs time on stream at 100°C. Reaction conditions: 0.4 g of SZ calcined *ex situ* in static air at 620°C for 3 h and *in situ* in flowing air at 500°C for 2 h; (●) $n\text{-C}_4 = 0.5 \text{ ml/min, He} = 30 \text{ ml/min}$; (○) $n\text{-C}_4 = 0.5 \text{ ml/min, H}_2 = 30 \text{ ml/min}$.

n-Butane conversion over Pt-containing SFMZ was strongly affected by hydrogen. Three reactions were carried out at 100°C over 0.4-g batches of PtSFMZ calcined *in situ* at 650°C for 3 h using *n*-C₄, He, and H₂ mixtures flowing at 30.5 ml/min. The feed compositions were *n*-C₄:He:H₂ = 0.5:30:0, 0.5:29:1, and 0.5:0:30. The

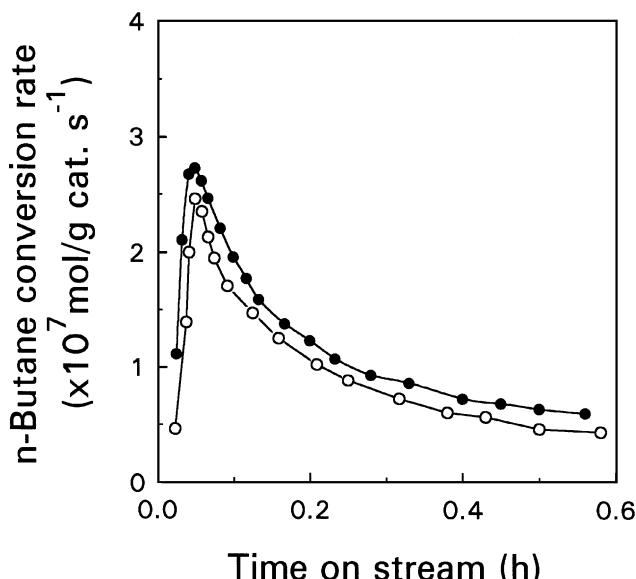


FIG. 6. *n*-Butane conversion rate over SFZ vs time on stream at 100°C; 0.4 g of SFZ calcined *ex situ* at 600°C for 16 h. All other conditions are the same as in Fig. 5.

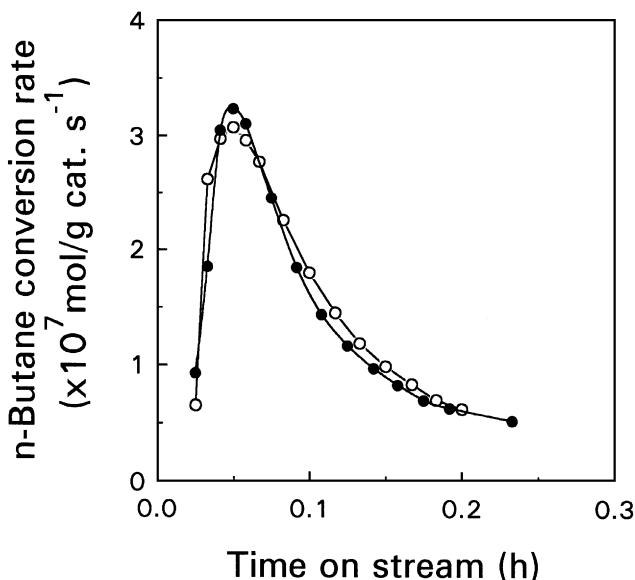


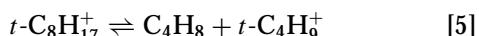
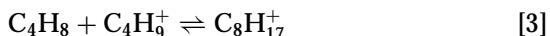
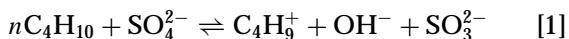
FIG. 7. *n*-Butane conversion rate over SFMZ vs time on stream at 100°C; 0.4 g of SFMZ calcined *ex situ* at 600°C for 16 h. All other conditions are the same as in Fig. 5.

maximum conversion rates were 1.4×10^{-7} , 0.3×10^{-7} , and 0.2×10^{-8} mol/g cat. s⁻¹. The induction period in the two first experiments was ca. 5 min.

DISCUSSION

Reaction Mechanism

There are essentially two proposed mechanisms for *n*-butane isomerization over acid catalysts (23, 27). The first one is a monomolecular mechanism involving abstraction of a hydride followed by isomerization of the secondary carbonium ion into a tertiary carbonium ion via methyl shift, hydride transfer, and isobutane desorption. This mechanism was reported by at least two research groups (28, 29) to occur in the presence of PtSZ. However, the majority of authors (9, 10, 12, 18–22, 24) have proposed that low-temperature *n*-butane conversion over SZ-based catalysts proceeds through a bimolecular mechanism. This mechanism can be represented as follows:



In this mechanism, the formation of butene takes place most likely through a redox process (Eqs. [1] and [2]). The butene thus formed can react with a C₄ carbonium ion to form a C₈ carbonium ion (Eq. [3]) which then undergoes skeletal rearrangement (Eq. [4]) and β -scission (Eq. [5]) to generate a tertiary C₄ carbonium ion. Finally, isobutane is formed as a result of hydride transfer between the *t*-C₄⁺ and a reactant molecule (Eq. [6]). Compared to a monomolecular *n*-butane isomerization process, the bimolecular pathway avoids the formation of primary carbonium ions, and thus requires a lower activation energy to initiate the reaction. Experimental evidence for such a mechanism is based mainly on the binomial distribution of ¹³C in the isomerization products of double-labeled *n*-butane (20–22), the negative effect of H₂ observed over SZ-based catalysts (10, 21, 22), and also the formation of C₈ disproportionation products (30).

Based on the above-mentioned investigations, in the following discussion of our results, we concur that *n*-butane isomerization at low temperature over SZ-based catalysts takes place via the bimolecular mechanism. Moreover, on the basis of our experimental data on hydrogen effect, we believe, as proposed by Coelho *et al.* (8, 10), that the role of the promoters is not only to facilitate the formation of unsaturated intermediates (C₄H₉⁺ and butene), but also to stabilize them on the catalyst surface. As a result of this stabilization effect, the surface concentration of the unsaturated species may be increased.

The bimolecular mechanism is consistent with many experimental observations associated with low-temperature *n*-butane conversion over SZ-based catalysts. For example, a common feature reported in the literature dealing with *n*-butane isomerization over SFMZ under inert atmosphere is the occurrence of an induction period of increasing conversion, followed by deactivation. The induction period corresponds to the time needed for the formation and accumulation of unsaturated intermediates (butenes). The activity decrease following the induction period is ascribed to the formation of coke precursors. Deactivation by coke deposition was suggested by several workers (25, 31) and confirmed recently by ESR and by direct observation by *in situ* Raman and UV-visible diffuse reflectance spectroscopies (32).

Based on the above reasoning, the effect of reaction temperature on the length of the induction period and the rate of deactivation (Fig. 1) can be rationalized as follows. The formation of C₄ carbonium ions and butenes is accelerated at higher temperature. The impact of the enhanced formation of butenes on the catalyst surface is twofold. On the one hand, it favors the bimolecular process, and therefore increases the conversion of *n*-butane. This leads to a shorter induction period and a higher maximum conversion at higher reaction temperature (Fig. 1). On the other hand, the increased butene concentration enhances

the polymerization of the olefins, leading to a more rapid formation of coke precursors and catalyst deactivation.

Obviously, butene plays an important role in the bimolecular process. Liu *et al.* (22) found that the *n*-butane conversion rate over a PtSZ catalyst decreased when the feed which contained 33 ppm butene was preequilibrated in hydrogen over a Pt/SiO₂ catalyst. Coelho *et al.* (10) found that preadsorption of a small amount of 1-butene on the catalyst resulted in a shorter induction period, a higher activity, and a faster deactivation.

As mentioned in the Introduction, the role of the promoters is still unclear. Several authors proposed that the promoters help generate butenes (7, 12, 20–22). Coelho *et al.* (10) argued that if the only role of the promoters is the formation of butene, addition of 1-butene in the feed should generate an activity level over SZ catalyst comparable to that observed over Fe- and Mn-promoted SZ. Since this was not the case they suggested that the role of the promoters is not only to generate butene, but also to enhance its concentration on the catalyst surface. To further examine the ability of the promoters to retain butene (and other hydrogen-deficient species) on the catalyst surface, we designed the experiments shown in Fig. 2. In the experiment represented by curve A, low *n*-butane conversions were observed because the residence time of the feed over the catalyst was short. With a longer residence time, the conversion increased significantly (curve B). It is inferred that at the same time on stream the amount of butene accumulated under the conditions in curve B is higher than that accumulated under the conditions in curve A. In the third experiment (curves C1 and C2), we started the reaction using the same long residence time as in curve B, and then stopped it

while the conversion was still increasing (curve C1). It was assumed that during this period butene forms and accumulated on the catalyst surface. Then, helium (30 ml/min) was introduced through the catalyst bed for 0.5 h, and the reaction was resumed under the same short residence time as in curve A. As shown in curve C2, a much higher conversion than under conditions (A) was observed. Clearly, this conversion difference is due to the presence of a higher surface concentration of butenes generated during the first reaction period represented by curve C1. These butenes remained on the SFMZ catalyst surface even after a 0.5-h purge with helium at 35°C. In agreement with Coelho *et al.* (9, 10), it is inferred that in the presence of SFMZ, butene is strongly stabilized on the catalyst surface. Moreover, as shown in Fig. 3, if the 30-min He purge were replaced by a 20-min H₂ treatment followed by a 10-min He purge at the same temperature (35°C), the activity obtained when the reaction is resumed at high residence time is significantly lower. This indicates that the accumulated intermediates are not stable in a pure hydrogen atmosphere, most likely because of their hydrogen-deficient character. In summary, these simple experiments provide convincing evidence of the occurrence of hydrogen-deficient intermediates species and the ability of the promoters to stabilize them.

Direct comparison of this behavior with SZ was unfortunately not possible because on the one hand SZ is not active at 35°C, and on the other hand if comparison is made at a temperature where SZ exhibits a reasonable activity, e.g., 150°C, the reaction intermediates over SFMZ are no longer stable under He. Moreover, at 150°C the reaction over SFMZ becomes extremely fast and the catalyst is deactivated very quickly (Table 1).

TABLE 1
n-Butane Isomerization over SFMZ under Different Conditions

| No. | Pretreatment | Reaction conditions | Reaction temp. (°C) | Maximum conv. (%) | Time (min) ^a |
|-----|--|--|---------------------|-------------------|-------------------------|
| 1 | Air, 650°C, 3 h ^b | 1 g cat., 0.5 ml/min <i>n</i> -C ₄ , 30 ml/min He or H ₂ | 35 | 1.2 | 48 |
| 2 | Same | Same | 50 | 3.4 | 19 |
| 3 | Same | Same | 100 | 29.5 | 3.5 |
| 4 | Air, 600°C, 16 h ^c ; air, 600°C, 2 h ^{b,d} | 0.4 g cat., 10.9 ml/min <i>n</i> -C ₄ , 20.6 ml/min He ^d or H ₂ | 100 ^d | 18 | 3.2 |
| 5 | Air, 500°C, 2 h ^{b,e} | Same | 100 | 14 | 4.1 |
| 6 | Air, 620°C, 3 h ^c | Same | 100 | 35 | 3.0 |
| 7 | Same as experiment (4) | Same | 180 | 23.8 ^f | t.s. ^g |

^a Time for maximum conversion.

^b *In situ* treatment.

^c *Ex situ* treatment.

^d Same conditions as in Ref. (10).

^e Regenerated catalyst.

^f First data point.

^g Too short.

Hydrogen Effect

According to the bimolecular mechanism of *n*-butane isomerization, hydrogen is supposed to display a negative effect on the reaction rate, because the formation of hydrogen-deficient species is obviously inhibited in the presence of hydrogen. This is clearly demonstrated in the case of SZ catalyst (Fig. 4). Several authors (21, 23, 32–34) have also observed that hydrogen suppresses the initial (intrinsic) *n*-butane conversion over SZ, although it increases the catalyst lifetime by reducing the accumulation of carbonaceous species on the catalyst surface. As shown in Fig. 4, the deactivation rate increases as the $H_2/n\text{-C}_4$ ratio decreases, and it was necessary to use the initial activity data in order to have a satisfactory Arrhenius plot. In some of the earlier investigations (22, 35), H_2 was found to have a positive effect on *n*-butane isomerization over SZ and PtSZ. However, this conclusion was drawn from steady state data or from data obtained after more than 30 min on stream. In our opinion, it reflects a strong decrease in the rate of deactivation in H_2 rather than a higher intrinsic activity of the catalyst.

Figure 5 shows the *n*-butane conversion rate over SZ during the early stages of the reaction. A clear induction period was observed when the reaction was carried out in helium, which is consistent with the occurrence of a bimolecular reaction mechanism. When the reaction was performed in hydrogen, the conversion was dramatically suppressed. However, it is interesting to observe that in the presence of Fe-promoted catalyst, the negative effect of hydrogen became much weaker (Fig. 6). Furthermore, over SFMZ catalyst the negative effect of hydrogen disappeared completely (Fig. 7). At variance with this finding, Coelho *et al.* (10) recently reported a strong negative effect of hydrogen on *n*-butane conversion over SFMZ catalysts.

In order to make sure that the data shown in Fig. 7 are representative of the behavior of our SFMZ catalyst, we compared *n*-butane isomerization in helium and in hydrogen over a wide range of temperature (35 to 180°C), feed compositions ($H_2/n\text{-C}_4 = 2$ to 60), and flow rates (5 to 31.5 ml/min). Table 1 provides typical data obtained under different pretreatment and reaction conditions. In all cases, no hydrogen effect was observed. Even though no butene impurity was reported by the supplier of the butane used in this study, we considered the possibility that trace amounts of butene present in the feed participate in the dimerization-cracking process (Eqs. [3]–[6]), leading to an apparent lack of hydrogen effect. In one experiment, a hydrogenation reactor was placed upstream of the isomerization reactor. The hydrogenation reactor contained 0.5 g of 5 wt% Pt/Al₂O₃ catalyst (Strem Chemicals, Inc.) which was prereduced *in situ* in flowing H_2 (30 ml/min) at 300°C for 1 h and then cooled to room temperature. The feed stream consisting of *n*-butane and H_2 flowed first through

the hydrogenation reactor and then through the isomerization reactor. The data obtained under these conditions were the same as those found without using the hydrogenation reactor. This confirms that no negative effect of hydrogen occurs over our SFMZ catalysts.

The absence of H_2 effect on *n*-butane isomerization over SFMZ catalyst is not necessarily inconsistent with the occurrence of a bimolecular mechanism. A reasonable explanation rests on the strong stabilization effect of Fe and Mn promoters on unsaturated intermediates (carbenium ions and butenes) on the catalyst surface, as already inferred from Figs. 2 and 3. The surface concentration of the unsaturated species depends not only on the partial pressure of hydrogen in the gas phase, but also on the ability of the catalyst to retain them on its surface. The more stable the species on the surface, the weaker the effect of H_2 on the rate of their formation or transformation. It is understood that if the stability of the reaction intermediate is high enough, the limited range of hydrogen pressure explored here may not be sufficient for the catalyst to experience a measurable hydrogen effect. It is inferred that (i) $C_4H_9^+$ and butene intermediates are held more strongly on the surface of SFMZ than on the SZ surface, and (ii) the strong stabilizing effect of Fe and Mn promoters on the reaction intermediates is at the origin of the remarkable increase in butane conversion over SFMZ compared to its unpromoted SZ counterpart. Lee *et al.* (36–38) studied the interactions of sulfated iron oxide with pyridine, ammonia, 1-butene, and butane by TPD and mass spectrometry. They found that contrary to butane, the other three molecules adsorb strongly on the catalyst by direct interaction between the nitrogen electron pair or the π -bond with coordinatively unsaturated iron. A similar stabilization process may occur during *n*-butane isomerization at low temperature over iron-containing catalysts.

Although no hydrogen effect was observed on SFMZ, we did observe a strongly negative effect of H_2 over Pt containing SFMZ catalysts. Furthermore, we found that the presence of even a small amount of hydrogen (3.3 mol%) in the feed causes a sharp decrease in *n*-butane conversion rate. In our previous reports we found that PtSZ catalyst calcined at 600°C exhibits metallic Pt (26, 39), and catalyzes propene hydrogenation at 35°C (24). This indicates that under these conditions PtSZ is capable of adsorbing H_2 dissociatively. It is inferred that this may also be the case for calcined PtSFMZ. Furthermore, because of the intimate contact between the Pt particles and the promoter species on the catalyst surface, it is reasonable to assume that the highly active atomic hydrogen will react readily on the catalyst surface with butenes. Under these conditions, hydrogenation of butenes will prevail over their association with $C_4H_9^+$ to form a C_8 carbenium ion. As a result, the bimolecular pathway is blocked, and the *n*-butane conversion decreases. It should be noticed that the occurrence

of hydrogen spillover over prerduced PtSZ has already been documented (35, 40). In this case, higher temperatures were needed because the catalyst was prerduced and consequently Pt was poisoned by sulfur during reduction.

CONCLUSION

Based on the fact that *n*-butane isomerization over sulfated zirconia and related catalysts takes place via an intermolecular mechanism, the following conclusions were reached. The induction period of the catalytic activity corresponds to the accumulation of unsaturated intermediates (butenes and carbenium ions). The length of the induction period is dependent on the reaction conditions (temperature, flow rate, and feed composition). The negative reaction order in hydrogen over SZ observed in this work and others is consistent with the intermolecular mechanism. The addition of promoters (Fe and Mn) to SZ dramatically decreases the negative effect of hydrogen. This finding indicates that transition metal oxides not only favor the formation of olefinic intermediates but also stabilize them strongly. The strong negative effect of H₂ on *n*-butane isomerization over PtSFMZ was attributed to the dissociative adsorption of hydrogen and the fast hydrogenation of unsaturated intermediates by atomic hydrogen.

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