

Effect of Pt and H₂ on *n*-Butane Isomerization over Fe and Mn Promoted Sulfated Zirconia

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The activity of a 0.4 wt% Pt-containing Fe and Mn promoted sulfated zirconia (PtSFMZ) catalyst in *n*-butane isomerization at 35°C was compared to that of a Pt-free catalyst (SFMZ). The maximum rate of *n*-butane conversion observed in helium over PtSFMZ was found to be 2.5 times higher than that over the SFMZ catalyst under the same conditions. It is believed that *n*-butane isomerization proceeds via a bimolecular mechanism in which the formation of hydrogen-deficient intermediates (carbenium ions and butenes) is necessary and the presence of transition metals such as Pt, Fe, and Mn on sulfated zirconia facilitates the formation/accumulation of these intermediates and increases their stability on the catalyst surface. The presence of H₂ had a strong negative effect on *n*-butane conversion over PtSFMZ, but had no effect over SFMZ. The negative effect of H₂ on PtSFMZ catalyst in *n*-butane isomerization reaction was attributed to the decreased concentration of butenes in the presence of hydrogen atoms which are formed by the dissociation of H₂ on Pt. The ability of calcined Pt-containing catalysts to activate hydrogen at 35°C was demonstrated. Reduced SFMZ with or without Pt was not active at 35°C regardless of the nature of the carrier gas. © 1996 Academic Press, Inc.

INTRODUCTION

About 15 years ago, Arata and co-workers (1) claimed that sulfate anion treated zirconia possesses superacidity with a Hammett acidity function $H_0 \leq -16$ and is capable of catalyzing *n*-butane isomerization at room temperature. The catalytic performance of these materials is unique compared to that of typical solid acid catalysts such as zeolites which show no activity for the reaction at such a low temperature. Since then, extensive studies have been devoted to this field, and several reviews are now available (2–8).

Recently, Hsu *et al.* (9) found that sulfated zirconia promoted with Fe and Mn (designated as SFMZ) is about three orders of magnitude more active than the unpromoted catalyst (SZ) for *n*-butane isomerization at near room temperature. This remarkable activity was later confirmed in several laboratories (10–13). Using TPD of substituted benzenes,

Lin and Hsu (14) reported that the promoted catalyst has more and stronger acid sites than the unpromoted one. However, the desorption peak they assigned to benzene adsorbed on extremely strong acid sites was later found to correspond not to desorbed benzene but to a mixture of CO₂, SO₂, and O₂ (10). Similar observations were also made by Adeeva *et al.* (11) and Sikabwe *et al.* (15) when they conducted TPD of acetonitrile, ammonia, pyridine, and benzene from SZ and Fe–Mn and Ni promoted SZ. The above facts imply that (i) SFMZ and SZ have sites capable of strongly adsorbing and oxidizing these adsorbate molecules and (ii) TPD of these adsorbates may not be a suitable technique for characterizing the acidity of SFMZ and SZ. Adeeva *et al.* (11) studied the acidity of SFMZ and SZ catalysts by means of FTIR and NMR spectroscopies of adsorbed bases. They found that both SZ and SFMZ are not superacids, and there is no significant difference in acid strength between these two catalysts. Using different means, several other authors concluded that SZ is not a superacid (16–18), and SZ and SFMZ have similar acid strengths (12, 13, 19).

Since there is a strong evidence that SZ and SFMZ have comparable acid strengths, but their butane isomerization activity at low temperature differs significantly from each other (SZ \ll SFMZ), it seems that the acidity and activity of these catalysts are not directly correlated. To explain the origin of the remarkable activity of SFMZ, Adeeva *et al.* (11) considered two hypotheses. The first one assumes that the presence of Fe and Mn promoters may enhance the stability of reaction intermediates such as chemisorbed carbenium ions. The other interpretation rests on the hypothesis that the promoters facilitate the formation of butane as a reaction intermediate. In this case, the isomerization of *n*-butane is supposed to proceed via a bimolecular mechanism (20, 21) involving the formation of C₈ species by interaction of C₄ carbenium ions with butane molecules, followed by rearrangement and β -scission, yielding fragments with iso-C₄ skeleton. The latter hypothesis was supported by a study using ¹³C-labeled butane (22) and a kinetic investigation (23). Recently, this reasoning has been extended to *n*-butane isomerization over SZ (24) and PtSZ (25).

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Both SFMZ and SZ deactivate fast during hydrocarbon isomerization. It has been shown that the addition of small amounts of Pt onto SZ greatly improves the catalyst stability under hydroisomerization and hydrocracking conditions (26–28). The initial purpose of the present work was to improve the stability of SFMZ by addition of Pt. We found that the presence of Pt has a positive effect on the activity of SFMZ toward *n*-butane isomerization provided that the reaction is carried out in helium and that the catalyst is calcined but not reduced. However, in the presence of hydrogen, *n*-butane conversion over PtSFMZ vanishes.

EXPERIMENTAL

ZrOCl₂ · 8H₂O (98%, Aldrich), NH₄OH (28–30%, Anachemia), Fe(NO₃)₃ · 9H₂O (98%, Aldrich), Cr(NO₃)₃ · 9H₂O (99%, Aldrich), Mn(NO₃)₂ · 6H₂O (98%, Aldrich), (NH₄)₂SO₄ (99%, Aldrich), and H₂PtCl₆ (99.9%, 38–40% Pt, Aldrich) were used for catalyst preparation. Zr(OH)₄ was prepared as described earlier (29) and crushed to below 100 mesh. SFMZ was prepared using the procedure of Jatia *et al.* (10). Pt (0.4 wt%) was impregnated on SFMZ by adding 1 ml of 1 wt% H₂PtCl₆ solution per gram of SFMZ catalyst. The resulting mixture was stirred at room temperature for 1 h and then dried at 110°C. The Pt-containing SFMZ catalyst is denoted hereafter as PtSFMZ. A chromium-containing catalyst (SCMZ) was prepared using the same procedure as for SFMZ except that Cr(NO₃)₃ · 9H₂O was used instead of Fe(NO₃)₃ · 9H₂O.

n-Butane isomerization was carried out in a fixed bed downflow quartz reactor (10 mm i.d.). The dried catalyst (1.0 g) was loaded in the reactor. Unless otherwise stated, the catalyst was first calcined at 650°C for 3 h in flowing air (30 ml/min) and cooled from 650 to 35°C under flowing helium. Then the mixture of *n*-butane (1 ml/min) with helium or hydrogen (4 ml/min) was fed into the reactor. The products were analyzed on-line using an HP 5890 gas chromatograph equipped with a capillary column (cross-linked methyl silicone gum, 50 m × 0.32 mm × 0.52 μm) and an FID. Consistent with the results of Hsu *et al.* (9) but in contrast with those of Jatia *et al.* (10), we found that deactivated SFMZ catalysts can be regenerated in flowing air at 500°C (3 h) and can be used repeatedly with reproducible behavior.

Hydrogenation of propene was performed under atmospheric pressure at 35°C using a 4:1 mixture of H₂/C₃H₆ flowing at 5 ml/min.

RESULTS AND DISCUSSION

The rate of *n*-butane conversion in helium versus time on stream over SFMZ and PtSFMZ catalysts is presented in Fig. 1. As seen, the PtSFMZ catalyst exhibits a higher activ-

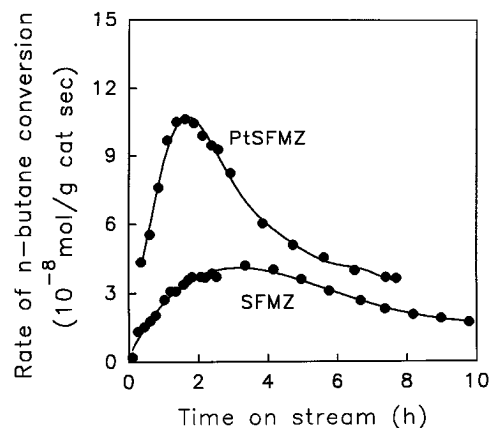


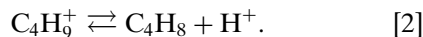
FIG. 1. Effect of Pt on the activity of SFMZ for *n*-butane isomerization in helium. Reaction conditions: 1 g of *in situ* air calcined catalyst (650°C, 3 h); *T*, 35°C; *n*-C₄, 1 ml/min; helium, 4 ml/min.

ity than SFMZ. The maximum rate of *n*-butane conversion obtained over PtSFMZ catalyst (1.1×10^{-7} mol/g cat s) was 2.5 times higher than that over SFMZ (4.4×10^{-8} mol/g cat s). Both catalysts showed an induction period followed by a fast deactivation. The induction period over PtSFMZ is shorter than that over SFMZ. Figure 1 indicates that Pt has an additional promoting effect on the already promoted SFMZ.

A similar promoting effect of Pt as well as Ir, Rh, Ru, Os, and Pd on SZ for *n*-butane conversion in helium was recently reported by Hino and Arata (30, 31). The authors attributed the increased activity of Pt loaded SZ catalysts (designated as PtSZ) to the enhancement of acid strength. Based on an empirical correlation between Hammett acid function (*H*₀) of SZ catalysts versus reaction temperature at constant *n*-butane conversion under similar conditions, they suggested that the PtSZ catalyst has an *H*₀ value of ≤ -20.5 and consequently is a stronger superacid than SZ. However, this correlation as well as the use of Hammett indicators for the characterization of the acidity of sulfated zirconia are questionable. According to Adeeva *et al.* (11), an exceptionally active catalyst for an acid-catalyzed reaction does not necessarily possess an extremely strong acidity. The high activity may originate from the occurrence of a energetically more favorable reaction pathway. As mentioned in the Introduction, *n*-butane isomerization can proceed via an oligomerization and cracking process, in which butene is formed as a reaction intermediate. This reaction pathway may be energetically favored over monomolecular isomerization, because it is expected to involve secondary and tertiary carbenium ions, whereas the monomolecular isomerization of *n*-butane takes place via the formation of highly unstable primary carbenium ions.

It is worth pointing out that the formation of butenes at low temperature ($<100^\circ\text{C}$) is likely to occur not through the direct dehydrogenation of butane but via an acid site

assisted process (20, 32) as shown in Eqs. [1] and [2], since the former reaction is thermodynamically favored only at very high temperatures (33):



It is inferred that any catalyst component (in combination with surface acid sites) that can facilitate the formation and accumulation of unsaturated intermediates (butenes or carbenium ions) because of increased stability of adsorbed carbenium ions will exhibit a promoting effect on *n*-butane isomerization over SZ based catalysts. Transition metal oxides such as Fe_2O_3 are known to possess dehydrogenation activity (34); their ability for hydrogen abstraction in combination with acid sites may help the formation, accumulation and stabilization of the unsaturated intermediate species. This may be at the origin of the remarkable catalytic activity of SFMZ for *n*-butane isomerization (11, 22). This interpretation is further corroborated by data we obtained in the presence of Cr and Cr-Mn promoted sulfated zirconia (SCZ and SCMZ) catalysts. Figure 2 shows that under the same reaction conditions as for SFMZ, the SCZ and SCMZ catalysts exhibit comparable behaviors to Fe and Fe-Mn promoted sulfated zirconia catalysts. It should be mentioned that chromium oxide is among the best dehydrogenation catalysts (35). Its strong hydrogen abstraction ability leads to the fast formation and accumulation of unsaturated species. This is likely the reason for the induction period, if there is any, to be very short (Fig. 2). The promoting effect of Pt on SFMZ may be explained on the same basis. The presence of Pt enhances the rate of hydrogen abstraction leading to butenes. Therefore, a shorter induction period is observed over PtSFMZ than over SFMZ. According to Adeeva *et al.* (11, 22, 24) and Coelho *et al.* (13, 32), the rate-limiting step in the early stage of the induction is the

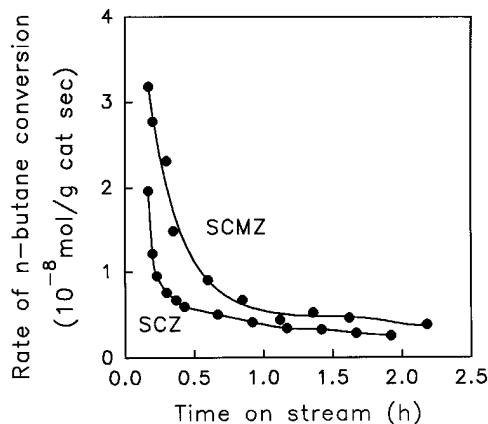


FIG. 2. *n*-Butane conversion rate over SCZ and SCMZ catalysts in helium versus time on stream. Reaction conditions: 1 g of *in situ* air calcined catalyst (650°C, 3 h); *T*, 35°C; *n*-C₄, 1 ml/min; helium, 4 ml/min.

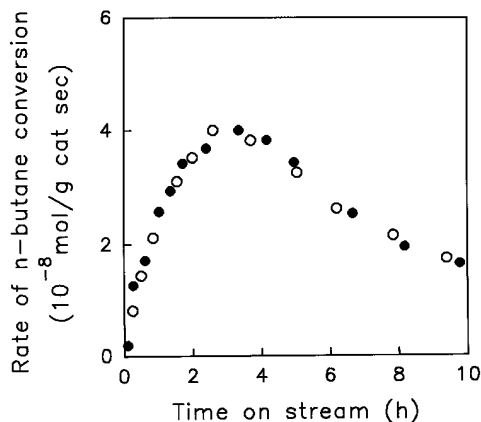


FIG. 3. *n*-Butane conversion rate over fresh SFMZ versus time on stream in helium (●) and in hydrogen (○). Reaction conditions: 1 g of *in situ* air calcined SFMZ (650°C, 3 h); *T*, 35°C; *n*-C₄, 1 ml/min; helium or hydrogen, 4 ml/min.

formation/accumulation of the unsaturated species. Thus the induction period is ascribed to the time needed for the building-up of these species. The role of these unsaturated species (particularly butenes) is twofold. They induce the bimolecular mechanism of butane isomerization by reacting with C₄ carbenium ions, but their accumulation on the catalyst surface leads to the formation of coke precursors. Therefore, the induction period and the subsequent deactivation stem from a common cause.

Based on the bimolecular mechanism of *n*-butane isomerization, it is expected that the formation of the hydrogen-deficient intermediate species (e.g., C₄H₉⁺ in Eq. [1]) will be suppressed in the presence of hydrogen. Indeed, Garin *et al.* (36) and Adeeva *et al.* (24) reported that *n*-butane isomerization over SZ at 180–250°C has much higher initial (intrinsic) rate in helium than in hydrogen. However, it is very surprising that we did not observe any negative effect of hydrogen over SFMZ. As shown in Fig. 3, the presence of H₂ did not decrease the activity of SFMZ under our reaction conditions (*P* = 1 atm, *t* = 35°C). This unexpected behavior is in disagreement with recent data by Coelho *et al.* (32). In order to make sure that data shown in Fig. 3 are representative of the behavior of our SFMZ catalyst we compared reaction rates in helium and in hydrogen under different temperatures (35–180°C) and H₂/*n*-C₄ ratios (4–60). In all cases, no hydrogen effect was observed. A tentative interpretation of these findings is as follows. In the two-step butene formation, H₂ pressure may affect only the formation of C₄H₉⁺ (Eq. [1]) but not its subsequent transformation into butene (Eq. [2]). Based on Eq. [1], it is understood that the magnitude of the effect of H₂ pressure depends on the stability of adsorbed carbenium ions. The more stable the intermediate the weaker the effect. Ultimately, if the intermediate is stable enough, the effect of H₂ may not be observed within a limited range of H₂ pressure. In the present study, it is inferred that C₄H₉⁺ in-

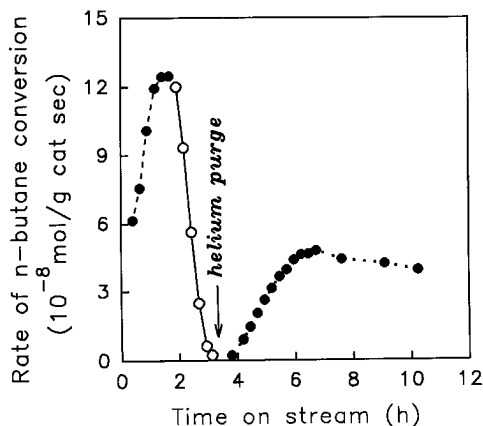


FIG. 4. Effect of carrier gas on *n*-butane conversion rate over PtSFMZ. Reaction conditions: 1 g of *in situ* air calcined catalyst (650°C, 3 h); *T*, 35°C; *n*-C₄, 1 ml/min; helium (●) or hydrogen (○), 4 ml/min.

intermediate is not adequately stabilized in the presence of SZ, while it is strongly stabilized over SFMZ. The latter statement is consistent with the proposal made by Adeeva *et al.* (11). Additional data in support of our interpretation of H₂ effect over SZ based catalysts will be reported in a forthcoming paper.

Over the Pt containing SFMZ catalyst, a strong negative effect of hydrogen was observed. For example, in one of our experiments (Fig. 4), *n*-butane isomerization reaction was started in helium and continued for 2 h, the time needed to reach the maximum conversion (Fig. 4, dashed curve). This part of the curve is similar to that obtained under the same conditions in Fig. 1 (curve PtSFMZ). After 2 h on stream, helium was replaced by hydrogen and the experiment was continued for another 1 h (Fig. 4, solid curve). By comparison to Fig. 1 (curve PtSFMZ), it is seen that under hydrogen, the activity decreases much more sharply than under helium. At 3 h on stream, the *n*-butane feed was stopped, and the catalyst was purged with helium (30 ml/min) at 35°C for 1.5 h. Then, the reaction was resumed in helium (Fig. 4, dotted curve). The purging time was not included in the time on stream in Fig. 4. The conversion rate was gradually restored to ca. 4.5×10^{-8} mol/g cat.s, the same level as that reached at the same time-on-stream by a catalyst which has not been exposed to hydrogen (Fig. 1, curve PtSFMZ). This implies that the negative effect of hydrogen on the activity of PtSFMZ at 35°C is reversible. To further check this conclusion, another experiment was carried out (Fig. 5). Instead of starting with a feed mixture of *n*-butane and helium, this experiment started with a mixture of *n*-butane and hydrogen (Fig. 5, dashed curve). It is seen in Fig. 5 that in the presence of hydrogen, the activity was negligible, even though the reaction was at its very early stages (compare with Fig. 4, dashed curve). At 0.8 h on stream in hydrogen, the *n*-butane flow was stopped, and the catalyst was purged with helium (30

ml/min) at 35°C for 1.5 h. Then the reaction was resumed in helium (Fig. 5, solid curve). The time for purging was not included in the time on stream. It is seen that the activity was almost completely restored in He to the same level as that of a fresh catalyst.

We believe that the suppressing effect of hydrogen on the activity of PtSFMZ involves the supply of active H atoms by dissociation of hydrogen on Pt, which strongly favors the hydrogenation of butene intermediates. Earlier reports indicate that, at least at room temperature, Pt in PtSZ does not exhibit common metallic properties such as H₂ and CO adsorption, or propene hydrogenation (28, 37, 38). However, in all these studies, the catalyst was reduced typically at 250–350°C before being tested. During the reduction, sulfur species migrate onto the Pt surface, most likely as S²⁻ or S⁰ species (37), and act as a strong poison. Consistent with these observations, the present study indicates that PtSFMZ reduced at 250°C has no isomerization activity at 35°C either in hydrogen or in helium, indicating that not only metallic Pt is poisoned by reduced sulfur species but also the other promoters. Actually, H₂ treatment at 250°C of a Pt-free SFMZ also leads to a nonactive material at 35°C. In contrast, calcination in air or in O₂ of Pt containing samples above 600°C, generates nonpoisoned metallic platinum (29, 39), most likely because of limited mobility of sulfate species and/or lack of affinity between Pt⁰ and sulfate. Indeed, we found that a PtSZ sample calcined *in situ* in air at 650°C and cooled in helium showed 100% conversion in propene hydrogenation at 35°C. This clearly indicates that in calcined PtSZ, and by inference in calcined PtSFMZ, Pt is not only in the metallic state, but its surface is accessible to reactants, in particular to the dissociative adsorption of H₂ at 35°C. Notice that the occurrence of the metallic state of Pt upon calcination of PtSZ, first proven by our group based on TPR, XPS, and XRD data (29, 39) was confirmed by several authors (30, 40–42).

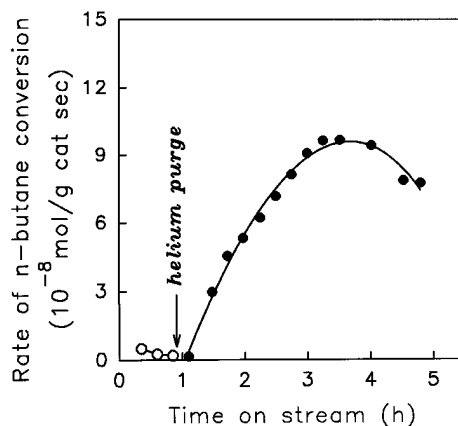


FIG. 5. Reversibility of the negative effect of H₂ on the activity of PtSFMZ for *n*-butane isomerization. Refer to the text for reaction conditions.

CONCLUSION

PtSFMZ was prepared and its catalytic activity for *n*-butane isomerization was compared with SFMZ catalyst. The maximum rate of *n*-butane conversion observed in helium over PtSFMZ was found to be 2.5 times higher than that over the SFMZ catalyst under the same conditions. It is believed that *n*-butane isomerization proceeds via a bimolecular mechanism in which the formation of hydrogen-deficient intermediates (carbenium ions and butenes) is necessary and the presence of transition metals such as Pt, Fe, and Mn on sulfated zirconia facilitates the formation/accumulation and increases the stability of these intermediates on the catalyst surface. The negative effect of H₂ on PtSFMZ catalyst in *n*-butane isomerization reaction is attributed to the decreased concentration of butenes in the presence of hydrogen atoms which are formed by the dissociation of H₂ on Pt. The absence of H₂ effect over SFMZ is most likely due to the strong stabilization of the C₄H₉⁺ intermediates. Reduced SFMZ with or without Pt was not active regardless of the nature of the carrier gas.

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