Effect of preparative conditions of Fe and Mn sulfated zirconia catalysts on their activities for n-butane isomerization

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This work investigates the effect of preparative conditions of Fe- and Mn-promoted sulfated zirconia catalysts on their activities for low-temperature n-butane isomerization. It was found that the active species on a promoted catalyst can be successfully regenerated in an oxidative treatment at 450 °C after the catalyst was deactivated either during the reaction or under a high-temperature treatment in helium. The loading sequence of Fe and Mn does not significantly affect the catalyst activity. Both Fe and Mn can individually promote the activity of sulfated zirconia catalysts. However, the promoting effect of Fe is much stronger than that of Mn; the catalyst containing only Fe is significantly more active than that containing both Fe and Mn and does not deactivate any more rapidly. The optimum Fe content was found to be 4 wt%.

Keywords: butane, isomerization, promoter, sulfated zirconia

1. Introduction

Sulfated zirconia (SZ) is a solid acid catalytic material that exhibits a high activity for low-temperature n-butane isomerization. A few years ago, Hsu and co-workers [1] first reported that the addition of Fe and Mn oxides to sulfated zirconia can significantly enhance the material's activity. Since then, many studies have been devoted to investigating the nature of the promoting effect, the acidity of the promoted catalyst, and the mechanism of low-temperature n-butane isomerization over the catalyst [2–12]. Most of these studies used the "standard" catalyst composition that was first described in the original work by Hsu et al. [1], i.e., 1.5 wt% Fe and 0.5 wt% Mn. To the best of our knowledge, there are virtually no reports about how the catalyst activity varies with the content of the promoters. In the present work, we investigate the effect of the content of the promoters and some other preparative conditions on the catalyst activity.

2. Experimental

Sulfated zirconium hydroxide was prepared using the method described in our previous communication [13]. Fe- and Mn-promoted sulfated zirconia catalysts were prepared as follows. Fe was loaded by mixing sulfated zirconium hydroxide with a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (98%, Aldrich). While stirring, the material was heated to remove the water. It was then powdered, impregnated with a solution of $Mn(NO_3)_2 \cdot 6H_2O$ (98%, Aldrich) and dried again. The amounts of added Fe and Mn were chosen to produce a catalyst with the desired contents of Fe and Mn. Some samples were prepared using different sequences for loading Fe, Mn and sulfate to investigate the influence of the sequence. In this communication, the catalyst samples are denominated according to their components (Z – zirconium hydroxide, S – sulfate, F – iron, M – manganese) and with the letters in reverse order of impregnation of the components. For example, MFSZ represents zirconium hydroxide which was first sulfated and then sequentially impregnated with iron and with manganese; SFZ represents zirconium hydroxide, first impregnated with iron and then with sulfate. The dried iron- and manganese-containing sulfated zirconium hydroxide samples were calcined at 650 °C for 3 h in static air, thus being transformed to iron-oxide- and manganese-oxide-containing sulfated zirconia.

n-butane isomerization was conducted in a fixed-bed downward-flow Pyrex or quartz reactor (9 mm i.d.) at either 55 or 80 °C under atmospheric pressure. The amount of the catalyst used was 0.25 g. The reaction feedstock was a mixture of n-butane (Instrument Grade, 99.5%) with helium (High Purity), which consisted of 1 ml/min of n-butane and 22 ml/min of helium. Prior to the reaction, calcined catalyst samples were activated in the reactor in flowing dry air (30 ml/min) at 450 °C for 2 h and cooled to reaction temperature under the activation gas stream. The reaction products were analyzed on-line using a gas chromatograph equipped with a stainless-steel column (3 mm o.d., 3 m long, packed with Porapak Q, 80/100 mesh) and a flame ionization detector. Since for all catalysts the plot of n-butane conversion versus time on stream exhibits a break-in period followed by a catalyst deactivation, the maximum conversion reached at the end of the break-in period was taken as a measure of the catalyst activity.

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Table 1
Regeneratability of Fe- and Mn-promoted SZ.

Entry	Catalyst[a]	Catalyst activation	n-butane conversion[b] (%)
1	Fresh MFSZ	Air, 450 °C, 2 h	41.0
2	Fresh MFSZ	He, 450 °C, 2 h	26.3
3	Used in entry 2	Air, 450 °C, 2 h	40.0
4	Fresh MFSZ	(He, 450 °C, 2 h) + (air, 450 °C, 2 h)	39.2

[a] All catalysts contain 1.5 wt% Fe and 0.5 wt% Mn.
[b] Reaction temperature: 80 °C.

3. Results and discussion

It has been found that at low reaction temperatures, n-butane isomerization over Fe- and Mn-promoted SZ catalysts takes place through a bimolecular mechanism which involves the formation of butene and C_4 carbenium ion, the reaction of the butene molecule with the carbenium ion to form a C_8 intermediate, and the skeletal rearrangement and β-scission of the C_8 intermediate to isobutane [4,7,9,10]. In this mechanism, the generation of butene molecules is essential, but these butene molecules can be protonated over even moderate acid sites; catalyst superacidity is not necessary. Sulfated zirconia is a material that possesses both acidic and redox properties [14,15]. Its redox property has been proposed to contribute to the formation of olefinic species from alkanes [15]. In addition, the presence of high-oxidation-state transition metals on SZ enhances the formation of the olefinic species from alkanes [10], through oxidative dehydrogenation, resulting in a higher catalytic activity. For example, Wan et al. [10] found that their SFMZ catalysts treated in dry air at over 450 °C are more active for n-butane isomerization than those treated in helium. The same observation was also made in other labs [13,16]. Wan et al. [10] suggested that an active iron oxy species (tentatively assigned as Fe(IV)) is responsible for the high activity of Fe- and Mn-sulfated zirconia near room temperature, because this species is capable of oxidative dehydrogenation of butane to generate butene which participates in the bimolecular reaction, leading to a high n-butane conversion. The proposed iron oxy species is considered to be quite labile and would be removed under a high-temperature treatment in helium [10,13,16].

3.1. Regeneration and thermal stability of iron oxy species

Given the above information about n-butane isomerization over Fe- and Mn-promoted sulfated zirconia catalyst, two questions may arise: Can the active iron oxy sites be regenerated by an oxidative treatment after deactivation in a reaction or after destruction in a high-temperature helium treatment? How thermally stable are the iron oxy species in helium? Tables 1 and 2 show our experimental results obtained in an effort to answer these questions. Table 1 (entries 1 and 2) shows that the MFSZ catalyst activated in air produces a higher activity than a catalyst activated in helium. The catalyst from entry 2 was regenerated in flowing air at 450 °C for 2 h, and its activity was found totally recovered (table 1, entry 3). In a separate experiment (table 1, entry 4), a catalyst was first treated in helium for 2 h at 450 °C to destroy the Fe–O species. Then, at the same treatment temperature (450 °C), the treatment gas stream was switched to dry air in an attempt to regenerate the Fe–O species. After these treatments, a n-butane conversion of 39.2% was obtained, indicating that the active Fe–O species were successfully regenerated.

Table 2
Thermal stability of iron oxy species.

He treatment following an air activation at 450 °C for 2 h[a]	n-butane conversion[b] (%)
80 °C, 2 h	42.0
250 °C, 2 h	42.9
350 °C, 2 h	41.9
400 °C, 2 h	39.7
450 °C, 2 h	36.0

[a] All catalysts contain 1.5 wt% Fe and 0.5 wt% Mn.
[b] Reaction temperature: 80 °C.

Another series of experiments was conducted to test the thermal stability of the Fe–O active sites in helium (i.e., the temperature at which the Fe–O sites begin to diminish in helium). Table 2 shows the activity data of MFSZ catalysts first activated in air at 450 °C for 2 h and then treated in helium at various temperatures for 2 h. Table 2 indicates that the helium treatment at temperatures up to 400 °C did not significantly affect the Fe–O sites on the catalyst. However, if treated at a higher temperature, the active Fe–O sites will start to diminish.

3.2. Order of Fe and Mn impregnation

In the literature, different sequences for impregnating Fe and Mn have been reported. Coelho et al. [8] compared the catalytic activities of Fe- and Mn-promoted catalysts prepared using various impregnation sequences (Fe–Mn co-impregnation, Mn(first)–Fe(last), Fe(first)–Mn(last)). They reported that the co-impregnated sample was the most active and the Fe(first)–Mn(last) sample was the least active. We also investigated the effect of the impregnation sequence and found that the sequence does not significantly affect the activity (see table 3). One possible reason for the different results obtained by Coelho et al. and by us is the different reaction temperatures. Coelho et al. conducted their catalytic testing at 250 °C and the activity data were taken at 5 min on stream. At this high reaction tempera-

Table 3
Catalytic activities of samples prepared using different sequences for impregnating Fe and Mn.

Catalyst preparation[a]	n-butane conversion[b] (%)
Fe loaded first, Mn last	16.1
Mn loaded first, Fe last	14.8
Fe and Mn co-impregnated	15.3

[a] In all the samples, Fe and Mn were impregnated on sulfated zirconium hydroxide; Fe: 1.5 wt%, Mn: 0.5 wt%. Calcination and pretreatment of each sample was the same, and this is described in section 2.

[b] Reaction temperature: 55 °C.

Table 4
Combined and individual promoting effect of Fe and Mn.

Catalyst composition	n-butane conversion[a] (%)
1.5 wt% Fe–0.5 wt% Mn/SZ	16.1
1.5 wt% Fe/SZ	21.0
0.5 wt% Mn/SZ	4.0
SZ	0

[a] Reaction temperature: 55 °C.

ture, the induction period could become too short to be observed, which makes it difficult to determine the maximum conversion. In this case, the conversion data obtained at a fixed time on stream may not represent the intrinsic activity of the catalyst because it involves the catalyst deactivation behavior as well. We believe that the maximum conversion achieved at the end of the induction period is a better parameter to represent the intrinsic activity. Therefore, we carried out our catalytic testing at low reaction temperatures ($\leqslant 80\,^\circ$C) and take the maximum conversion as a measure of the catalyst activity.

3.3. Effect of Fe and Mn contents

Most documented studies on Fe- and Mn-promoted sulfated zirconia used catalysts that contain 1.5 wt% Fe and 0.5 wt% Mn, as reported by Hsu et al. in their original paper [1]. The individual role played by Fe or Mn is not clear yet. In this study, we investigated the activity of the catalysts containing 1.5% Fe + 0.5% Mn ("standard" catalyst composition), 1.5% Fe only, and 0.5% Mn only, respectively. The results in table 4 indicate that both Fe and Mn can promote the activity of SZ catalysts, with Fe being a much more effective promoter than Mn. However, there is no accumulation of the promoting effects of Fe and Mn – in fact, the presence of Mn actually reduces the effectiveness of the Fe. When both Fe and Mn are present on the catalyst surface, the less effective promoter Mn presumably covers a fraction of Fe active sites and this causes the lower activity.

We considered the possibility that the role of the Mn might be to prolong the lifetime of the catalyst. Under our experimental conditions, however, this is clearly not the case: we extended the reaction on the 1.5% Fe + 0.5% Mn catalyst and on the 1.5% Fe (no Mn) catalyst to 3 h, well past the time at which the maximum conversion (<40 min) was reached. The Fe-only catalyst attained a significantly higher maximum conversion (see table 4), but it did not deactivate any more rapidly. Based on these results, it appears that an Fe-only catalyst is preferable to one containing both Fe and Mn.

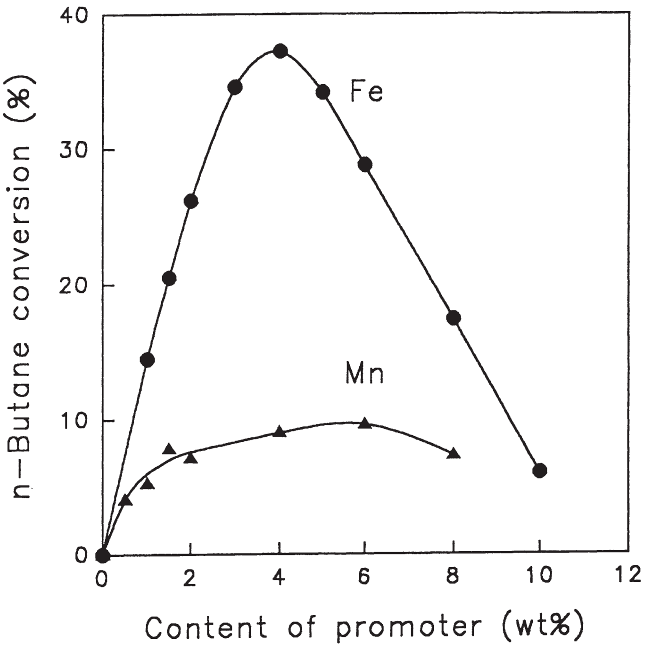

Figure 1. Effect of promoter content. Catalysts contained either Fe or Mn. Reaction temperature: 55 °C.

To systematically investigate the effects of the content of each promoter (Fe or Mn), we tested the activity of Fe-only- and Mn-only-promoted sulfated zirconia catalysts with varying contents of each promoter. The results, as shown in figure 1, confirm that the promoting effect of iron is much more significant than that of manganese at all loadings. The activity of an Fe-promoted catalyst is very sensitive to the content of Fe, while for Mn-promoted catalysts, the activity becomes essentially unchanged when the Mn content exceeds 2%. The catalyst containing 4 wt% Fe has the highest activity. This result is different from that reported by Coelho et al. [8], who found that the maximum in activity for the Fe-only catalysts occurred at a loading of 0.2 wt%. We believe that this difference is due to the way in which the activities were determined and the much higher reaction temperature used in their experiments (250 vs. 55 °C). Coelho et al. used the conversion to isobutane after a fixed time (20 min) on stream as a measure of activity. Using a fixed time does not ensure that the maximum in the curve of conversion vs. time is measured. For all catalysts, the conversion first increases with time on stream, reaches a maximum, then begins to decrease; for active catalysts (higher loadings of Fe) the maximum is reached much more quickly than for less active catalysts [17]. When using a fixed time, one would be comparing the activities of the catalysts at different reaction stages (e.g., the conversion well down on the deactivation part of the curve for

Table 5
Effect of sulfation sequence.

Entry	Catalyst preparation	n-butane conversion[a] (%)
1	1.5% Fe loaded on sulfated $Zr(OH)_4$	21.0
2	1.5% Fe loaded on $Zr(OH)_4$, then sulfated	17.7
3	4% Fe loaded on sulfated $Zr(OH)_4$	37.9
4	4% Fe loaded on $Zr(OH)_4$, then sulfated	32.0

[a] Reaction temperature: 55 °C.

an active catalyst vs. a conversion near the maximum for a less active catalyst).

As stated in our early papers [13,18], we believe that sulfated zirconia is a bifunctional catalyst for n-butane isomerization, i.e., it contains acid functionality and redox functionality. The acidity is provided by the sulfate ions grafted onto the zirconia surface. The redox capability is provided by the sulfate ions in SZ and by both sulfate ions and Fe oxides in Fe-promoted SZ. The reactivity of SZ-based catalysts for isomerization requires a contribution from both acid and redox functions. The redox sites are responsible for the generation of alkenes and the acid sites are responsible for the formation of carbenium ions and their subsequent transformations. An active FSZ catalyst requires a proper balance between acid and redox functions, which, in turn, requires a suitable ratio of acid and redox sites. When impregnated on an SZ surface, Fe will cover some acid sites on the surface. If too much Fe is loaded on, the number of acid sites will be significantly decreased, resulting in an insufficient acid function.

3.4. Effect of sulfation sequence

Since Fe exhibits the major promoting effect, we used Fe-only SZ catalysts to investigate the effect of the sequence for sulfating $Zr(OH)_4$. As seen in table 5, entry 1, the sulfation of $Zr(OH)_4$ was done before 1.5% Fe was impregnated, while in entry 2, the sulfation was done after 1.5% Fe was loaded on $Zr(OH)_4$. It was found that the former catalyst is more active than the latter. The same tendency was observed for samples containing 4% Fe, the optimal Fe content (table 5, entries 3 and 4). A possible explanation of the observation is that, if Fe is loaded on top of sulfated zirconium hydroxide, it has a better exposure to oxygen in the activation gas (air) and thus has a greater chance to form the active iron oxy species during the oxidative activation.

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