The effect of pretreatment procedures on the activities of Fe- and Mn-promoted sulfated zirconia catalysts

Steven X. Song and Ronald A. Kydd *

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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The effect of activation and calcination conditions on the activities of Fe- and Mn-promoted sulfated zirconia (MFSZ) catalysts for the isomerization of n-butane at low temperatures ($\leqslant 90\,^\circ$C) was investigated. Activation in air resulted in a higher activity of MFSZ than did activation in helium; this is in contrast to the situation for unpromoted sulfated zirconia (SZ) catalysts where the activation atmosphere did not affect the activity. The maximum activity of MFSZ was found to occur when the activation temperature was $450\,^\circ$C, while for unpromoted SZ, the optimum activation temperature was $250\,^\circ$C. Comparison of the n-butane conversions at these two temperatures showed that MFSZ was only about 1.6 times as active as SZ. This activity difference is much less than that reported before in the literature where comparison was made at the same activation temperature. This activity difference is attributed to the different degree of synergism between redox and acid sites on the two catalysts.

Keywords: butane, isomerization, promoter, sulfated zirconia

1. Introduction

Compared with acidic zeolite catalysts, sulfated zirconia (SZ) exhibits superior activity for the isomerization of alkanes, particularly light alkanes such as butane. The addition of some transition metal (e.g., Fe, Mn, etc.) oxides has been found to further increase the activity [1]. This observation has inevitably raised the question: what is the role played by the transition metal oxides? There are essentially two explanations about this matter which have been offered. An early investigation suggested that the presence of Fe and Mn oxides increases both the number and the strength of SZ surface acid sites [2]. This postulate seems to gain support from recent reports [3,4] of ethane and propane conversions over Fe- and Mn-promoted sulfated zirconia (designated as MFSZ here). In contrast to the above assessment, there is an increasing number of reports which suggest that the addition of Fe and Mn promoters does not result in an increase in the strength and density of the surface acid sites [5–9]. Rather, the reason proposed for the higher activity of the promoted catalysts is that the promoters help produce butenes from butane due to either their capability of oxidative dehydrogenation [8,10] or their facility to provide acid-base bifunctional dehydrogenation [11,12]. Recently, it has been convincingly demonstrated that n-butane isomerization on SZ-based catalysts proceeds through a bimolecular mechanism involving the formation of C_4 carbenium ion and butene, the reaction of the carbenium ion with butene to form a C_8 intermediate, and the skeletal rearrangement and β-scission of the C_8 intermediate to isobutane [13–16]. Obviously, the increased formation of olefinic C_4 species would accelerate the reaction.

It is well known that the acidic and catalytic properties of SZ-based catalysts depend on their preparative history from the formation of $Zr(OH)_4$ precursor to the *in situ* activation of the final catalysts prior to reactions. Investigations of the effects of the preparation and pretreatment conditions have been well documented for unpromoted SZ catalysts. However, most of the studies on MFSZ have so far focused on the role of the promoters and the reaction mechanism. The information about their catalytic properties versus their pretreatment conditions is very limited. We believe that a study of the effect of the pretreatment conditions on the activity of MFSZ catalysts is important because it not only can lead to finding the optimum conditions, but it also may provide useful information about the functions of the promoters. In the present work, we investigate the effect of calcination and activation conditions of MFSZ catalysts on their activity for n-butane isomerization and compare the results with those obtained over unpromoted SZ catalysts.

2. Experimental

A volume of 600 ml of 0.45 M solution of $ZrOCl_2{\cdot}8H_2O$ was hydrolyzed by dropwise addition of 75 ml aqueous ammonia (28–30 wt% NH_3) with vigorous mechanical stirring to produce $Zr(OH)_4$ precipitate. After the hydrolysis, the pH of the mixture was about 9, and the mixture was stirred for another 30 min. The $Zr(OH)_4$ precipitate was then separated from the liquid by filtration and washed thoroughly with distilled water until no chloride ions were detected. The $Zr(OH)_4$ was then dried overnight and powdered to below 100 mesh. Sulfation was carried out by adding the $Zr(OH)_4$ powder to a 0.5 molar solution of H_2SO_4 (1 g solid/10 ml liquid) followed by stirring the mixture for 1 h.

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[*] To whom correspondence should be addressed.

The solid was separated from the liquid by filtration without washing and then dried overnight. Unpromoted SZ catalysts were obtained by calcining the dried sulfated $Zr(OH)_4$ in a furnace at 620 °C for 3 h in static air. The calcined samples were cooled and stored under ambient conditions before being placed in a reactor.

Fe- and Mn-promoted SZ catalysts were prepared as follows. Iron was loaded by impregnation of the sulfated $Zr(OH)_4$ with a 0.1 M solution of $Fe(NO_3)_3{\cdot}9H_2O$ (98%, Aldrich). The material was dried, powdered, impregnated with a 0.1 M solution of $Mn(NO_3)_2{\cdot}6H_2O$ (98%, Aldrich), and then dried again. The amounts of added Fe and Mn were chosen so that their weight percentages were 1.5 and 0.5, respectively. The dried Fe- and Mn-containing sulfated $Zr(OH)_4$ was calcined either *ex situ* or *in situ*. In an *ex situ* calcination, samples were calcined at 450–800 °C in the same manner as described above for SZ catalysts. In an *in situ* calcination, samples were calcined in the quartz catalytic reactor (described below) at a given temperature (550–750 °C) for 3 h under a dry air stream (30 ml/min).

n-butane isomerization was carried out in a fixed bed downward-flow quartz reactor (9 mm i.d.) at either 45 or 90 °C under atmospheric pressure. The amount of the catalyst used was 0.3 g for reactions at 45 °C and 0.25 g for those at 90 °C. 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 4 ml/min of helium for reactions at 45 °C, and 1 ml/min of n-butane and 22 ml/min of helium for reactions at 90 °C. Prior to the reaction, *ex situ* calcined catalyst samples were activated in the reactor in flowing dry air (30 ml/min) at a given temperature (100–600 °C) for 2 h and cooled to reaction temperature under the activation gas stream. *In situ* calcined catalysts were cooled from the calcination temperature directly to reaction temperature under the dry air stream; in this case, care was taken to prevent contact of the catalyst with moisture before the activity testing. All the catalyst samples were purged with flowing helium (30 ml/min) at the reaction temperature for 10 min before being exposed to the reaction feedstock. The reaction products were analyzed on-line using a HP 5890 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.

3. Results

The reactivity patterns of n-butane conversion versus time on stream observed in this work exhibited an induction period of increasing conversion followed by a subsequent deactivation. This is a common feature for n-butane isomerization over SZ-based catalysts [5–8,16–24], and the length of the induction period has been reported to depend on the catalyst activity [25] and reaction conditions such as temperature, n-butane partial pressure and residence time [21,24,26]. For example, when the reaction temperature is sufficiently high, the induction period can become too short to be observed experimentally. In this work, the reaction conditions were carefully chosen based on two considerations. One is to make the observation of the induction period and thus the observation of the maximum n-butane conversion possible; the % conversion at this maximum is taken as a measure of the catalyst activity, rather than simply taking the conversion at some fixed time. The other consideration is to keep the n-butane conversion sufficiently below the equilibrium value so that the activity of different catalysts can be easily distinguished.

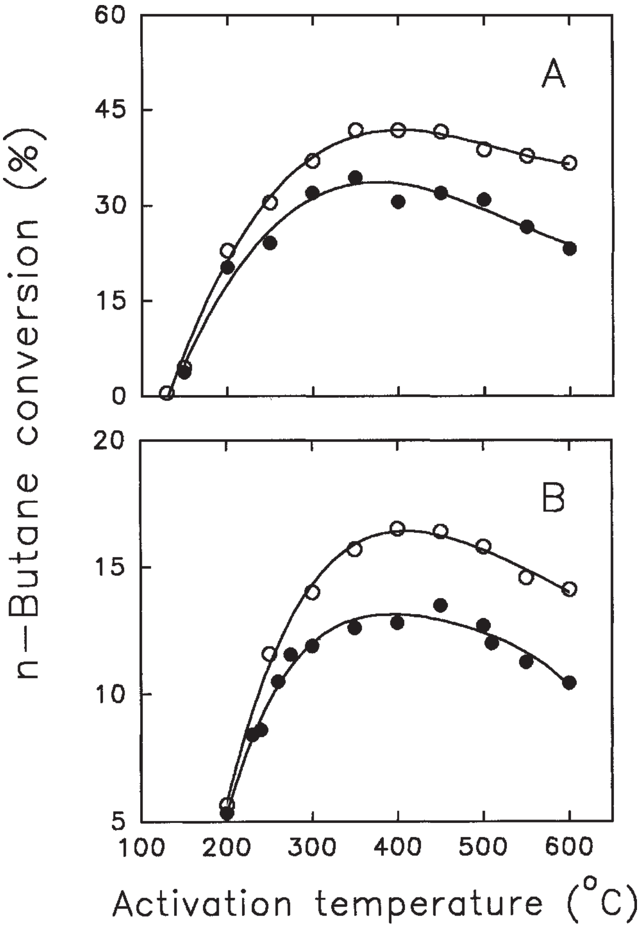

Figure 1. Effect of activation temperature and atmosphere on the activity of MFSZ catalysts. (A) Reaction at 90 °C; (B) reaction at 45 °C. The catalysts were *ex situ* calcined at 620 °C for 3 h in air prior to the activation. Activation gas: (○) air; (●) helium.

Figure 1(A) shows the activity data, at a reaction temperature of 90 °C, of MFSZ catalysts activated in air or in helium at 130–600 °C. Three features can be noticed in this figure. First, the catalyst activation atmosphere had a significant effect on the activity. The catalysts activated in air (oxidative atmosphere) exhibited higher activities than those activated in helium (inert atmosphere). Second, this activity difference increased with the activation temperature. At low activation temperature (<200 °C), the difference was not significant. Third, regardless of the activation atmosphere (air or helium), the catalyst activity first increased with the activation temperature, reaching a max-

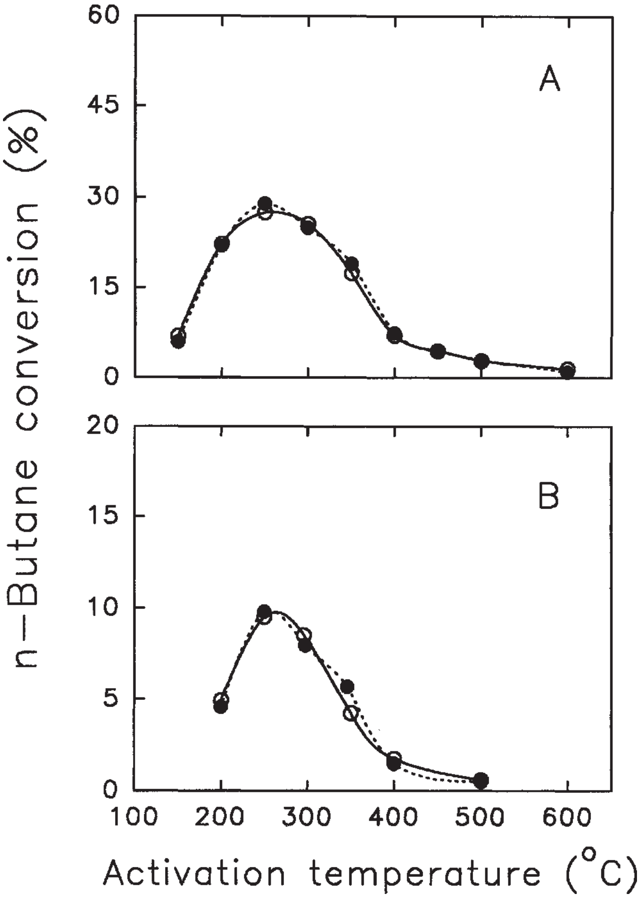

Figure 2. Effect of activation temperature and atmosphere on the activity of SZ catalysts. (A) Reaction at 90 °C; (B) reaction at 45 °C. The catalysts were *ex situ* calcined at 620 °C for 3 h in air prior to the activation. Activation gas: (○) air; (●) helium.

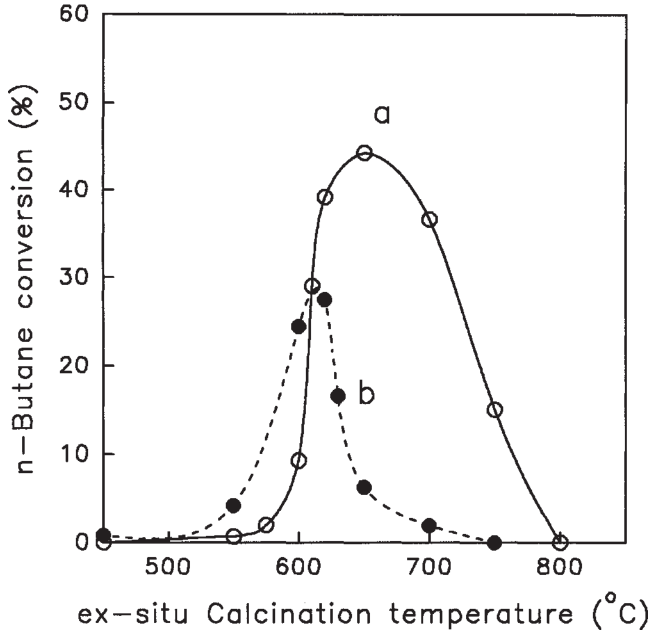

Figure 3. Effect of *ex situ* calcination temperature on the activities of MFSZ (curve a) and SZ (curve b) catalysts. The catalyst was activated at 450 °C for MFSZ and at 250 °C for SZ in flowing dry air. Reaction temperature = 90 °C.

imum at 350–450 °C, and then decreased. In addition, the MFSZ catalysts activated in air had shorter induction periods than those activated in helium (data not shown).

A similar set of experiments was conducted with unpromoted SZ catalysts, and the results are shown in figure 2(A). The activity of SZ catalysts also first increased with the activation temperature and then decreased. However, the maximum activity resulted when the activation temperature was between 250 and 300 °C, which is lower than that observed for MFSZ (350–450 °C). In addition, it is interesting to note that, in contrast to MFSZ, unpromoted SZ catalysts exhibited similar activity no matter whether the activation atmosphere is oxidative (air) or inert (helium). The induction period observed over SZ was longer than over MFSZ (data not shown). The tendencies shown in figures 1(A) and 2(A) were also observed in reactions run at a lower reaction temperature (e.g., 45 °C, figures 1(B) and 2(B)).

The pretreatment of SZ-based catalysts normally includes a calcination procedure followed by an activation step. For *ex situ* calcined samples, the purpose of the activation step is to achieve a preliminary surface dehydration. It was assumed that if after calcination the catalyst was not exposed to the atmosphere (for example, in the case of *in situ* calcination), the activation step is no longer necessary, as the surface dehydration achieved in the calcination step is maintained [27]. Therefore we investigated the effect of calcination temperature on the activity of MFSZ and SZ catalysts, for both *ex situ* and *in situ* calcination. Figure 3 shows the results with *ex situ* calcination followed by *in situ* activation in flowing air at an appropriate temperature (450 °C for MFSZ and 250 °C for SZ, according to figures 1 and 2). Both MFSZ and SZ exhibited a maximum activity at a given calcination temperature which is higher for MFSZ (∼650 °C) than for SZ (∼610 °C). The maximum activity of MFSZ is as about 1.6 times high as that of SZ. This is in sharp contrast with earlier reports claiming that MFSZ is about 2–3 orders of magnitude more active than SZ [1,17]. To ensure that this result was not simply a matter of our MFSZ being “inactive”, we ran the reaction under the same conditions as those used by Jatia et al. [17] and found that our MFSZ catalyst gave conversions which were very similar to theirs. Another feature which is worth noting in figure 3 is that, at a calcination temperature below 610 °C, the activity of SZ was higher than that of MFSZ, while above 610 °C MFSZ became more active.

In this work, we calcined our catalysts at various temperatures but for a constant period of time (3 h). It should be mentioned that the activity of SZ catalysts may also depend on the length of their calcination time. For example, it has been reported [28] that the activity of a Pt/SZ catalyst was negligible after calcination at 500 °C for up to 10 h. However, after 67.5 h of calcination, the catalyst activity became significantly higher, being equivalent to that of catalysts calcined at 725 °C for 2 h.

Figure 4 (curve a) depicts the effect of *in situ* calcination temperature on the activity of MFSZ. The *in situ* calcination

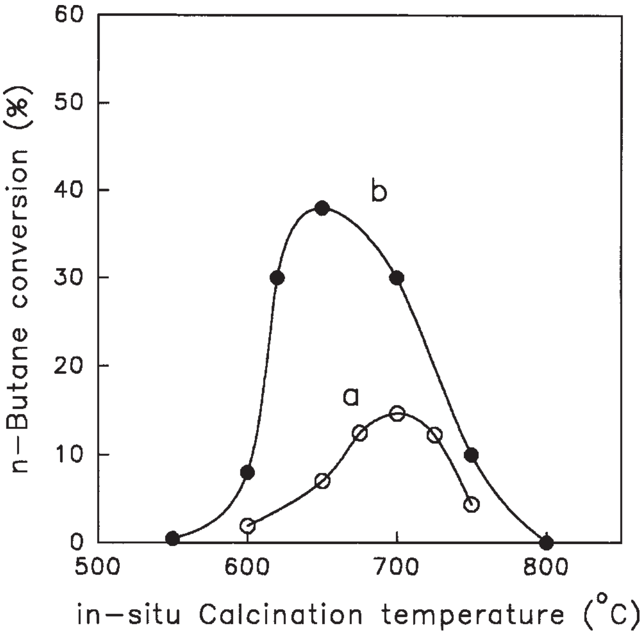

Figure 4. Effect of *in situ* calcination temperature (curve a) and hydration (curve b) on the activity of MFSZ catalysts. Reaction temperature = 90 °C.

was carried out at 500–800 °C for 3 h in flowing dry air (30 ml/min). The catalyst was then cooled in the calcination stream, without exposure to air, to reaction temperature (90 °C). A comparison between figure 3 (curve a) and figure 4 (curve a) indicates that *in situ* calcination is much less effective than *ex situ* calcination. In a previous report [29], we found that a proper hydration of *in situ* calcined SZ catalysts resulted in similar catalytic behavior to that of *ex situ* calcined SZ catalysts. Therefore, we performed the same hydration procedures over the *in situ* calcined MFSZ catalysts: After Fe- and Mn-containing sulfated $Zr(OH)_4$ were *in situ* calcined at 550–800 °C in a dry air stream for 3 h and then cooled to 100 °C, a helium stream (22 ml/min) passing through a bubbler containing water at 16 °C was admitted into the reactor for 5 min. The wetted catalyst was then activated in a dry air stream at 450 °C for 2 h and cooled to the reaction temperature (90 °C). After the hydration treatment, the *in situ* calcined catalyst regained its effectiveness, behaving like *ex situ* calcined samples in n-butane isomerization (see figure 4 (curve b) and figure 3 (curve a)).

4. Discussion

Figures 1 and 2 indicate that different activation atmospheres (oxidative or inert) did not result in any significant difference in the catalytic activity of SZ but strongly affected the activity of MFSZ. The fact that the activity of MFSZ was significantly influenced by the activation atmosphere does not seem to support the suggestion that the introduction of Fe and Mn increases the acidity of SZ, because the active acid sites of the unpromoted SZ were not affected by the activation atmosphere.

There is an emerging consensus now that Fe and Mn promoters do not increase the acid strength on the surface of the catalyst [5–9]. Recent studies [13,16] using double ^{13}C-labeled butane convincingly indicated that at low reaction temperature, n-butane isomerization over Fe- and Mn-promoted SZ catalysts takes place via a bimolecular mechanism in which the participation of butene molecules is essential, but catalyst superacidity is not necessary. In a recent investigation, Wan et al. [8] found that MFSZ catalysts exposed to dry air at over 450 °C are more active for n-butane isomerization than those calcined in helium. They suggested that an active iron oxy species (tentatively assigned as Fe(IV)) is responsible for the high activity of MFSZ near room temperature because this species is capable of oxidative dehydrogenation of butane to form the butene which participates in the bimolecular reaction, leading to high n-butane conversion. The proposed oxy species is thought to be rather labile, and would be removed under such conditions as room temperature vacuum or high temperature treatment in helium. Our observation made in catalytic testing is similar to that described by Wan et al. In addition, X-ray photo-electron spectroscopy (XPS) analysis of two MFSZ samples heated at 450 °C in different atmospheres (air or helium) showed that the chemical states of Fe on the two samples are identical, being 3+, which is consistent with the XPS results obtained by Hino and Arata [30]. We believe that the Fe oxy species, even though formed in high temperature air calcination, were removed under the ultra high vacuum in the sample chamber of the XPS instrument. As a result, only Fe^{3+} was detected by XPS; as the helium calcined samples also contain Fe^{3+}, no difference was seen.

The study by Adeeva et al. [14] indicates that the bimolecular mechanism occurs not only on MFSZ but also on unpromoted SZ. This implies that SZ may also have an ability to generate butene molecules from butane. The formation of dimers over SZ has also been indicated in the conversion of other hydrocarbons [31]. Ghenciu and Fărcaşiu [10] proposed a mechanism of aliphatic alkane conversion on SZ. In this mechanism, the first step is a one-electron oxidation of the alkane, leading to an ion–radical pair, followed by recombination and rearrangement to generate sulfite esters on the surface; these esters either ionize generating carbocations, or eliminate forming olefins. Ghenciu and Fărcaşiu believed that the higher catalytic activity of MFSZ compared to SZ in hydrocarbon reactions is due to its higher oxidizing potential when the transition metal is in a high oxidation state (Fe^{3+}, Mn^{x+}).

In a previous report we have indicated that an active SZ catalyst should possess an appropriate amount of Brønsted acid sites, which in turn requires a proper degree of catalyst hydration [29]. Taking account of the contribution of both redox and acid sites to the activity of SZ-based catalysts, we concur with earlier suggestions that the high activity of SZ-based catalysts towards n-butane isomerization is due to a synergism of its redox capability and its acidity [8,10]. The acidity is provided by the sulfate ions grafted onto the

Table 1
n-butane isomerization at 45 °C over *in situ* calcined MFSZ.

Experiment no.	Catalyst	Air calcination	Conversion (%)
1	MFSZOH[a]	*In situ*, 650 °C	5
2	From exp. no. 1	Regeneration, 500 °C	9
3	From exp. no. 2	Regeneration, 500 °C	11
4	From exp. no. 3	Regeneration, 500 °C	12

[a] Fe- and Mn-containing sulfated $Zr(OH)_4$.

zirconia surface. The redox capability is provided by the sulfate ions in SZ and by both sulfate ions and Fe and Mn oxides in MFSZ. 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.

Based on the above considerations, our data in figures 1 and 2 can be understood as follows. On SZ, no metal oxy species exists. The activation atmosphere (dry air or helium) does not significantly influence the surface sulfate ions which are responsible for the oxidative formation of butenes; therefore, no activity difference was observed. For SZ catalyst, the maximum activity, at an activation temperature of 250 °C, corresponds to an optimum synergism of the oxidative formation of butene and the catalyst acidity. On the catalyst activated at this temperature, the acid sites must have appropriate strengths, and the optimum ratio of Brønsted to Lewis acidities must exist, allowing the fastest transformation of the butenes formed on the redox sites. Metal oxy species are labile and can be removed during helium activation; the higher the activation temperature, the more this species will be removed. This explains why the catalytic activity difference between air and helium activations increases with activation temperature (figure 1). Although the optimized acid sites apparently are formed at an activation temperature of ~250 °C, the formation of optimized metal oxy species needs higher temperatures. This explains why the optimum activation temperature for MFSZ is higher than that for SZ. At even higher activation temperature, the decreased acidity will become the determining factor, resulting in a reduced catalyst activity, even though redox sites are present.

In addition to requiring an increased activation temperature, the formation of an active MFSZ catalyst usually needs more severe calcination conditions (higher calcination temperature or longer time) than does SZ. It is seen in figure 3 that the optimum calcination temperature for SZ is ~610 °C while that for MFSZ is ~650 °C. This also indicates that the development of active metal oxide redox sites needs higher calcination temperatures than the formation of optimum acid sites. Upon calcination at temperatures above 610 °C, MFSZ showed much higher activity than SZ. This implies that a MFSZ catalyst with well-formed metal oxy redox sites can exhibit considerable activity even though the contribution from its acidity is greatly reduced due to the removal of sulfate ions at high calcination temperatures. Hino and Arata [30] reported that their active sulfated Fe_2O_3/Zr_2O_3 catalysts calcined at 700 °C had only small amounts of sulfur (0.3–0.5 wt%) compared to the sulfur content of SZ calcined at 650 °C (1.27 wt%) which showed no activity under their reaction conditions.

It is interesting to note in figure 3 that when the calcination temperature was below 610 °C, the activity of MFSZ was lower than that of SZ. There are several studies reporting that the strength and the density of the acid sites on MFSZ do not exceed those of SZ [5–7]. Moreover, a recent investigation using a calorimetry-adsorption titration of SZ-based catalysts with pyridine indicates that doping SZ with Fe and Mn results in a lower measured acidity, indicating that Fe and Mn have occupied the strongest acid sites [9]. This may account for the lower activity of MFSZ seen in figure 3. At relatively high calcination temperatures, the oxy species can be well developed and their increased contribution to the reaction may compensate for the decreased contribution from the acidity, resulting in the same, or even increased, catalytic activity.

Another point we want to address is that the catalyst acidity also plays an important role in producing the high activity. Compared to *ex situ* calcined MFSZ, the *in situ* calcined catalysts were much less active (figure 4 (curve a)). The reason, as discussed previously for SZ [29], is that the *ex situ* calcined samples could adsorb moisture from the atmosphere during cooling and storage. After proper activation, the catalyst would have appropriate amounts of the Brønsted acid sites which are needed to catalyze the carbenium reaction. In contrast, in an *in situ* calcined sample, the Brønsted sites are scarce. Therefore, even though there are redox sites on the surface, the catalyst was less active. In figure 4 (curve a), a maximum activity was observed at an *in situ* calcination temperature of 700 °C. This activity presumably resulted primarily from the contribution of the strong redox sites formed at this high calcination temperature, as the number of acid sites would be low after 700 °C calcination. A proper hydration generates Brønsted acid sites and promotes the activity to a significant extent, as shown in figure 4 (curve b). Actually, any approach which can produce minor amounts of water over the *in situ* calcined catalysts will enhance the catalyst activity. For example, we carried out experiments after successive regenerations as shown in table 1 and found that the catalyst activities observed in the second and subsequent experiments were significantly higher than that in the first experiment. It is believed that during the catalyst regeneration, a minor amount of water was formed due to the burning of coke and butane adsorbed in the catalyst bed. The water thus produced adsorbed on the catalyst, leading to the formation of some Brønsted acid sites which enhance the catalyst activity.

It was earlier reported that Fe- and Mn-promoted SZ is 2–3 orders of magnitude more active than unpromoted SZ [1,6,17]. In those studies, both types of catalyst were usually activated at the same temperature (typically 450–500 °C). Our data also show a large difference under such conditions; for example, if both catalysts are activated at 450 °C, which is the optimal temperature for MFSZ, then MFSZ is about 10 times more active than SZ. However, if SZ activated at 250 °C (its optimal temperature) is compared to MFSZ activated at 450 °C, then the MFSZ is only about 1.6 times more active than the SZ. This activity difference should not be taken as the indication of significant difference in the acidity of both catalysts, but may suggest that the degree of concerted action between the redox and acid sites is different for the two catalysts.

In conclusion, activation in air resulted in a higher activity of MFSZ than in helium, but the activation atmosphere did not affect the activity of unpromoted sulfated zirconia (SZ) catalysts. The maximum activity of MFSZ (activated at 450 °C) was found to be only as about 1.6 times as that of SZ (activated at 250 °C). The activity difference is not as great as that reported before in the literature. This activity difference is attributed to the different synergism between redox and acid sites on the two catalysts.

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