Probing the Low Temperature Initiation Sites in Fe-, Mn-Promoted Sulfated Zirconia via CO and H$_2$ Adsorption

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Exposure of freshly activated Fe-, Mn-promoted sulfated zirconia (SFMZ) to carbon monoxide at temperatures up to 50°C induced permanent loss of activity, while the addition of CO after the beginning of the reaction had a reversible effect, regardless of whether the butane flow has been interrupted or not. Similar experiments using dissociated hydrogen instead of CO led to irreversible poisoning in all cases. These finding were interpreted based on (i) the occurrence of initiation sites that are consumed stoichiometrically and very rapidly upon exposure to butane, (ii) such initiation sites which are also consumed by CO or dissociated hydrogen, (iii) CO which competes effectively for adsorption sites without affecting accumulated reaction intermediates, and (iv) such intermediates that are removed in the presence of dissociated hydrogen. © 1999 Academic Press

Key Words: *n*-butane isomerization; active sites; sulfated zirconia; CO poisoning.

INTRODUCTION

Owing to their exceptional ability to isomerize saturated hydrocarbons at low temperature, sulfated zirconia-based catalysts (SZ) attracted much attention (1). Careful characterization studies played an essential role in the evolution of our understanding of such catalysts. For example, it took a long time before it was realized that SZ catalysts are not superacidic (2, 3), which has significant implications on reaction mechanisms. There was also a widespread belief that Pt in Pt/SZ is difficult to reduce by hydrogen. Our XPS, TPR, and XRD studies demonstrated that Pt in properly calcined samples is essentially in the metallic state (4, 5), and no hydrogen reduction is needed.

As experimental and theoretical evidence that SZ-based catalysts are not superacidic accumulated (2, 3, 6, 7), direct protolysis as the initial step in the mechanism of hydrocarbon isomerization was abandoned (8). Attention was then focused on the redox properties of SZ catalysts, and a one-electron oxidation process was proposed as the initial step for alkane activation (9). For nonpromoted SZ catalysts,

sulfate ions were considered to be the oxidizing species. However, Fe- and Mn-promoted SZ catalysts (SFMZ) are not only, under some conditions, two to three orders of magnitude more active than pristine SZ, but they are active even at room temperature. This enhanced activity was attributed to a new redox site, believed to be an iron oxy group. Support for such a proposal was provided by Wan *et al.* (10) based on a CO poisoning experiment. It was reported that the addition of CO to the feed during butane isomerization at 30°C poisoned the catalyst completely and irreversibly. Moreover, contacting freshly activated SZ by CO in a helium stream gave rise to CO$_2$, the amount of which was used to estimate the number of low-temperature active sites in the catalyst. More recently, Morterra *et al.* (11) conducted a similar experiment at 50°C and reported conflicting findings. They observed that catalyst poisoning via the addition of CO to the feed was reversible and no CO$_2$ was formed. Thus, they associated the low-temperature activity to Lewis acid sites. The current work dealt with the nature of the sites responsible for near-room-temperature catalytic activity for butane isomerization over SFMZ catalysts. Particular attention was devoted to understanding the discrepancy between literature data (10, 11).

EXPERIMENTAL

The SFMZ catalyst used in the current study was prepared as described elsewhere (12). The precursor Zr(OH)$_4$ was first synthesized by dropwise addition of ammonium hydroxide (28 wt% NH$_3$, Anachemina) into a ZrOCl$_2$ · 8H$_2$O (98%, Aldrich) solution under vigorous stirring until a pH of 8. Then, the precipitate was filtrated, washed by distilled water to remove all chloride ions, then dried at 110°C for 12 h, and grinded to below 100 mesh. Sulfation was performed by impregnation using 0.5 M sulfuric acid solution (15 ml/g of solid). Then, 1.5% Fe and 0.5% Mn were loaded on dried sulfated zirconium hydroxide by the incipient wetness method using 0.3 M Fe(NO$_3$)$_3$ and 0.15 M Mn(NO$_3$)$_2$ solutions at the same time. The as-made catalyst was dried at 110°C, calcined in static air at 620°C for 6 h, and stored in ambient conditions.

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Catalytic reactions were carried out in a fixed-bed down-flow quartz microreactor with 10-mm inner diameter. Calcined SFMZ (0.4 g) was loaded in the reactor between glass wool layers. For all experiments, the catalyst was first activated in flowing dry air (30 ml/min) at 500°C for 2 h, cooled to the reaction temperature (35–100°C), and then purged in flowing helium (30 ml/min) for 15 min to remove air from the reactor system. Butane isomerization was conducted using a 1 : 4 mixture of n-butane and He at different total flow rates, depending on the reaction temperature. Depending on the purpose of the experiment, pure carbon monoxide was either fed (30 ml/min for 20 min) through the freshly activated catalyst followed by helium purge and then an n-butane/helium mixture or fed (1 ml/min) during the isomerization reaction along with butane and helium. A third type of experiment was conducted as follows: the reaction mixture was stopped, CO was fed at 30 ml/min for 30 min, the catalyst was then purged with He for 30 min, and the reaction resumed. Similar experiments were carried out using H_2 instead of CO. Quantitative analysis of the reaction products was performed by an online gas chromatograph (HP 5890 series II) equipped with a capillary column (crosslinked methyl silicone gum, 50 m × 0.32 mm × 0.52 mm) and a flame ionization detector.

RESULTS AND DISCUSSION

Figure 1 shows the conversion rate vs time on stream for standard n-butane isomerization over SFMZ at 50°C (open symbols) and the effect of CO addition to the reaction feed

FIG. 1. Effect of CO on the catalytic activity of SFMZ at 50°C. Reaction conditions: 0.4 g of precalcined catalyst (620°C, 6 h); total flow rate, 5 ml/min; (□) n-C_4 : He = 1 : 4; (■) n-C_4 : He : CO = 1 : 3 : 1.

during both the phase of increasing activity and the deactivation phase (filled symbols). It is seen that the activity decreases to zero almost immediately after CO addition and recovers fully as soon as CO is removed. Similar results were obtained at 35°C. Morterra et al. (11) introduced CO in the reaction feed during the deactivation phase and found the poisoning effect to be fully reversible. Our findings not only confirm this behavior but also show that the poisoning is also reversible during the so-called induction period (Fig. 1).

In our first few attempts to run such CO-poisoning experiments, we found that once the CO feed is switched off, the activity recovers only after a long period of time, often exceeding 2 h. This potentially misleading artifact was due to a "dead" volume in the experimental setup. A similar artifact may be a possible reason CO poisoning seemed irreversible in Wan et al.'s investigation (10). Moreover, to completely dismiss the possibility that the observed effect of CO may be due to irreversible adsorption of CO at 30°C, Wan et al. purged the catalyst in flowing He at 200°C for 2 h. Such a catalyst was found to have no activity at 30°C. However, treatment in He at 200°C is likely to affect the catalyst surface more than merely remove potentially adsorbed CO. The following experiment was designed to investigate such effects. After activation, the catalyst was exposed to a He–butane mixture at 50°C for 14 min, CO at 50°C for 10 min, and then He at 200°C for 2 h. In agreement with Wan et al. (10), when cooled to 50°C, this catalyst exhibited no isomerization activity. Furthermore, even when the step involving CO is skipped, the catalyst showed no activity. In an early investigation from this laboratory (12), it was reported that interruption of the n-butane flow at 35°C followed by He purge at the same temperature did not affect the reaction intermediates as the same conversion was obtained upon resumption of n-butane isomerization. Independent work by Alvarez et al. (13) showed that such intermediates are stable in He up to a temperature between 100 and 150°C. Therefore, He purge at 200°C after interrupting the flow of butane leads to the complete removal of reaction intermediates. As will be shown later, the so-called low-temperature *active* sites are actually *initiation* sites that can be used only once. Therefore, regardless of the effect of CO, no activity can be recovered at 35°C after interruption of the butane flow and elimination of adsorbed reactive intermediates.

More importantly, the types of CO-poisoning experiments reported by Wan et al. (10) and Morterra et al. (11) have no direct bearing on catalyst sites responsible for the isomerization activity at low temperature. Indeed, recent mechanistic proposals show that butane isomerization over SZ-based catalysts at low temperature is a chain reaction with the usual three steps, initiation, propagation, and termination (8, 14). At high temperature, the initiation step may be dehydrogenation over a Zr–O site in the sulfate
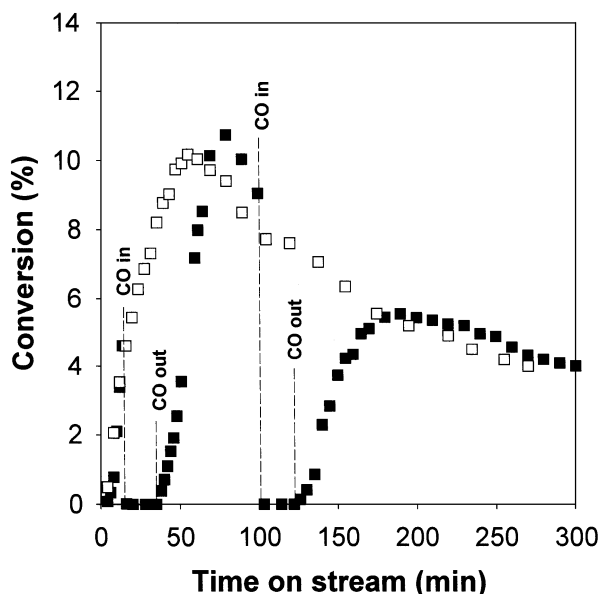
cluster (8) or a one-electron oxidation process involving sulfate species (9). In the current situation of butane isomerization over SFMZ at near room temperature, both of these possibilities are unlikely since the temperature is too low for dehydrogenation to occur and for sulfate species to oxidize butane. Otherwise, contrary to experimental evidence, nonpromoted sulfated zirconia would also be active at room temperature. Assuming, as proposed by Wan *et al.* (10), that we are dealing with an iron oxy species, the initiation step would be a noncatalytic (i.e., stoichiometric) reaction (14) involving abstraction of active oxygen. This reaction is likely to be very fast with all oxy species being eliminated at once upon exposure of the catalyst to the reaction feed. If this is the case, then contacting the catalyst with CO (or other reactive species) *before* the reaction feed within the temperature range where no other active sites are triggered would eliminate any isomerization activity completely. Our findings, described hereafter, fully support this contention.

In a series of experiments, the freshly activated catalyst was contacted with pure CO (30 ml/min) for 30 min at different temperatures and purged with helium before conducting butane isomerization at the same temperatures. Experimental data obtained at 35°C are shown in Fig. 2. As seen, exposure of the catalyst to CO before reaction had a deleterious effect on its activity. At this stage, two different interpretations may be considered: (i) CO irreversibly destroys the sites responsible for low-temperature catalytic activity and (ii) CO was not removed by the helium purge at 35°C, i.e., the active sites remained blocked by adsorbed
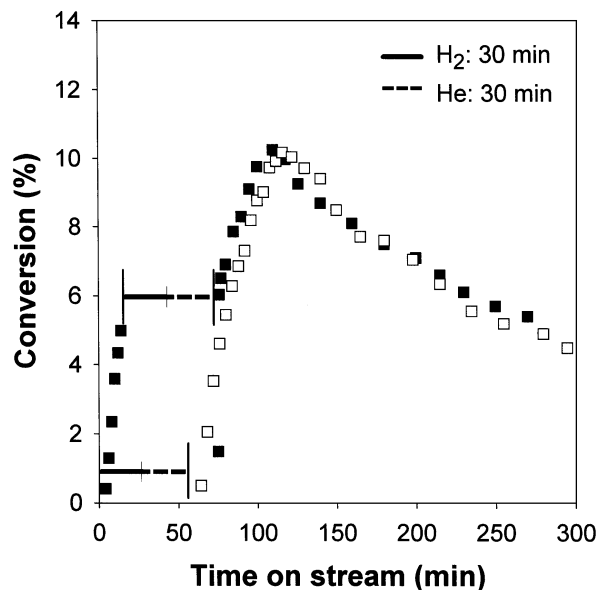
FIG. 3. Effect of H_2 on the catalytic activity of SFMZ at 50°C. Reaction conditions: 0.4 g of precalcined catalyst (620°C, 6 h); total flow rate, 5 ml/min; n-C_4 : He = 1 : 4; (□) H_2 (30 ml/min, 30 min) was added before the beginning of the reaction followed by He purge (30 ml/min, 30 min); (■) similar treatment was performed after interruption of the reaction.

CO, leading to complete deactivation. The latter possibility was dismissed on the basis of the following experiment. After CO introduction at 35°C, we switched to flowing He, increased the temperature to 100°C, and purged with He for 1 h before cooling to 35°C and conducting butane isomerization. The catalyst did not recover any activity, even though the temperature of 100°C was not high enough for He to remove reaction intermediates if they were present on the catalyst surface (13). It was then clear that, regardless of its nature, the low-temperature initiation site is irreversibly eliminated by CO. Using mass spectrometry, Wan *et al.* (10) detected the formation of CO_2 upon exposure of freshly activated SFMZ to CO in He at 30°C. They suggested that CO_2 was formed via the oxidation of CO by iron oxy species. Our current results are consistent with such a proposal.

Similar experiments using H_2 instead of CO, either before or during the reaction, did not affect the catalyst behavior (Fig. 3). This is consistent with our early finding that H_2 has no effect on n-butane isomerization over SFMZ at atmospheric pressure (12, 15). It may thus be concluded that the proposed labile oxygen part of the initiation site does not react with molecular hydrogen. However, this oxygen is likely to react readily with dissociated hydrogen. The following experiment was designed to support this proposal. The SFMZ catalyst (0.4 g) was activated at 500°C, cooled to 100°C in air, and exposed to flowing He. Freshly reduced 0.5 wt% Pt/Al_2O_3 (0.2 g) was then poured on top of SFMZ. The two-component catalyst was shaken and cooled to
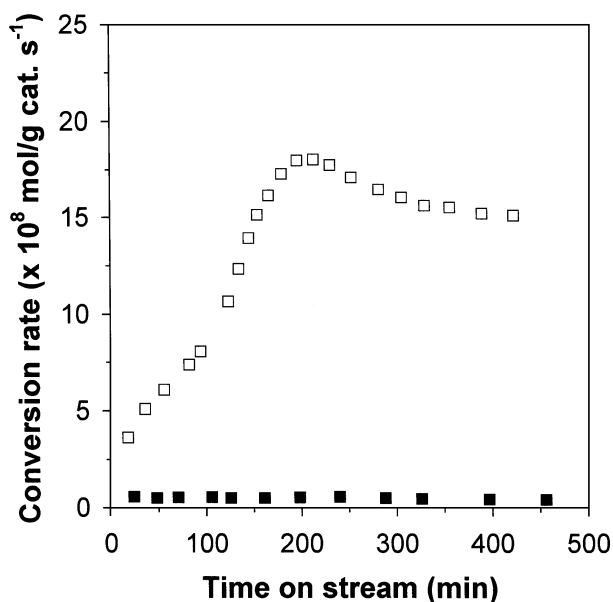
FIG. 2. Effect of CO on the catalytic activity of SFMZ at 35°C. Reaction conditions: 0.4 g of precalcined catalyst (620°C, 6 h); total flow rate, 5 ml/min; n-C_4 : He = 1 : 4; (□) activated SFMZ; (■) CO-poisoned SFMZ.

TABLE 1

Effect of Added Species before or after the Beginning of n-Butane Isomerization at 50°C

Species added	Before reaction[b]	During reaction[c]	After butane interruption[d]
CO	Irreversible effect	Reversible effect	No effect
H_2	No effect	No effect	No effect
Dissociated H^a	Irreversible effect	Irreversible effect	Irreversible effect

[a] A mixture of reduced 0.5% Pt/Al_2O_3 and activated SFMZ was used. Added hydrogen was dissociated on Pt (see text).

[b] The species added (30 ml/min, 30 min) was purged with He (30 ml/min, 30 min) before switching to the $1:4$ C_4 : He mixture.

[c] The $1:4$ C_4 : He mixture was replaced by a $1:3:1$ C_4 : He : X mixture for about 15 min, X being CO or H_2.

[d] The reaction was stopped and pure CO, He, or H_2 (30 ml/min) was used for 30 min and then purged with He when necessary.

35°C, exposed to flowing H_2 (30 ml/min) for 30 min, and purged with He. Such a catalyst was found to be completely inactive for n-butane isomerization at 35°C, indicating that the initiation sites were consumed by atomic hydrogen which is formed via dissociative adsorption on Pt/Al_2O_3 and spilled over the SFMZ catalyst. Addition of hydrogen after the beginning of the reaction and interruption of n-butane also poisons the catalyst irreversibly. Table 1 summarizes the effect of different species added either before or after the beginning of the isomerization at temperatures below ca. 50°C.

The effect of CO exposure, before reaction, on the catalyst activity was found to be strongly dependent on the temperature. For example, at 100°C, the effect was significantly reduced (Fig. 4). The maximum activity of the catalyst contacted with CO was more than 80% of its original value, i.e., 4.9×10^{-6} vs 6.0×10^{-6} mol/(g of catalyst s^{-1}). This indicates that, at such a temperature, other types of active sites which are not irreversibly destroyed by interaction with CO are triggered. Additional data shown in Table 2 indicate that the threshold temperature for these sites to be catalytically active is ca. 50°C. Indeed, at this temperature, the catalyst that has been exposed to CO before reaction exhibited some isomerization activity (1.5% conversion). Consistent with Wan *et al.*'s proposal (10), there must be another kind of nonacid site which is responsible for n-butane isomerization in the temperature range of 50–100°C since, under the same conditions, unpromoted sulfated zirconia has much lower activity, and yet promoted and nonpromoted catalysts exhibit comparable acidity. These active sites are most likely comprised of Fe(III) oxide formed during precalcination in air at high temperature.

As mentioned earlier, n-butane isomerization at near room temperature over SFMZ is a surface chain reaction; the initiation step is a fast redox process involving Fe oxy as an oxidizing species. As shown in Scheme 1, the over-
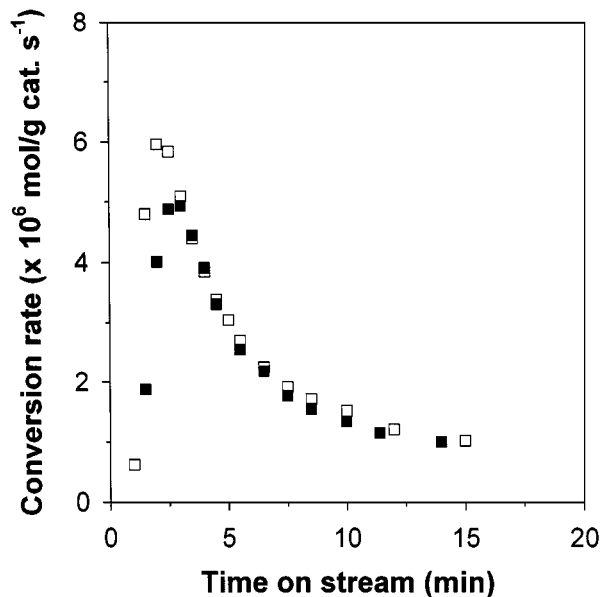

FIG. 4. Effect of CO on the catalytic activity of SFMZ at 100°C. Reaction conditions: 0.4 g of precalcined catalyst (620°C, 6 h); total flow rate, 50 ml/min; n-C_4 : He = 10 : 40; (□) activated SFMZ; (■) CO-poisoned SFMZ.
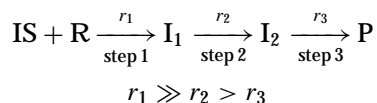
all reaction may be represented as a three-step process. The initiation step is a noncatalytic reaction between the reactant (R) and the initiation sites (IS), presumably Fe oxy species. The obtained intermediate I_1 transforms into a second intermediate I_2 (step 2), most likely butene, which undergo propagation and eventually termination (step 3). Because of the high reactivity of the iron oxy species, step 1 is likely to be very fast. To accumulate I_2 during the so-called induction period, its consumption should be slower than its formation, i.e., $r_3 < r_2$. As suggested earlier (12), such intermediates could be stabilized by the promoters.

TABLE 2

Catalytic Data for n-Butane Isomerization over SFMZ with or without CO Treatment at Different Temperatures

Entry	Reaction temperature (°C)	Feed comp. (ml/min)		Maximum conv. (%)	Maximum rate (mol/(g of catalyst s^{-1}))
		n-C_4	He		
1	35	1	4	6	1.8×10^{-7}
2	35	1	4	0	0
3	50	1	9	17	5.0×10^{-7}
4	50	1	9	1.5	2.0×10^{-8}
5	75	5	20	22.5	3.3×10^{-6}
6	75	5	20	18	2.7×10^{-6}
7	100	10	40	20.2	6.0×10^{-6}
8	100	10	40	15.8	4.9×10^{-6}

Note. Reaction entries 1, 3, 5, and 7 are measured on CO-free SFMZ; entries 2, 4, 6, and 8 are measured on CO-poisoned SFMZ.

$$IS + R \xrightarrow[\text{step 1}]{r_1} I_1 \xrightarrow[\text{step 2}]{r_2} I_2 \xrightarrow[\text{step 3}]{r_3} P$$

$$r_1 \gg r_2 > r_3$$

SCHEME 1. *n*-Butane isomerization over SFMZ at near room temperature. IS = initiation site, R = reactant, I_1 and I_2 = reaction intermediates, P = final product, r_i = overall reaction rate of step *i*.

The effect of CO addition at different stages of *n*-butane isomerization can be rationalized on the basis of Scheme 1. Exposure of the catalyst to CO before the introduction of *n*-butane destroys the initiation sites; thus, the catalyst will not exhibit any activity. Complete and irreversible inhibition was also observed upon exposure of the catalyst to spilled-over atomic hydrogen under otherwise similar conditions. Addition of CO during either the induction or the deactivation period essentially puts the reaction on hold because, at low temperature, CO competes efficiently for adsorption sites that are required for steps 2 and 3. Such sites may be acidic in nature (8, 11). Earlier work from this laboratory (16) showed that the competitivity of CO for adsorption sites during isomerization of hydrocarbons over SZ catalysts increases as the reaction temperature decreases. In addition, our findings (Fig. 1) are consistent with the contention that the surface concentrations of I_1 and I_2 are hardly affected by flowing CO at near room temperature, even if the *n*-butane flow is interrupted. Similar behavior was observed in the presence of flowing He or H_2. Once CO is removed, the reaction resumes unperturbed. However, it is important to mention that the intermediates are removed in the presence of dissociated hydrogen, leading to irreversible loss of activity.

The effect of CO exposure at $100°C$ before the reaction was not as dramatic as that observed at 35 or $50°C$ because another active site (as opposed to initiation site), presumably Fe (III), was triggered. Such an active site was not affected by CO.

In summary, literature discrepancies regarding the effect of CO on *n*-butane isomerization over SFMZ at low temperature were lifted. It was found that the CO-poisoning effect may be irreversible or reversible, depending on whether CO addition took place before or after the start of *n*-butane isomerization. The irreversible effect was associated with the destruction of the initiation sites, while the reversible effect was attributed to competitive adsorption of CO on the catalyst surface. Experiments using other species, i.e., molecular and atomic hydrogen, provided strong support to this interpretation. The strong and irreversible negative effect of dissociated hydrogen (Table 1) was due to either the destruction of the initiation sites or to the removal of reaction intermediates, depending on whether it was generated before or after the beginning of the reaction.

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