Influence of hydrogen on n-butane isomerization over sulfated zirconia catalysts

Steven X. Song, Debra J. McIntosh and Ronald A. Kydd
Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Received 9 November 1999; accepted 14 January 2000

This work investigates the influence of hydrogen on the catalytic activity of Fe- and Mn-promoted sulfated zirconia catalysts. It was found that the effect of hydrogen on the activity of Fe-promoted SZ in n-butane isomerization significantly depended on the Fe content of the catalyst. It was also discovered that the negative effect of hydrogen is more significant at lower temperatures. The reason for the decreased activity in hydrogen is thought to be due to the interaction of hydrogen with reaction intermediates.

Keywords: butane, isomerization, hydrogen effect, sulfated zirconia

1. Introduction

Sulfated zirconia (SZ) is a solid acid catalytic material that exhibits a high activity for low-temperature n-butane isomerization. One explanation for this high activity is that SZ can facilitate a bimolecular mechanism [1] that involves the formation of butene and C_4 carbenium ions. The butene molecule reacts with the carbenium ion to form a C_8 intermediate, and the skeletal rearrangement and β-scission of the C_8 intermediate forms isobutane. Experimental evidence to support this explanation is the negative effect of hydrogen on the isomerization of n-butane over SZ catalysts [1–5]; i.e., the presence of hydrogen in the reaction feedstock causes a lower n-butane conversion to isobutane. The higher the hydrogen partial pressure, the lower the conversion. This negative hydrogen effect has been considered to result from the decreased butene concentration on the catalyst surface due to the presence of hydrogen. The negative effect of hydrogen has been reported without exception from studies on unpromoted SZ catalysts [1,2,4,5]. For Fe- and Mn-promoted SZ catalysts (FMSZ), however, different observations about the hydrogen effect have been reported. In one report, a reduced n-butane conversion was observed when hydrogen was present in the reaction feedstock [3]. However, other reports showed that hydrogen does not show a negative effect on n-butane conversion over FMSZ catalysts [4,6]; this was explained on the basis of a strong stabilization effect by Fe and Mn promoters on unsaturated intermediates (carbenium ions and butene on the catalyst surface) [4]. A recent study [7] suggested that the difference in the observed hydrogen effect may result from the different butene concentrations in n-butane feedstocks used by the research groups. A high concentration of butene in the feed tends to diminish the negative effect of hydrogen, because a high accumulation of olefins is present on the catalyst surface initially (and throughout the course of the reaction).

The purpose of the present study is to clarify the influence of hydrogen on butane isomerizations conducted at different temperatures over both promoted and unpromoted SZ catalysts. In addition to the temperature, the effects of varying the Fe and Mn content were studied.

2. Experimental

Sulfated zirconium hydroxide was prepared using the method described in our previous communication [8]. Fe- or Mn-promoted sulfated zirconia catalysts were prepared by mixing sulfated zirconium hydroxide with a solution of $Fe(NO_3)_3 \cdot 9H_2O$ (98%, Aldrich) or $Mn(NO_3)_2 \cdot 6H_2O$ (98%, Aldrich). While stirred, the mixture was heated to remove water. The amount of Fe or Mn added was chosen to produce a catalyst with the desired content of Fe or Mn. The dried iron- or manganese-containing sulfated zirconium hydroxide samples were calcined at 650 °C for 3 h in static air, thus being transformed to iron-oxide- or manganese-oxide-containing sulfated zirconia.

n-butane isomerization was conducted in a fixed-bed downward-flow quartz reactor (9 mm i.d.) at 60–80 °C under atmospheric pressure. The amount of the catalyst used was 0.25 g. The reaction feedstock was a mixture on n-butane (Instrument Grade, 99.5%) with helium (High Purity) or hydrogen (High Purity), which consisted of 1 ml/min of butane and 22 ml/min of helium or hydrogen. 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 air 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

© J.C. Baltzer AG, Science Publishers

maximum conversion reached at the end of the break-in period was taken as a measure of the catalytic activity.

3. Results and discussion

One interesting finding of our present work is that the effect of hydrogen on the activity of Fe-promoted SZ in n-butane isomerization significantly depends on the content of Fe in the catalyst. This is the first time that the H_2 effect and Fe variation have been studied together and the result is shown in figure 1. All of the reactions were run at 60 °C, except for the reactions run with catalysts containing no iron. These reactions were run at 80 °C since their activity at 60 °C was too low to measure. For catalysts containing low contents of Fe, the catalytic activity in H_2 is significantly lower than that in He. When the Fe content exceeds 6 wt%, the negative H_2 effect becomes negligible, although the catalytic activity declines from its peak value at about 4 wt% Fe. A plot of the ratio of conversion in H_2 over conversion in He is also shown (figure 1(b)). From this figure, it can be seen that the magnitude of the H_2 effect decreases by a factor of 15 as the Fe content changes from 0 to 8%.

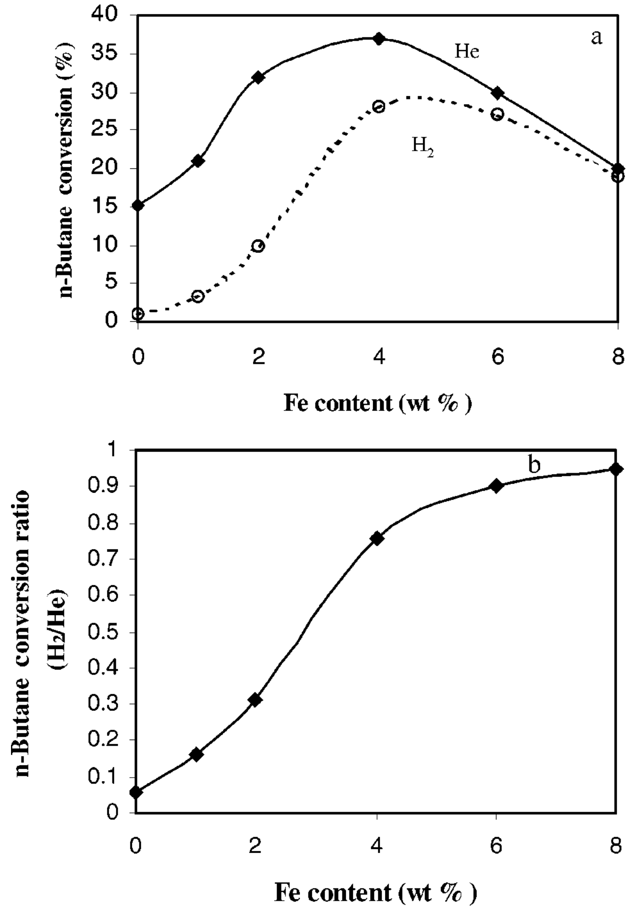

Figure 1. Influence of Fe content on H_2 effect. Reactions were carried out at 60 °C (excluding first data point, which was taken at 80 °C) in H_2 or He as indicated: (a) n-butane conversion and (b) ratio of n-butane conversions in H_2 and He, as a function of Fe content.

To ensure that the decreased catalytic activity is not because of the interactions between the catalytic active sites and the hydrogen at the reaction temperature used, the following experiments were carried out. First, a catalyst sample containing 2 wt% Fe was pretreated in air at 450 °C for 2 h and its activity was tested in He. In a second experiment, another sample of the same catalyst was first pretreated in air (under the same conditions) and subsequently exposed to hydrogen for 2 h at 60 °C before a reaction in He was started. The results shown in table 1 indicate that the exposure of the catalyst in hydrogen at 60 °C does not affect the catalytic activity. This suggests that the interaction between the catalytic active sites and the H_2 at 60 °C is negligible and the reason for the decreased catalytic activity in H_2 is due to the interaction of H_2 with reaction intermediates, rather than with the active sites.

As a support to our speculation two different reactions were carried out over 2 wt% Fe: one in He and the other initially in H_2 and then switched to He. Figure 2 shows that during a reaction in H_2, when a He stream was introduced to replace the H_2, the catalytic activity increased immediately. This clearly indicates that H_2 does not deactivate the active sites on the catalyst surface or no immediate change in activity would be observed. By comparing figures 1 and 2, it can be seen that after switching to He from H_2 the activity does not increase to the maximum observed when using He; this is because the catalyst has been exposed to butane and some deactivation has already occurred before switching gases.

We investigated the influence of hydrogen at different reaction temperatures (60 and 80 °C). It was found (table 2) that the negative effect of H_2 is more significant at lower

Table 1
Regeneratability of Fe-promoted SZ after exposure to H_2.

Entry	Catalyst[a]	Catalyst activation	n-butane conversion[b] (%)
1	FSZ	Air, 450 °C, 2 h	32
2	FSZ	Air, 450 °C, 2 h + H_2, 60 °C, 2 h	31

[a] All catalysts contained 2 wt% Fe.
[b] At 60 °C, in He flow.

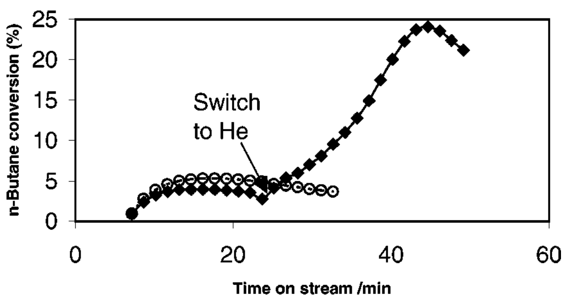

Figure 2. Influence of H_2 on catalyst surface. Reactions were carried out at 60 °C with 2% Fe. Reaction carried out in H_2 only is shown with (○). (◆) represent reaction where H_2 carrier gas was used up to 24 min and then switched to He carrier gas.

Table 2
Influence of reaction temperature on H_2 effect.

Reaction conditions[a]	Reaction temperature	
	60 °C	80 °C
Conversion in He	27.8	50.7
Conversion in H_2	4.8	48.3

[a] All reactions used 2% Fe-SZ.

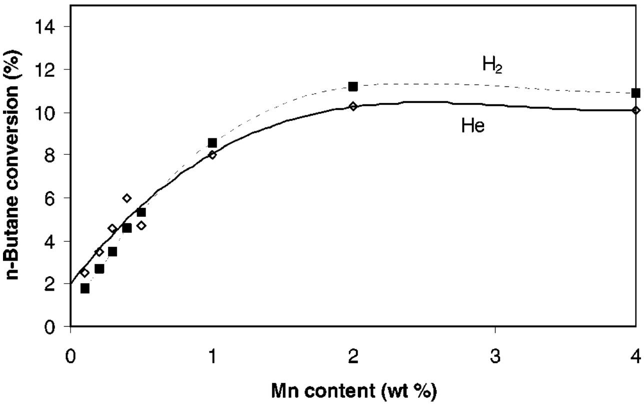

Figure 3. Influence of Mn content on H_2 effect. Reactions were carried out at 60 °C in H_2 or He as indicated.

temperatures. This observation is consistent with that reported by Tran et al. [5].

We also tested the activity of catalysts containing only Mn in He and H_2, respectively. The results are shown in figure 3. Although the activities of these catalysts are much lower than that of Fe-SZ, the hydrogen effect is much weaker over Mn-SZ than over Fe-SZ. In fact at higher Mn content, the activity in H_2 appears to be slightly larger than in He. The reason for this behaviour is not clear at this time.

It has been well-accepted that at low reaction temperatures, n-butane isomerization over SZ catalysts takes place through a bimolecular mechanism that 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 forms isobutane [1]. In this mechanism, butene molecules (generated by catalyst or present as an impurity in the feed) are required for catalytic activity. Butene along with H_2 can be produced through an oxidative dehydrogenation process over SZ catalysts [9] and the H_2 evolution has been detected during n-butane isomerization [10]. It was also found that butene presented in a n-butane feed as an impurity tends to increase the n-butane conversion [3,11].

Other researchers have speculated about the role H_2 plays in the catalytic isomerization of n-butane over SZ catalysts [1–8]. The consensus is that hydrogen in the feed inhibits n-butane isomerization by decreasing the butene concentration on the catalyst surface. Taking into consideration the literature data and the results presented in the work, we conclude that while this is true, there are also many other factors that affect the magnitude of the hydrogen effect over promoted and unpromoted SZ catalysts.

First, it depends on the composition of SZ catalysts. As observed in the present work, the presence of Fe oxide strongly affects the magnitude of the hydrogen effect. The higher the Fe content, the smaller the hydrogen effect. We concur with the rationalization proposed in [4,6] regarding the roles played by Fe oxide as a promoter, i.e., it can stabilize the reaction intermediates (such as C_4 carbenium ions and butene molecules) on the catalyst surface. Due to the stabilization effect, a higher concentration of butenes may be able to accumulate when the Fe content is high even when hydrogen exists in the feed; this increases the catalyst activity. This large accumulation of butenes on the catalyst surface also causes the hydrogen effect to be diminished until it is insignificant at high Fe content (greater than 4 wt%).

Second, the negative hydrogen effect is reported to depend on butene contents in the feed [7]. Butene exists in n-butane as an impurity. Small amounts of butenes in the feed can significantly diminish the hydrogen effect at low reaction temperatures. As mentioned in section 1, this factor is thought to have contributed to the different results obtained by the researchers in [3,4,6].

And third, the magnitude of the negative hydrogen effect is also dependent on reaction temperature. At lower temperatures, n-butane isomerization over SZ catalysts is thought to occur via a bimolecular reaction pathway in which the formation of butene is critical. The presence of hydrogen will limit the number of butene molecules present, thereby limiting the activity. At higher temperatures the monomolecular pathway will start to be more significant and this pathway will not be affected by the presence of hydrogen. In [4] (where no hydrogen effect was found) the results were obtained at 100 °C, where the hydrogen effect is insignificant.

References

[1] V. Adeeva, G.D. Lei and W.M.H. Sachtler, Appl. Catal. A 118 (1994) L11; Catal. Lett. 33 (1995) 135.
[2] H. Lui, V. Adeeva, G.D. Lei and W.M.H. Sachtler, J. Mol. Catal. 100 (1995) 35.
[3] M.A. Coelho, W.E. Alvarez, E.C. Sikabwe, R.L. White and D.E. Resasco, Catal. Today 28 (1996) 415.
[4] A. Sayari, Y. Yang and X. Song, J. Catal. 167 (1997) 346.
[5] M.-T. Tran, N.S. Gnep, M. Guisnet and P. Nascimento, Catal. Lett. 47 (1997) 57.
[6] X. Song, K.R. Reddy and A. Sayari, J. Catal. 161 (1996) 206.
[7] W.E. Alvarez, H. Liu and D.E. Resasco, Appl. Catal. A 162 (1997) 103.
[8] S.X. Song and R.A. Kydd, Catal. Lett. 51 (1998) 95.
[9] K.T. Wan, C.B. Khouw and M.E. Davis, J. Catal. 158 (1996) 489.
[10] Z. Hong, K.B. Fogash, R.M. Watwe, B. Kim, B.I. Masqueda-Jimenez, M.A. Natal-Santiago, J.M. Hill and J.A. Dumesic, J. Catal. 178 (1998) 489.
[11] J.E. Tábora and R.J. Davis, J. Am. Chem. Soc. 118 (1996) 12240; J. Catal. 162 (1996) 125.