Catalysis Letters 37 (1996) 5–8

Pentane isomerization and disproportionation catalyzed by sulfated zirconia promoted with iron and manganese

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Received 11 September 1995; accepted 23 October 1995

Fe- and Mn-promoted sulfated zirconia was used to catalyze the conversion of *n*-pentane in a flow reactor at temperatures in the range of −25 to 40°C and *n*-pentane partial pressures in the range of 0.005 to 0.01 atm. The rates of reaction increased with time on stream during an induction period and then decreased rapidly. The predominant reaction at −25°C and short times on stream was isomerization to give isopentane; no dibranched products were observed. The selectivity for isomerization decreased and that for disproportionation increased with increasing temperature, with disproportionation becoming predominant at 40°C; the principal product was then isobutane. The product distribution data are consistent with acid–base catalysis and carbocation intermediates. However, there appears to be more to the reaction mechanism than acid–base chemistry, and the roles of the iron and manganese promoters are not yet explained.

Keywords: pentane; disproportionation; isomerization; sulfated zirconia; *n*-pentane

1. Introduction

Alkane isomerization at low temperatures favors branched, high-octane-number products, but to be practically valuable, it requires a highly active catalyst. Sulfated ZrO_2 incorporating Fe and Mn has been shown to be highly active for butane isomerization, catalyzing the reaction even at room temperature [1]. There are still almost no data indicating how this catalyst functions for conversion of reactants other than butanes. Our goal was to investigate sulfated ZrO_2 incorporating Fe and Mn as a catalyst for the conversion of *n*-pentane at low temperatures.

2. Experimental

The catalysts, sulfated zirconia and sulfated zirconia containing 1.0 wt% Fe, 0.5 wt% Mn, and 1.8 wt% sulfur, were prepared from sulfated zirconium hydroxide (Magnesium Elektron, Inc.). The unpromoted sulfated zirconia was first dried at 120°C for 24 h and then impregnated by the incipient wetness method with an aqueous solution of iron and manganese nitrates; 26.756 g of the dried sulfated zirconia was brought in contact with a solution consisting of 5.0 ml of water, 2.307 g of $Fe(NO_3)_3 \cdot 9H_2O$, and 0.555 g of $Mn(NO_3)_2 \cdot 6H_2O$. The resultant promoted material was dried at 120°C for 24 h, calcined in static air as the temperature was raised at a rate of 3°C/min from room temperature to 650°C, and then held for 3 h. The preparation of the unpromoted catalyst involved drying at 120°C for 24 h followed by contacting with water (the same amount as used with the promoted catalyst) and drying at 120°C for 24 h and calcining in static air as stated above.

Before each catalytic reaction experiment, the catalyst in flowing N_2 (30 ml(NTP)/min) was heated from 20 to 450°C at a rate of 7.1°C/min, and the temperature was then held at 450°C for 1.5 h. After this pretreatment, the catalyst was cooled to the desired reaction temperature in N_2 flowing at 30 ml/min. Reactions were carried out in a thermostatted stainless steel U-tube reactor. The mass of catalyst varied from 0.1 to 1.0 g.

In the flow reactor experiments, 1.01 mol% *n*-pentane in N_2 containing 0.002 mol% isopentane and 0.00077 mol% neopentane impurities was used as the feed; this was occasionally diluted with a stream of N_2. Reactions were carried out at 1 atm and at temperatures in the range of −25 to 40°C. The total volumetric flow rate of feed was 20 ml(NTP)/min. Products were analyzed with an online gas chromatograph with a J&W alumina PLOT column 0.53 mm in diameter and 30 m in length. The first injection was made after 5 min on stream, and subsequent injections were made at intervals of 20 min.

3. Results

The unpromoted sulfated zirconia was barely active for conversion of *n*-pentane under the conditions investigated. Only trace amounts of one product, isopentane, were observed at temperatures up to 40°C.

In contrast, the promoted sulfated zirconia was active for *n*-pentane conversion. At the lower reaction tem-

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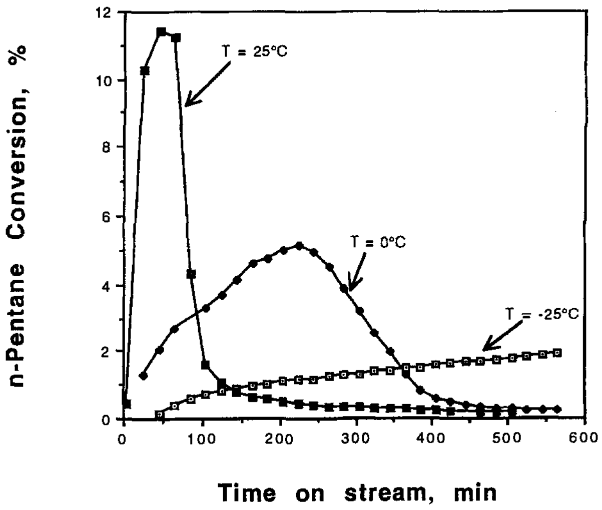

Fig. 1. Effect of temperature on conversion of *n*-pentane catalyzed by Fe- and Mn-promoted sulfated zirconia in a flow reactor. Catalyst mass: 0.500 g; *n*-pentane partial pressure 0.010 atm; feed flow rate 20 ml(NTP)/min.

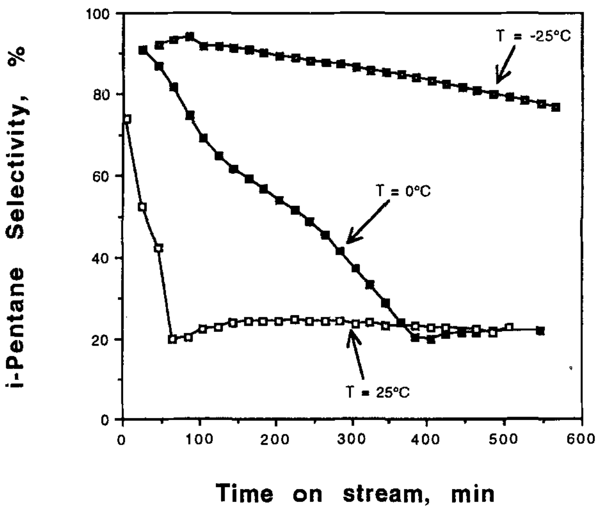

Fig. 3. Effect of temperature on selectivity for formation of isopentane formed from *n*-pentane in the presence of Fe- and Mn-promoted sulfated zirconia catalyst. Other conditions as stated in caption of fig. 1.

peratures (−25 to 0°C), the promoted sulfated zirconia catalyzed the formation of isobutane, isopentane, and traces of 2-methylpentane and 3-methylpentane. In addition to these products, small amounts of *n*-butane and traces of propane, *n*-hexane, and heptanes were observed at 25 and at 40°C. No dibranched products were observed.

n-pentane conversion as a function of time on stream is shown in fig. 1 for reaction at −25, 0, and 25°C. Conversion to individual products at 0°C is shown in fig. 2. At each temperature, the conversion to each product increased toward a maximum as a function of time on stream. The time to reach maximum conversion (the induction period) decreased with increasing temperature, and the maximum conversion increased with increasing temperature. The pattern is consistent with that observed for conversion of *n*-butane and of isobutane in the presence of the same catalyst [2].

The selectivities (in mol%) for formation of isopentane and isobutane are shown as a function of time on stream in figs. 3 and 4, respectively. As isopentane and isobutane were the major products, the decrease in selectivity for isopentane formation with time on stream was nearly compensated by the increase in selectivity for isobutane formation.

Conversion data for the reaction of *n*-pentane catalyzed by the iron- and manganese-promoted sulfated zirconia at 40°C are summarized in table 1 and compared with data taken under nearly the same conditions [3] for conversion of *n*-butane. The comparison is based on the

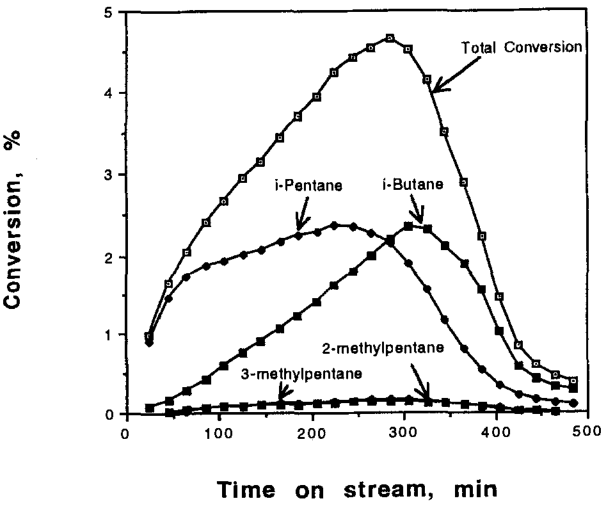

Fig. 2. Conversion and product distribution in conversion of *n*-pentane catalyzed by Fe- and Mn-promoted sulfated zirconia at 0°C. Other conditions as stated in caption of fig. 1.

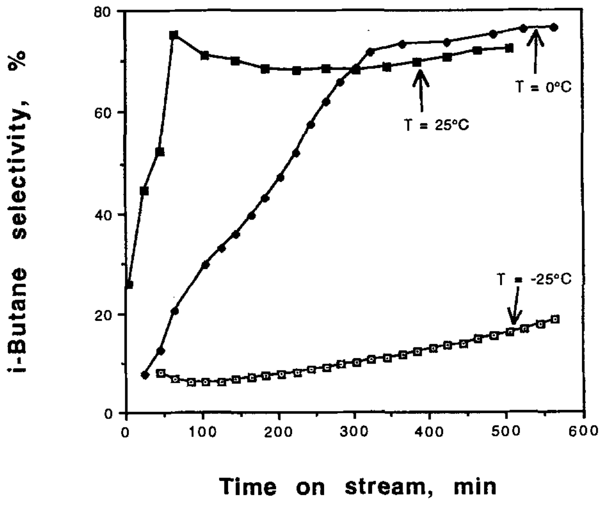

Fig. 4. Effect of temperature on selectivity for formation of isobutane formed from *n*-pentane in the presence of Fe- and Mn-promoted sulfated zirconia catalyst. Other conditions as stated in caption of fig. 1.

Table 1
Comparison of reactivities of *n*-pentane and *n*-butane for reactions catalyzed by Fe- and Mn-promoted sulfated zirconia at 40°C[a]

Reactant	Conversion	Space velocity (mol of *n*-alkane/(g s))	Product	Selectivity (mol%)	Ref.
n-butane	0.127	2.0×10^{-7}	propane	3.1	[3]
			isobutane	95	[3]
			isopentane	1.7	[3]
n-pentane	0.126	6.0×10^{-7}	propane	1.5	this work
			isobutane	75	this work
			isopentane	20	this work
			3-methylpentane	1.3	this work
			2-methylpentane	2.2	this work
			n-hexane	trace	this work

[a] The feed flow rate was 80 ml(NTP)/min; the alkane reactant partial pressure was 0.005 atm.

conversions at the maximum as a function of time on stream.

The decreases in conversion following the induction period indicate catalyst deactivation. The pattern of conversion as a function of time on stream is qualitatively consistent with that observed for conversion of *n*-butane with the same catalyst [2,3b,4]. The promoted catalyst was unchanged in color after use, remaining beige, but it took on a red-brown tinge upon coming in contact with air after removal from the reactor. When the catalyst had been used at a low temperature ($\leqslant 0$°C), undergoing deactivation, and then (without removal from the reactor) used at a higher temperature, the performance at the higher temperature agreed exactly with that observed with a fresh catalyst at the higher temperature.

4. Discussion

4.1. Product distributions

The product distribution data observed for the Fe- and Mn-promoted sulfated zirconia show that isomerization of *n*-pentane was the predominant reaction at the lowest temperatures (−25 and 0°C) and the shortest times on stream. We stress that only the monobranched isomerization product was observed.

The observation of butanes and hexanes as products suggests the occurrence of *n*-pentane disproportionation, although a stoichiometric ratio of these products was not observed. As stoichiometric disproportionation of *n*-butane has been observed with this catalyst under similar conditions [2,3b,5], we suggest that stoichiometric disproportionation occurred and was accompanied by relatively rapid secondary reactions that led to preferential conversion of hexanes. Consistent with this hypothesis, propane was observed as a product (presumably of a secondary reaction). The observation of heptanes is also consistent with the occurrence of disproportionation (of hexane).

4.2. Comparison of reactivities of n-pentane and n-butane

The data (table 1) show that the reactivity of *n*-pentane is three times greater than the reactivity of *n*-butane in the presence of the Fe- and Mn-promoted sulfated zirconia at 40°C.

4.3. Comparison of unpromoted and promoted sulfated zirconia

Hino and Arata [6] observed that sulfated zirconia catalyzed the conversion of *n*-pentane into isobutane and isopentane at 80°C in a pulse reactor. The same products were observed in this work (among others).

The data reported here demonstrate that the Fe- and Mn-promoted sulfated zirconia is markedly more active than unpromoted sulfated zirconia, but there is not a basis for a quantitative comparison. The promoted catalyst has been found to be two to three orders of magnitude more active than the unpromoted catalyst for isomerization of *n*-butane [1].

4.4. Implications for reaction mechanism

The product distribution data are consistent with acid–base catalysis, whereby isomerization and disproportionation take place via carbocation intermediates. For example, Ipatieff and Schmerling [7] observed product distributions similar to ours when *n*-pentane was converted in the presence of $HCl/AlCl_3$. Pines [8] interpreted these and related data in terms of isomerization and disproportionation reactions.

Butane isomerization catalyzed by the Fe- and Mn-promoted sulfated zirconia has been suggested to take place by a bimolecular mechanism, with the evidence for the suggestion including results of tracer experiments [9], kinetics [10], and the occurrence of disproportionation characterized by induction times the same as those observed for isomerization [11]. In this work, the induction times observed for *n*-pentane disproportionation were not the same as those observed for *n*-pentane isomerization, which suggests that the two reactions did not proceed through a common intermediate. Thus, assuming that *n*-pentane disproportionation was bimolecular, we might then suggest that *n*-pentane isomerization was acid-catalyzed and monomolecular. Acid-catalyzed monomolecular isomerization of *n*-pentane does not require a high-energy primary carbenium ion intermediate, whereas acid-catalyzed monomolecular isomerization of *n*-butane does [12]. If these monomolecular and bimolecular mechanisms suggested for *n*-pentane and *n*-butane, respectively, were correct, it would seem likely that the difference in reactivity between the two reactants would be large. However, the difference is only threefold (table 1). Consequently, we suggest that there may be more to the mechanism of the catalysis than simple acid–base chemistry.

The color change of the used catalyst in contact with air suggests an increase in the oxidation state of the iron, consistent with the proposal of Wan et al. [13] that iron centers are active for oxidative dehydrogenation to generate butene from *n*-butane during *n*-butane isomerization catalysis. Wan's suggestion is in agreement with the postulate of Adeeva et al. [9] that *n*-butane isomerization catalyzed by Fe- and Mn-promoted sulfated zirconia proceeds through butene intermediates formed by dehydrogenation of *n*-butane. However, any butenes formed on the catalyst surface would be expected to be protonated rapidly and almost completely by the strongly acidic sites. Thus it is doubtful that butenes are reaction intermediates, and the roles of the iron and manganese promoters remain to be fully explained.

5. Conclusions

Fe- and Mn-promoted sulfated zirconia catalyzed the isomerization and disproportionation of *n*-pentane at temperatures in the range of −25 to 40°C. The products were isobutane, isopentane, and traces of 2-methylpentane and 3-methylpentane; in addition, small amounts of *n*-butane and traces of propane, *n*-hexane, and heptanes were observed at 25 and at 40°C. The rates of reaction increased with time on stream during an induction period and then decreased rapidly. At 40°C and the end of the induction period, the reactivity of *n*-pentane was three times greater than that of *n*-butane. The pentane isomerization took place selectively at −25°C and short times on stream, but the selectivity for disproportionation increased with increasing temperature, becoming predominant at 40°C; the principal product was then isobutane. The product distribution data are consistent with acid–base chemistry and carbocation intermediates; however, there appears to be more to the catalysis than acid–base chemistry, and the roles of the iron and manganese promoters are not yet explained.

Acknowledgement

We thank R.E. Jentoft and C. Neville for help in the experimentation. This research was supported by the University of California Energy Institute.

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