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Butane disproportionation catalyzed by sulfated zirconia promoted with iron and manganese

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The disproportionation of *n*-butane (and of isobutane) was catalyzed by sulfated zirconium oxide containing 1.5 wt% Fe, 0.5 wt% Mn, and 4.0 wt% sulfate at 2.0 atm and temperatures in the range of 30–60°C. The reaction accompanies isomerization, which under some conditions is as much as one or two orders of magnitude faster than disproportionation. The conversion to each of the products increased with time on stream in a flow reactor, and then declined. The time on stream for maximum conversion was the same for each product. The results suggest that the disproportionation and isomerization reactions proceed through a common C_8 intermediate. Rates of the disproportionation reaction were determined at the time on stream corresponding to the maximum conversion at each temperature; for example, the rate of conversion of *n*-butane into isopentane at 60°C with an *n*-butane partial pressure of 0.58 atm was about 1×10^{-7} mol/(g of catalyst s).

Keywords: butane; disproportionation; isomerization; sulfated zirconia; *n*-butane; isobutane

1. Introduction

Sulfated zirconia promoted with Fe and Mn is one of the most active known catalysts for *n*-butane isomerization, catalyzing the reaction even at room temperature, but undergoing rapid deactivation [1–4]. Disproportionation accompanies the isomerization reactions [1,3,4], but there are almost no quantitative data characterizing this reaction. As a companion to a report of butane isomerization [3], this paper includes data for disproportionation of *n*-butane and of isobutane accompanying the isomerization reactions catalyzed by Fe- and Mn-promoted sulfated zirconia. The data reported here were collected during the experiments described earlier [3].

2. Experimental

The catalyst, sulfated zirconia containing 1.5 wt% Fe, 0.5 wt% Mn, and 4.0 wt% sulfate, and the experiments, carried out with a once-through flow reactor fed with *n*-butane, isobutane, or mixtures of the two, have been described [3]. Products were analyzed by on-line gas chromatography. The temperature range was 30–60°C and the pressure 2.0 atm. In the experiments reported here, the feed contained *n*-butane or isobutane, but not both.

3. Results

The products of the reaction of *n*-butane were isobutane, propane, isopentane, and *n*-pentane. The products of the reaction of isobutane were *n*-butane, propane, isopentane and *n*-pentane. The conversions to C_3 and C_5 products were zero to two orders of magnitude less than the conversions to C_4 products, depending on the temperature. The isopentane to *n*-pentane ratio in the product was > 1 and depended on the reaction conditions.

Measurements of conversion of each of the butane isomers to each of the products as a function of time on stream showed an initial period (the induction period) of increasing conversion followed by a rapid decline associated with catalyst deactivation (figs. 1–6). The pattern of conversion vs. time on stream for butane dispropor-

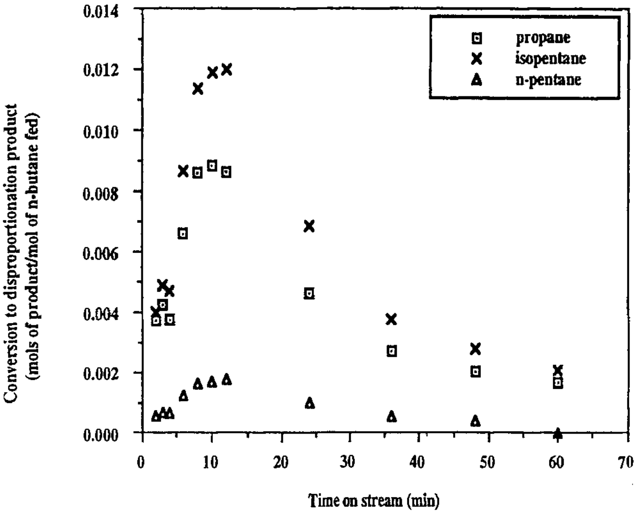

Fig. 1. Conversion profile for disproportionation products. Reactant: *n*-butane. Reaction conditions: temperature = 50°C; mass of catalyst, 2.33 g; inverse space velocity = 2.80×10^5 (g of catalyst s)/(mol of butane fed); partial pressure of *n*-butane = 0.58 atm.

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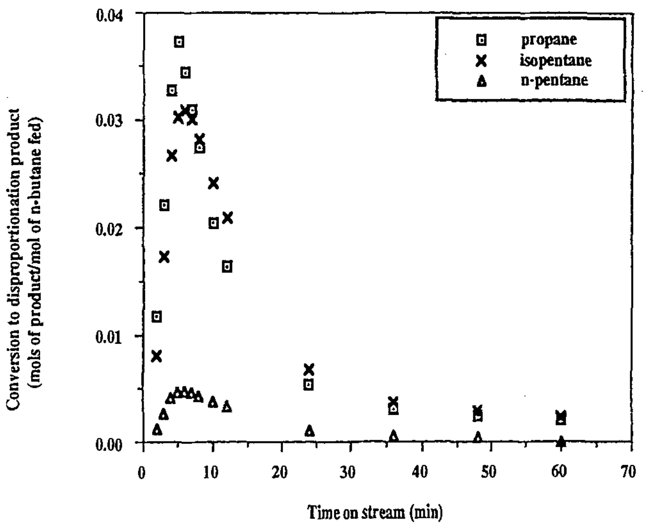

Fig. 2. Conversion profile for disproportionation products. Reactant: *n*-butane. Reaction conditions: temperature = 60°C; other conditions as stated in caption of fig. 1.

tionation (figs. 1–3) is almost the same as that observed for butane isomerization (figs. 4–6), but the selectivity for isomerization increased slightly as the catalyst deactivated. The times on stream corresponding to the maximum in conversion were found to be the same for each product in an experiment (figs. 1–6).

The conversions observed at the end of the induction period were taken to be those characteristic of the undeactivated catalyst, as these gave a more consistent set of data than the conversions extrapolated to zero time on stream (with only the data taken following the maximum conversion being included in the extrapolation); details are given elsewhere [5]. The conversions were low and approximated as differential, providing estimates of reaction rates [5], which are summarized in table 1. Temperature dependencies of the rates (determined under the conditions stated in table 1) are represented by the apparent activation energies summarized in table 2; details are given elsewhere [5].

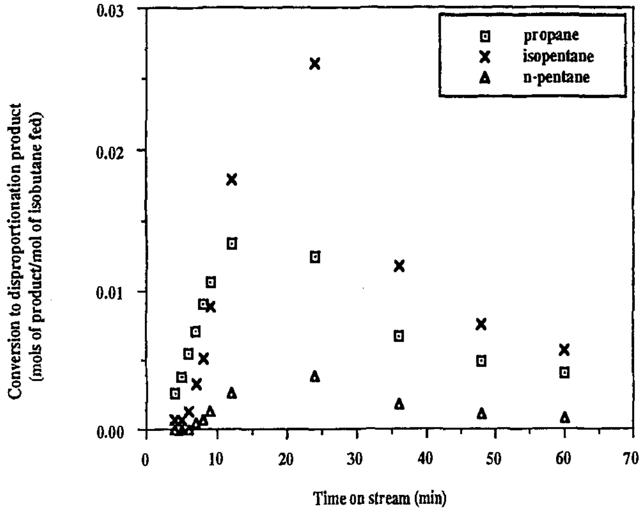

Fig. 3. Conversion profile for disproportionation products. Reactant: isobutane. Reaction conditions: temperature = 50°C; inverse space velocity = 8.41 × 10^5 (g of catalyst s)/(mol of butane fed); other conditions as stated in caption of fig. 1.

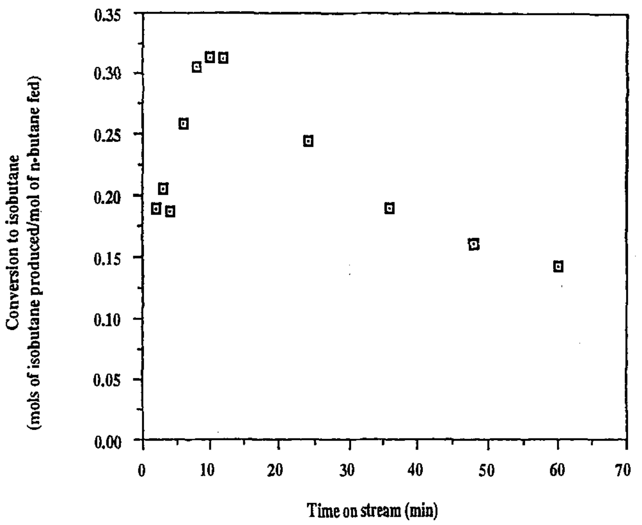

Fig. 4. Conversion profile for isomerization product, isobutane. Reactant: *n*-butane. Reaction conditions as stated in caption of fig. 1.

The induction times were dependent on the temperature, as shown in fig. 7.

4. Discussion

The data show that the predominant reaction of each of the butanes was isomerization, which was accompanied by disproportionation:

$$2\ n\text{-butane} \rightarrow \text{propane} + \text{pentane} \quad (1)$$

$$2\ \text{isobutane} \rightarrow \text{propane} + \text{pentane} \quad (2)$$

The product distributions initially do not all correspond exactly to the stoichiometric occurrence of isomerization in parallel with disproportionation; however, at the

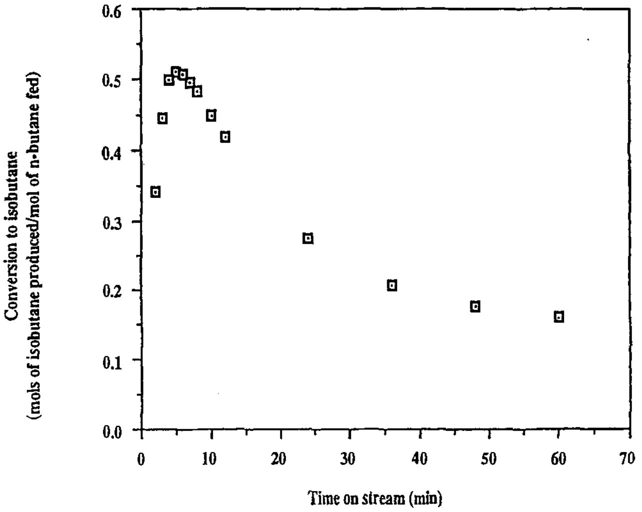

Fig. 5. Conversion profile for isomerization product, isobutane. Reactant: *n*-butane. Reaction conditions as stated in caption of fig. 2.

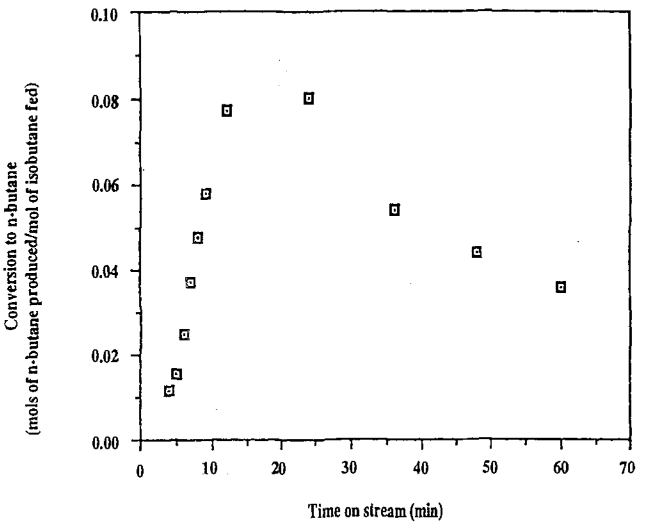

Fig. 6. Conversion profile for isomerization product, *n*-butane. Reactant: isobutane. Reaction conditions as stated in caption of fig. 3.

Table 2
Temperature dependence of rates of butane disproportionation catalyzed by iron- and manganese-promoted sulfated zirconia[a]

Reaction product	Apparent activation energy (kcal/mol)	Temperature range (°C)
isobutane [b]	14 ± 4	30–60
n-butane [c]	19 ± 1	30–60
propane [b]	27 ± 4	30–60
n-pentane [b]	19 ± 11	45–60
isopentane [b]	22 ± 4	30–60

[a] Reaction conditions stated in table 1.
[b] Reactant: *n*-butane; partial pressure 0.58 atm.
[c] Reactant: isobutane; partial pressure 0.58 atm.

longer times on stream, the stoichiometric proportions were closely approached (figs. 1–3), consistent with the observations of Cheung et al. [4].

Calculations show that the rates of catalytic reaction were not influenced by mass or heat transport and that the flow in the reactor was well approximated as plug flow [6]. Thus the rate data are inferred to represent the intrinsic activity of the catalyst. These are the first data quantifying the rates of disproportionation with a catalyst of the sulfated zirconia type, and they are almost the only data quantifying this reaction for any catalyst.

The rate data show that the catalyst is highly active for disproportionation; the rates of disproportionation reported here are higher than others reported – however, hardly any rates of this reaction have been reported. For example, the rate of conversion of *n*-butane into isopentane observed in this work at 60°C with an *n*-butane partial pressure of 0.58 atm was about 1×10^{-7} mol/(g of catalyst s); for comparison, the rate of formation of isopentane from *n*-butane in the presence of aluminum chloride supported on sulfonic acid resin at 100°C and an *n*-butane partial pressure of 0.41 atm was only about 8×10^{-10} mol/(g of catalyst s) [7], although the latter catalyst was partially deactivated prior to the measurement.

The mere fact of the occurrence of disproportionation suggests that this reaction proceeded through a C_8 intermediate. There is evidence that butane isomerization also proceeds through C_8 intermediates; presumably, the intermediates are the same for both the isomerization and disproportionation reactions. The evidence is as follows:

(1) The reaction profiles for the isomerization and disproportionation reactions are nearly the same (figs. 1–6), suggesting that the reactions proceed through the same intermediates.

(2) The form of the kinetics of each of the butane isomerization reactions suggests a bimolecular reaction [3].

(3) The results of ^{13}C labeling experiments indicate a bimolecular reaction and a C_8 intermediate [8], consistent with what had been found by Guisnet et al. for butane isomerization catalyzed by H-mordenite at a much higher temperature, 350°C [9,10].

The classical mechanism for such a bimolecular reaction catalyzed by an acid [7,9,10] involves alkylation, isomerization, and cracking reactions, with carbenium ion and alkene intermediates; the latter could be formed by butane dehydrogenation on Fe or Mn promoter sites [8]. Alternatively, the strength of the acidity of the catalyst leads to the suggestion that the presumed alkene

Table 1
Rates of formation of isobutane, propane, *n*-pentane, and isopentane from *n*-butane catalyzed by iron- and manganese-promoted sulfated zirconia[a]

Reactant	Temp. (°C)	$10^7 \times$ rate of isomerization[b]	$10^7 \times$ rate of propane formation[a]	$10^7 \times$ rate of isopentane formation[a]	$10^7 \times$ rate of *n*-pentane formation[a]
n-butane	30	2.3	0.02	0.04	–
n-butane	40	6.8	0.11	0.19	–
n-butane	45	9.8	0.26	0.33	0.05
n-butane	50	11.2	0.32	0.43	0.06
n-butane	60	18.2	1.33	1.10	0.17
isobutane	50	0.95	0.16	0.31	0.05
isobutane	60	2.12	1.65	0.68	0.11

[a] Reaction conditions: partial pressure of butane (*n*-butane or isobutane), 0.58 atm; partial pressure of N_2: 1.44 atm.
[b] Units of rate: mol of butane/(g of catalyst s).

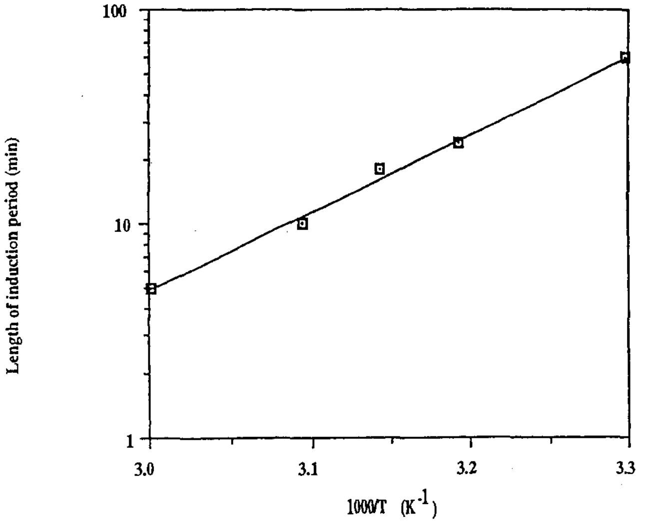

Fig. 7. Temperature dependence of the length of the induction period. Feed: *n*-butane with a partial pressure of 0.58 atm.

intermediates would be unimportant because they are unstable and readily converted into species such as carbenium ions (which could be equilibrated with other species, such as alkoxides), with the chemistry paralleling that in liquid superacids. Such a possibility has been pointed out to explain the reactions of propane in the presence of Fe- and Mn-promoted sulfated zirconia [11].

At the short times on stream, the conversion to isopentane exceeded that to propane at the lower temperature, whereas the reverse was true at the higher temperatures (figs. 1 and 2). Presumably, the isopentane was converted in secondary reactions, but the conversions were too low to allow detection of the presumed secondary reaction products. Consistent with this presumption, experiments done at higher temperatures confirm that cracking occurred [12].

The cause of the induction period is still unknown; the strong temperature dependence of this period shown in fig. 7 suggests that this period is characteristic of a chemical change in the catalyst, perhaps associated with the Fe and Mn sites.

5. Conclusions

Fe- and Mn-promoted sulfated zirconia is an active catalyst for the disproportionation and isomerization of *n*-butane and of isobutane at temperatures in the range of 30–60°C. The rates of *n*-butane disproportionation observed with this catalyst are higher than those reported for other catalysts. The products are the following, stated in the most typical order of decreasing yield: isomerized butane, isopentane, propane, and *n*-pentane. The time on stream of the maximum conversion was approximately the same for each product. This result suggests that the isomerization and disproportionation reactions proceed via the same reaction intermediate, which is inferred to be a C_8 species.

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