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Butane Cracking Catalyzed by the Zeolite H-ZSM-5

Catalytic cracking reactions are not well characterized, in part because they are complicated by numerous side reactions, including coke formation. Our objective was to characterize catalytic cracking with a minimum of complicating side reactions. The reactants were chosen to be *n*-butane and isobutane because they have few primary cracking products and are recommended probe reactants for testing strongly acidic catalysts (*1*). The catalyst was H-ZSM-5, which has little tendency to form coke (*2*). The results, obtained at low butane conversions with a pulse flow microreactor, demonstrate simple product distributions different from those usually associated with cracking via carbenium-ion intermediates.

The ZSM-5 catalyst, originally in the ammonium form, was provided by Mobil. Samples were characterized by X-ray diffraction with a Philips automated powder diffractometer (APD 3500), the results agreeing well with those in the literature (*3*). A sample was also characterized by X-ray fluorescence, the results being in agreement with those observed with a standard sample having a Si : Al atomic ratio of 70. Examination of the catalyst with transmission electron microscopy and scanning electron microscopy showed that most of the particles had sizes in the range 0.2 to 0.5 μm. Some apparently noncrystalline material was also observed, including particles much larger than the typical particles.

A few experiments were also done with crystallites of H-mordenite (Zeolon 900, Norton).

The conversion of *n*-butane and of isobutane catalyzed by H-ZSM-5 was investigated with a standard pulse microreactor (*4, 5*). The reactor was a quartz tube, 4 mm in inside diameter and 50 cm in length. He carrier gas flowed through the reactor to a gas chromatograph (GC), an Antek 300 equipped with a flame ionization detector. Crystallites on the catalyst (typically, 20 mg) were held in a 2.5-mm layer in the middle of the reactor, which was packed with quartz particles having diameters between 0.3 and 0.8 mm. The small mass of catalyst was used to minimize back-mixing and the occurrence of secondary reactions. Pulses of butane (10 μl) were injected with a syringe into the carrier gas at the upstream end of the reactor. Each hydrocarbon pulse (including products and unconverted butane) was separated in a 0.25-in. × 4-ft. GC column packed with activated alumina and thermostated at 120°C. The flow rate of He was 42 cm^3/min, and the pressure at the exit of the reactor was 1.1 atm. The catalyst samples were pretreated in the reactor in flowing He at 500°C; some samples were used without this high-temperature pretreatment, and there was little difference in performance.

The *n*-butane (research grade, Matheson) had the following impurities as measured by GC: propane, 0.008 mol%; isobutane, 0.055 mol%; and butenes, trace. The isobutane (Matheson) contained 0.045 mol% propane impurity.

Product analyses were obtained for individual reactant pulses at each temperature; the catalyst was held in flowing He for 30 to 40 min at each temperature prior to injection of the reactant pulse. In a typical sequence, data were obtained for a series of increasing or decreasing temperatures, and then the experiment at the initial temperature was repeated to test for catalyst deacti-

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TABLE 1

Product Distribution in *n*-Butane Conversion Catalyzed by H-ZSM-5[a]

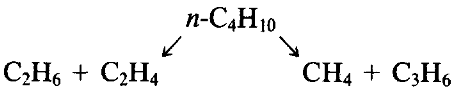
T (°C)	Conversion	Product distribution, mol%							
		CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_8	C_5H_{12}	C_5H_{10}
498	0.024	18	17	21	0.1	19	21	—	2
448	0.0063	16	16	20	0.3	18	26	—	3
410	0.0023	13	13	18	0.1	14	39	—	2
373	0.00075	13	11	18	4	12	42	—	—
342	0.00019	17	11	33	14	16	9	—	—
498	0.023	19	18	22	0.1	20	18	—	3

[a] The catalyst was held in flowing He at 500°C for 2 h then in He (without flow) for 4 h additionally, prior to injection of the first reactant pulse.

vation. Representative data are summarized in Tables 1 and 2; results are listed in order of measurement. The total conversion of each pulse of butane is represented as the number of moles of products divided by the number of moles of reactant injected. This is an empirical measure of conversion that does not account for the reaction stoichiometries.

The product analyses[1] show that the conversion of *n*-butane in the presence of H-ZSM-5 led to the formation of methane, ethane, ethylene, and propylene as the principal products; butenes and pentenes were also found (Table 1). No isobutane was detected under the conditions of these experiments. The results of experiments with the reactor containing no catalyst indicate that noncatalytic cracking was negligibly slow in comparison with that observed in the presence of the catalyst. Catalyst deactivation was negligible, as indicated by repeated results obtained at standard conditions.

The data of Table 1 suggest a simple reaction network for cracking of *n*-butane catalyzed by H-ZSM-5:



$$C_2H_6 + C_2H_4 \longleftarrow n\text{-}C_4H_{10} \longrightarrow CH_4 + C_3H_6$$

TABLE 2

Product Distribution in Isobutane Conversion Catalyzed by H-ZSM-5[a]

T (°C)	Conversion	Product distribution, mol%							
		CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_8	C_5H_{12}	C_5H_{10}
496	0.038	22	0	1.3	—	36	37	—	3
348	0.00069	10	0	0	—	8	83	—	—
388	0.0014	11	0	0	—	15	74	—	—
429	0.0037	17	0	1.3	—	21	55	—	6
465	0.014	19	0	0.8	—	25	54	—	2
500	0.035	26	0	1.5	—	32	37	—	4

[a] Catalyst pretreated for 2 h at 500°C in flowing He then in He (without flow) for 4 h additionally.

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[1] Since the fractional conversions were low (<0.01 in most of the experiments), there were inaccuracies in the product distributions resulting from the feed impurities; the propane yields shown in Table 1 are attributed to impurity.

The observation of butenes and of higher yields of ethylene than ethane indicates that dehydrogenation occurred simultaneously with cracking, but we were unable to detect H_2 in the products because of the small pulse sizes and the lack of sensitivity of the flame ionization detector.

A simple product distribution was also observed when pulses of isobutane were converted in the presence of H-ZSM-5 (Table 2). The reactivity of isobutane was nearly the same as that of *n*-butane. The isobutane cracked to give methane and propylene, but the ratio was not stoichiometric and the data showed more scatter than those obtained with *n*-butane. Ethane was undetectable in the isobutane conversion products. Butenes were formed in higher yields than from *n*-butane. At the highest conversions, C_5 hydrocarbons were also formed.

These results suggest the following simple reaction network for cracking of isobutane catalyzed by H-ZSM-5:

$$i\text{-}C_4H_{10} \rightarrow CH_4 + C_3H_6$$

The side reactions were more important for isobutane than for *n*-butane conversion in the presence of H-ZSM-5. The appearance of C_5 and ethylene in the products suggests the occurrence of some C–C bond-forming reactions followed by cracking. Such reactions are typical of "classical" cracking proceeding via carbenium-ion intermediates. The product distribution observed with *n*-butane and H-mordenite catalyst is representative of this more typical cracking pattern. In contrast to the ZSM-5, the mordenite (1) underwent rapid deactivation resulting from coke formation; (2) catalyzed the formation of isobutane in high yields; (3) catalyzed the formation of relatively high yields of C_{5+} products; and (4) gave only low yields of C_1 and C_2 products.

The conversions were too low to determine the reaction orders, but the data obtained with the H-ZSM-5 catalyst are consistent with and conveniently represented by first-order kinetics. With this assumption, apparent activation energies of 30 and 31 kcal/mol were calculated from the conversion data of Tables 1 and 2 for the cracking of *n*-butane and isobutane, respectively.

We infer, as follows, that the rates of reaction catalyzed by H-ZSM-5 were not influenced by intraparticle transport: Haag *et al.* (*6*) investigated the H-ZSM-5-catalyzed cracking of paraffins (e.g., *n*-hexane, *n*-nonane, *n*-dodecane, and 3-methylpentane) at higher temperatures than used in this work, finding that the effect of the zeolite crystallite size (i.e., the intracrystalline mass transport resistance) was negligible. Since, in comparison with the data of Haag *et al.*, our reaction rates were much less, our reactant and product molecules smaller, and our zeolite crystallites about the same size, we conclude that the transport resistance was negligible in our case as well.

The striking results are the simple product distributions and the absence of paraffin isomerization observed for butane cracking in the presence of the ZSM-5 catalyst. These results are much different from what is usually expected in acid-catalyzed cracking, as exemplified by the data obtained with H-mordenite. The product distributions are similar to those reported recently by McVicker *et al.* (*7*) for isobutane cracking catalyzed by amorphous solid acids (e.g., SiO_2–Al_2O_3) at 450–700°C; they apparently differ from the results of Hilaireau *et al.* (*8*), who observed isomerization and disproportionation accompanying cracking of isobutane catalyzed by H-ZSM-5 at 350°C; the difference is difficult to interpret, since Hilaireau *et al.* did not state their conversions or experimental methods.

The product distributions reported here for H-ZSM-5 are suggestive of free-radical rather than carbenium-ion cracking. McVicker *et al.* (*7*) speculated that their similar results (observed with isobutane and amorphous solid acids) indicated radical cation intermediates. Further investigations are warranted, and H-ZSM-5 seems to be an appropriate catalyst.

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Y. W. BIZREH[2]
B. C. GATES

Center for Catalytic Science
and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716

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[2] Present address: Damascus University, Faculty of Sciences, Department of Chemistry, Damascus, Syria.