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Acid Catalysis over CuY Zeolites

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Isobutane and *n*-pentane cracking were studied over Cu zeolite catalysts and these results were compared with their HY analogues at low conversions and at temperatures of 673 K and below. Three forms of the catalysts were used: those reduced in CO at 773 K; those reduced with H_2 at 473 K; and those in the oxidic form (following flushing with He at 773 K). In contrast with an earlier publication (*1*), very little difference in activity was found between the two reduced forms. The oxidic form that had not been investigated previously, however, was found to be considerably more active than either of the other two. The product distributions from the reduced forms of the catalysts did not differ significantly from each other nor from the H-form of the zeolite. They were typical of a Brønsted acid catalysis. The oxidic form of the catalyst produced excess H_2 in increasing amounts with time on stream. This could be quantitatively accounted for by the coking of the catalyst. These results negate the previous claim (*1*) that Lewis acid sites are effective in the cracking of light hydrocarbons over Cu zeolites.

INTRODUCTION

Recently there has been considerable interest in the Cu–ZSM-5 catalysts for the selective reduction of NO by light hydrocarbons for the purpose of atmospheric pollution abatement. These catalysts appear very promising under clean laboratory conditions. They are not poisoned by SO_2 and are inhibited only by large quantities of H_2O. Catalyst stability appears to be a problem under the more rigorous conditions required for commercial applications. The present work was undertaken to provide a foundation for an in-depth study of these problems.

The cracking of isobutane, neopentane, and normal butane was studied briefly over CuY by Beyer *et al.* (*1*). Although their data were fragmentary, they indicated that the catalyst reduced with CO was considerably more active than that reduced with H_2 and indeed more active than the HY catalyst made from the same zeolite. This finding was interpreted on the basis of the model for the reduction of Cu zeolites of Jacobs and Beyer (*2*). Thus, it was assumed that lattice oxygen was removed on reduction with CO forming a stoichiometric amount of CO_2. This was said to lead to dealumination of the zeolite, making an equivalent amount of Lewis acid sites depicted as AlO^+ centers. Reduction with H_2 under mild conditions, on the other hand, was thought to lead exclusively to the formation of Brønsted sites. As a result it was suggested that the Lewis acid sites catalyzed the cracking of butanes and neopentane, while both Lewis acid and Lewis base sites were involved in dehydrogenation of these reactants. More recently it has become evident that when acid catalysis is involved, dehydrogenation is the result of the initiation process where carbenium ions are formed by decomposition of the pentacoordinated carbonium ions resulting from protonation of the paraffin molecules by Brønsted acid sites (*3–9*). Moreover it has been shown that a characteristic product distribution is diagnostic for this reaction when isobutane is the reactant (*7*). Accordingly, we decided to extend the work of Beyer *et al.* to obtain these distributions. This was one of two rea-

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sons for using CuY in this work rather than Cu–ZSM-5. The other reason was that the much lower Si/Al ratio of the Y zeolites made measurement of the extent of dealumination possible (*10*). As reported recently (*11*), when this was done it was discovered that CO reduction did not effect dealumination after all and that both Brønsted acid sites and extralattice oxygen are introduced into the zeolite during base exchange of Cu^{2+} for Na^+. The decomposition mechanisms of isobutane, *n*-butane, and *n*-pentane are, by now, well understood (*7–9*). The effects of introduction of a reducible cation such as Cu^{2+} have not been previously studied in detail and the possibility existed that this ion could act as a Lewis acid center. Another matter of concern was the stability of the catalyst under the strongly reducing reaction conditions. All of these various factors provided motivation for the present work.

EXPERIMENTAL

Catalysts and materials. The CuY zeolite (Cu74) used was graciously supplied by H. K. Beyer; methods used in its preparation have been described elsewhere (*12*). The catalysts were analyzed for Si, Al, Cu, and Na by Galbraith Laboratories. The normal unit cell composition, based on 192 T units/uc, from that analysis was $Cu_{20}Na_{14}(AlO_2)_{55}(SiO_2)_{137}$ and (2Cu + Na)/Al = 0.98.

For purposes of quantitative NMR measurements and as a reference sample in our catalytic experiments, the Cu-containing sample was repeatedly back-exchanged in a 2 *M* solution of NH_4Cl (Fisher A 661-500). The zeolite/solution ratio was 10 g/liter. The solution was heated to reflux temperature, and the exchange was conducted overnight. The samples were filtered, washed, and contacted repeatedly with fresh NH_4Cl solution. After the final exchange, the samples were dried at 393 K. The degree of back exchange was determined by Cu analysis using X-ray fluorescence analysis. In this way HY74 was prepared with >99% of the Cu^{2+} removed. Before running a cracking reaction with this material, the NH_4Y zeolite was converted into the hydrogen form by heating to 673 K under flowing O_2 and then nitrogen (3 h each).

Instrument grade 10% isobutane (i-butane) in nitrogen, obtained from Matheson, was used as received. It contained 0.02% propane and 0.03% *n*-butane as impurities. Gold label 99.3% *n*-pentane with trace impurities of 0.4% i-pentane and 0.3% *n*-hexane was obtained from Aldrich. This *n*-pentane was stored over 5A molecular sieves in an inert atmosphere. Propane was from Matheson (research purity 99.97%). Nitrogen was obtained from Linde (99.999% purity); it contained $H_2O < 3$ ppm, total hydrocarbons < 1 ppm, and $O_2 < 1$ ppm. It was passed through an oxy-absorbent (Altech) trap.

Apparatus and procedures. As described previously (*7b–d*), the catalytic tests were made in the steady-state flow mode under atmospheric pressure in a quartz U-tube (8 mm i.d) reactor. The downflow side served as a preheater, and the catalyst was packed into a 20-cm-long bed held between plugs of quartz wool in the upflow side (typically 0.43- to 0.83-mm particle size was used). The reactor was held at constant temperature (±0.2 K) inside an electrically heated furnace. The temperature was monitored by a thermocouple placed externally adjacent to the center of the catalyst bed. The flow rate of the reactant was kept constant and adjusted using a Brooks flow controller.

The catalysts were given a standard pretreatment. The samples were dehydrated in flowing dried O_2 as the temperature was slowly increased (1 K/min) from 298 to 423 K, where it was maintained for 3 h. Bulk H_2O was removed in this step. The temperature was then increased at the same rate to 773 K (673 K in the case of the HY and NH_4Y samples), where it was held for 8 h. Finally the reactor was flushed for 15 min with dried prepurified grade N_2 and cooled to the preselected reduction or reaction temperature. This procedure was designed to avoid structural damage effected by steaming. Of course partial dehydroxylation of

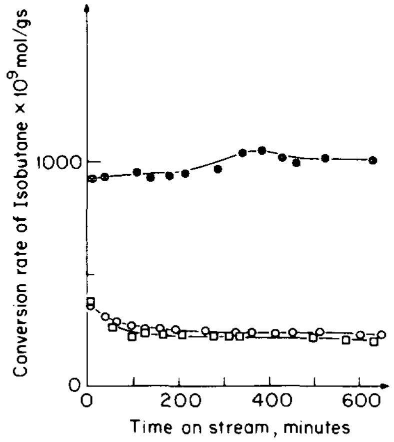

FIG. 1. Variation in rate of isobutane conversion (average of B and C) with time on stream over Cu74 zeolite. (●) After standard pretreatment (oxidized sample); (○) after CO (4% in He) reduction at 773 K for 3 h; (□) after H_2 reduction at 473 K for 1 h. Catalyst loading was 0.400 g; $F/W = 3.4 \times 10^{-5}$ mol/gs; reaction temperature was 673 K.

HY undoubtedly ocurred as it always does on heating to 673 K, but not as extensively as with samples heated to 800 K and above. This process is essential for development of the strong Brønsted sites required for paraffin cracking. A more quantitative assessment can be made from the ^{27}Al MAS–NMR data published elsewhere (*11*).

The samples were reduced *in situ*. A 4% CO in He stream was passed through the bed for 3 h at 773 K. After reduction, the catalysts were flushed with N_2 for 15 min and then cooled in this gas. Alternatively, pure H_2 was passed at a flow rate of about 100 cm^3/min for 1 h at 473 K. The reduced samples were then purged with N_2 at the reduction temperatures.

During *n*-pentane cracking, N_2 was bubbled through a pool of this hydrocarbon in a 30-cm-long saturator maintained at 273 K. This stream was further diluted with N_2 to yield 10 mol% C_5H_{12} in N_2 using a Brooks dual-channel mass flow controller unit. The reaction was started by switching streams from pure N_2 to the reactant mixture.

The effluent gas was sampled and analyzed by on-line GLC. The first sample was taken after 5 min on stream. Subsequent samples were taken at convenient intervals as indicated by the points plotted in Figs. 1–6. Two columns were connected in series, and N_2 was used as carrier gas. In the first, hydrogen was separated and determined on a 5A molecular sieve column ($\frac{1}{8}$ in. × 3 ft. stainless steel) at 273 K using a TCC detector. In the second, hydrocarbons were separated at 273 K and determined by using an FID unit after passing over two packings in series ($\frac{1}{8}$ × 8 in. column) containing dibenzylamine followed by propylene carbonate, both on Chromosorb (PAW 80/100 from Analabs). Satisfactory separation of H_2 and all C_1 to C_5 hydrocarbons was obtained.

Treatment of the data was as outlined previously (*7b–d*). The composition of the effluent was calculated as the mole fraction of the *i*th species, X_i, of the total product (including reactant) after correcting for impurities in the feed. Differential conversion levels were maintained in all the activity measurements; i.e., the conversion was kept below 3.0% and usually around 1%.

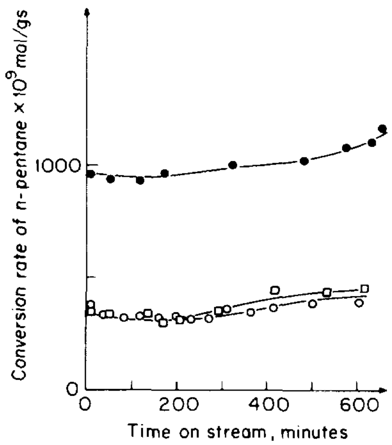

FIG. 2. Variation in conversion rate of *n*-pentane (average of B and C) with time on stream over Cu74 zerolite. (●) After standard pretreatment (oxidized sample); (○) after CO (4% in He) reduction at 773 K for 3 h; (□) after H_2 reduction at 473 K for 1 h. Catalyst loading was 0.400 g; $F/W = 4.0 \times 10^{-5}$ mol/gs; reaction temperature was 673 K.

TABLE 1

Initial Rates of Product Formation from Reaction of Isobutane over Y Zeolites at 673 K[a]

Catalyst:	CuY74			HY74[b]
Reducing gas:	None	CO (4% in He)	H_2 (100%)	None
Reduction:	—	3 h at 773 K	1 h at 473 K	—
Product		(mol/gs× 10^9)		
H_2	360	64	79	158
CH_4	46	27	38	44
C_2H_6	28	5	6	8
C_3H_8	96 (220)	27 (60)	36 (72)	65 (105)
C_3H_6	124	33	36	40
n-C_4H_{10}	238	105	94	178
1-C_4H_8	184	81	86	157
1-C_4H_8	67	28	39	46
t-C_4H_8	45	26	24	36
i-C_5H_{12}	195 (241)	44 (71)	50 (188)	51 (95)
Initiation[c]	406	91	117	202
Propagation[d]	529	183	186	302
Termination[e]	448	168	191	279
Conversion A[f]	935	274	303	505
Conversion B[g]	968	349	376	574
Conversion C[h]	967	333	361	567
% Conversion[i]	2.81	0.94	1.02	1.61
Chain length A[j]	1.3	2.01	1.59	1.5
Chain length B	1.2	1.09	0.97	1.1

[a] Catalyst loading was 400 mg; F/W was 3.4×10^{-5} mol/gs; time on stream was 5 min. Shown in parentheses are the sum of the C_3 products and the sum of the CH_4 and i-C_5 products.

[b] Obtained after back exchange with NH_4Cl of CuY74. See Experimental for detail.

[c] Initiation = $H_2 + CH_4$.

[d] Propagation = $\Sigma_2^5\, C_nH_{2n+2}$.

[e] Termination = $\Sigma_2^4\, C_nH_{2n}$.

[f] Conversion A = $H_2 + CH_4 + \Sigma_2^5\, C_nH_{2n+2}$.

[g] Conversion B = $(\frac{1}{4})\, \Sigma_1^5\, jC_i$, where j is the number of carbon atom in the ith product.

[h] Conversion C = $(\frac{1}{10})\, \Sigma_1^5\, jH_i$, where j is the number of hydrogen atoms in the ith product.

[i] % Conversion = average percentage conversion A, B, C.

[j] Chain length A, propagation/initiation; chain length B, propagation/termination.

Under these conditions, the rate of formation of each product could be taken as $C_i = X_i(F/W)$ mol/g, where F and W are the corresponding flow rate and weight of the catalyst tested.

As described previously (7), the Brønsted acid catalysis of isobutane is a carbenium ion chain reaction carried chiefly by isomerization of the t-butylcarbenium ion followed by H-transfer from the reactant ($\geq$98% of the gas phase) to the sec-butyl ion forming the corresponding paraffin product and regenerating the chain carrier. Termination occurs when the carbenium ion decomposes to the corresponding olefin regenerating the Brønsted site. Thus, conversion A was calculated by adding the rate of consumption of reactant in the unimolar step (initiation) to the rate of consumption by H-transfer to existing carbenium ions in a bimolecular step (propagation). For isobutane, these data are the sum of the rates of formation of H_2, CH_4, and all other alkanes. Conversions B and C were obtained on the basis of carbon and hydrogen balances over the products, respectively. Thus, the contributions of initiation, propagation, and termination steps were separated

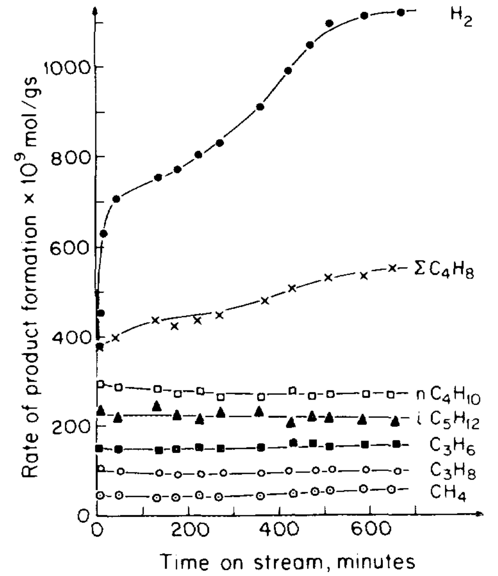

FIG. 3. Variation of rates of formation of individual products from isobutane reaction over oxidized Cu74 with time on stream. (●) H_2, (×) Σ C_4H_8, (□) n-C_4H_{10}, (▲) i-C_5H_{12}, (■) C_3H_6, (○) C_3H_8, (⊙) CH_4. Catalyst loading was 0.400 g; $F/W = 3.4 \times 10^{-5}$ mol/gs; reaction temperature was 673 K.

based on the Brønsted acid-catalyzed cracking mechanism of i-butane and n-pentane (*7b–d*).

Chain length A was defined as the ratio of rate of the propagation to the rate of the initiation reaction; i.e., the i-butane molecules reacted by H-transfer in a bimolar propagation to those reacted in the unimolecular initiation. Alternatively, chain length B is the ratio of the rates of propagation and termination, i.e., the number of times the carbenium ion chain propagates before it terminates leaving behind the original Brønsted acid site. In the steady state, both chain length A and B should be the same, provided that no olefin is lost (coking) or found in extraneous side reactions (polymerization cracking).

The carbonaceous residue (coke) retained by the zeolite was determined in a BET system with a circulation loop similar to the one used before (*6a*). After the reaction study was completed, the reactor was sealed and then connected to the vacuum apparatus. Before admitting the oxygen, it was evacuated at room temperature to ~5×10^{-5} Torr. Then 150 Torr of O_2 was circulated over the catalyst at a temperature of 773 K. The CO_2 and H_2O formed were removed from the circulating gas in an in-line trap cooled with liquid nitrogen. The CO_2 could be released at 195 K and the H_2O retained. Thus the gases could be separated and measured separately in a gas burette.

Total product formation was calculated by graphic integration of the plot of rates of product formation against time on stream. The H_2 released from the carbon deposited as coke was calculated from the H/C ratio determined in the burnoff and the values of 2.5 and 2.4 for isobutane and n-pentane, respectively. This properly gives the amount of hydrogen that has been lost from the carbonaceous residue. Where it goes is discussed later in connection with Table 5.

XRD powder patterns were obtained using a Diano Model 700 diffractometer employing Ni-filtered Cu$K\alpha$ radiation (λ = 1.5418 Å). The X-ray tube was operated at 45 kV and 25 mA. The samples after the desired treatment were finely ground and pressed into a pellet. X-ray diffraction patterns were obtained in the range $10° < 2\theta < 60°$ scanning at 0.2°/min.

EPR spectra were recorded with a Varian E-4 ESR spectrometer. Spectra were determined at X band at room temperature. Samples were evacuated for 10 min before collecting the EPR spectra. To obtain spectra before and after reaction or pretreatment, a quartz reactor having a 4-mm-o.d. ESR sidearm was used. The sealed reactor was removed from its fixed position and the catalyst was transferred into the sidearm by tipping the tube. This sidearm could then be inserted into the EPR microwave cavity.

NMR. ^{27}Al MAS–NMR spectra were recorded using a Bruker MSL-300 spectrometer at 78.205 MHz and a spinning rate of 3.5 kHz. As in our previous study (*11*), a flip angle of 10° and a 2-μs pulse were used. Typically, 1000 scans were collected with a

TABLE 2

Rates of Product Formation from Reaction of Isobutane over Oxidized Cu74: Effect of the Reaction Temperature[a]

Reaction temp.:	623 K		643 K		673 K	
Time on stream (min):	35	300	35	300	35	300
Product			(mol/gs × 10^9)			
H_2	19	20	61	79	560	796
CH_4	4	3	10	8	46	49
C_2H_6	6	4	9	6	19	21
C_3H_8	12 (27)	12 (18)	23 (45)	20 (44)	86 (209)	81 (219)
C_3H_6	15	6	22	24	123	138
n-C_4H_{10}	49	39	84	91	237	232
1-C_4H_8	—	—	—	9	199	270
1-C_4H_8	11	10	13	25	71	83
t-C_4H_8	—	—	5	11	49	56
i-C_5H_{12}	23 (27)	16 (19)	46 (56)	47 (55)	186 (232)	172 (221)
Initiation[b]	23	23	71	87	606	845[j]
Propagation[c]	90	71	162	164	509	485
Termination[d]	26	20	40	69	461	568
Conversion A[e]	113	94	233	251	1116	1330
Conversion B[f]	113	88	200	232	968	1043
Conversion C[g]	113	89	207	234	1007	1260
% Conversion[h]	0.33	0.26	0.6	0.71	3.07	3.61
Chain length A[i]	3.91	3.1	2.3	1.88	0.86	0.78
Chain length B[i]	3.46	4.4	4.0	2.38	1.10	0.95

[a] Catalyst loading was 400 mg; *F*/*W* was 3.35×10^{-5} mol/gs. Before reaction the standard pretreatment was given. Shown in parentheses are the sum of the C_3 products and the sum of the CH_4 and i-C_5 products.

[b] Initiation = $H_2 + CH_4$.

[c] Propagation = $\Sigma_2^5\, C_nH_{2n+2}$.

[d] Termination = $\Sigma_2^4\, C_nH_{2n}$.

[e] Conversion A = $H_2 + CH_4 + \Sigma_2^5\, C_nH_{2n+2}$.

[f] Conversion B = $(\frac{1}{4})\, \Sigma_1^5\, jC_i$, where j is the number of carbon atoms in the ith product.

[g] Conversion C = $(\frac{1}{10})\, \Sigma_1^5\, jH_i$, where j is the number of hydrogen atoms in the ith product.

[h] % Conversion = average percentage conversion A, B, C.

[i] Chain length A, propagation/initiation; chain length B, propagation/termination.

[j] Excess H_2.

repetition time of 1 s. ^{27}Al chemical shifts were determined relative to $Al(H_2O)_6^{3+}$ as a standard. The spectra were recorded with the pore system filled with H_2O. The absolute intensity method was used for quantitative determination. The NaY zeolite (parent material) after pretreatment in O_2 was used as reference. The amount of octahedral Al that appeared with a chemical shift of −1 ppm was obtained from the integration of the Al signal.

^{29}Si spectra were recorded at 59.627 MHz using a spinning rate of 4 kHz, a 90° pulse of 6 μs length, and a repetition time of 10 s. From 4000 to 7000 scans were necessary to obtain a satisfactory signal-to-noise ratio.

For the calculation of the framework Si/Al ratio, the ^{29}Si spectrum was deconvoluted using the method developed by Engelhardt and co-workers (*13*) and the ratio was obtained using (*10*)

$$(\mathrm{Si/Al}) = \sum_{n=0}^{n=4} I_{\mathrm{Si}(n\mathrm{Al})} \Big/ \sum_{n=0}^{n=4} (n/4) I_{\mathrm{Si}(n\mathrm{Al})},$$

where $I_{\mathrm{Si}(n\mathrm{Al})}$ is the integrated intensity attributable to Si(nAl) units.

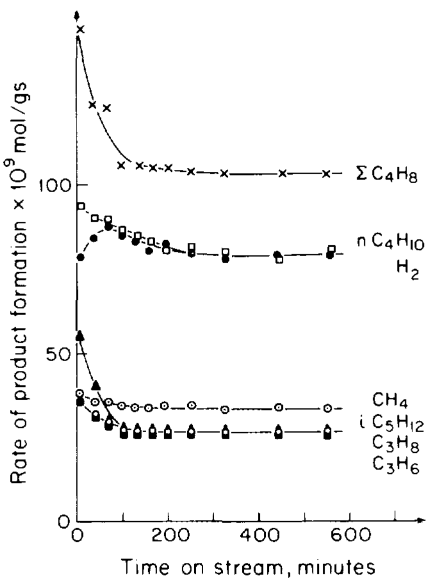

FIG. 4. Variation of rate of product formation with time on stream from reaction of isobutane over Cu74 after reduction with flowing H_2 (1 h at 473 K). (●) H_2, (×) ΣC_4H_8, (□) n-C_4H_{10}, (▲) i-C_5H_{12}, (■) C_3H_6, (○) C_3H_8, (⊙) CH_4. Catalyst loading was 0.400 g; $F/W = 3.4 \times 10^{-5}$ mol/gs; reaction temperature was 673 K.

The lattice aluminum ion concentration, i.e., Al/uc, was calculated from the experimental Si/Al by assuming the unit cell composition was $(CuNaH)_x(AlO_2)_x(SiO_2)_{192-x}$.

RESULTS

Isobutane decomposition. Data for i-butane as a function of time on stream over Cu74 zeolites after different treatments are shown in Fig. 1. Catalysts reduced with either CO at 773 K or H_2 at 473 K were reproducible and showed no significant difference in activity at 673 K. Moreover, they were less active than the oxidized sample. These observations are in disagreement with Beyer's findings (*1*). The same trend was observed when n-pentane was used instead of isobutane as reactant (Fig. 2).

The selectivity data and some properties calculated therefrom for the catalyst after different treatments are compared with those for the HY preparation in Table 1. These data were taken after 5 min of reaction. The changes in selectivity with time on stream are depicted in Figs. 3 and 4. The data for the oxidized and reduced catalysts all followed a similar pattern. The chief products were C_4 olefins and n-butane, but significant amounts of isopentane were also formed. In all cases the amount of i-pentane + methane was closely related with the amount of propane + propene. (This comparison is made in the tables by the figures in parentheses.) Dehydrogenation was favored over demethanation by roughly a factor of 2 in the reduced samples and by about 8 times in the oxidized samples. With the latter the H_2 production increased with time on stream (Fig. 3), while in the reduced catalyst it increased slightly and then remained constant.

The results for the oxidized form of Cu74 showed that a dehydrogenation reaction accompanied the cracking. In the initial stage of the reaction the rate of initiation was in reasonable agreement with the rate of termination but after a short time on stream the rate of dehydrogenation increased considerably (compare Tables 1 and 2; see Fig. 3). Hence, the calculated rate of initiation increased markedly, exceeding that of termination. This was not the case with the rate of hydrocarbon product formation, which was almost constant (except for the C_4 alkenes, which increased with increasing H_2 production). This could be attributed to reaction over a set of weak Brønsted sites created as the catalyst was coked, but *vide infra*.

Interestingly, on reduced Cu74 the sum of the alkenes (tabulated as the termination rate) was generally greater than the corresponding rate of initiation (Table 1 and Fig. 4). This feature was also observed for the HY preparation and confirmed earlier observations of Hall and co-workers (*7c*). The effect of the temperature and/or conversion level on selectivity for i-butane cracking on oxidized Cu74 is shown in Table 2. As expected, at low values of these variables closer agreement with the reaction model was obtained. In particular, the dehydroge-

TABLE 3

Rates of Product Formation from Reaction of Isobutane over Cu74 at 673 K: Effect of Pretreatment[a]

Pretreatment:	st + 1 h H_2/473 K + 1 h N_2/823 K		st + 1 h H_2/473 K + 1 h N_2/823 K + O_2/773 K	
Time on stream (min):	35	270	35	270
Product		(mol/gs × 10^9)		
H_2	77	48	535	1183
CH_4	42	36	48	70
C_2H_6	5	5	24	35
C_3H_8	30	24	212	200
C_3H_6	24	18	111	179
n-C_4H_{10}	93	69	332	410
1-C_4H_8	61	47	172	286
1-C_4H_8	24	23	61	96
t-C_4H_8	21	13	45	60
i-C_5H_{12}	26	19	235	336
Initiation[b]	119	84	583	1253
Propagation[c]	154	117	803	981
Termination[d]	136	101	389	621
Conversion A[e]	273	201	1386	2234
Conversion B[f]	228	175	1170	1591
Conversion C[g]	207	171	1106	1401
% Conversion[h]	0.70	0.53	3.30	4.30
Chain length A[i]	1.30	1.40	1.34	0.80
Chain length B	1.10	1.16	2.06	1.59

[a] Catalyst loading was 400 mg; F/W was 3.50×10^{-5} mol/gs; reaction temperature was 673 K.

[b] Initiation = $H_2 + CH_4$.

[c] Propagation = $\Sigma_2^5 C_nH_{2n+2}$.

[d] Termination = $\Sigma_2^4 C_nH_{2n}$.

[e] Conversion A = $H_2 + CH_4 + \Sigma_2^5 C_nH_{2n+2}$.

[f] Conversion B = $(\frac{1}{4}) \Sigma_1^5 jC_i$, where j is the number of carbon atoms in the ith product.

[g] Conversion C = $(\frac{1}{10}) \Sigma_0^5 jH_i$, where j is the number of hydrogen atoms in the ith product.

[h] % Conversion = average percentage conversion A, B, C.

[i] Chain length A, propagation/initiation; chain length B, propagation/termination.

nation rate strongly decreased. In fact, at 623 K the carbenium ion chain reaction and the rates of initiation and termination were comparable during the time that the reaction was studied (more than 1000 min).

In another set of experiments the effect of the additional dehydroxylation was explored. The CuY zeolite was reduced with pure H_2 at 473 K for 1 h [which has been claimed (*1*) to generate Brønsted sites]. The H_2 was then replaced by N_2 and the temperature increased up to 823 K to affect dehydroxylation of such sites. On cooling to reaction temperature (673 K), it was found (Table 3) that these results were quite similar to those for the H_2 reduced preparation in Table 1 (next to last column). Reoxidation of this preparation led to behavior reminiscent of the original unreduced catalyst.

n-Pentane reactions. The mechanistic features of this reaction have been described previously (*7c*). Table 4 and Figures 5 and 6 show selectivity data obtained at 673 K on oxidized and reduced Cu74. In all cases, H_2 was the single largest product even after a very short time on stream (the data in Table 4 were taken after 5 min of reaction). This was also true for the HY catalyst in contradiction with the report of Shertukde *et al.* (*7c*), who failed to detect any H_2 during

TABLE 4

Rates of Product Formation from Reaction of *n*-Pentane over Y Zeolites at 673 K[a]

Catalyst:		CuY74		HY74[b]
Pretreatment:	st	st	st	st
Reducing gas	None	CO (4% in He) 3 h	H_2 (100%) 1 h	None
Reduction temp. (K):	—	773	473	—
Product		(mol/gs × 10^9)		
H_2	651	208	156	120
CH_4	85	40	40	39
C_2H_6	226	123	132	120
C_3H_8	158	69	67	59
C_3H_6	125	74	68	65
i-C_4H_{10}	217	64	52	28
n-C_4H_8	49	14	17	12
1-C_4H_8	37	12	13	60
i-C_4H_8	15	—	—	—
t-C_5H_{12}	10	—	—	—
i-C_5H_{12}	404	122	123	60
Initiation[c]	962	371	334	278
Propagation[d]	828	269	259	279
Termination[e]	187	86	81	125
Conversion A[f]	1790	640	674	338
Conversion B[g]	944	337	332	270
Conversion C[h]	976	351	349	298
% Conversion[i]	2.89	0.74	0.74	0.30
Chain length A[j]	2.66	1.65	1.45	1
Chain length B	4.42	3.1	3.2	2.2

[a] Catalyst loading was 400 mg; *F/W* was 4.0 × 10^{-5} mol/gs; time on stream was 5 min.

[b] Obtained after back exchange with NH_4Cl of CuY74. See Experimental for details.

[c] Initiation = $H_2 + CH_4 + C_2H_6$.

[d] Propagation = $\Sigma_2 C_nH_{2n+2}$.

[e] Termination = $\Sigma_2^4 C_nH_{2n}$.

[f] Conversion A = $H_2 + CH_4 + \Sigma_2^5 C_nH_{2n+2}$.

[g] Conversion B = $(\frac{1}{5}) \Sigma_1^5 jC_i$, where *j* is the number of carbon atoms in the *i*th product.

[h] Conversion C = $(\frac{1}{12}) \Sigma_1^5 jH_i$, where *j* is the number of hydrogen atoms in the *i*th product.

[i] % Conversion = average percentage conversion B, C.

[j] Chain length A, propagation/initiation; chain length B, propagation/termination.

n-pentane cracking on HY zeolites. Despite this difference, the hydrocarbon distributions were similar in all cases. The rate of formation of C_2H_6 was higher than the rate of formation of CH_4 (2.5 and 3 times for the oxidized and reduced sample, respectively). Isomerization selectivity to i-pentane was around 40%. Among the other alkanes, isobutane and propane were major products. Note that the amount of C_3 product formed was adequate to balance the rate of C_2H_6 formation, but that more C_4 compounds were produced than required to balance the CH_4 formed. The reason for this becomes clear subsequently.

Coke formation on Cu74 after more than 10 h on stream at 673 K was determined for both reactants. The results obtained after different pretreatments of the catalysts are given in Table 5. The amount of coke removed from the oxidized catalysts was similar for both reactants, but in the case of *n*-pentane it occurred after a shorter time on stream. The amount of H_2 released, cal-

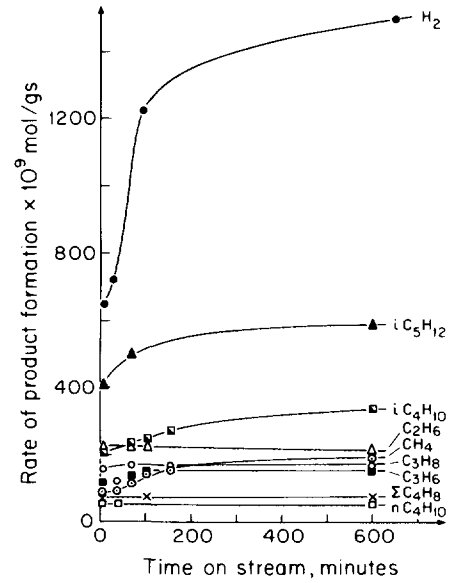

FIG. 5. Variation of rates of product formation from *n*-pentane reaction over oxidized Cu74 with time on stream. (●) H_2, (▲) i-C_5H_{12}, (◪) i-C_4H_{10}, (△) C_2H6, (⊙) CH_4, (○) C_3H_8, (■) C_3H_6, (×) Σ C_4H_8, (□) *n*-C_4H_{10}. Catalyst loading was 0.400 g; $F/W = 4.0 \times 10^{-5}$ mol/gs; reaction temperature was 673 K.

culated from the H/C ratio of the carbon deposited on the catalysts, properly measures the hydrogen transferred somewhere. It was in reasonable agreement with the amount obtained form the total H_2 found in the gas phase corrected for the total production of alkenes. This correction is equivalent to the H_2 produced in the monomolecular initiation step. It ignores, however, the disproportionation of adsorbed oligomeric olefins into desorbed paraffins and adsorbed diolefins, aromatics, polynuclear aromatics, etc. The carbon deposition was much greater for those catalysts given the standard pretreatment than for the reduced catalysts. In all cases, however, *n*-pentane deposited carbon more readily than isobutane.

An experiment using propane as reactant (10% in He) over the oxidized Cu74 was performed. Some dehydrogenation was detected at 673 K; equivalent amounts of H_2 and propene were produced; and the conversion was about 0.1%. No cracked products were detected in these experiments.

Catalyst characterization. Measurements of the Si/Al ratios were made by ^{29}Si and ^{27}Al MAS-NMR before and after the isobutane cracking reaction and after removal of the Cu^{2+} by back exchange with NH_4^+. The results are presented in Table 6. In agreement with our previous findings (*11*), the Cu^{2+}-exchanged zeolite showed only a minor degree of dealumination after the standard pretreatment or reduction with CO or with H_2. The lattice aluminum concentration changed from 55 Al/uc in the fresh material to 53, 52, and 52, respectively. No further changes were observed after 25 h on stream (10% isobutane, $F/W = 3.4 \times 10^{-5}$ mol/gs, temperature of 673 K).

To follow the oxidation state of Cu zeolite during cracking, EPR measurements were taken in the following manner: After a certain time on stream, the gas mixture was replaced by N_2 and the catalyst purged for 15 min at 673 K. Then it was cooled and the reactor sealed and connected to a vacuum line where it was degassed for 15 min before recording the EPR spectra. The data are

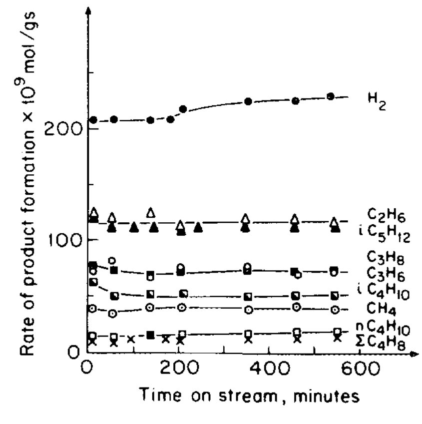

FIG. 6. Variation of rates of product formation from *n*-pentane reaction over Cu74 after reduction with flowing CO (4% in He) for 3 h at 773 K. (●) H_2, (△) C_2H_6, (▲) i-C_5H_{12}, (○) C_3H_8, (■) C_3H_6, (□) i-C_4H_{10}, (⊙) CH_4, (□) *n*-C_4H_{10}, (×) Σ C_4H_8. Catalyst loading was 0.400 g; $F/W = 4.0 \times 10^{-5}$ mol/gs; reaction temperature was 673 K.

TABLE 5

Hydrogen Mass Balance after Isobutane and *n*-Pentane Reaction on Cu74[a]

Pretreatment	Reactant	Time on stream (min)	On Catalyst		H/C	H_2 Released from Coke (mmol/g)	
			C/G (mmol/g)	H/g (mmol/g)		Calculated[b] I	Observed[c] II
st	i-Butane	1500	16.0	4.60	0.29	36.0	45
CO (4% in He) 3 h at 773 K	i-Butane	1200	0.3	0.28	0.93	0.3	—
H_2 (100%) 1 h at 473 K	i-Butane	1200	0.4	0.38	0.95	0.3	—
st	*n*-Pentane	800	21.0	6.00	0.29	46.0	55
CO (4% in He) 3 h at 773 K	*n*-Pentane	600	2.3	0.80	0.35	2.5	3
H_2 (100%) 1 h at 473 K	*n*-Pentane	600	2.3	0.80	0.35	2.5	3

[a] Catalyst loading was 400 mg, *F*/*W* was 3.4×10^{-5} mol/gs; reaction temperature was 673 K.

[b] Calculated as follows: $H_2 = 1.25C - H/2$ from the fourth and fifth columns and $H_2 = 1.2C - H/2$ for isobutane and *n*-pentane, respectively.

[c] Excess H_2 produced in the gas phase from coke formation. This was calculated from H_2 (total) − Σalkenes.

summarized in Fig. 7, where the variations of the EPR signal as a function of time on stream are shown. The fresh Cu74 after standard pretreatment (Fig. 7a) gave the characteristic spectrum of the CuY zeolite with a high spin concentration of Cu^{2+} (*14*). Spectrum b was recorded after 15 min on stream. The spin density decreased by a factor of about 10^4; i.e., only about 0.01% of the paramagnetic Cu^{2+} remained. Now the line shape typical of the dilute spin system from residual Cu^{2+} appeared and a line having $g = 2.038$ could also be observed. The latter increased with time on stream, and after overnight under reaction it was the only species detectable (Fig. 7e). This spectrum was in good agreement with the one reported in the literature by Collins *et al.* (*15*) for carbon blacks. After reoxidation, the spectrum was almost identical with that of the fresh sample (compare Figs. 7a and 7f). Similar results were obtained when *n*-pentane was used instead of isobutane as reactant. In this case, however, an EPR spectrum resembling Fig. 7e appeared after only 3 h on stream.

XRD measurements were made to assess the extent of the changes brought about by carrying out the hydrocarbon decomposition reaction at 673 K. The diffractograms from freshly prepared samples before and after treatment with flowing O_2 (to burn off coke) are presented in Figs. 8A and 8B, respectively. Patterns a and f were from a sample of Cu74 given the standard pretreatment, but before contact with isobutane; b and g were the same materials after 24 h on stream in isobutane cracking at 673 K; and lines for Cu^0 were clearly evident, but those for CuO were not. Patterns c and h and d and i were from catalysts reduced in CO at 773 K and in H_2 at 473 K, respectively, before contact with isobutane. After 24 h of cracking, both these reduced catalysts showed further reduction to Cu^0, but no clear evidence for CuO after burnoff. Patterns e and j were from preparations where Cu74 was doped to the extent of 10% with Cu metal particles and a CuO powder, respectively, to provide reference samples. In earlier work (*16*) carried out at 1023 K, CuO lines did appear in similar experiments.

TABLE 6

Lattice Aluminum Content of Cu74 before and after Isobutane Cracking Reaction[a]

Catalyst	Oxidized[b]		CO reduced[c]		H_2 reduced[d]	
	Before	After	Before	After	Before	After
Si/Al[e]:	2.62	2.63	2.68	2.72	2.72	2.70
Al[f] Atoms per unit cell						
Octahedral[g]	2	2	3	3	3	3
Tetrahedral[h]	53	53	52	52	52	52
Total[i]	55	55	55	55	55	55
Extralattice[j]	2	2	3	3	3	3

[a] Catalyst loading was 0.4 g; F/W was 3.4×10^{-5} mol/g; reaction temperature was 673 K; time on stream was 1500 min.

[b] After standard pretreatment.

[c] Reduced with flowing CO (4% in He) at 773 K for 3 h.

[d] Reduced with flowing H_2 at 473 K for 1 h.

[e] From ^{29}Si MAS–NMR after back exchange with NH_4Cl.

[f] Calculated assuming Al + Si – 192 per unit cell.

[g] Taken from ^{27}Al MAS–NMR.

[h] Lattice Al by ^{29}Si MAS–NMR.

[i] Total from chemical analysis.

[j] (Total – tetrahedral) aluminum.

Otherwise, in the present experiments no significant difference in the whole range of $10° < 2\theta < 60°$ was found between the "as prepared" (both after and before standard pretreatment) and "used" (after reaction) catalysts, either before or after burning off the deposited coke. Thus, the zeolitic structure was little perturbed by the long time under reaction conditions ($F/W = 3.4\ 10^{-5}$ mol/g, 673 K), but when attention is focused on the $40° < 2\theta < 55°$ regoion, peaks appear to be characteristic of Cu° metal.

DISCUSSION

The present work has demonstrated that, first, there is no real difference in catalytic activity or selectivity introduced into the catalyst by reduction with H_2 versus CO and, second, that in both cases the results resemble closely those of the HY preparations made by back exchanging the Cu^{2+} from the catalyst. Third, the product distributon found in all three cases is rather similar to that expected (7) for the carbenium ion chain process (Table 1). The chief difference was the extra amount of H_2 produced, and this was traced to additional coking in the presence of copper. The product distribu-

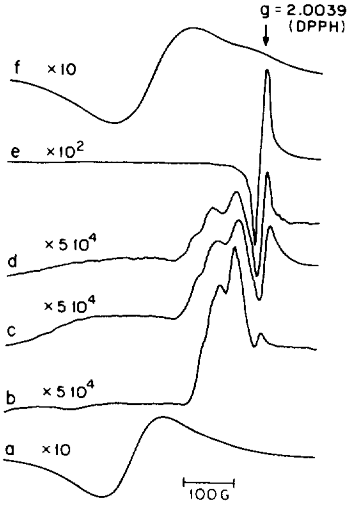

FIG. 7. EPR spectra of Cu74 after the following successive treatments: (a) Standard pretreatment; (b, c, d, e) after 15, 90, 270 min and overnight on stream catalyzing the isobutane cracking reaction at 673 K ($F/W = 3.4 \times 10^{-5}$ mol/gs); (f) after burning off the carbon deposited (O_2 at 773 K).

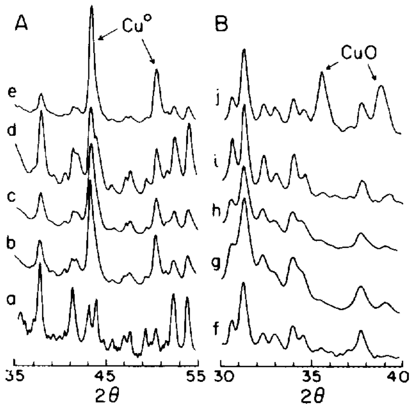

FIG. 8. XRD powder patterns (I vs 2θ) of the Cu74 obtained before (A) and after (B) burning off the carbon deposited following 24 h on stream isobutane cracking at 673 K and $F/W = 3.4 \times 10^{-5}$ mol/gs. Before the reaction samples were pretreated as follows: (a) fresh sample; (b, g) standard pretreatment; (c, h) reduced with CO (4% in He) 3 h at 773 K; (d, i) reduced with H_2 (100%) 1 h at 473 K; (e) mechanical mixture Cu metal (10%) Cu74, and (j) mechanical mixture CuO (10%) Cu74.

tion data generally conformed to a carbenium ion chain reaction. Note that the $\Sigma C_3 \sim CH_4 + i\text{-}C_5H_{12}$, i.e., that produced by the initiation reaction plus that from disproportionation. However, the H_2 formed did not generally agree well with the ΣC_4 olefins. The imbalance resulted from several factors. Mainly extra C_4 products can be formed repetitively in the carbenium chain process (not simply by chain initiation). This point is emphasized when the rates of initiation are compared with the rates of termination. These should be equal and, in the case of these catalysts, this if far from true. On the other hand, in some cases an excess formation of H_2 was observed and this corresponded to the formation of carbonaceous residue left on the catalyst.

A surprising result was that the unreduced catalyst was more active than either form of the reduced catalyst. Moreover, H_2 was produced in increasingly excessive amounts with time on stream. This evolved from residue or coke that had an H/C ratio less than 1, suggesting that it was a highly condensed polynuclear aromatic "coke-like" system.

Evidently, the Brønsted acidity is introduced together with Cu^{2+} ions during base exchange. This is in accord with our recent finding (*11*) that both extralattice oxygen and Brønsted sites are produced in this step. Thus, on reduction with H_2 or with CO the stoichiometric amount of H_2 and CO_2 is formed from the extralattice oxygen, and this does not introduce a significant amount of additional acidity into the catalyst. The higher activity of the unreduced catalyst may be affected by the formation of olefin by the dehydrogenation in the residue producing process, which is highest for the unreduced form of the catalyst. Perhaps the extralattice oxygen is involved in establishing a larger bank account of reaction centers.

It must be mentioned that these findings are in direct experimental contradiction with those published by Beyer *et al.* (*1*). There were, however, differences in experimental procedures. His work was conducted in a static recirculation reactor with the removal of olefins from the circulating gas before it was returned to the catalyst. Our work was conducted at low conversion in the steady-state flow mode. Their work was not very extensive; ours was much more thorough.

As pointed out previously (*6*), the cracking of small paraffin molecules catalyzed by Lewis acid sites can hardly be expected. There are no well-documented cases where H^- abstraction by a Lewis site on an aluminum silicate has been demonstrated. Oxidation of a paraffin to an olefin + H_2O is much more likely.

Interestingly, both the EPR and XRD results showed that the catalyst underwent reduction during the reaction (Figs. 7 and 8). With the former, the resonance signal from Cu^{2+} rapidly disappeared while that for carbonaceous or graphitic carbon appeared. Similarly, the XRD pattern showed the presence of metallic Cu. This suggested the formation of an HY zeolite carrying a carbonaceous deposit from the original Cu^{2+} form. On combustion, the Cu° form was completely reoxidized, but a well-defined pattern corresponding to CuO did not appear. Possibly this should not be expected, as the catalyst was at least partially converted back to the Cu^{2+} zeolite. These experiments demonstrate a source of instability for this type of catalyst.

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