JOURNAL OF CATALYSIS **157**, 721–729 (1995)

Induced Catalytic Activity of Fluorided Alumina in the Reactions of Isobutane

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Received May 30, 1995; revised August 10, 1995

The reaction chemistry for the conversion of isobutane on pure and fluorided aluminas was compared to continuous flow experiments. Catalysts with 0, 2.6, 4.5, and 6.5% F were pretreated in flowing oxygen either at 500 or 650°C. Only the products of dehydrogenation and demethanation were obtained on pure alumina; the rate of reaction was about one order of magnitude higher when the catalyst was pretreated at 650°C than when it was pretreated at 500°C. Paraffins, including neopentane, were also produced over fluorided aluminas; on catalysts pretreated at 650°C while dehydrogenation and demethanation decreased, paraffin formation increased with time on stream (TOS). Over the catalysts with 4.5 and 6.5% F the rate of hydride transfer-producing paraffins exceeded that of initiation (H_2 + CH_4 formation) by a factor of from 2 to 3. All of the catalysts were more active than silica-alumina for i-butane conversion. IR spectra from pyridine adsorbed on catalysts with 0–4.5% F and pretreated either at 500 or 650°C showed no evidence of a band of 1540–50 cm^{-1} assignable to pyridinium ion formed by interaction between pyridine and Brønsted acid sites. On the catalyst with 6.5% F this band appeared when the catalyst was pretreated at either 500 or 650°C. Isobutane can be dehydrogenated and demethanated over the dual acid–base pair sites of the alumina. The increasing paraffin formation with TOS may result from new and additional Brønsted sites introduced during dehydrogenation.

INTRODUCTION

Alumina is frequently said to be an acid catalyst, yet its surface chemistry is vastly different from that of H zeolites or silica-alumina catalysts. The latter have strong to moderate Brønsted acid sites while the surface chemistry of alumina is centered around Lewis acid–base pair sites accompanied by residual terminal hydroxyls that may (reluctantly) function as Brønsted sites when this is required by the reaction mechanism. Thus Tung and McInnich (1) reported 97% conversion of cumene to equal amounts of propylene and benzene at 350°C over silica-alumina, whereas 500°C was required to produce 35% of these products over alumina, and this was accompanied by an about equal conversion to products formed by dehydrogenation and demethylation. Gerberich and Hall (2) found that rates of double-bond isomerization of 1-butene increased with hydroxyl concentration over silica-alumina whereas dehydroxylation enhanced the rates over alumina. *Cis-/trans-* ratios near unity were obtained over the former and either much higher ratios or near equilibrium values with the latter. These results are characteristic (3) of proton catalyzed vs allylic mechanisms, respectively. With cyclopropane, the results were different (4). Here the conversion rates over both alumina and silica-alumina increased with the residual hydroxyl concentration, but silica-alumina was much more active than alumina, reminiscent of the data for cumene (1).

The changes in surface chemistry on fluoriding have been exhaustively studied (5, 12–15). On contacting an alumina with aqueous HF, the F^- ions are quantitatively removed from the solution; they replace terminal surface OH^- groups (5). As the fluoride content increased from 0 to 6 wt%, the hydroxyl concentration decreased from about 3 to 0.06 nm^{-2}. The rates of cracking of 2,3-dimethylbutane and isomerization of cyclopropane attained maximum values at 2.7 and 1.2 wt% F, respectively; the corresponding rates increased by factors of 25 and 4000 and were now higher than those produced by silica-alumina under comparable conditions. Pure alumina also catalyzed the isomerization, but at over 100°C higher temperature than required for silica-alumina. Cyclopropane isomerization, like cumene dealkylation, is proton catalyzed. Evidently the aluminas can act as poor Brønsted acid catalysts.

McVicker *et al.* (6) were first to study the cracking of isobutane over these systems. In order of increasing activity, they reported: γ-Al_2O_3 < silica-alumina < 0.9% Cl–Al_2O_3 < 0.9% F–Al_2O_3 $\ll$ LZ-Y82 zeolite. The last they regarded as a mild superacid; F–Al_2O_3 was an order of

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0021-9517/95 $12.00

magnitude more active than the silica-alumina catalyst and alumina was the least active. Except for the H zeolite, the product consisted primarily of CH_4, C_3H_6, i-C_4H_8 (and presumably H_2). It was suggested that these were produced via free radical (radical cation) intermediates and that the olefin product could then be protonated to produce carbenium ions and acid catalysis. The order of activity for the skeletal isomerization of i-C_4H_8 to *n*-C_4H_8 fell in the same order as that above; equilibrium values were approached indicating acid catalysis. Hydride transfer to produce paraffin was not observed with γ-Al_2O_3 and only trace amounts were found over the halided alumina at 500°C, while these were the major products over HY zeolite (LZ-Y-82). Perhaps it was for this reason that McVicker *et al.* (6) thought it necessary to assume a dual mechanism for this reaction: dehydrogenation by a radical pathway to form olefins and CH_4 followed by acid catalysis. The latter became detectable over silica-alumina and halided aluminas at 600°C and important over HY at 500°C. More recently most workers (7–11) have come to think that Brønsted sites may protonate paraffin molecules forming transient pentacoordinated carbonium ions that decompose forming H_2 or smaller paraffin molecules and the corresponding carbenium ion. The present work raises the question whether the same or different processes are operating over alumina and halided alumina.

H zeolites catalyze the reaction of isobutane (7, 10) by proton attack on the C–H or C–C bonds. The transient pentacoordinated carbonium ions thus formed decompose into more stable *t*-butyl and 2-propyl carbenium ions and the products of the initiation reactions, viz. H_2 and CH_4. Weak acids reacted with isobutane at higher temperatures than stronger acids, and deprotonation of carbenium ions occurred immediately resulting in the formation of mainly isobutene and propylene. Stronger acids effected reaction at lower temperatures and skeletal isomerization of the *t*-butylcarbenium ion to the sec-butyl ion. Bimolecular chain processes accompanied hydride and methide transfer between the reactant and various carbenium ions resulting in the formation of C_3–C_5 paraffins.

EXPERIMENTAL

In the present work the reaction of isobutane was studied in steady-state flow experiments over alumina catalysts with varying fluorine content. These preparations have been described and used extensively in earlier work (2, 5). The parent alumina was prepared by the neutral hydrolysis of redistilled aluminum isopropoxide. The fluorided catalysts contained 0, 2.6, 4.5, and 6.5% F; their surface areas were 158, 138, 149, and 130 m^2/g, and 20–40 mesh fractions (0.425–0.85 mm) were employed.

For comparison, similar experiments with isobutane were carried out on amorphous and crystalline aluminum silicates. Pellets of M-46, an amorphous silica-alumina, obtained from Houdry over 40 years ago, were crushed and sieved. Its surface area was 270 m^2/g. Powders of LZ-Y62 zeolite and LZ-Y82 ultrastable zeolite supplied by AlliedSignal were pressed into pellets without binder, crushed, and sieved. The former had a Si/Al = 2.5 and 25×10^{20} lattice Al T sites/g and the latter a Si/Al = 5.1 and 16×10^{20} T sites/g. Turnover frequencies may be calculated from the specific rates listed in the tables using these data.

The catalytic tests were carried out at atmospheric pressure in a continuous flow reaction system. The U-shaped reactor was held at temperatures constant to ±0.2°C inside an electrically heated furnace. The temperature was monitored by a thermocouple placed externally near the center of the about 2-cm-long catalyst bed.

Before use, the calcined catalysts (400-mg aliquots) were transferred to the quartz reactor where they were treated overnight in dry flowing O_2 either at 500 or 650°C and cooled to the reaction temperature (400°C) in flowing N_2. Studies of the decomposition of isobutane (isobutane/N_2 = 1/9) were made at atmospheric pressure and constant temperature with a feed rate of 1×10^{-5} mol isobutane g^{-1} s^{-1}.

The reaction was started by switching the reactor from nitrogen to the reactant mixture stream. The effluent gas from the reactor was sampled and analyzed by on-line GC. Two GCs were connected in parallel, and N_2 was used as carrier gas. In the first, hydrogen was separated and determined on a 5A molecular sieve column at 0°C using a thermal conductivity detector. In the second, hydrocarbons were separated at 0°C over two packings in series (dibenzylamine and propylene carbonate on Chromosorb) and determined using a flame ionization detector.

The composition of products was calculated as the mole fraction (X_i) of the total product. Differential reaction rates were calculated at low conversion as $C_i = X_i(F/W)$, where (F/W) is the entering reactant in moles per gram per second. Percentage conversions were expressed as moles of reactant converted to products per 100 moles of reactant passed.

For the IR spectroscopic measurements self-supporting wafers of about 8–10 mg cm^{-2} thickness were pressed from the powdered catalyst. Mounted on a quartz bracket the wafers were placed in an IR cell which was equipped with KBr windows and a furnace region into which the wafer could be raised. The wafers were treated for 2 h in dry flowing O_2 at either 500 or 650°C and the under vacuum at the same temperature for 1 h. After contacting with isobutane and/or pyridine at given temperature and pressure under static conditions, the wafers were lowered into slots between the optical windows for spectroscopic measurement at room temperature. Spectra were obtained by accumulating 32 scans with a Nicolet 5 PC FT-IR spectrometer.

RESULTS

As shown in Figs. 1 and 2, the rates of product formation in the reaction of isobutane varied significantly with time on stream (TOS). The results obtained at 400°C and TOS of 5 min are collected for comparison in Table 1. Only the products of dehydrogenation and demethanation were obtained over pure alumina pretreated at 500°C. These rates were about one order of magnitude higher when the catalyst was pretreated at 650°C, and *n*-butene appeared in the product showing that skeletal isomerization had occurred. Conventionally this process is thought to be proton catalyzed. Pretreatment at 650°C greatly increased paraffin formation over the fluorided aluminas as the TOS increased (Fig. 2).

Results obtained at different temperatures and TOS of 5 min on pure alumina and on alumina containing 2.6% F are plotted in Arrhenius fashion in Fig. 3. For pure alumina pretreated at either 500 or 650°C the points of CH_4 and C_3H_6 as well as H_2 and ΣC_4H_8 characteristically fell almost on the same straight lines. The rate of demethanation was lower than the rate of dehydrogenation. The activation energies calculated on the basis of Arrhenius plots are listed in Table 2. The activation energies decreased with increasing heat treatment and were lower on fluorided than on pure alumina.

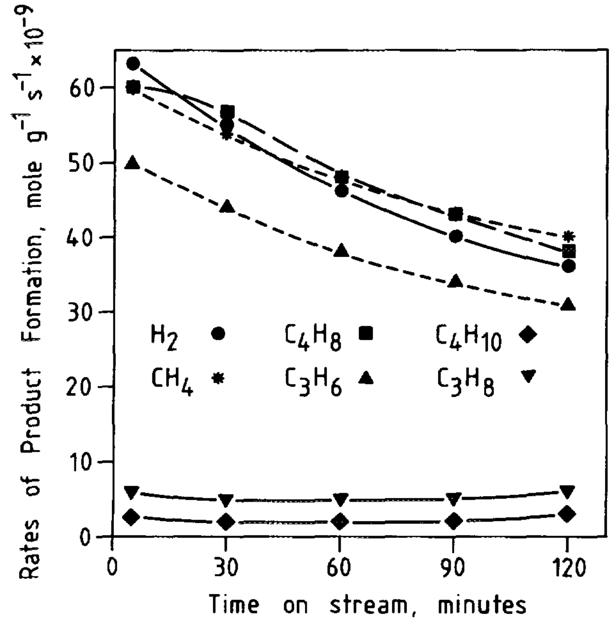

FIG. 1. The rates of individual product formation from isobutane at 400°C as a function of TOS: 400 mg of catalyst containing 4.5% F and pretreated at 500°C was used. F/W was 1×10^{-5} mol g^{-1} s^{-1}.

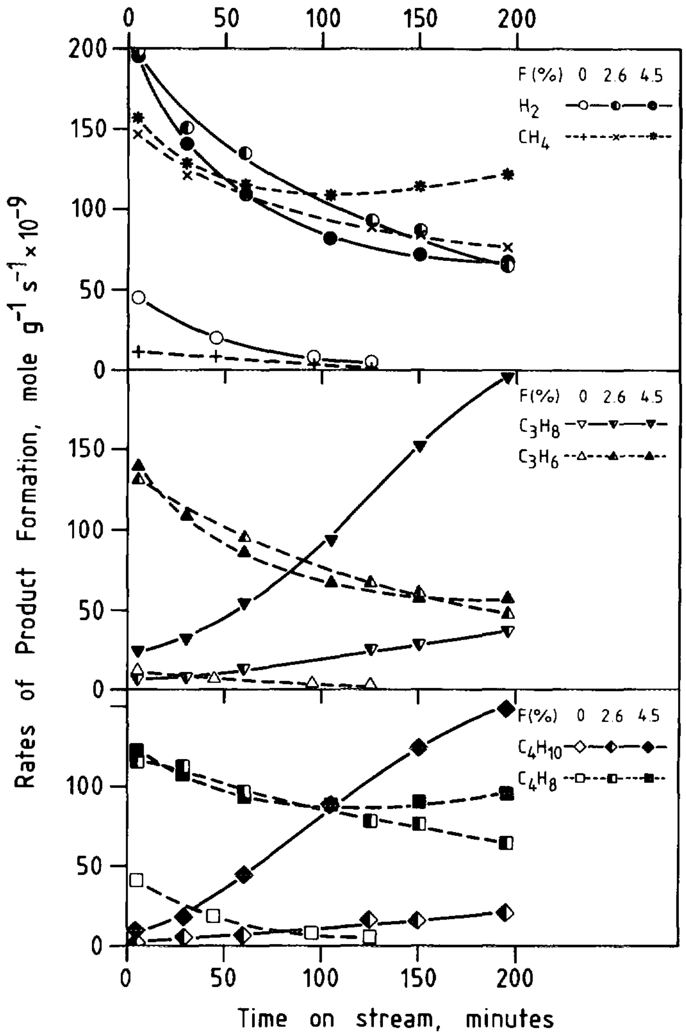

FIG. 2. The rates of individual product formation from isobutane at 400°C as a function of TOS; 400 mg of catalysts pretreated at 650°C were used. F/W was 10×10^{-5} mol g^{-1} s^{-1}.

Although some paraffin formation was observed over the catalyst containing 2.6% F and pretreated at 500°C (Table 1), the character of the Arrhenius plot was similar to that for pure alumina except, of course, that the rates at identical temperatures were much higher. The results obtained on catalysts pretreated at 650°C were still more complex. The points representing the rate of formation of H_2, ΣC_4, CH_4, and ΣC_3 each fell on different straight lines, showing that dehydrogenation and demethanation were not the only processes taking place.

In general, the product composition obtained over fluorided alumina differed from that over pure alumina (Table 1). Paraffins were produced over the former indicating that H^- transfer from isobutane to existing carbenium ions was taking place. The most significant changes in catalytic characteristics were obtained on catalysts pretreated at 650°C

TABLE 1

Rates of Product Formation from the Reaction of Isobutane at 400°C on Alumina Catalysts Pretreated at 500 or 650°C[a]

Pretreatment temp. (°C):	500				600			
Fluorine content (%)	0	2.6	4.5	6.5	0	2.6	4.5	6.5
H_2	3.1	131	63	33	44	198	189	75
CH_4	1.3	82	60	37	12	146	157	64
C_2H_4	0	3.5	2.5	1.0	1.0	15	23	3.0
C_2H_6	0	0	0	0	0	0	0	0
C_3H_6	1.0	68	50	21	12	131	139	59
C_3H_8	0	3.3	5.6	10	0	5.9	22	15
iso-C_4H_8	2.9	48	32	19	36	74	68	30
n-C_4H_8	0	42	27	19	4.8	42	54	18
n-C_4H_{10}	0	8	1.6	4.5	0	1.8	9.0	9.0
neo-C_5H_{12}	0	0	0	0	0	25	40	25
iso-C_5H_{12}	0	0	0	0	0	4.4	9.1	3.1
n-C_5H_{12}	0	0	0	0	0	0	0	0
$H_2 + CH_4$	4.5	213	123	70	56	344	346	139
Σ_3^5 olefin	3.9	158	109	59	53	247	261	107
Σ_3^5 paraffin	0	11.3	7.2	14.5	0	37	80	52
Conversion A[b]	4.5	224	130	85	56	381	426	191
Conversion B[c]	4.0	174	119	76	53	301	364	165
% Conversion B	0.04	1.55	1.06	0.68	0.47	2.69	3.25	1.48

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of each catalyst was used. The flow rate of isobutane, F/W, was 1×10^{-5} mol g^{-1} s^{-1}; it was diluted with N_2 (N_2/i-C_4H_{10} = 10). Values obtained at 5 min on stream are shown. These specific rates may be converted into rates per unit area by dividing by the surface areas listed in the Experimental section.

[b] Conversion A = $H_2 + CH_4 + \Sigma_3^5$ paraffin.

[c] Conversion B = $\frac{1}{4} \Sigma_1^5 jC_i$, where j is the number of carbon atoms in each of the i products.

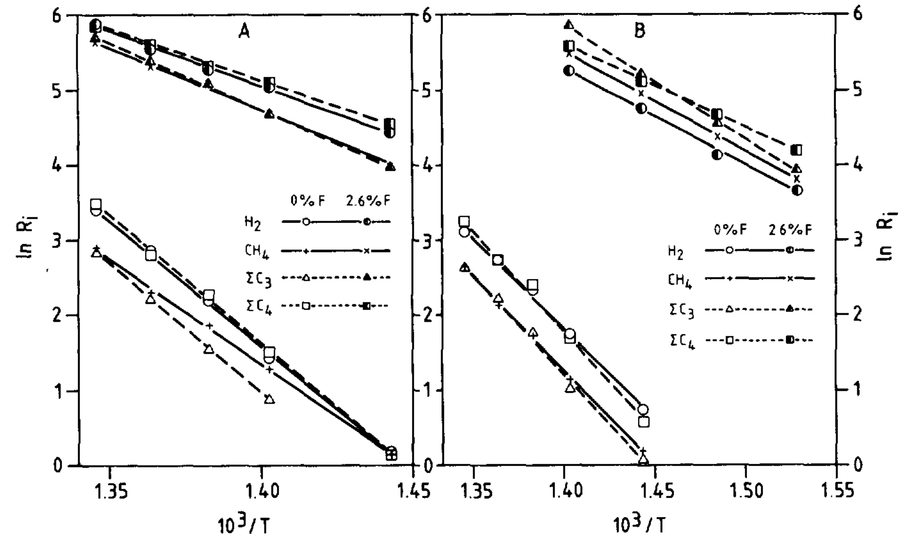

FIG. 3. Arrhenius plots for the rate of individual product formation from isobutane; 400 mg of catalysts pretreated at (A) 500°C and (B) 650°C were used. F/W was 1×10^{-5} mol g^{-1} s^{-1}; data at 5 min TOS are shown.

TABLE 2

Activation Energies of Product Formation Calculated on the Basis of Arrhenius Plots

F content of alumina (%)	Activation temperature (°C)	Product	E_a kcal mol^{-1}	E_a kJ mol^{-1}
0	500	H_2	66.6	278.5
		ΣC_4	66.1	276.9
		CH_4	64.0	267.9
		ΣC_3	67.5	282.6
	650	H_2	47.9	200.3
		ΣC_4	52.9	221.5
		CH_4	48.7	203.6
		ΣC_3	53.3	223.1
2.6	500	H_2	28.4	118.9
		ΣC_4	25.9	108.3
		CH_4	32.7	136.8
		ΣC_3	35.6	149.0
	650	H_2	24.5	102.6
		ΣC_4	21.2	88.8
		CH_4	25.5	106.7
		ΣC_3	29.2	122.1

and thus having less Brønsted sites and more Lewis acid-base centers, as well as a more highly strained surface. Paraffin formation increased; furthermore, not only was isopentane formed, but also neopentane. The latter reaction was not observed in any of our previous work with acid catalysts (7, 10) although our chromotograph was calibrated for this compound, which was used previously as a reactant (7, 10). Its retention time was distinct from all other hydrocarbons which could have been present. Isopentane formation was common. It has been suggested (10) that the latter results from H_3C^- transfer from isobutane to the sec-butylcarbenium ion. If this is true then neopentane formation should also result. We have looked for it but have not previously found it. Again, the formation of paraffins suggests the existence of carbenium ion intermediates. $C_6(+)$ hydrocarbons were not detected although the chromatographic capability existed.

The rates of paraffin formation on the fluorided alumina catalysts were rather low at 5 min on stream (Figs. 1 and 2). These values remained practically constant with TOS; however, the total conversion decreased continuously (for catalyst with 4.5% F see Fig. 1). The rates of paraffin formation increased, while the rates of initial product formation decreased on fluorided catalysts pretreated at 650°C (Figs. 2 and 4); i.e., hydride transfer increased with TOS at the expense of other products. On each catalyst, including pure alumina, the rate of dehydrogenation decreased faster than the rate of demethanation. On the catalyst with 2.6% F the rise in paraffin formation did not compensate for the loss in other products; therefore, the conversion decreased with TOS. On catalysts with 4.5 and 6.5% F (the latter is not shown in Fig. 2), however, due to the larger increase in paraffin formation, the conversion increased with TOS. As can be seen in Fig.

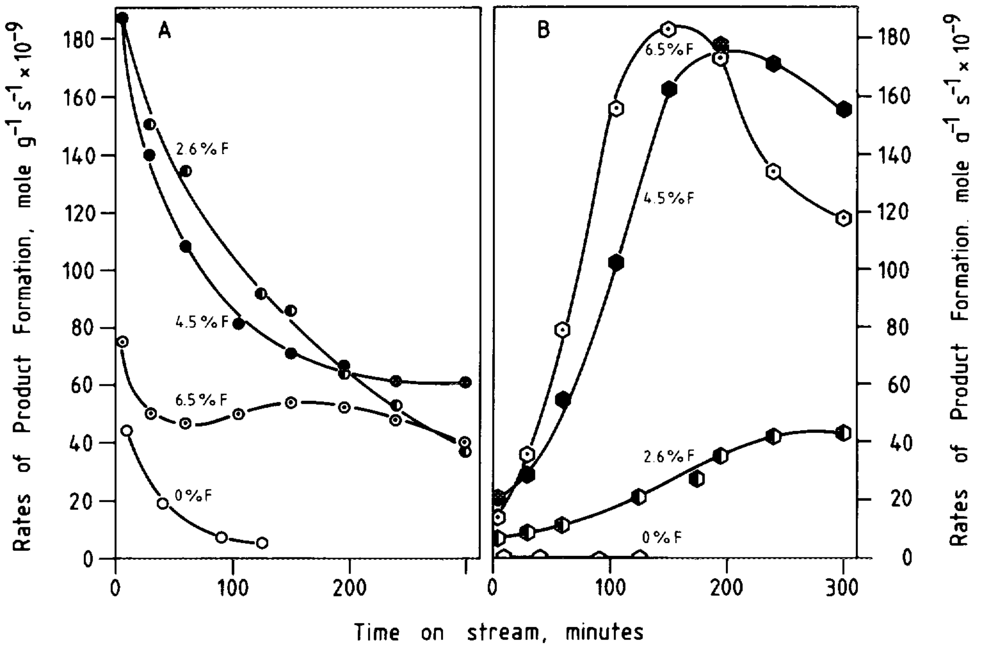

FIG. 4. The rates of (A) hydrogen and (B) Σ_3^5 paraffin formation from isobutane at 400°C as a function of TOS; 400 mg of catalysts pretreated at 650°C were used. *F*/*W* was 1 × 10^{-5} mol g^{-1} s^{-1}.

TABLE 3

Rates of Product Formation from the Reaction of Isobutane at 400°C on Alumina Catalysts Pretreated at 650°C (Values in the Conversion Maxima)[a]

Fluorine content (%):	0	2.6	4.5	6.5
TOS (min)	5	300	195	150
H_2	44	37	66	54
CH_4	12	62	121	92
C_2H_4	1	4	26	16
C_2H_6	0	0	1	1
C_3H_6	12	32	57	40
C_3H_8	0	46	196	151
iso-C_4H_8	36	28	46	41
n-C_4H_8	5	29	49	41
n-C_4H_{10}	0	30	148	151
neo-C_5H_{12}	0	0	0	0
iso-C_5H_{12}	0	9	59	59
n-C_5H_{12}	0	0	0	0
$H_2 + CH_4$	56	99	187	146
Σ_3^5 olefin	53	89	152	122
Σ_3^5 paraffin	0	85	403	361
Conversion A[b]	56	194	590	507
Conversion B[c]	53	174	557	485
% Conversion B	0.47	1.55	4.97	4.33
Chain length[d]	0	0.9	2.2	2.5

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of each catalyst was used. The flow rate of isobutane, F/W, was 1×10^{-5} moles g^{-1} s^{-1}; it was diluted with N_2 (N_2/i-C_4H_{10} = 10). Surface areas are given in the Experimental section.

[b] Conversion A = $H_2 + CH_4 + \Sigma_3^5$ paraffin.

[c] Conversion B = $\frac{1}{4} \Sigma_1^5 jC_i$, where j is the number of carbon atoms in each of the i products.

[d] Σ_3^5 paraffin/($H_2 + CH_4$).

4, the rate of paraffin formation reached a maximum, then decreased continuously.

The rates of product formation at the conversion maxima on catalysts pretreated at 650°C are collected in Table 3. Maximum conversion was observed at 5, 300, 195, and 150 min TOS on catalysts with 0, 2.6, 4.5, and 6.5% F, respectively. Over catalysts with 4.5 and 6.5% F the rates of paraffin formation exceeded those of $H_2 + CH_4$ formation by a factor of from 2 to 3, showing that carbenium ion chain length was greater than unity. It is important to note that in contrast to other paraffins, formation of neopentane decreased with TOS. Partly for this reason and partly because of the high n-C_4H_{10} peak, neopentane production was not observable chromatographically at the conversion maximum.

Isobutane conversion experiments were carried out on amorphous silica-alumina catalyst pretreated in flowing dry O_2 at either 500 or 650°C (Table 4). The conversion at 460°C was comparable with that obtained on pure alumina at 400°C under otherwise identical conditions. The conversion of isobutane was lower on silica-alumina pretreated at 650°C than after 500°C treatment and dehydrogenation was favored over demethanation. No paraffin formation was observed.

Under identical conditions, the conversion of isobutane was lower on HY zeolites (Table 4) than over fluorided alumina. The H^- transfer reaction played a more significant role than the initiation reaction over zeolites. Neopentane formation, however, in contrast to fluorided alumina catalysts, was not observed.

IR spectra of pyridine adsorbed on catalysts with 0–4.5% F and pretreated either at 500 or 650°C showed no evidence of a band at 1540–50 cm^{-1} assignable to pyridinium ion formed by interaction between pyridine and Brønsted acid sites. Typical spectra are shown for the catalyst with 2.6% F in Fig. 5. The band at 1440 cm^{-1} corresponds to pyridine coordinated to Lewis acid sites. This result indicates either a very low concentration or absence of Brønsted sites strong enough to protonate pyridine at room temperature. This result is well known for pure alumina, but appears inconsistent with the cracking data for the F/Al_2O_3.

Figure 6 illustrates IR spectra of pyridine adsorbed at 200°C on catalysts with 4.5% (A) and 6.5% F (B). On a catalyst with 6.5% F, the band at 1540–50 cm^{-1} appeared when the catalyst was pretreated either at 650 (1) or at 500°C (3). This band assigned to pyridinium ion was also observed when the wafers were contacted with 76 Torr of isobutane at 400°C for 2 h before adsorption of pyridine (2, 4). Under the same conditions the band at 1540–50 cm^{-1} was hardly noticeable on the catalyst with 4.5% F.

The broadbands in the 3550 to 3720 cm^{-1} region attributable to hydroxyl groups were much weaker when the catalyst was pretreated at 650 rather than at 500°C. Significantly, in both cases the intensity increased after contact with isobutane. Typical spectra are shown for the catalyst with 2.6% F in Fig. 7.

DISCUSSION

Perhaps the most significant feature of the present work is the contrast in the character of the results obtained from these alumina-based catalysts and the aluminosilicate studies reported earlier (7, 10). This could be explained by recognizing, as did McVicker *et al.* in their first paper (6), that dehydrogenation and demethanation of isobutane resulting in formation of CH_4, H_2, C_3H_6, and i-C_4H_8 (the primary products) over these alumina-based catalysts occurs as a separate initial step. With pure alumina the reaction stops here (except for a small amount of skeletal isomerization on the more active catalyst which had been pretreated [dehydroxylated] at the higher temperature). With the H zeolites, the strong Brønsted sites protonate

TABLE 4

Rates of Product Formation from the Reaction of Isobutane on Amorphous Silica-Aluminas and HY Zeolites[a]

Catalyst:	Pure alumina		M-46		LZ-Y62	LZ-Y82
Reaction temp. (°C):	400		460		400	400
Pretreatment temp. (°C):	500	650	500	650	500	500
H_2	3.2	44	5.9	3.3	1.8	9.4
CH_4	1.3	12	1.6	0.8	1.9	15.7
C_2H_4	0	0	0	0	0	0.4
C_2H_6	0	0	0	0	0.5	1.6
C_3H_6	1.0	12	1.5	0.7	0.6	8.1
C_3H_8	0	0	0	0	10.4	47.0
iso-C_4H_8	2.9	36	5.7	3.4	5.1	16.5
n-C_4H_8	0	5	0	0	0.1	6.6
n-C_4H_{10}	0	0	0	0	9.4	102.7
iso-C_5H_{12}	0	0	0	0	1.1	34.3
n-C_5H_{12}	0	0	0	0	0	0
$H_2 + CH_4$	4.5	56	7.5	4.1	3.7	25.1
Σ_3^5 olefin	3.9	53	7.2	4.1	5.8	31.2
Σ_3^5 paraffin	0	0	0	0	21.0	184.0
Conversion A[b]	4.5	56	7.5	4.1	24.7	209.1
Conversion B[c]	4.0	53	7.2	4.1	25.0	214.7
% Conversion B	0.04	0.47	0.06	0.04	0.23	1.9
Chain length[d]	0	0	0	0	5.7	7.4

[a] Rates are given as 10^{-9} mol g^{-1} s^{-1}; 400 mg of each catalyst was used. The flow rate of isobutane, *F*/*W*, was 1.1×10^{-5} mol g^{-1} s^{-1}; it was diluted with N_2 (N_2/i-C_4H_{10} = 10). Values obtained on alumina and amorphous silica-alumina at 5 min and on zeolites at 200 min on stream are shown.

[b] Conversion A = $H_2 + CH_4 + \Sigma_3^5$ paraffin.

[c] Conversion B = $\frac{1}{4} \Sigma_1^5 jC_i$, where j is the number of carbon atoms in each of the i products.

[d] Σ_3^5 paraffin/($H_2 + CH_4$).

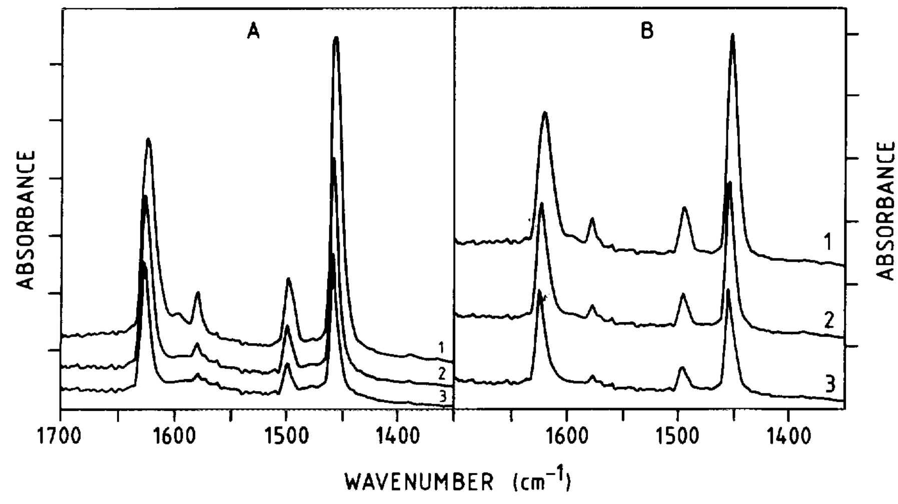

FIG. 5. Infrared spectra of pyridine adsorbed on alumina with 2.6% F and pretreated at (A) 500°C or (B) 650°C after contact with 15 Torr pyridine at 25°C; pellets were evacuated for 0.5 h at (1) 200°C, (2) 300°C, (3) 400°C.

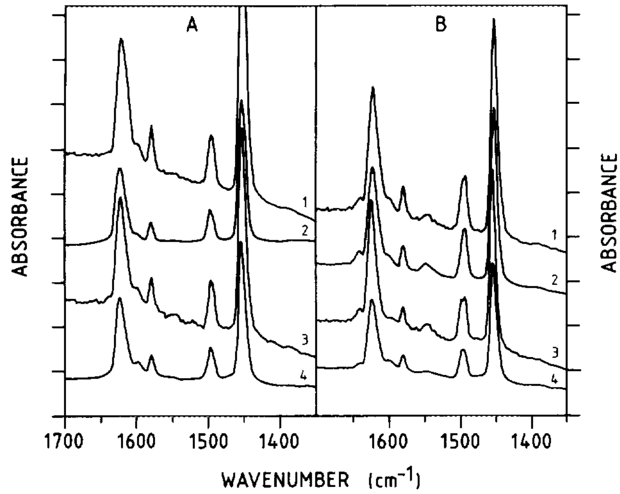

FIG. 6. Infrared spectra of pyridine adsorbed at 200°C on alumina with (A) 4.5% F and (B) 6.5% F and pretreated at 650°C (1, 2) or 500°C (3, 4); pyridine was adsorbed after pretreatment (1, 3) or after contact first with 76 Torr isobutane at 400°C for 2 h (2, 4).

the paraffin directly producing the active carbenium ions. These are not active dehydrogenation catalysts. Of course the olefins produced over the alumina-based catalysts may be protonated by the sparse Brønsted sites of the fluorided aluminas; evidently this occurs since paraffins are produced and skeletal isomerization is observed. The overall activity of these catalysts was significantly increased by further dehydroxylation. This is shown by the comparison made in Table 1.

The explanation offered above finds considerable support in the literature. Dehydrogenation and demethanation of cumene-forming α-methylstyrene, styrene, and CH_4 has been reported (1) for alumina at 500°C. The exchange rates of CH_4 and CD_4 with each other or with D_2 or H_2 at 135°C showed a primary isotope effect for the cleavage of a C–H vs a C–D bond (16). Selective poisoning with CO_2 showed that these reactions occurred on a small fraction of the available acid–base pair sites (0.04 nm^{-2}). Pure alumina is a relatively poor catalyst for opening the cyclopropane ring, temperatures above 200°C being required for the isomerization to propene. On the other hand, it is an excellent catalyst for exchange of D_2 with unsaturated molecules. Even cyclopropane-d_6 could be made in 77% yield and 98% purity at room temperature (17). Moreover, when cyclic olefins such as cyclopentene were exchanged with D_2 below 100°C, only the two vinyl hydrogens were replaced with a kinetic isotope effect, $k_H/k_D = 2.8$. Thus cyclopentene-d_2 was formed without double-bond isomerization (18). This could only occur if the vinyl C–H bond was first cleaved and then replaced with addition of a D atom. H_2/D_2 exchange occurs readily at temperatures below -100°C (19); again the rates increased markedly as the surface was "activated" by dehydroxylation at increasing temperatures. These are characteristics of an alumina surface and involve a portion of the dual Lewis acid–Lewis base sites.

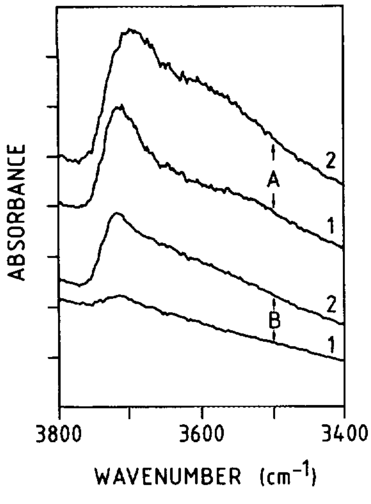

FIG. 7. Infrared spectra of alumina with 2.6% F and pretreated at (A) 500°C or (B) 650°C determined after pretreatment (1), or after contact with 76 Torr isobutane at 400°C for 30 min (2).

Lombardo *et al.* (20) made a comparison of the isomerization reactions of the *n*-butenes over ZnO and pure alumina using kinetic and tracer methods. The mechanism over ZnO had been previously well defined by Kokes and co-workers (21) who were able to obtain IR spectra of all of the intermediate species. These included both the three π-complexes and the syn- and anti-π-allyl species; they followed the changes with time as the reaction proceeded. The key result was that this same chemistry was found for the alumina surface, viz., cleavage of the allylic C–H bond of the olefin forming the intermediate π-allyl associated with the exposed cation (Lewis acid) and an adjacent OH group on the basic surface oxygen (Lewis base).

Finally, Kazansky *et al.* (22) were able to show spectroscopically that H_2 chemisorbs on alumina heterolytically in exactly the same way as it does on ZnO. At liquid N_2 temperature, a polarized molecular adsorption of H_2 that was infrared active was formed. Above -80°C this molecular species rapidly dissociated into Al–H paired with OH. Similarly, adsorbed heterolytically dissociated methane (Al–CH_3 and OH) was observed at room temperature on the same sites that dissociated H_2. Dehydrogenation of larger paraffins to olefins at temperatures above about 425°C was reported as was the hydrogenation of olefins at 475°C. Presumably the latter reaction occurred by insertion of the olefin into the Al–H bond formed by the dissociative chemisorption of H_2. The alkyl thus formed then reacted more slowly with the paired O–H, just as demonstrated (21) for ZnO. The reverse reaction, dehydrogenation, could then occur by the reverse pathway. In summary, these kinetic and tracer studies show that dehydrogenation of isobutane on the dual acid–base pair sites of alumina may be expected on both alumina and fluorided alumina catalysts. On the latter, a few strong Brønsted sites exist, which can lead to observation of the results of acid catalysis involving carbenium ion intermediates, just as postulated by McVicker *et al.* (6), although we do not think the primary products are produced by a radical mechanism, but by dehydrogenation on the Lewis acid–base pair sites. Basic oxides are noted for their ability to dehydrogenate. This is a subtle, but important distinction.

The striking changes in paraffin production over the fluorided catalyst pretreated at 650°C are interesting. Formation of paraffins is ordinarily attributed to bimolecular hydride transfer from the substrate (isobutane) to carbenium ions. In the present case the conversion level was maintained at less than 2.5%. Other aspects of the product distribution clearly support the concepts of acid catalysis.

Pyridinium ions were not detected with pure alumina, nor were C_3–C_5 paraffins, but they did appear concomitant with the formation of important amounts of these paraffins. The unanswered questions are Why did the rates of paraffin formation increase so dramatically with TOS when the catalysts were pretreated at 650°C, and how can the formation of carbenium ions be rationalized with the known surface chemistry of alumina? One can only speculate that these ions are *not* formed over the dual acid–base pair sites of alumina. The isobutane can be dehydrogenated and demethylated over these sites. On fluoriding, the site concentration is diminished as the surface hydroxyls (the precursors of the dual sites) are substituted by stable F^- ions. This process is accompanied by an increase in the intrinsic acid strength of the remaining hydroxyl groups. Now protonation of the olefins becomes possible and isomerization and paraffin production result. The changes with TOS may result from new and additional Brønsted acidity induced in the fluorided catalyst during dehydrogenation. Alternatively, small amounts of HF may be produced. Clearly there are still some things to be learned about these systems.

ACKNOWLEDGMENTS

Support for this work by the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Research (Grant DE-FG02-87ER13774 A000) is gratefully acknowledged. Two of us (J.E. and G.O.) also thank the National Scientific Research Foundation (OTKA), (Project No. T017770) for support.

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