Nature of the Sites on Fluorided Alumina

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The reactions of 1-butene with fluorided alumina containing 1.0, 7.5, and 12.1% have been investigated using ammonia-blocking and deuterium-tracer techniques. On all catalysts there was initial formation of a polymeric complex. Isomerization then continued under steady-state conditions. Ammonia-blocking studies indicate that complex formation is confined more to the higher energy sites than is the same reaction on silica–alumina. These data also suggest that the isomerization activity is associated with the presence of the complex. Products obtained from passing pulses of 1-butene over perdeuterobutene-treated catalyst contain significantly more deuterium than does the starting material. This is evidence that the complex participates in the isomerization reaction. The complex probably furnishes the protons to form carbonium ions necessary for reaction. The possibility that water present in low concentrations on fluorided alumina may participate in the reaction cannot be excluded. The evidence indicates that complex formation depends at least in part on fluoride content and that isomerization depends on both fluoride content and the presence of the complex.

I. INTRODUCTION

It is well known that fluoridation enhances the activity of alumina for acid-catalyzed reactions. The acidic properties developed are similar to those of silica–alumina. There is, however, considerable divergence in opinion concerning the nature of the acidity responsible for the catalytic activity (*1–8*). Recent results of ammonia-blocking and deuterium-tracer studies of 1-butene reactions over silica–alumina indicate that isomerization activity depends in part on the presence of an adsorbed phase (polymeric complex) formed initially in the reaction (*9–13*). The conclusion is that the polymeric complex furnishes the protons to form the carbonium ions necessary for isomerization. The question arises whether a similar mechanism operates during 1-butene isomerization over fluorided alumina. The present report gives results of ammonia-blocking and deuterium-tracer studies showing that 1-butene forms a polymeric complex on fluorided alumina and

that this complex is associated with the isomerization reaction.

II. EXPERIMENTAL METHODS

The catalysts used in the investigation were prepared by coprecipitating aluminum nitrate with a mixture of ammonia and the amount of ammonium fluoride required to give the desired fluoride concentration. The resulting gels were washed thoroughly and dried at 125°C. These materials were heated in a stream of dry air at 400°C for 4 hr to decompose the nitrates and then at 550°C for 16 hr to effect dehydration. The fluorine contents of the catalysts were determined by activation analysis. Catalysts containing 0, 1.0, 7.5, and 12.1 wt % F had surface areas of 223, 230, 192, and 168 m²/g, respectively.

About 2.5 g of catalyst, ground 15 to 60 mesh, was activated *in situ* for each continuous flow experiment. One-half-g samples were used for the pulse experiments. Activation consisted of heating the catalyst under flowing nitrogen for 2 hr at 500°C.

The catalysts were treated with ammonia under static conditions. The amount of ammonia required to produce a measurable pressure, 50 μ or less, over the catalyst was taken as the saturation concentration. After activation the catalyst was cooled *in vacuo* to the desired temperature and known amounts of ammonia were added in increments until pressure was observed. The equilibration process was allowed to continue at least 1 hr. If too much ammonia was added, the calibrated gas-handling system was used as a Toeppler pump to reduce the pressure below 50 μ. The catalyst was isolated from the vacuum system and allowed to cool to room temperature before the flow studies were commenced. The saturation concentrations found here compare well with those determined by Webb for catalysts of similar composition (1).

Phillips Research Grade 1-butene was used as received. The mixture of *cis*- and *trans*-perdeuterobutene was obtained from Merck, Sharp and Dohme. Helium carrier gas, Matheson Ultra High Purity, was dried by passage through a Dry Ice trap. The anhydrous ammonia obtained from Matheson was attached directly to the gas-handling system.

The flow apparatus consisted of a gas chromatograph (Perkin-Elmer Model 154D) in which the column normally used for analysis was replaced by an external column of catalyst. The column was attached to a gas-handling system, making it possible to treat it statically with gases, e.g., ammonia at a variety of temperatures and pressures. The basic apparatus was arranged to do either pulse or continuous flow studies.

In studies using the pulse technique, a Perkin-Elmer sample valve with a loop of known volume was used to introduce pulses or slugs of 1-butene into the carrier gas stream. The amount of butene recovered from a pulse after passing through the catalyst was determined from peak area using a calibration chart. The product butenes were trapped for further analysis.

In the continuous flow method, a sampling valve was arranged to continuously inject 1-butene into the helium carrier stream. The details of the apparatus have been described previously (14). Figure 1 is a schematic drawing of a typical flowgram showing the quantities measured. These quantities are defined: $A = B - C$, the amount of residue (polymeric complex) remaining on the catalyst after stripping; B = the amount of olefin adsorbed and reacted on the catalyst under steady-state conditions; and C = the amount of olefin desorbed after termination of injection.

All flow experiments were conducted at atmospheric pressure and 25°C. The helium carrier flow was approximately 50 ml/min STP. The partial pressure of the 1-butene in the carrier was about 35 mm. Injection of olefin into the carrier was terminated at 87 min at which time the isomer distribution in the effluent was determined with an auxiliary chromatograph.

The rate constants reported here were calculated on the basis of first-order kinetics using the expression $kt = 2.3 \log X_e/(X_e - X)$ where X_e is the fraction of 2-butene in an equilibrium mixture at 25°C, X is the fraction converted, and t in seconds is the time spent by the butene in the catalyst bed. The latter is based on the time required for the butene–helium mixture to flow through 2.5 g of catalyst having a void volume of 1.67 ml. These rate constants are significant for comparison purposes only.

III. RESULTS AND DISCUSSION

Ammonia-Blocking Studies

The reactions of 1-butene with catalysts containing 0, 1.0, 7.5, and 12.1 F were investigated by the continuous flow method. Our objective was to establish the existence and magnitude of the polymeric complex and not to determine the optimum fluoride concentration for the polymerization and isomerization reactions. The polymeric complex formation and isomerization activities of the four catalysts are summarized in Table 1. It requires as long as 60 min before the adsorption–polymerization reaction is complete (Area B, Fig. 1) after which adsorption–desorption of the butenes continues under steady-state conditions.

TABLE 1
1-BUTENE ON $Al_2O_3 \cdot F$ CATALYST

Fluoride conc		Polymeric complex, A				
Wt %	F^-/cm^2 $\times 10^{-14}$	Moles of $C_4H_8/g \times 10^4$	Molecules/ $cm^2 \times 10^{-13}$	P_0 (mm)	% Conv. to 2-C_4H_8	k (sec^{-1})
0	0	0.37	1.0	32.4	2.7	0.015
1.0	1.38	6.64	17.4	32.4	6.8	0.043
		6.74	17.7	29.3	8.0	0.050
7.5	12.4	6.48	20.4	28.3	35.4	0.0247
		6.76	21.2	29.5	34.0	0.246
12.1	22.8	2.64	9.46	32.5	15.2	0.097
		2.84	10.2	32.0	17.2	0.112

The concurrent isomerization reaction declines with time which suggests that the surface is undergoing some change. Once the steady-state condition is reached the amount of butene easily desorbed under helium flushing (Area C, Fig. 1) does not vary with injection time. Hence, we conclude that this butene is physically adsorbed on the weak sites of the catalyst. On all of the catalysts except pure alumina the amount of butene adsorbed and polymerized was much larger than the amount desorbed indicating the formation of significant amounts of polymeric complex (A). These properties of fluorided alumina are similar to those observed for silica–alumina (12, 13).

The data in Table 1 show that pure alumina, which has been shown to possess principally aprotic sites (15), produces little polymeric complex. This appears to dis-

count the possibility that the polymeric complex resides exclusively on the aprotic sites of the fluorided catalysts. We note that the rate of isomerization is not proportional to the amount of complex for all fluoride concentrations. In particular the catalysts containing 1.0 and 7.5% F produce the same quantity of complex, yet the rate of isomerization is four to five times greater for the catalyst with the higher fluorine content. This indicates that factors in addition to the quantity of polymeric complex influence the rate of isomerization.

The polymeric complex and isomerization reactions were investigated over all three fluorided catalysts as function of ammonia-saturation temperature. The results along with the ammonia-saturation concentrations are summarized in Table 2. The quantity of ammonia required for satu-
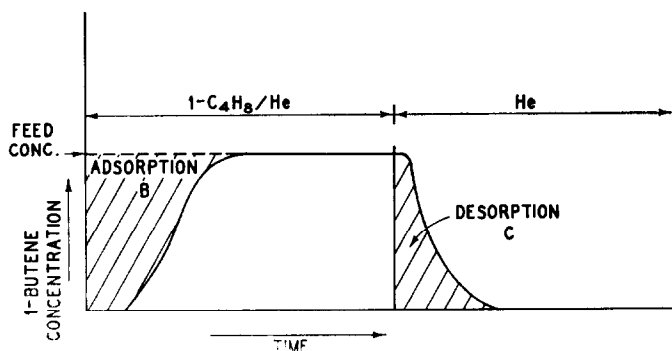

FIG. 1. Adsorption of 1-C_4H_8 on fluorided alumina.

TABLE 2
1-BUTENE ON NH_3-SATURATED $Al_2O_3 \cdot F$ CATALYST

		NH₃ saturation conc		Polymeric complex, A				
F⁻ Conc Wt %	NH₃ ads T (°C)	Moles of NH_3/g $\times 10^4$	Molecules/ cm² $\times 10^{-13}$	Moles of C_4H_8/g $\times 10^4$	Molecules/ cm² $\times 10^{-13}$	P_0 (mm)	% Conv. to $2\text{-}C_4H_8$	k (sec⁻¹)
1.0	25	6.20	16.2	0.05	0.13	30.9	0	—
	100	3.52	9.22	0.06	0.16	31.0	0	—
	200	2.20	5.76	0.16	0.42	32.1	0	—
	300	0.98	2.57	0.11	0.29	29.7	0	—
	300	0.98	2.57	0.19	0.50	32.0	0	—
	400	0.44	1.15	0.16	0.42	31.0	0.2	0.0026
	450	0.22	0.58	0.40	1.05	32.4	1.3	0.0091
7.5	25	5.75	18.1	0	0	34.1	0	—
	100	3.27	10.3	0.16	0.50	31.2	0	—
	100	3.42	10.7	0.10	0.31	34.2	0	—
	200	2.40	7.54	0	0	29.1	0	—
	200	2.39	7.51	0	0	34.6	0	—
	300	1.45	4.55	0	0	29.2	1.3	0.007
	300	1.35	4.24	0	0	33.3	1.1	0.008
	400	1.02	3.20	1.17	3.67	32.5	13.5	0.085
	400	0.97	3.05	1.81	5.68	34.9	12.3	0.072
	450	0.49	1.54	3.44	10.8	35.5	23.6	0.160
12.1	25	4.96	17.7	0.03	0.11	30.2	0	—
	100	3.48	12.5	0.06	0.21	31.6	0	—
	200	2.12	7.59	0.08	0.29	32.0	0	—
	300	1.15	4.12	0.08	0.29	33.7	1.2	0.0094
	400	0.72	2.58	0.56	2.00	33.6	5.8	0.036
	500	0.41	1.47	1.57	5.62	34.4	10.4	0.065
	500	0.40	1.43	1.56	5.59	34.4	10.2	0.066

ration at a given temperature showed little dependence on fluoride content. This is consistent with the observations of Webb (1). Actually the amount of ammonia adsorbed per unit area at each temperature is nearly constant for all three catalysts, the data for the 7.5 and 12.5% F catalysts agreeing better than those for the 1.0% F catalyst. The results in Table 2 show that only when the ammonia-saturation temperature exceeds 300°C (perhaps higher for the 1.0% F catalyst) do we observe complex formation and accompanying isomerization. Saturation at temperatures less than 300°C virtually destroy all isomerization activity. These observations are illustrated graphically in Fig. 2 using the data for the 7.5% F catalyst.

The increase in isomerization with increasing polymeric complex formation suggests that there is an association between the two reactions. The correlation for the 7.5 and 12.1% F catalysts is particularly good. The large amount of complex present on the 1.0% F catalyst showing little isomerization activity is puzzling and deserves further study in the range of 0 to 1.0% F. The possibility that polymeric complex formation occurs predominantly on aprotic sites appears unlikely because pure alumina having only aprotic sites forms little complex. This discounts, but does not deny unequivocally, the possibility that isomerization and polymerization occur independently on two different kinds of acid sites. Repeated adsorption–desorption cycles on the same catalyst show that once the complex is
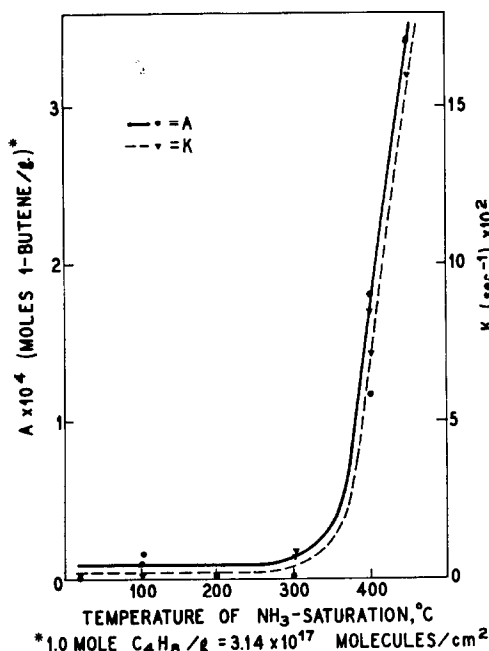
FIG. 2. Isomerization and polymeric complex formation of 1-butene over NH$_3$-saturated Al$_2$O$_3$·F (7.5% F).

formed in the initial cycle no more butene is polymerized on the surface in subsequent cycles. We interpret this to mean that the complex remains adsorbed on catalyst sites. It seems unlikely that parallel reactions could occur independently on the same kind of site on which one of the products, polymer, is permanently adsorbed.

The results of the ammonia-blocking study can be rationalized by assuming a continuous distribution of site energies on the surface in which there is a sharp boundary with respect to kT between sites capable and incapable of holding ammonia. The higher the preadsorption temperature the higher the lower boundary required for fixed adsorption. Thus ammonia saturation at 300°C marks the point at which ammonia just covers all the sites involved in polymeric complex formation and accompanying isomerization. Saturation at 400°C leaves the sites capable of holding ammonia at 300 to 400°C available for reaction with butene. It follows that over untreated catalyst the reaction takes place on sites capable of holding ammonia

at 300°C and above. In general the data in Table 2 show the increase in polymeric complex formation and accompanying isomerization as more sites become available for reaction. Admittedly this increase is small for the 1.0% F catalyst, but as pointed out earlier, the lower boundary for fixed adsorption on this catalyst may be higher than 300°C. This may occur because the catalyst is too dilute in fluorine to show typical behavior.

The results of our ammonia-blocking studies on silica–alumina indicated that the lower boundary for fixed adsorption of butenes is 200°C (12, 13). Then a lower boundary at 300°C for fluorided alumina indicates that the fixed adsorption is confined more to higher energy sites than is the same reaction on silica–alumina. Dividing the amount of polymeric complex formed in the absence of blocking by the amount of ammonia adsorbed at the lower boundary for fixed adsorption gives the average number of butene molecules per occupied site. For the fluoride concentrations 1.0, 7.5, and 12.1%, the number of molecules per occupied site is 6.6, 4.6, and 2.3, respectively. This implies that the complex varies from the heptamer to dimer in the range of fluoride concentrations studied. These values seem reasonable because a similar calculation for silica–alumina based on the lower boundary at 200°C indicates that the average composition of the complex is tetramer. All these calculations assume that one ammonia molecule occupies one site. Hence these values may be lower limits because the ammonia may reside on some sites that are not active.

Determining the Role of the Polymeric Complex in the Isomerization Reaction Using Deuterium-Tracer Techniques

Deuterium-tracer studies provide evidence that the polymeric complex is associated with isomerization activity. We chose the catalyst containing 7.5% F because we felt that its behavior was most representative of the three concentrations used here. The perdeuterobutene polymeric complex, 1.2×10^{-4} moles of C$_4$D$_8$, was formed on 0.5 g of catalyst in the static

reactor using a mixture of *cis*- and *trans*-2-perdeuterobutene. Pulses of 1-butene, 3.85 ml STP, were passed over the per-deuterobutene-treated catalyst in helium carrier flowing at 50 ml/min. The products from each pulse were analyzed by a combination of gas chromatography and mass spectrometry for deuterium content. Table 3 lists the results of the experiment. We have retained the symbol, F_D, used by Ozaki and Kimura to indicate the mole fraction of deuterobutene in each isomer (9). Using the notation of Hightower and Hall, the quantities presented in the last two columns of Table 3 are defined as follows (11):

No. D atoms exchanged

$$= \frac{(\text{total product recovered, ml})}{2.24 \times 10^4 \text{ ml/mole}}$$
$$\times \left(6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}}\right)$$
$$\times (\% \text{ isomer}/100) \, \Sigma i d_i,$$

where d_i is the mole fraction of deutero-butene containing i D atoms.

No. D atoms exchanged/molecule $= \Sigma i d_i$

Practically all of each pulse was recovered as gaseous products indicating that little additional polymeric complex was formed after contact with the perdeutero-butene in the static system. Silica–alumina showed similar behavior under continuous flow conditions (12, 13). This demonstrates the sequential nature of the reactions: polymeric complex formation, which ceases shortly after contact, followed by isomerization. Isomerization activity declines with each pulse much in the same manner that it declines with time during continuous flow experiments. The decline in the percentage of deuterated isomers would be expected because of the "dilution" of the perdeuterobutene complex with hydrogen atoms during the isomerization process. This occurs because a carbonium ion formed from a perhydrobutene molecule and a surface deuteron is, assuming all substituent positions equally labile, eight times more likely to return a proton than a deuteron to the surface.

The quantities, mole fraction of deutero-butene, number of D atoms exchanged, and number of D atoms exchanged per molecule, listed in Table 3 all indicate that a preponderance of the deuterium is in the isomerized products. The number of deuterium atoms exchanged per molecule is 16 to 56 times greater for the products, *cis*- and *trans*-2-butene, than for the starting material. Clearly this indicates that the polymeric complex is associated in some manner with the isomerization activity. The small amount of deuterium found in the starting material is due presumably to H–D exchange not associated with the isomerization event and to the reverse reaction. Products containing no deuterium probably came from reactions where the carbonium ions returned their deuterons to the surface and from reaction over sites which lost deuterons in prior isomerization events.

The role of the surface and the adsorbed polymeric complex in the isomerization reaction is not completely understood. It appears that the polymeric complex furnishes the protons to form the carbonium ions necessary for the isomerization reaction. This does not necessarily mean that the polymeric complex is the seat of the isomerization activity. For example the data could be explained using the following assumptions:

1. The isomerization reaction occurs on a small number of highly active protonic sites.

2. The polymeric complex deuterates the small number of active sites.

3. The deuteration reaction is slower than the isomerization process. Under these conditions the initial products would consist predominantly of deutero-2-butene as is observed. In addition the slower deuteration step would eventually result in a decline in the number of deuterium atoms transferred per molecule of product even in the presence of an abundance of deuterium.

Our study of 1-butene polymerization and isomerization over silica–alumina shows that polymer complex formation depends in part on the water content and

TABLE 3

ISOMERIZATION OF 1-BUTENE OVER PERDEUTEROBUTENE-TREATED Al₂O₃·F CATALYST (7.5% F)

He flow 22.0 × 10⁻⁴ moles/min; polymeric complex 1.2 × 10⁻⁴ moles of C₄D₈ on 0.5 g; T = 25°C.

Pulse No.	Pulse size (cc-STP)	Percentage recovered	Product	Conc. isomer (%)	Isotopic composition of products (%)					F_D[a]	No. of D atoms exch. 10^{-19}[b]	No. of D atoms exch./molecule[c]
					d_0	d_1	d_2	d_3	d_4			
1	3.85	~100	1-C₄	61.0	98.7	1.1	0.2			0.013	0.095	0.015
			t-2-C₄	16.2	68.1	28.0	3.4	0.5		0.319	0.624	0.370
			c-2-C₄	22.8	66.0	31.2	2.5	0.3		0.340	0.880	0.371
2	3.85	~100	1-C₄	81.8	98.4	1.2	0.2	0.1	0.1	0.016	0.196	0.023
			t-2-C₄	6.1	66.7	26.1	5.0	1.5	0.7	0.333	0.275	0.434
			c-2-C₄	12.1	63.9	29.3	4.7	1.5	0.6	0.361	0.575	0.456
3	3.85	~100	1-C₄	80.2	98.8	1.0	0.1	0.1		0.012	0.125	0.015
			t-2-C₄	6.2	62.0	25.8	10.7	0.8	0.7	0.380	0.338	0.524
			c-2-C₄	13.6	67.3	28.5	2.3	1.3	0.6	0.327	0.556	0.394
4	3.85	~100	1-C₄	82.0	99.2	0.7	0.1	0.1		0.008	0.0717	0.009
			t-2-C₄	6.0	73.1	21.7	3.8	1.4	0.4	0.273	0.226	0.351
			c-2-C₄	12.0	70.1	25.6	3.5	0.8		0.299	0.437	0.350
5	3.85	~100	1-C₄	72.6	98.2	1.8	0.1			0.018	0.136	0.018
			t-2-C₄	9.2	77.4	18.5	2.0	1.2	0.9	0.226	0.284	0.297
			c-2-C₄	18.2	73.8	24.4	1.8			0.262	0.531	0.280
6	3.85	~100	1-C₄	79.7	99.6	0.4				0.004	0.0334	0.004
			t-2-C₄	6.2	82.4	16.4	1.2			0.176	0.121	0.188
			c-2-C₄	14.1	74.8	23.9	1.3			0.252	0.388	0.265

[a] F_D [After Ozaki and Kimura (9)] is the mole fraction of deuterobutene in each isomer.

[b] No. D atoms exchanged [after Hightower (11)] = $\dfrac{\text{(total product recovered, ml)}}{2.24 \times 104 \ \text{(ml/mole)}} \ \dfrac{\text{(% isomer present)}}{100} \ (6.02 \times 10^{23}) \ (\Sigma i d_i)$, where d_i is mole fraction of deuterobutene containing i D atoms.

[c] No. atoms exchanged/molecule [after Hightower (11)] = $\Sigma i d_i$.

that isomerization depends on both water content and the presence of the complex (*13*). Gerberich *et al.* (*3*) have shown by H–D exchange methods that the water content of alumina impregnated with 5% or more fluorine is nil. We examined the H_2O content of two coprecipitated fluorided alumina catalysts containing 2.6 and 6.9% F by these methods and found 0.3 and 0.2% H_2O, respectively, for activation at 500°C. Although these H_2O contents are only 0.25 and 0.38 of that found for silica–alumina (Houdry M46) at 500°C they still correspond to more than 1×10^{14} OH groups/cm^2. Hence, we cannot rule out the possibility that water in low concentrations may influence catalytic activity. We noted earlier that our catalysts containing 1.0 and 7.5% F produce the same amounts of polymeric complex and yet the 7.5% F catalyst isomerizes 1-butene four to five times the rate of the 1.0% F catalyst. Collectively these observations indicate that the polymeric complex formation depends in part on fluoride concentration and that isomerization depends on both fluoride content and the presence of the complex.

ACKNOWLEDGMENT

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