JOURNAL OF CATALYSIS 13, 147-153 (1969)

The Nature of the Sites on Silica-Alumina for Propylene Polymerization

J. N. FINCH AND ALFRED CLARK

From the Phillips Petroleum Company, Bartlesville, Oklahoma 74003

Received August 20, 1968; revised October 3, 1968

The nature of the sites on silica-alumina for propylene polymerization has been investigated using adsorption, deuterium tracer, and ammonia blocking techniques. Adsorption studies indicate that propylene, like 1-butene, rapidly undergoes polymeric complex formation which ceases after a few minutes. The polymeric complex remains adsorbed on catalyst sites. 1-Butene readily isomerizes over the propylene complex. Deuterium tracer studies indicate that little propylene isomerization occurs over silica-alumina at 25°C. The ammonia blocking studies show that polymeric complex formation for propylene and 1-butene over silica-alumina is very similar. In both cases the average degree of polymerization is four. Catalyst sites of intermediate energy appear to be the most active in polymeric formation.

INTRODUCTION

The results of several deuterium tracer studies, including those conducted in this laboratory, demonstrate conclusively that a strongly adsorbed phase is involved in the isomerization of 1-butene over silica-alumina (*1–4*). In addition we have used ammonia blocking techniques to show that the strongly adsorbed phase is polymeric and that it is the seat of activity for the isomerization reaction. These results suggest that reaction over an adsorbed polymeric phase may be a general catalytic phenomenon. The purpose of the present report is to give evidence showing that (1) propylene forms an adsorbed polymeric complex, (2) 1-butene will isomerize over the propylene complex, and (3) the polymeric complex reactions for propylene and for 1-butene over ammonia-poisoned silica-alumina are very similar.

EXPERIMENTAL

The silica-alumina, designated M-46 by the Houdry Process Corporation, contained 87% SiO_2 and 13% Al_2O_3. It had a surface area of 300 m^2/g, a bulk density of 0.55 g/cc, and a void volume of 0.9 cc/g. About 2.5 g of catalyst, ground 30 to 60 mesh, was activated *in situ* for each experiment. The catalyst was activated at 500°C for 4 hr, 2 hr in a stream of dry air and 2 hr in a stream of nitrogen.

The catalyst was pretreated with ammonia under static conditions. The activated catalyst was first heated under vacuum to the desired temperature and then a known amount of ammonia was admitted to the system. The adsorption process was allowed to continue at the elevated temperature for 1 hr. The quantity of ammonia required to produce a pressure of less than 50 μ Hg after equilibration over the catalyst at a given temperature was taken as the saturation concentration. For all concentrations less than saturation the ammonia pressure over the catalyst was essentially zero at the end of the equilibration period. The catalyst was isolated from the vacuum system and allowed to cool to room temperature before the flow studies were commenced.

The propylene and 1-butene, both Phillips Research Grade products, were used as received. The cis and trans mixture of perdeutero-2-butene used in the deuterium tracer studies was obtained from Merck, Sharp, and Dohme. The helium carrier gas, Matheson Ultra High Purity, was dried by passage through a Dry Ice trap.

The continuous flow apparatus used in the investigation was essentially the same as that described previously (*5*). It consisted of a gas injection system and flow-measuring devices coupled to a gas chromatograph (Perkin-Elmer 154D) in which the column normally used for analysis was replaced by a column of catalyst. The column or reactor was attached to a gas-handling system. Thus it was possible to evacuate the catalyst and treat it statically with gases at a variety of temperatures and pressures. A second chromatograph arranged to sample the effluent from the flow apparatus was used to determine the concentration of butene isomers in the product. Figure 1 is a schematic drawing of a typical flowgram showing the quantities measured with the continuous flow apparatus. Argon was used to determine the "dead space" of the reactor. The following quantities are defined: $A = B - C$, the amount of residue remaining on the catalyst after helium stripping; B, the amount of olefin adsorbed and reacted on the catalyst under steady state conditions; C, the amount of olefin desorbed after termination of injection.

All flow experiments were conducted at atmospheric pressure and at 25°C. The helium carrier flow was approximately 50 cc/min STP. At 35 mm partial pressure of 1-butene the space velocity was about 700 volumes of feed per volume of catalyst per hour. Injection of the olefin into the carrier gas was usually terminated after 87 minutes. In studies involving the butenes, the isomer distribution used in the rate calculations was determined at the time of termination of olefin injection.

RESULTS AND DISCUSSION

Reactivity of Propylene and 1-Butene Residues for Isomerization

Our studies on silica-alumina indicate that propylene, like 1-butene, rapidly undergoes polymeric complex formation which ceases after a few minutes. Further contact with propylene produces no more polymeric complex, and adsorption is completely reversible. Since the polymeric complex is estimated to cover less than 10% of the surface of the catalyst, it cannot be argued that the surface is blocked by product. Therefore, we conclude that the propylene polymeric complex is adsorbed on catalyst sites. We reached the same conclusion in other studies with 1-butene on silica-alumina (*4*).

To determine whether propylene polymeric complex is active for 1-butene isomerization, we first formed the complex on the surface, stripped off the reversibly adsorbed propylene, and then passed 1-butene over the residue. Experimentally this amounted to running a propylene flowgram followed by a 1-butene flowgram on the same sample of catalyst. The zero-order rate constant for 1-butene isomerization, 25°C and 35 mm, over propylene polymeric complex is 8.16 mm/sec. This compares

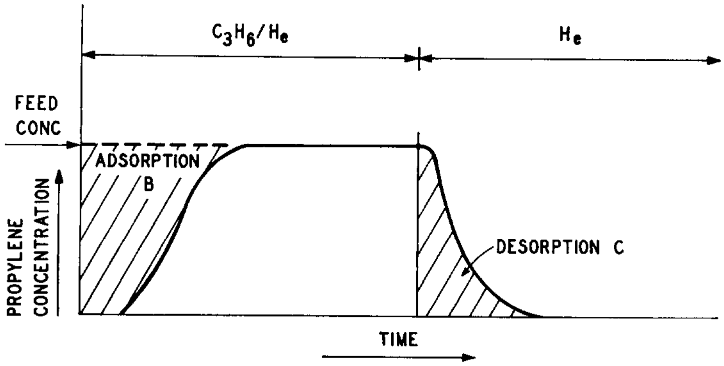

FIG. 1. Adsorption of C_3H_6 on silica-alumina.

favorably with 9.24 and 10.9 mm/sec found in two different experiments for 1-butene isomerization over its own residue. From these data we conclude that propylene polymeric complex is almost as effective for 1-butene isomerization as the butene residue.

The results of the two flowgrams recorded in the foregoing experiment are shown in Fig. 2. The difference between *B* and *C* for propylene indicates the formation of the expected complex. The difference between *B* and *C* for 1-butene indicates that some additional polymeric complex, equivalent to 0.74×10^{-4} moles 1-butene/g, was formed. When the order of the experiment is reversed, i.e., propylene is passed over butene polymeric complex, then no additional polymer is formed. Figure 3 shows the data for such an experiment. These data suggest that 1-butene reacts with a broader distribution of site energies than does propylene.

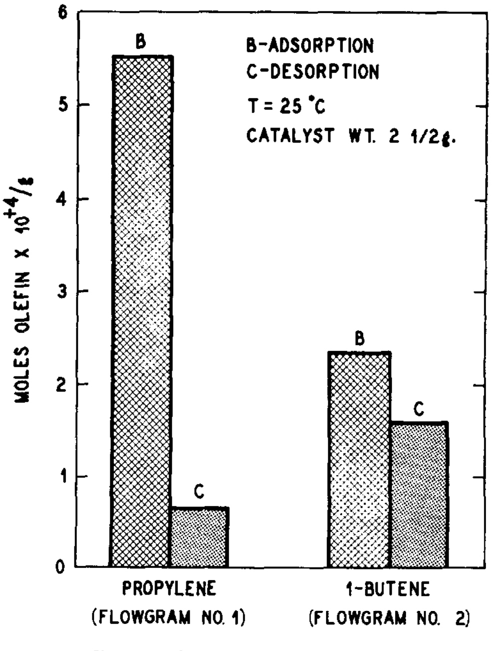

FIG. 2. Consecutive flowgrams: (1) propylene and (2) 1-Butene on silica-alumina.

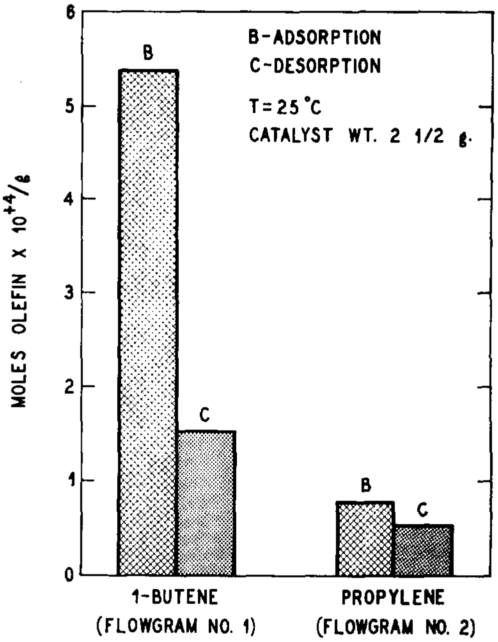

FIG. 3. Consecutive flowgrams: (1) 1-Butene and (2) propylene on silica-alumina.

To determine whether propylene is isomerized to any appreciable extent over the butene residue at 25°C we have used deuterium tracer techniques similar to those employed in our 1-butene isomerization studies (*4*). We injected pulses of propylene (1.14×10^{-4} moles/min for 1.8 min) into helium flowing at 22.1×10^{-4} moles/min over 1.5 g of silica-alumina having perdeuterobutene polymeric complex on its surface. A similar experiment was conducted using exhaustively deuterated silica-alumina. The perdeuterobutene polymeric complex, 2.03×10^{-4} moles C_4D_8/g catalyst, was formed by treating the catalyst with a mixture of *cis-* and *trans*-2-butene at 25°C in our static apparatus. The exhaustively deuterated catalyst was prepared according to Ozaki and Kimura (*1*). The products of each propylene pulse were trapped and analyzed by mass spectrometry for deuterium content. The results of both experiments are presented in Table 1.

Examination of the data for the exhaustively deuterated catalyst in Table 1 reveals that nearly all of the first pulse and portions of each succeeding pulse were consumed to form the expected polymeric complex. If one disregards the results for the first pulse because of the small amount of propylene recovered, the isotopic compositions of the succeeding pulses compare well with those

TABLE 1

Reaction of Propylene over Exhaustively Deuterated (A) and Perdeuterobutene-Treated (B)[a] Silica-Alumina

Pulse No.	Pulse size (moles/g $\times 10^{+4}$)	Total recovered (moles/g $\times 10^{+4}$)	Isotopic composition of products (%) d_0	d_1	d_2	d_3	d_4	d_5	d_6	$\frac{\text{g atoms D exch.} \times 10^{+4}}{\text{g catalyst}}$	$\frac{\text{g atoms D exch.}}{\text{mole product}}$
A-1	1.24	0.078	23.9	51.0	18.3	6.5	—	—	—	0.086	1.071
A-2	1.24	0.555	82.0	10.8	5.8	1.4	—	—	—	0.149	0.266
A-3	1.24	0.78	86.9	8.0	4.1	1.0	—	—	—	0.148	0.192
A-4	1.20	0.815	90.5	7.1	1.7	0.7	—	—	—	0.102	0.125
A-5	1.19	0.85	89.6	6.8	2.8	0.8	—	—	—	0.125	0.148
B-1	1.37	1.29	83.7	10.7	0	0	5.6	—	—	0.427	0.331
B-2	1.35	1.29	91.9	3.3	3.6	0.3	0.9	—	—	0.194	0.150
B-3	1.35	1.24	91.3	5.2	2.6	0.2	0.7	—	—	0.171	0.138
B-4	1.35	1.37	91.5	5.9	1.7	0.2	0.7	—	—	0.174	0.127
B-5	1.35	1.29	92.8	5.0	1.4	0.1	0.7	—	—	0.141	0.109

[a] Polymeric complex, 2.18×10^{-4} moles C_4D_8/g catalyst. Reaction temp. 25°C; 1.5 g catalyst; He flow 22×10^{-4} moles/min.

reported by Larsen, Gerberich, and Hall for a similar experiment (*6*). What is surprising here is the amount of deuterium transferred to the propylene by the exhaustively deuterated catalyst. About 0.8% of the 14.8×10^{-4} g atoms D/g catalyst assumed available is transferred with each pulse. In contrast, similar experiments with 1-butene show that less than 0.2% of the available deuterium is carried away with each pulse (*4*). The data for the perdeuterobutene-treated catalyst also indicate that after passage of the first pulse each succeeding pulse carried away about 0.8% of the 17.6×10^{-4} g atoms D/g catalyst available on the surface. In fact, the number of g atoms of deuterium exchanged per gram of catalyst for the two experiments (except for the first pulses) is essentially the same. These data indicate that (1) only a small fraction of the deuterium available on either catalyst, less than 1%, is transferred to the propylene, and (2) the perdeuterobutene-treated catalyst is no more effective in transferring deuterium to propylene than is the exhaustively-deuterated catalyst. If the seat of isomerization activity is the adsorbed polymeric complex, as has been shown for the normal butenes (*1–4*) and the alkyl-substituted cyclopropanes (*7*), then these results imply that little propylene isomerization is occurring and that the principal reaction is H–D exchange.

In other experiments catalysts were saturated with either cyclohexene, 1-octene, or tetramethylethylene (2,3-dimethylbutene-2) and then stripped with helium. When these catalysts were contacted with 1-butene no additional polymeric complex was formed; i.e., *B* and *C*, illustrated in Fig. 1, were equal; and the butenes were recovered extensively isomerized. From this we conclude that these other olefins form residues that are active for 1-butene isomerization.

IDENTIFICATION OF THE CATALYTICALLY IMPORTANT SITES USING AMMONIA BLOCKING TECHNIQUES

The effect of preadsorbed ammonia on the propylene polymeric complex reaction was investigated as a function of preadsorption temperature for two ammonia coverages, 0.243×10^{-4} moles/g and the saturation concentration for each temperature. The saturation concentrations for the preadsorption tempertures 25°, 100°, 200°, 300°, and 400°C were 3.35×10^{-4}, 1.72×10^{-4}, 0.945×10^{-4}, 0.464×10^{-4}, and 0.241×10^{-4} moles NH_3/g, respectively. The polymeric complex reaction was carried out at 25°C and 35 mm partial pressure of propylene.

Figure 4 shows the curve for propylene polymeric complex formation as a function of preadsorption temperature for 0.243×10^{-4} moles NH_3/g catalyst. A minimum clearly exists in the curve between 200° and 300°C. Since the number of sites available to propylene is constant, the differences in the amount of polymeric complex formed must indicate differences in the effectiveness of ammonia blocking. To determine the effectiveness of the ammonia as a blocking agent, the number of moles of propylene denied per mole of ammonia at each preadsorption temperature was calculated from the relation $(A_{\text{untreated}} - A_{NH_3\text{-treated}})/NH_3$ conc. For $A_{\text{untreated}}$, 4.1×10^{-4} moles propylene/g, the calculation indicates that the ammonia preadsorbed at 25°, 100°, 200°, 300°, and 400°C denied 5.8, 7.1, 8.7, 8.7, and 6.2 moles propylene/site, repectively. This assumes that one ammonia molecule occupies one active site. These results show that the maximum ammonia blocking occurs on sites capable of holding ammonia between 200° and 300°C.

The minimum in the polymeric complex–preadsorption temperature curve between 200° and 300°C is consistent with the concept that there is a distribution of site energies on the catalyst in which those of intermediate energy are most important in reaction (*8*). At 25°C concentrations of ammonia less than saturation will cover some, but not all, sites completely down the energy scale as shown in Fig. 5. The ammonia is so "smeared out" over all site energies that few sites important in reaction are affected. The results are that the amount of polymeric complex formed is not reduced appreciably. At 100°C the same quantity of ammonia must distribute itself over a much

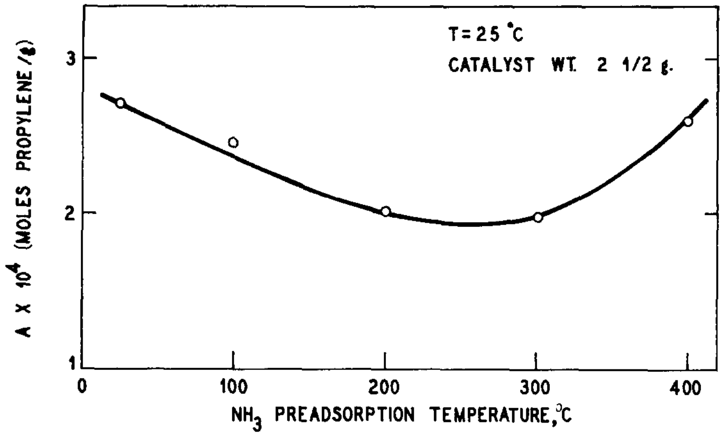

FIG. 4. Polymeric complex on silica-alumina as a function of preadsorption temperature for constant NH_3 coverage, 0.240×10^{-4} moles/g.

narrower range of site energies. More sites important in reaction are now poisoned, and there is a concomitant decrease in the amount of polymeric complex formed. This trend continues at 200°C. At 300°C, however, there are sites of intermediate energy that can no longer retain ammonia and are available for reaction. This reverses the downward trend in polymeric complex formation and produces the minimum in the polymeric complex–temperature curve. Ammonia preadsorbed at 400°C resides largely on sites at the high-energy end of the scale, which are less active for complex formation, leaving the sites of intermediate energy most important in reaction less affected. Hence, for quantities of ammonia less than saturation there is a point between 200° and 300°C where a small change in preadsorption temperature just redistributes the ammonia over the active sites leaving the number of active centers unchanged.

The data for propylene polymeric complex formation as a function of ammonia saturation temperature are plotted in Fig. 6. The polymeric complex–preadsorption temperature curve for the saturation concentrations is almost identical with that for 1-butene (*4*). In both cases polymeric complex formation does not commence until the preadsorption temperature exceeds 200°C. Calculation of the number of propylene molecules denied per mole of ammonia preadsorbed at 200°C indicates that the propylene is adsorbed on the average as tetramer—the same as that calculated for 1-butene. In

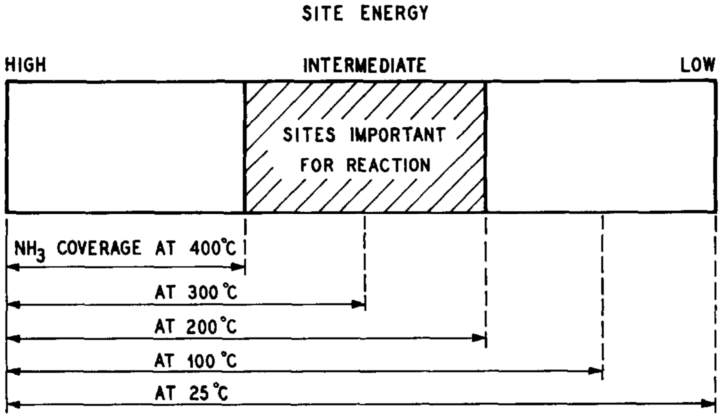

FIG. 5. Site energy scale.

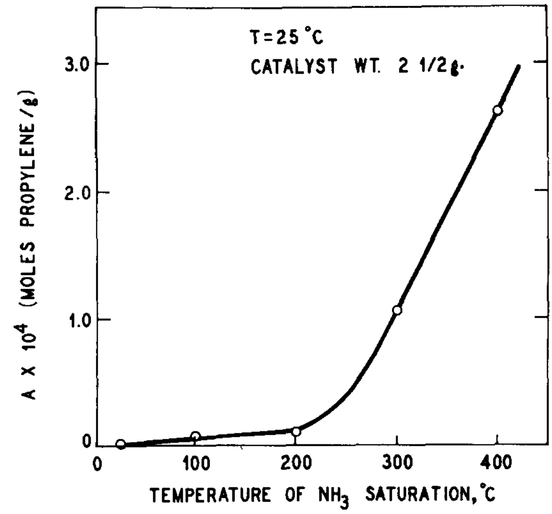

FIG. 6. Propylene polymeric complex formation on NH_3-saturated silica-alumina.

view of these similarities it is not surprising that the propylene polymeric complex is just as effective for 1-butene isomerization as is the butene polymeric complex.

The site energy model shown in Fig. 5 can be used to explain the data presented in Fig. 6. Here the ammonia saturates all sites down the energy scale to the point where the sites have insufficient energies with respect to kT to hold the molecules. According to Fig. 6 it is necessary for the saturation temperature to exceed 200°C before any sites of intermediate energy are available for reaction. This is just the point where the onset of polymeric complex formation is observed. Saturations at 300° and 400°C leave more sites of intermediate energy and high energies available for reaction, as evidenced by the increase in polymeric complex formation.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Phillips Petroleum Company for permission to publish this work and to Mr. R. L. Brown who carried out most of the experimental measurements.

REFERENCES

1. OZAKI, A., AND KIMURA, K., *J. Catalysis* **3**, 395 (1964).
2. GERBERICH, H. R., LARSEN, J. G., AND HALL, W. K., *J. Catalysis* **4**, 523 (1965).
3. HIGHTOWER, J. W., AND HALL, W. K., *J. Am. Chem. Soc.* **89**, 778 (1967).
4. CLARK, A., *Ind. Eng. Chem.* **59**, 29 (1967); CLARK, A., AND FINCH, J. N., Preprints of Fourth International Congress On Catalysis, Moscow, June 1968, Paper No. 75.
5. CLARK, A., FINCH, J. N., AND ASHE, B. H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, p. 1010.
6. LARSEN, J. G., GERBERICH, H. R., AND HALL, W. K., *J. Am. Chem. Soc.* **87**, 1880 (1965).
7. HIGHTOWER, J. W., AND HALL, W. K., "Preprints of the Division of Petroleum Chemistry, American Chemical Society meeting, Chicago, Illinois, 1967," Vol. 12, No. 3, p. 191.
8. HOLM, V. C. F., AND CLARK, A., *J. Catalysis* **2**, 16 (1963).