JOURNAL OF CATALYSIS 2, 16–20 (1963)

The Nature of Silica-Alumina Surfaces II. Cracking of *n*-Octane, Polymerization of Propylene, o-Xylene Isomerization, Hydrogen Transfer, and H-D Exchange

VERNON C. F. HOLM AND ALFRED CLARK

From the Phillips Petroleum Company, Research Division, Bartlesville, Oklahoma

Received June 4, 1962

In Part I the thermodynamics of ammonia adsorption on eleven silica-alumina gels ranging from pure alumina to pure silica was presented. In this paper, thermodynamic quantities are shown to correlate qualitatively with catalytic reactions occurring on these materials. The catalyst compositions showing highest activity for acid-type reactions are those possessing the highest differential surface entropies, indicating mobile adsorption.

I. INTRODUCTION

The importance of acid-type catalysts in petroleum processing has stimulated a considerable amount of research on the adsorptive and acid properties of solid surfaces and the correlation of these properties with catalytic activities (*1–12*).

A previous paper (*13*) in this series presented thermodynamic data for the adsorption of ammonia on eleven silica-alumina gels ranging from pure alumina to pure silica. In this paper the activities of these catalysts are given for the reactions: *n*-octane cracking, propylene polymerization, *o*-xylene isomerization, hydrogen transfer (1-butene-decalin), and H-D exchange.

II. EXPERIMENTAL

Catalyst preparation. The silica-alumina compositions were coprecipitated from solutions of sodium silicate and sodium aluminate as described previously (*12*). Silica gel was made by a similar procedure from sodium silicate. Alumina was obtained by heat treatment of high-purity β-alumina trihydrate from Davison Chemical Corporation; the resulting material was η-alumina. All adsorbents were heated in granular form for 16 hr at 550°C in a stream of dry air and stored prior to use under dry conditions. Surface areas and other properties are given in a previous publication (*13*).

Apparatus and procedures. The apparatus employed for the *o*-xylene isomerization and the *n*-octane cracking tests was basically the same as that used for studying propylene polymerization, described previously (*14*). It consisted of a 16-mm outside diameter glass reactor, furnace, temperature controller, a feed buret for liquids or flow meter for gases, and conventional product-collection accessories appropriate to the reaction being studied. In each of the above tests, 10 ml of catalyst was employed.

Normal octane cracking tests were carried out at 550°C and a liquid hourly space rate of one with a run duration of 1 hr. The *ortho*-xylene isomerization tests were 1-hr runs at 350°C with a liquid hourly space rate of two. The hydrogen transfer reaction between decalin and 1-butene was carried out at 340°C, a liquid hourly space rate of decalin of 1.6 and a gaseous hourly space rate of 1-butene of 350, as described in a previous publication (*15*). Propylene polymerization tests were carried out, as previously described, in a rising-temperature reactor with a gaseous hourly rate of 250. The results are reported for the temperature of maximum conversion which was approximately 210°C for all catalysts. The hydrogen-deuterium exchange tests at 200°C have been described previously (*16*). The hydrogen transfer and hydrogen-deuterium exchange data represent tests made on a different series of silica-alumina catalysts but which were prepared by the same procedure described above.

III. Results and Discussion

The results for propylene polymerization, hydrogen transfer, and H-D exchange, reported previously (*14, 15, 16*), are included here along with new information on *n*-octane cracking and *ortho*-xylene isomerization. In Fig. 1, the conversion per square meter of catalyst surface for each of the five reactions is plotted against catalyst composition. All of the reactions except H-D exchange behave similarly. Conversions show maxima between 70 and 85% silica, fall off sharply on the high-silica side and more gradually on the low-silica side. They can be related to the differential entropies ($\bar{S}_\Gamma$) of adsorbed ammonia reported in Part I (*13*). There it was shown that $\bar{S}_\Gamma$ isotherms start at low values at low coverages, rise rapidly, level out, then fall if adsorbate–adsorbate interaction occurs. The maximum value attained by $\bar{S}_\Gamma$ varies with silica-alumina composition and is a measure of the maximum mobility attained.

In Fig. 2, the difference between maximum $\bar{S}_\Gamma$ (at 150°C) and the calculated differential entropy ($\bar{S}_{\Gamma m}$) of an ideal two-dimensional gas at the same concentration and temperature is plotted against silica-alumina composition. This is equivalent to adjusting entropies ideally to a standard surface state with the calculated entropy $\bar{S}_{\Gamma m}$ as the zero of reference. (The data for this curve were taken from the original plots of Fig. 6, Part I (*13*). The curve in Fig. 2 shows the same general pattern as the curves in Fig. 1. Plots of (max. $\bar{S}_\Gamma - \bar{S}_{\Gamma m}$) at other temperatures are relative to the plot at 150°C shown in Fig. 2. They differ by the addition of approximately 3–4 entropy units to the ordinate value of each point for each increase of 50°C in temperature, as may be seen from Fig. 6, Part I (*13*).

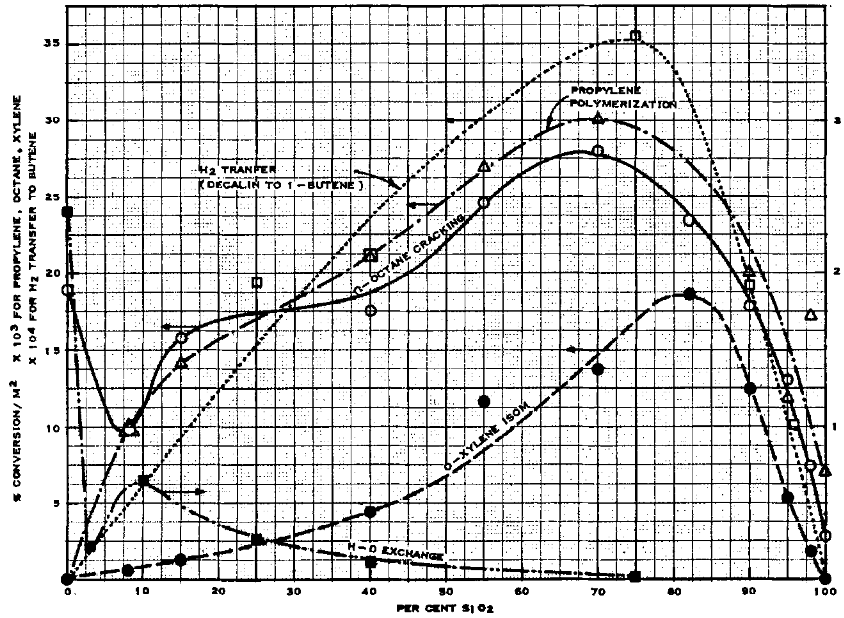

Fig. 1. Activity vs. silica-alumina composition.

Provided ammonia molecules reflect the

same relative adsorption characteristics as other electron-donating adsorbates, it is reasonable to infer that carbonium ion reactions such as propylene polymerization, xylene isomerization, hydrogen transfer, and *n*-octane cracking proceed most rapidly in the neighborhood of weak sites where the mobility of adsorbate is high and desorption of products is rapid. It should be stressed that the correlation obtained between entropy and catalytic activity does not prove conclusively that reaction proceeds on the weak sites. This is an inference that will require further work to prove.

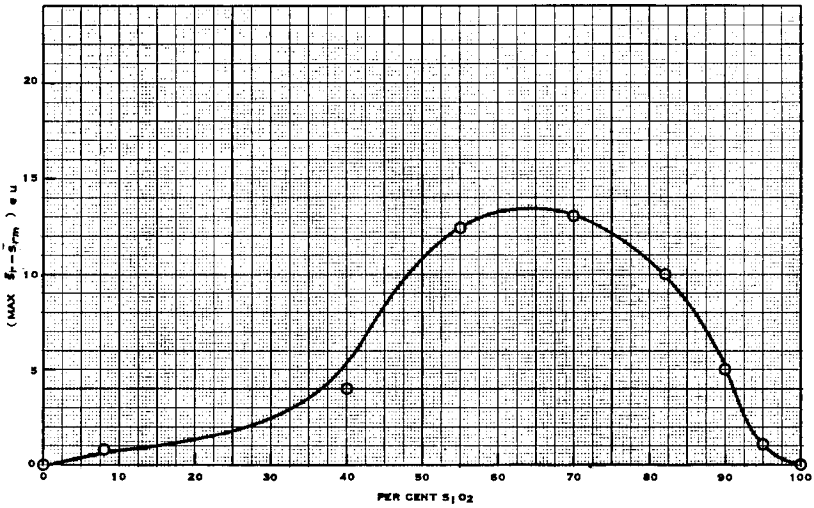

Fig. 2. Relative maximum mobility of adsorbed ammonia (max $\bar{S}_\Gamma - \bar{S}_{\Gamma m}$) vs. silica-alumina composition.

Conversions for the H-D exchange reaction behave differently (Fig. 1). Highest conversions are obtained in the high-alumina region. Since H–H and D–D bonds must be broken for this reaction to proceed, high concentrations of strong adsorption sites are probably required. This is in agreement with the data presented in Part I (*13*) where it was shown that there is a rapid increase in the concentration of strong sites as the composition approaches that of pure alumina. We have no clear explanation for the small loop between 0 and 10% silica. The presence of this loop has been verified repeatedly.

Figure 1 shows a sharp rise in the conversion of *n*-octane as pure alumina is approached. We believe that in the region to the left of the maximum the over-all reaction is a composite of reactions favored by weak sites (alkane scission, etc.) and those favored by strong sites (alkane dehydrogenation and dehydrocyclization). Close to the pure alumina axis, the concentration of strong sites with adsorption entropies for ammonia less than those of an ideal two-dimensional gas increases rapidly. Conversion by dehydrogenation and dehydrocyclization increases correspondingly.

In Fig. 3, information is presented on the changing nature of the products formed from *n*-octane cracking as a function of silica-alumina composition. The mole ratio of isoalkenes to *n*-alkanes (C_4–C_5) reaches a maximum at approximately 80% silica where the concentration of weak sites (mobile adsorption) is high. The mole ratio of olefins to alkanes (C_2–C_5) reaches a minimum at the same point. The ratio is significantly below unity at this point, indicating that some of the olefins formed by scission of *n*-octane have been used up in further reactions. At the high-silica end, beyond the minimum, the olefin: alkane ratio rises steeply. The total conversion of *n*-octane is very small in this region because of the low concentration of adsorption sites on these compositions. A large part of the conversion is thermal. At the high-alumina end, the ratio drops. This is attributed to increase in production of aromatics as shown in Fig. 3 by plots of the mole ratios of aromatics:*n*-octane cracked and hydrogen:*n*-octane cracked.

The data plotted in Fig. 3 are based on runs at constant space velocity and temperature and represent a range of conversions. The general shapes of the selectivity curves with their maxima and minima are not critical with respect to conversion level. For example, when the conversions of the high-alumina catalysts (0–30% SiO_2) are increased until they are equal to those of catalysts containing higher silica contents (50–85% SiO_2), the selectivity ratios are not changed by more than 10%, approximately. The selectivities shown are not due to kinetic effects dependent on conversion levels, but are primarily functions of the catalyst composition.

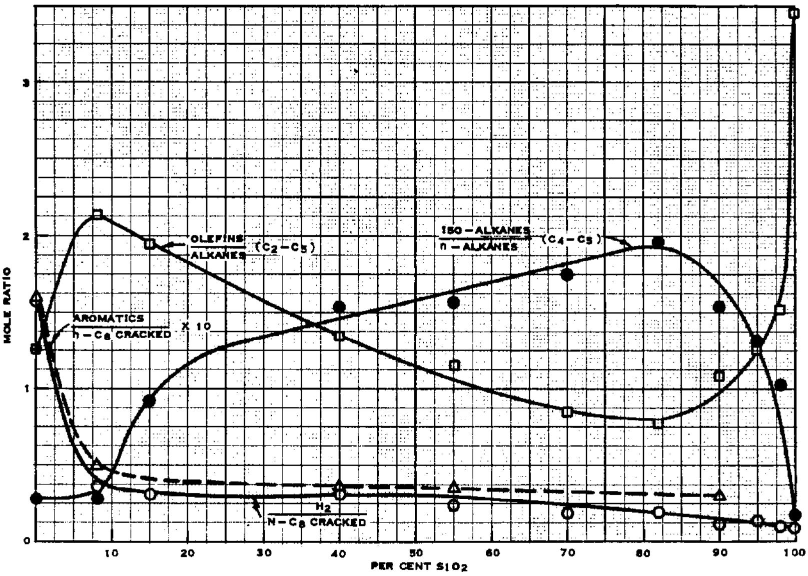

FIG. 3. Mole ratios showing variation in hydrogen formation, ratio isoalkanes to *n*-alkanes, ratio olefins to alkanes, and ratio aromatics to *n*-C_8 cracked in *n*-C_8 cracking over silica-aluminas.

Of all the reactions that show maxima at the high-silica end in Fig. 1, *ortho*-xylene isomerization follows the entropy curve of Fig. 2 in detail better than the others. We can only speculate about the differences in detail at present. It is interesting to note that the *n*-octane curve in Fig. 1 assumes the character of the H-D curve near the alumina axis where dehydrogenation and dehydrocyclization play a more prominent role in the various reactions of *n*-octane cracking. It will also be noted in Fig. 1 that the reactions of propylene polymerization and hydrogen transfer do not fall off as rapidly in conversion as *ortho*-xylene isomerization on the alumina side beyond the maximum. Possibly the former reactions do not depend strictly on the weak sites alone. For example, propylene chains may grow on strong sites as long as there are sufficient weak sites from which adsorbate can be fed rapidly to the growing chains. Conversions would still decrease with decreasing concentrations of weak sites, but not so rapidly. *Ortho*-xylene isomerization, on the other hand, presumably is a monomolecular reaction whose rate is more strictly a function of the weak sites alone.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Phillips Petroleum Company for permission to publish this work.

REFERENCES

1. OBLAD, A. G., MILLIKEN, T. H., JR., AND MILLS, G. A., *Advances in Catalysis* **3,** 199 (1951).
2. THOMAS, C. L., *Ind. Eng. Chem.* **41,** 2565 (1949).
3. TAMELE, M. W., *Disc. Faraday Soc.* **8,** 270 (1950).
4. JOHNSON, O., *J. Phys. Chem.* **59,** 827 (1955).
5. TRAMBOUZE, Y., *Compt. rend.* **233,** 648 (1951).
6. TRAMBOUZE, Y., DE MOURGUES, L., AND PERRIN, M., *J. Chim. Phys.* **51,** 723 (1954).
7. STRIGHT, P., AND DANFORTH, J. D., *J. Phys. Chem.* **57,** 448 (1953).
8. MAPES, J. E., AND EISCHENS, R. P., *J. Phys. Chem.* **58,** 1059 (1954).
9. HANSFORD, R. C., *Ind. Eng. Chem.* **39,** 849 (1947).
10. OBLAD, A. G., HINDEN, S. G., AND MILLS, G. A., *J. Am. Chem. Soc.* **77,** 535, 538 (1955).
11. PLANK, C. J., *J. Phys. Chem.* **57,** 284 (1955).
12. HOLM, V. C. F., BAILEY, G. C., AND CLARK, ALFRED, *J. Phys. Chem.* **63,** 129 (1959).
13. CLARK, ALFRED, HOLM, V. C. F., AND BLACKBURN, D. M., *J. Catalysis* **1,** 244 (1962).
14. HOLM, V. C. F., BAILEY, G. C., AND CLARK, ALFRED, *Ind. Eng. Chem.* **49,** 250 (1957).
15. BLUE, R. W., AND ENGLE, C. J., *Ind. Eng. Chem.* **43,** 494 (1951).
16. HOLM, V. C. F., AND BLUE, R. W., *Ind. Eng. Chem.* **43,** 501 (1951).