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Selective Hydrogenolysis of Methylcyclopropane over Bifunctional Catalysts

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Hydrogenation of methylcyclopropane proceeds at vastly different rates to yield isobutane or *n*-butane. The ratio of these rates at 0°C, called here selectivity, has been studied at 0°C on a platinum catalyst supported on silica gel. The selectivity was about 20 when the catalyst was used alone or was mixed with a 19-fold excess of Vycor or Cabosil silica gel. But when the catalyst was mixed with alumina or silica gel diluents containing more acidic sites, the selectivity dropped to values as low as 0.1. This change is attributed to isomerization on the diluent to *n*-butene followed by hydrogenation to *n*-butane on the metal. True bifunctional catalysis is indicated by enhanced activity of the acidic function as a result of its being kept clean by the hydrogenating function of the metal.

INTRODUCTION

One of the major novel applications of heterogeneous catalysis in the past twenty years has been the reforming of petroleum to produce high-quality gasolines. Our understanding of the many reactions that take place during catalytic reforming has increased considerably since Haensel first patented a catalyst found to be particularly effective for certain reforming reactions (*1*). The initial report contained few details about the catalyst or its mode of action, but data were presented to show that the platinum-containing catalyst was well suited for isomerizing and dehydrogenating saturated hydrocarbons (*2*).

Such was the beginning of the study of bifunctional catalysts, so-called because they contain a metal component such as platinum, palladium or nickel for catalyzing hydrogenation and dehydrogenation and an acidic component such as alumina or silica–alumina for promoting skeletal isomerization via carbonium ion intermediates. The latter were first clearly recognized by Ciapetta from the product distribution of several reactions over a nickel catalyst supported on silica–alumina (*3*). Mills and coworkers provided a more detailed description of the reaction network by testing the catalytic properties of each "function" (hydrogenation–dehydrogenation or acidic) of their catalyst separately and comparing the results with those for their bifunctional catalyst (*4*). For isomerization, their data indicate that a saturated hydrocarbon is first dehydrogenated to an olefin on the metal, then transfers to the acidic support to be isomerized, and finally returns to the metal for rehydrogenation. This basic explanation of the mode of action of a bifunctional catalyst is generally accepted today.

The mechanism for the transfer of the intermediates between the two types of catalytic sites was clarified for isomerization reactions by Weisz and Swegler (*5*) and for dehydroisomerization reactions by Hindin, Weller and Mills (*6*). By isolating the dehydrogenation and isomerization sites on separate particles, these authors were able to show that transport of intermediate species can take place via the gas

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phase. Such gas-phase olefin intermediates were invoked quite convincingly by Sinfelt, Hurwitz and Rohrer to explain their kinetic results for the bifunctional catalysis of petane isomerization (*7*).

In the course of our study of supported platinum catalysts for hydrogenation reactions, we observed an example of bifunctional catalysis that differs from the general pattern described above where the initial interaction of the hydrocarbon reactant with the catalyst is on the metallic sites. By contrast, we have found that methylcyclopropane is first isomerized on the acid sites with subsequent hydrogenation on the metal of the olefin produced in the previous reaction. The details of the experiments that led us to this conclusion are given in this paper.

EXPERIMENTAL

The reaction of methylcyclopropane with hydrogen was studied in a Pyrex batch-recirculation system under conditions designed to eliminate gradients in both concentration and temperature (*8*). The reactor itself was a glass chamber 30-mm in diameter and about 15-mm high with a medium grade fritted disc to support the catalyst. One experiment required a special reactor, similar in design to the normal one but made taller to provide for two fritted discs so that the catalyst mixtures could be separated. The temperature was measured with a thermocouple inserted into a well extending through the reactor wall to a point just above the center of the fritted disc. A glass coil above the reactor served to preheat or precool the reaction gases. The gases were recirculated over the catalyst by a Teflon bellows pump capable of producing well-controlled and reasonably steady flow rates (*9*). The pump was driven by compressed nitrogen rather than air to avoid any possibility of contamination resulting from the diffusion of oxygen through the bellows. A flow rate of 500 cc/min was used in a system of 2.55-liter total volume, and 23-cc samples were withdrawn at ten-minute intervals for chromatographic analysis.

The methylcyclopropane was an API Standard Sample containing 0.052 ± 0.006 mole % impurity (shown to be normal butane), and it was used without further purification. The hydrogen, starting at 99.93% purity, was diffused through a palladium thimble to remove trace impurities, while the helium was designated as 99.995% and was only passed through a glass coil at −195°C before use.

Catalysts containing 0.5% and 2.5% platinum, prepared according to the method of Benesi, Curtis and Studer (*10*) and provided by Dr. H. A. Benesi, were reduced in flowing hydrogen at 400°C before being put into the reactor. The platinum surface areas were determined according to the technique of Benson and Boudart (*11*); the dispersion (ratio of surface to total platinum atoms) was 0.61 for the 0.5% Pt/SiO_2 catalyst and 0.58 for the 2.5% Pt/SiO_2 sample. These values were obtained both before and after the pretreatment described below. The Vycor used as a diluent was simply tubing crushed in a mortar and pestle; no attempt was made to determine its surface area. The Cabosil, Cabot Corporation's HS-5, was pressed at 10,000 psi and then crushed to the desired particle size. Cabot reported its surface area to be 325 ± 25 m^2g^{-1}. The alumina was the η-form prepared by calcination of Davison β-alumina trihydrate for four hours at 593°C; it was supplied by Esso Research and Engineering Company with a reported surface area of 296 m^2g^{-1}. The Davison silica gel was Grade 40, 6/12 mesh, and it was crushed and calcined four hours at 540°C before use. The surface area was believed to be about 400 m^2g^{-1}. The silica–13% alumina was also from Davison, who indicated an area of 550 m^2g^{-1}. It was supplied in pellet form and was crushed before use. All diluents were used as 48/100 mesh (150–300 μm) particles; the catalysts were 60/200 mesh. The components were mixed by shaking in the reactor until the 25 mg of catalyst particles appeared to be uniformly distributed in the 475 mg of diluent.

The pretreatment of the mixture involved a one-hour evacuation at 150°C after which hydrogen flowing at 100 cc/

min was started through the reactor while the temperature was raised to 400°C. After four hours at 400°C the sample was cooled in flowing hydrogen and evacuated for ten minutes just prior to admitting the reactant mixture. If after the reaction the hydrogen flow was restarted through the reactor while the temperature was raised to 400°C for two hours, the activity of the catalyst was retained.

The reactant mixture consisted of 10 Torr methylcyclopropane, 50 Torr hydrogen, and 700 Torr helium diluent to give one atmosphere total pressure. While the catalyst was being cooled to 0°C for a run, the reactants were circulated through the system (bypassing the catalyst) to provide a uniform composition. The reaction was followed by periodic analysis of gas samples in a Varian-Aerograph A-90-P chromatograph equipped with a 10-ft dimethylsulfolane on firebrick column at room temperature. This column gave good resolution of the butanes and 1-butene, but the *cis*-2-butene overlapped the large methylcyclopropane peak that completely hid the *trans*-2-butene. However, none of the three *n*-butenes dominated the products of the isomerization reaction (*12*), and since a quantitative measure of the individual butenes present was not essential the separation was considered adequate.

The reaction rate was taken as the initial slope of the plot of product concentration *vs* time. The detectability limit of our chromatograph was about 10^{-6} mole in the system; so rates below 0.03×10^{-8} mol/sec (no visible product after one hour) were recorded as zero reaction. Conditions were such that all the catalyst mixtures gave convenient levels of conversion; the lowest rates, about 0.15% per pass (2% overall), were well within the sensitivity of the analysis, while the highest rate (exclusive of SiO_2–Al_2O_3 mixtures) of 1.2% per pass could still be studied in the absence of gradients in the system. In most cases the plots of the data were linear: where slight curvature appeared it was still easy to determine the initial slope. The high activity and variety of reactions over SiO_2–Al_2O_3 caused more pronounced curvature in the data, but the resulting uncertainties did not affect the interpretation of the results.

RESULTS

The reaction of methylcyclopropane with hydrogen can produce either of two products, isobutane or normal butane. In the work presented here, the selectivity, that is, the ratio of the rates of formation of the two products, varied over more than two orders of magnitude, when the catalyst was mixed with various diluents.

The data in Table 1 show that the selectivity falls into three distinct groups. The uncertainty in the rates is about 10% (20% in the case of rates lower than 0.1×10^{-8} mol/sec), but this does not alter the basic conclusions to be drawn. It also should be noted that in cases where normal butane was formed in appreciable quantities the rate deteriorated slightly during the run even though the isobutane activity remained constant. The catalyst alone gave primarily isobutane with the same selectivity as has been observed by others (*13*), and the addition of crushed Vycor glass or Cabosil to the catalyst had little effect. When alumina was added, however, the selectivity dropped by a factor of four. The isobutane formation was slightly faster than in the other runs, but the dominant new feature was the five-fold increase in normal butane production. This latter rate could be further increased by a higher temperature (500°C) pretreatment although the isobutane rate remained nearly the same.

Davison silica gel had an even more pronounced effect on the normal butane rate which now surpassed the rate over alumina mixtures by a factor of 20–30. The rate of isobutane formation, however, was the same as observed with the apparently inert diluents, Vycor and Cabosil. It was interesting to find also that when the catalyst and diluent were separated in the two-level reactor with the catalyst on the lower level, the diluent on the upper level and the gases flowing from above to below, the selectivity was maintained although the absolute activities dropped somewhat. The

TABLE 1
PRODUCTS OF METHYLCYCLOPROPANE HYDROGENATION OVER DILUTED PLATINUM CATALYSTS

Catalyst[a]	Diluent[a]	Rate (10^{-8} mol/sec) at 0°C				Selectivity = $\frac{i\text{-butane}}{n\text{-butane}}$
		i-C_4H_{10}	n-C_4H_{10}	1-C_4H_8	*cis*-2-C_4H_8	
	SiO_2	0	0	1	<1	
	SiO_2-13% Al_2O_3	0	0	30	50	
0.5% Pt/SiO_2		1.4	~0.06	0	0	23
0.5% Pt/SiO_2	Vycor	1.1	~0.06	0	0	19
0.5% Pt/SiO_2	Cabosil	1.1	~0.05	0	0	22
2.5% Pt/SiO_2	Cabosil	1.8[b]	0.08[b]	0	0	22
0.5% Pt/SiO_2	Al_2O_3	1.5	0.3	0	0	5.0
0.5% Pt/SiO_2	Al_2O_3[c]	1.8	0.7	0	0	2.6
0.5% Pt/SiO_2	SiO_2	1.2	8.	0.2	0	0.15
0.5% Pt/SiO_2	SiO_2[d]	0.6	6.	0	0	0.10
0.5% Pt/SiO_2	SiO_2-13% Al_2O_3	0	16.	24	84	0

[a] 25 mg catalyst and 475 mg diluent in all cases.
[b] corrected for platinum surface area.
[c] 500°C pretreatment.
[d] catalyst separated from diluent.

silica alone was inert for hydrogenation under the standard reaction conditions, but it showed a slight ability to isomerize the methylcyclopropane to butenes. There was a much larger isomerization activity with the silica–alumina sample, again in the absence of hydrogenation products. When the platinum catalyst was mixed with the silica–alumina, there was no isobutane observed at all; yet the normal butane rate was twice that observed for any other catalyst, and appreciable butene concentrations were observed.

DISCUSSION

The most striking feature of the tabulated data is the relative constancy of the isobutane rate while the normal butane rate ranges over two orders of magnitude. The mixture containing silica–alumina is a somewhat special case, and it will be discussed later. Clearly, the platinum favors isobutane formation over normal butane, and the reasons for that are discussed elsewhere (*13*, *14*). The addition of Vycor or Cabosil as a diluent diminishes the overall activity slightly but otherwise does not affect the reaction pattern. Small amounts of contaminants could account for both the activity decrease of the 0.5% catalyst and the higher specific activity of the sample with 2.5% platinum.

The other diluents which were tried—alumina, Davison silica, and Davison silica–13% alumina—all form normal butane to a lesser or greater degree when mixed with the catalyst. This is a clear-cut example of bifunctional catalysis since individually neither component forms the normal butane product. The path of the reaction involves the adsorption and isomerization of methylcyclopropane to one of the normal butenes (*12*) on the acidic oxide sites and then transport via the gas phase to the platinum for hydrogenation. The conclusion that the transport of butenes is through the gas phase is based on the fact that separating the two components does not change the selectivity. The isomerization reaction of cyclopropane and its derivatives has been exhaustively studied (*12*, *15*, *16*), and the relative activities for the isomerization reaction are SiO_2–Al_2O_3 > Al_2O_3 > > SiO_2. This order is in agreement with our data except in the case of the Davison silica, which is more active than alumina for isomerization in our system. The explanation must be that acidic silica–alumina impurities are present in the Davison silica and that these are responsible for its unusually high isomerization activity. This was at least qualitatively verified using a measurement of surface acidities by ammonium ion adsorption; the Davison SiO_2 has about three times as many Brönsted sites ($\sim 1.5 \times 10^{13}$ cm^{-2}) as the Cabosil. It can be inferred also that the deterioration in the rate of production of normal butane results from the deactivation of the diluent; this explains why the isobutane activity is not affected.

The data show that the hydrogenation of the butenes is much faster than the hydrogenation of the methylcyclopropane; thus the platinum is very efficient in keeping the gas-phase butene concentration low. This is especially obvious in the mixtures with the Davison silica since the normal butane is being formed at seven times the rate of isobutane despite the existence of only a minute amount of gas-phase butene. The silica–13% alumina is a special case because of its very high isomerization activity at 0°C. The butenes are produced in such large quantities that the entire platinum surface is converting them to normal butane; the methylcyclopropane is not active enough to give a detectable amount of isobutane under these conditions. This represents a significant shift away from the situation with the other diluents. In those cases the platinum forms isobutane from methylcyclopropane at its normal, i.e., undiluted, rate and still has sufficient surface sites to convert any butenes formed on the diluent to normal butane. The silica–alumina, on the other hand, forms butenes so fast that the hydrogenation sites on the metal are not active enough to prevent a large build-up of butenes in the gas phase. The olefins must be adsorbed much more strongly than the methylcyclopropane since, in spite of the fact that at their highest concentration the total butenes never exceed 50% of the methylcyclopropane, the absence of isobutane indicates that the methylcyclopropane is not reaching the platinum surface in measurable quantities. Bond, Newham and Wells reached the same conclusion when they studied the reaction of methylenecyclopropane with hydrogen on a platinum–pumice catalyst (*17*).

A feature of this reaction which differentiates it from the classical examples of dual-function catalysis, is initiation on the acidic sites rather than on the hydrogenation–dehydrogenation sites as is normally the case. At first glance this might appear to be a trivial example of dual-function catalysis since the two successive reactions can and do occur even when the catalytic functions are separated by a considerable distance. A comparison of the isomerization activity of the Davison silica with the normal butane rate over the silica in the presence of platinum shows, however, that there is in fact a synergistic effect when both components are present in the system. It seems likely that *by hydrogenating the gas-phase olefins as fast as they are formed the platinum reduces the poisoning of the isomerization sites.* In this sense the work reported here bears some similarities to the hydro-isomerization of butane on a catalyst consisting of platinum supported on very acidic sites as discussed by Haensel and Bloch (*18*). These authors believe that, in that reaction also, the reactant *n*-butane first reacts by hydride abstraction on the acidic function. This initiation process is followed by a chain reaction on the acidic sites. Platinum is believed, in that case, to maintain catalyst cleanliness by hydrogenation of precursors of carbonaceous residues.

CONCLUSION

The selectivity of a reaction can be affected substantially by running it on a bifunctional catalyst, the first function of which involves carbonium ion intermediates with the second function being of the hydrogenating type. While both functions can be separated in principle, a sizable gain in activity can be achieved with cooperation between the acidic and the metallic functions, presumably because the latter keeps the former clean, as has been assumed previously in catalytic practice (*18*).

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REFERENCES

1. Haensel, V., U. S. Patents 2,479,109 and 2,479,110 (1949).
2. Haensel, V., and Donaldson, G. R., *Ind. Eng. Chem.* **43**, 2102 (1951).
3. Ciapetta, F. G., *Ind. Eng. Chem.* **45**, 162 (1953).
4. Mills, G. A., Heinemann, H., Milliken, T. H., and Oblad, A. G., *Ind. Eng. Chem.* **45**, 134 (1953).
5. Weisz, P. B., and Swegler, E. W., *Science* **126**, 31 (1957).
6. Hindin, S. G., Weller, S. W., and Mills, G. A., *J. Phys. Chem.* **62**, 244 (1958).
7. Sinfelt, J. H., Hurwitz, H., and Rohrer, J. C., *J. Phys. Chem.* **64**, 892 (1960).
8. Schlatter, J. C., and Boudart, M., *J. Catal.*, unpublished.
9. Bernard, J. R., and Teichner, S. J., *Bull. Soc. Chim. Fr.*, **36**, 3798 (1969).
10. Benesi, H. A., Curtis, R. M., and Studer, H. P., *J. Catal.* **10**, 328 (1968).
11. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
12. Hightower, J. W., and Hall, W. K., *J. Amer. Chem. Soc.* **90**, 851 (1968).
13. Bond, G. C., and Newham, J., *Trans. Faraday Soc.* **56**, 1501 (1960).
14. Irwin, W. J., and McQuillin, F. J., *Tetrahedron Letters* **18**, 2195 (1968).
15. Hall, W. K., Lutinski, F. E., and Gerberich, H. R., *J. Catal.* **3**, 512 (1964).
16. Larson, J. G., Gerberich, H. R., and Hall, W. K., *J. Amer. Chem. Soc.* **87**, 1880 (1965).
17. Bond, G. C., Newham, J., and Wells, P. B., *Proc. Int. Congr. Catal. 2nd,* **1177** (1960).
18. Haensel, V., and Bloch, H. S., *Platinum Metals Rev.* **8**, 2 (1964).