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The Structure and Activity of Chromium Oxide Catalysts

II. Influence of Catalyst Structure on Activity for Reactions of Cyclopropane

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The initial rates for cyclopropane isomerization and hydrogenolysis on amorphous (catalyst A) and crystalline (catalyst C) chromium oxide are reported. Based on the overall specific rates or turnover numbers, cyclopropane hydrogenolysis is sensitive and isomerization insensitive to the catalyst structure. The activation energies for both reactions are greater on catalyst C than on A, but a strong compensation effect is operative. The changes in activity which accompany catalyst structural changes do not appear to be closely related to changes in pore size, site density or mechanism, but are interpreted in terms of the influence of catalyst structure on site activity.

INTRODUCTION

In the preceding paper (*1*) we reported on a detailed structural analysis of two forms of chromium oxide catalysts. Catalyst A was shown to be amorphous in the usual sense but appears to possess local order of the same kind as α-chromium oxide over a dimension of the order of 10 Å. Catalyst C contains a broad distribution of α-chromium oxide microcrystallites with an average crystallite size of the order of 100 Å. The influence of the structure change (i.e., when the catalyst form is converted from A to C) on the catalytic activity of chromium oxide for the isomerization and hydrogenolysis of cyclopropane is the subject of the present paper. Some preliminary results on the same reactions of methylcyclopropane are also included.

It has been found that with supported metal catalysts hydrogenation, dehydrogenation and hydrogenolysis reactions are generally insensitive to the structure of the catalyst (facile reactions) while isomerizations tend to be structure-sensitive (demanding reactions) (*2*). In the present study the hydrogenolysis and isomerization of cyclopropane were selected to provide one test reaction in each of these categories for study with respect to the structure of an oxide catalyst. It was hoped that experimental conditions could be found where the two reactions could be run competitively, allowing direct measurement of a selectivity between the two parallel reaction paths as a function of catalyst structure and avoiding the difficult problems associated with comparison of rates measured in separate experiments (*2*). Unfortunately, these conditions were not attainable, so in the present work we resort to a comparison of specific activity of the two catalyst forms for the two test reactions.

The hydrogenolysis of cyclopropane on chromium oxide has been observed as a side reaction in a study of deuterium exchange of cycloalkanes (*3*); the isomeri-

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zation of cyclopropane on chromium oxide has not been previously investigated.

EXPERIMENTAL

Materials. The materials and the preparation and activation of the chromium oxide catalyst have been described in the preceding paper (*1*). Hydrogen was purified by diffusion through a palladium–25% silver thimble supplied by Englehard Industries, Inc.; helium was purified by diffusion through a glass capillary cell supplied by Electron Technology, Inc. The cyclopropane used was Matheson C. P. grade and the methylcyclopropane was supplied by Chemical Procurement Laboratories; gas chromatographic analyses indicated a purity for these materials of 99.86 and 96.42 mol %, respectively. The cycloalkanes were passed through an olefin adsorbent of mercuric acetate and mercuric nitrate prepared according to the prescription of Kerr and Trotman-Dickenson (*4*) and then over Linde 4A molecular sieves (cooled by a Dry Ice–acetone bath when cyclopropane was the reactant), prior to use.

Procedure. The reactions were carried out in a differential flow reactor containing about one gram of catalyst. Samples of the gas stream were removed with a Beckman pneumatic sample valve and analyzed chromatographically on a 30 ft 2:1 dimethylsulpholane–hexamethylphosphoramide on Anakrom column operated at 0°C. The initial specific reaction rates (moles converted per unit time per unit surface area) were calculated in the usual manner assuming negligible pressure changes to occur through the reactor at conversions of only a few per cent. The catalyst activity was observed to decrease steadily with time, but in all cases a Voorhies (*5*) type plot of specific reaction rate vs the square root of the time of catalyst utilization was found to be linear. Thus the initial reaction rates on the unpoisoned catalyst surface were determined by extrapolation of the linear decay function to zero time and a consistent comparison of catalytic activity could be obtained from these values. Between each run the catalyst was reactivated by slow heating to 400°C in flowing helium.

In order to minimize activity variations from one sample to the next, the activity of the same sample in both catalyst forms are compared. Thus, a sample of chromia gel was activated as previously described to give catalyst in form A and the activity for both isomerization and hydrogenolysis measured. Half the sample was then removed for X-ray analysis and BET surface area measurements. The remainder of the sample was reactivated to produce catalyst form C and the activity for both reactions again measured.

Calculations and experiments, which assure us that the observed reactions are not influenced by intraphase or interphase gradients or other extraneous effects, are given by Dyne (*6*). This reference should also be consulted for additional experimental details.

RESULTS AND DISCUSSION

The initial rates measured for cyclopropane isomerization on both chromium oxide catalyst A (amorphous) and C (crystalline) at 200°C are given in Table 1. One observes that the reproducibility of the rate on a given sample of either form is good (compare Experiments 23/7 with

TABLE 1
RATES OF CYCLOPROPANE ISOMERIZATION AT 200°C

Experiment[a]	Catalyst form	CP partial pressure (Torr)	Initial reaction rate (mmol/hr m^2)	R_C/R_A
21/7	C	762	0.0084	2.2
20/5	A	747	0.0038	
23/7	C	759	0.0144	2.1
23/9	C	764	0.0157	
22/7	A	763	0.0069	
22/9	A	766	0.0073	

[a] Experiments performed on the same sample of chromium oxide are grouped together. For example, following a series of experiments including 20/5 the same sample was converted into form C for the series of experiments including 21/7.

23/9 and 22/7 with 22/9) but is highly variable from sample to sample (compare Experiments 21/7 and 23/7 or 20/5 and 22/7). However, we are primarily interested in the effect of the structure change on the activity. If we use, for individual samples, the ratio of the initial rates on the two catalyst forms (which were prepared in the consecutive fashion described above) as a measure of this structural effect, we again obtain reproducible results. Since the activity ratios, R_C/R_A, for cyclopropane isomerization on chromium oxide at 200°C given in Table 1 are all of the order of unity, we conclude that this reaction is structure-insensitive or facile. It is interesting to compare this behavior with that of the side reactions which accompany the isomerization of cyclopropane. Small quantities of methane, ethane, ethylene and propane are formed from cracking and self-hydrogenation of cyclopropane at 200°C. The sum of these side products never exceeds 3 mol % of the major product, propylene, on catalyst A, but tends to be about twice as large on catalyst C, that is, the catalyst structure affects the side reactions in the same manner as it does the isomerization. This may suggest that all of the observed products are formed from the same intermediate.

The initial rates of cyclopropane hydrogenolysis on both chromium oxide catalyst forms A and C at 200°C are given in Table 2. Again, reproducible results are obtained from experiments on individual samples and again there is variation from sample to sample. The ratio of initial rates R_C/R_A, on the two forms is about 20, indicating that the hydrogenolysis of cyclopropane on chromium oxide at 200°C is a structure-sensitive or demanding reaction. This is contrary to common experience on supported metal catalysts where reactions between hydrogen and hydrocarbons are generally structure insensitive (*2*). On reflection, however, this result is perhaps to be expected. The deuterogenation of olefins on metals results in a wide spread of isotopically exchanged alkanes (*7*), but the same reaction on chromium oxide is very specific for the *cis*-addition of two atoms of deuterium across the double bond (*8*). That is, reactions between hydrocarbons and hydrogen on chromium are very specific (selective) and one intuitively assumes that a specific (selective) reaction will be a demanding reaction.

TABLE 2
CYCLOPROPANE HYDROGENOLYSIS AT 200°C

Experiment	Catalyst form	CP partial pressure (Torr)	Initial reaction rate (mmol/hr m^2)	R_C/R_A
21/5[a]	C	240[b]	0.0053	17.5
20/3	A	232	0.0003	
23/3	C	288	0.0113	21.8
23/5	C	250	0.0125	
22/3	A	263	0.0005	
22/5	A	243	0.0006	

[a] The sample used in experiments 21/5 and 20/3 is different from that used in 23/3, 23/5, 22/3 and 22/5.

[b] The total pressure was made equal to one atmosphere with hydrogen.

The activity ratios, R_C/R_A, for cyclopropane isomerization and hydrogenolysis given in Tables 1 and 2, respectively, indicate the degree to which catalyst structure influences activity at 200°C. These activity ratios might be expected to be temperature dependent, and in order to obtain a measure of this temperature dependence the activation energies for isomerization and hydrogenolysis of cyclopropane were determined on both forms of chromium oxide in the temperature range 125–240°C. These results are given in Table 3. Given the large error bars quoted in Table 3, the question as to whether the difference between the activation energies is significant deserves comment. The least-square Arrhenius plots from which the activation energies for isomerization were obtained are shown in Fig. 1. Each point in Fig. 1 is itself the result of a least-squares analysis, that is, the specific differential rate was plotted vs the square root of catalyst utilization time (Voorhies plot) (*5*) and extrapolated to zero time to correct for deactivation of the catalyst. This sort of correction for catalyst

TABLE 3
ACTIVATION ENERGIES FOR HYDROGENOLYSIS AND ISOMERIZATION OF CYCLOPROPANE ON CHROMIUM OXIDE IN THE RANGE 125-240°C

	Catalyst form	
	A	C
Hydrogenolysis	11.6 ± 2.5[a] kcal/mol	14.7 ± 2.5 kcal/mol
Isomerization	17.9 ± 2.5	23.5 ± 2.5

[a] The activation energy for hydrogenolysis on catalyst form A has been previously reported to be 12 kcal/mol (*3*).

deactivation appears to be adequate. For example, in the Arrhenius plot for isomerization on crystalline catalyst we obtain essentially the same slope if we consider only those points immediately after reactivation (points 15/3(a), 15/5(a), 15/7(a), and 15/9(a) at temperatures 149, 138, 157, and 230°C, respectively) or all of the points. Since there appears to be somewhat less scatter when only a single rate is obtained following a reactivation, this was the procedure used to obtain the activation energies for hydrogenolysis (and all other data given in this paper, Tables 1 and 2). The error bars on the hydrogenolysis activation energies are still large due to the uncertainty arising in the Voorhies plot. It is the authors' opinion that the data given in Table 3 establish that the activation energies for both hydrogenolysis and isomerization increase when the catalyst form is changed from A to C and that the change is larger for the isomerization reaction. The exact magnitude of these changes is uncertain, but the values given in Table 3 will be used in the following discussion. It is somewhat surprising that the isomerization of cyclopropane, which appeared insensitive to the structure of chromium oxide when only the overall rate was considered, must be judged as very sensitive based on the difference in apparent activation energies on the two catalyst forms. The 5.6 kcal/mol difference in activation energies represents a 370-fold smaller rate on the crystalline catalyst, a difference which is essentially completely compensated for by change in the pre-exponential factor.

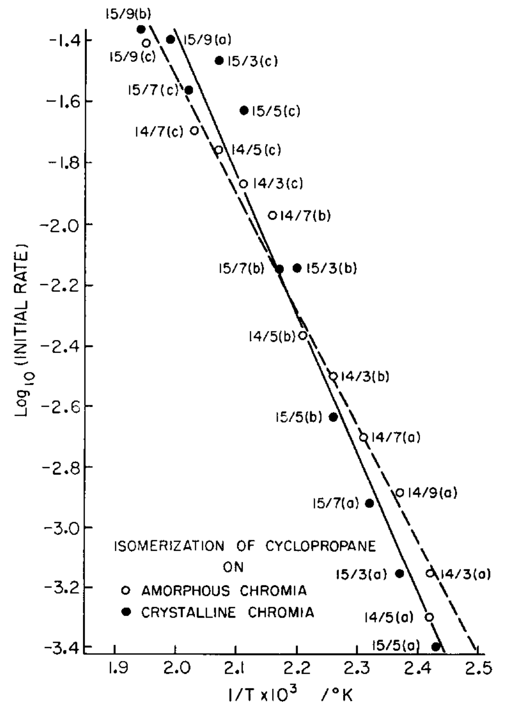

FIG. 1. Arrhenius plots for the isomerization of cyclopropane on catalyst forms A and C. The code for each point is: catalyst form/reactivation number (reaction letter). For example, on catalyst form C the points were obtained in the following order 15/3(a), 15/3(b), 15/3(c), 15/5(a), etc.

It is probable that the rate behavior described above is determined by how the activity of a given site is affected by macroscopic changes in catalyst structure. However, other factors are also possibly important, in particular the three questions posed below: (1) How does the change in catalyst structure affect site density? (2) Is the change in activity an effect of the change in pore size which accompanies crystallization (see Figs. 9 and 10 of ref. (*1*)? (3) Is it likely that the change in catalyst structure results in a different mechanism for either the isomerization or hydrogenolysis reaction? In the following we consider each of these questions in turn.

Carbon monoxide acts as a poison for olefin hydrogenation on chromia catalysts and the amount adsorbed correlates roughly with its activity (*9*). Therefore, we can take the amount of irreversible carbon monoxide adsorption at −78°C, 1.1 and 3.3 molecules/100 Å^2 on catalyst form A and C, respectively (*9*), as a measure of site density. The rates of isomerization and hydrogenation measured in experiments 20/3–23/9 and tabulated per unit BET surface area in Tables 1 and 2 are given in units of molecules reacted per site per second (turnover number) in Table 4. The isomerization reaction was found to be about first order in cyclopropane pressure; this information was used to adjust the isomerization rates to the same partial pressure as used in the hydrogenation reaction. Even when the rates are expressed as turnover numbers (TN), the ratios of overall rates $(R_C/R_A)_{TN}$, suggest that cyclopropane isomerization is insensitive to the catalyst structure at 200°C. MacIver and Tobin (*10*) have measured chemisorption of 3.8 molecules of carbon monoxide per 100 Å^2 of surface on reduced and stabilized chromia (~100% α-Cr_2O_3). This represents a reasonable upper limit for site density corresponding to completely crystalline material (*11*). On comparison with the 1.1 sites/100 Å^2 for amorphous chromia it is apparent that the increase in site density upon crystallization is small in comparison with the magnitude of the compensation effect observed, but may account, in part, for the increased activation energies that are associated with the crystallization of the catalyst (Table 3) if one assumes that the reactions occur at high surface coverage where intermolecular interactions are operative.

TABLE 4

Cyclopropane Isomerization and Hydrogenation at 200°C and 260 Torr

	Catalyst form	Turnover number ×10^4 (sec^{-1})	$\left(\frac{R_C}{R_A}\right)_{TN}$
Isomerization	C	2.6	0.72
	A	3.6	
Hydrogenolysis	C	6.0	7.2
	A	0.83	

It has been observed (*8*) that both catalyst forms are microporous and that the mean pore radii increases when catalyst A is converted into C. Let us assume that some portion of the pores on form A are so small that they either exclude the cyclopropane molecule altogether or require an activated deformation of the cyclopropane molecule for entry into the pore. The former assumption leads to the prediction of a greater rate for both reactions on catalyst form C as is, in fact, observed (Tables 1 and 2). Neither assumption, however, can provide an explanation for the larger activation energies measured for both reactions on catalyst C. Thus, we make a similar argument here as for the question of site density: The change in pore size may account for a part of the compensation of increased activation energy when catalyst A is converted to C, but is probably not the dominant factor nor the mechanism by which the activation energies are affected.

There is no direct evidence available concerning the effect of catalyst structure on the mechanism of either the isomerization or hydrogenolysis of cyclopropane. However, the nearly identical patterns of isotopically labeled products produced in the deuterogenation of olefins and deuterium exchange of alkanes, olefins and aromatics on the two catalyst forms (*9*) indicates that mechanism of these reactions does not differ with structure. Perhaps our present observations on the selectivity for straight chain products in reactions of methylcyclopropane are more pertinent. The selectivity for *n*-butenes in the isomerization reaction and *n*-butane in hydrogenolysis reaction approaches 100% on both catalyst forms while the rates of these reactions were found to be a strong function of the catalyst structure. This suggests that only the rate and not the mechanism is affected by the change in catalyst structure for the isomerization and hydrogenolysis of methylcyclopropane, and it is not unreasonable to expect similar behavior for the same reactions of cyclopropane. Moreover, we make the following observations concerning the mechanism of hydrogenolysis of cyclopropane on both forms of chromium oxide catalysts. Since the rate of olefin hydrogenation (*8*, *9*) is several orders of magnitude faster than cyclopropane hydrogenolysis, we do not expect to observe propylene as an intermediate in the hydrogenolysis even if this reaction occurs in consecutive isomerization and hydrogenation steps. But, the rate of cyclopropane isomerization in the absence of hydrogen on either catalyst form is always greater than the rate of hydrogenolysis (for example, compare 21/7 and 20/5 with 21/5 and 20/3, respectively, see Tables 1 and 2) and is larger by about an order of magnitude on catalyst A. Thus, either the hydrogenolysis proceeds directly from cyclopropane to propane or the isomerization is partially poisoned in the presence of hydrogen.

Since none of the three factors discussed above seem very important in accounting for the observed activity behavior of the two forms of the catalyst, it appears that the explanation must necessarily be found in the changes in the nature (structure) of the active sites on chromium oxide when it is converted from the amorphous to the crystalline form. Even subtle changes in the nature of an active site may be expected to modify the energy and stereochemistry of an activated complex formed on it which, in turn, will modify the observed entropy and enthalpy of activation, and it is well known that such changes provide a plausible rationalization for the compensation effect (*12*). In our discussion here we will assume that the active site involves a coordinately unsaturated chromium ion [see Burwell *et al.* (*8*, *9*)] and consider three possible alterations it may undergo in the process of crystallization: (1) it may change oxidation state; (2) the chemical nature of one or more ligands may change; (3) the number of ligands and/or the symmetry about the chromium ion may be altered. Although these are considered below individually, it is realized that any combination presents yet another possibility.

Oxidation states greater than three are very improbable, given the fact that the preparation of both catalyst forms requires heating to 300°C in hydrogen (*1*), but the reduction of surface chromium (III) to chromium (II) must be considered (*9, 13, 14*), particularly in the case of catalyst form C which is heated to 400°C in hydrogen (*1*). In experiments where catalyst C was exposed to air at 25°C (chromium (II) is known to be easily oxidized (*9, 14*)) and reactivated in helium the activity before and after this exposure for both isomerization and hydrogenolysis did not show variation greater than the sample to sample variation indicated in Tables 1 and 2. Additional evidence against oxidation states other than three is given by Burwell *et al.* (*9*).

If the chemical nature of one or more ligands of the surface chromium ion changes upon transformation of catalyst form A into C, the most probable ligand replacement reaction would involve the formation of an oxide ion by the condensation of two hydroxyls. It is recognized that catalyst form A retains water (presumably as surface hydroxyls) following activation at 400°C and above (*8, 9, 13*) and it is also known that most of this water is lost during crystallization (*8, 9, 15*). The question as to whether this water desorbed upon crystallization is removed only from the coordination sphere of chromium ions which end up in the bulk of the crystallites, or both from these and those ions that remain on the surface, has not been answered. We have attempted to measure surface hydroxyl concentrations using infrared spectroscopy, but have not been able to prepare samples of unsupported chromium oxide which are transparent in the infrared. The relative concentration of surface hydroxyls on the two catalyst forms thus remains an open question.

The third possible alteration, a change in the number of ligands and/or the symmetry of an active site (coordinately unsaturated chromium (III) ion) seems very probable in light of our structural analysis of the two catalyst forms (*1*). Consider first the idealized picture whereby the structure of catalyst form A is represented by the Cr_8O_{12} model depicted in Figs. 3

and 4 of ref. (*1*), and catalyst form C by 100 Å crystallites of α-Cr_2O_3. In the Cr_8O_{12} "crystal" there are two "bulk" chromium ions (6-coordinated) and six surface ions (3-coordinated). It has been previously reasoned that 5-coordinate chromium can be expected on several faces of α-Cr_2O_3, i.e., the 100 Å crystallites (*9*). To make this representation of catalyst A somewhat more realistic we must associate the Cr_8O_{12} "crystals" randomly to form the larger agglomerates seen in the electron micrographs (*1*) and add surface hydroxyls, both of which would increase the average coordination number of a surface chromium ion relative to the idealized Cr_8O_{12}. To obtain a better representation of catalyst form C, we must account for the noncrystalline portion [see Fig. 1 of ref. (*1*)]. Since the noncrystalline part of catalyst C is likely to be very similar in structure to catalyst A, the average coordination number of a surface chromium ion relative to the idealized α-Cr_2O_3 crystallite will be lowered. On balance then, we consider both catalyst forms to have a distribution of coordination numbers for surface chromium ions, but the average coordination number and/or symmetry of these surface chromium ion sites on form C is greater than on form A.

Conclusions

The cyclopropane hydrogenolysis is structure-sensitive and isomerization structure-insensitive on chromium oxide at 200°C if only the overall rate is considered. On the basis of measured activation energies both reactions are sensitive to the structure of the catalyst. We believe this effect is best interpreted in terms of an increase in the average coordination and/or symmetry of the active site when catalyst A (amorphous) is transformed into C (crystalline). This stabilization of the site leads to higher activation energies on catalyst C for both reactions, but a strong compensation effect results in an increase in the rate of hydrogenolysis and little change in the rate of isomerization on form C relative to A at 200°C.

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