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Kinetic Study of the Catalytic Oxidation of Isopropyl Alcohol to Acetone on Divided Cupric Oxides

J. C. VOLTA, P. TURLIER AND Y. TRAMBOUZE

Institut de Recherches sur la Catalyse, 39, Bd du 11 Novembre 1918, 69626-Villeurbanne, France

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The partial oxidation of isopropyl alcohol has been studied on dispersed cupric oxides.

The catalytic behavior is strongly dependent on operating conditions and especially on the composition of the gaseous phase above the solids. The acetone produced seems to be adsorbed on two energetically different sites. During the catalytic run, cupric oxide is slightly reduced, its reoxidation proceeding slowly.

The kinetic study has shown that the partial oxidation of isopropyl alcohol on copper oxide catalysts occurs according to the Mars and Van Krevelen [*Chem. Eng. Sci. Spec. Suppl.* 3, 41 (1954)] mechanism.

When the solids are initially reduced, catalysis proceeds by dehydrogenation of alcohol, the reaction being disturbed by the complete oxidation to carbon dioxide which occurs at lower temperatures than for nonreduced solids.

I. INTRODUCTION

In a previous paper (*1*), the authors have shown that it was possible to obtain dispersed cupric oxides starting with copper hydroxides. Depending on the treatment, their specific areas can vary from 16 to 78 m^2/g. The use of different techniques has made possible the determination of their composition and texture, and the great influence of water vapor on the development of their porosity has been clearly shown.

The aim of this study was to compare the catalytic activity of these solids in a reaction occurring at moderate temperatures, lower than those chosen for the preparation of the samples. Afterwards, the study of the catalytic behavior of the solids under the influence of the reactants and reaction products is presented. Since the reduction state of the catalyst is difficult to control, simultaneous thermogravimetric and gas chromatographic measurements have been performed. The study of the reaction kinetics is then presented, and finally a reaction scheme is proposed to explain the results.

II. METHODS

A. Preparation of Samples

Three kinds of sample were used: they were those designated as Samples 1, 5 and 6 in the textural study (*1*):

Sample 1 was obtained by decomposition of copper(II) hydroxide at 150°C in an atmosphere of water vapor (4.6 Torr) during 24 hr.

Sample 5 was obtained by sintering in air at 300°C a solid obtained from the copper(II) hydroxide decomposition in water vapor.

Sample 6 was prepared by a fast heating at 150°C of copper(II) hydroxide in air, followed by a treatment at the same temperature during 24 hr.

The previous study (*1*) has shown the similarity of the aspect and granulometry of Samples 1 and 6. Nevertheless, they differ in their surface properties.

B. Measurement of the Catalytic Activity

The apparatus used was a differential dynamic reactor connected with a gas chromatograph and adapted for simultaneous gravimetric measurements. Air was used as the carrier gas and was passed through a bubbler containing isopropyl alcohol. The catalyst in a thin bed was supported on a sintered glass filter. The temperature was controlled by means of a thermocouple located in a cavity enclosed in the catalyst. The analysis of reactants and products was made by gas chromatography, using a flame ionization detector. The column (6 mm in diameter and 2 m in length) was filled with Carbowax 20 M on Chromosorb WAW-HMDS.

For 75 mg of catalyst, the gas flow rate had to be higher than 2 liters hr^{-1} to avoid external diffusion phenomena. For 3 liters hr^{-1}, the absence of intergranular diffusion was verified between 50 and 200 mg of solid. Furthermore, the calculation of the Weisz factor (*2*) showed that the laws of the kinetic control are followed.

C. Gravimetric Measurements

The determination of the oxidation state of our catalysts, since they are unsupported catalysts, is possible using gravimetric analysis with a simple microbalance. It rapidly became clear that this gravimetric information needed to be linked with the chromatographic analysis of gases. Thus, a microdynamometric balance CI model Mark II of 5 μg sensitivity was included in the chromatographic circuit, as shown in Fig. 1. One of the vessels contained the catalyst, supported by a quartz wool bed, and the other contained inert material. The same gas flowed through the two laboratory tubes. In these conditions, the vessel with the catalyst can be compared to a dynamic reactor.

The temperature of the catalytic bed was controlled by means of a thermocouple ("thermocoax"). To estimate the delay between the gravimetric and chromatographic information, the flowing time of gases between the catalyst vessel and the chromatograph detection cell was measured.

Determinations of specific areas by the BET method could be carried out gravimetrically before and after the catalytic runs. Moreover, since the balance could be pumped down to 5×10^{-5} Torr, it was possible to prepare the catalyst *in situ* and to perform kinetic and specific area measurements.

III. Results and Discussion

A. Comparison of the Catalytic Activity of the Three Types of Sample

In a first series of experiments, the catalytic activity of Samples 1, 5 and 6 were compared at 150°C. Considering the ob-

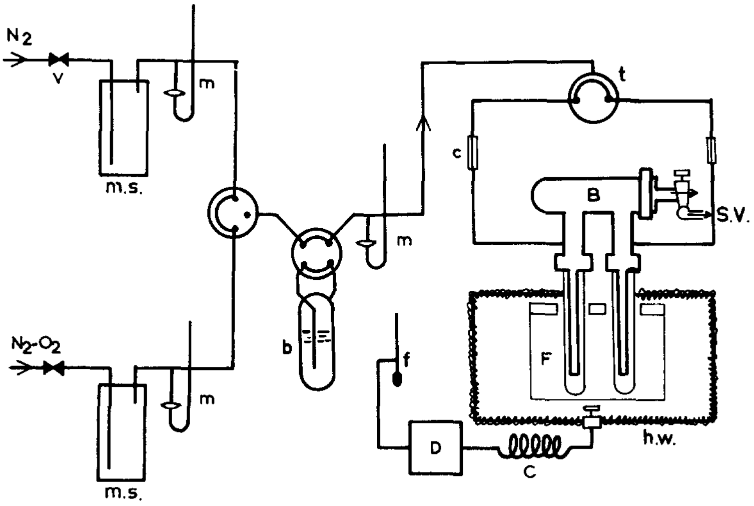

FIG. 1. Apparatus for coupled thermogravimetric and chromatographic analysis: (v) valve, (m.s.) molecular sieves trap, (m) manometer, (b) bubbler, (t) "vestale" tap, (c) capillary, (B) balance, (S.V.) secondary vacuum, (F) furnace, (h.w.) heating wire, (C) column, (D) detector, (f) flowmeter.

TABLE 1

CHARACTERISTICS AND CATALYTIC ACTIVITIES OF SAMPLES

Sample no.	Conditions of preparation	Carbonate content (%) before catalytic experiments	$Cu(OH)_2$ content (%) before catalytic experiments	Specific surface (m^2/g)		Catalytic activity (mole/s/g) $T = 150°C$	Activation energy (kcal/mole)	Specific activity (mole/s/m^2) $T = 150°C$
				Before catalytic experiments	After catalytic experiments			
1	Decomposition of $Cu(OH)_2$ 24 hr 150°C 4.6 Torr of water vapor	4.4	8	28.5	27	8.0×10^{-7} before stab. 1.0×10^{-7} after stab.	31 25	3.7×10^{-9} after stab.
6	Fast heating of $Cu(OH)_2$ in air 150°C + 24 hr 150°C	5	5	44	40	8.6×10^{-7} before stab. 3.3×10^{-7} after stab.	31 20	8.2×10^{-9} after stab.
5	Decomposition of $Cu(OH)_2$ 24 hr 150°C in water vapor + 24 hr 300°C in air	2.5	3	20	20	8.0×10^{-7} before stab. 1.9×10^{-7} after stab.	20.5 20.5	9.5×10^{-9} after stab.

served aging of the catalysts when staying in air (*1*), specific area measurements were performed before and after the catalytic runs. Water and carbonate contents were measured before any catalytic experiments. The results obtained are summarized in Table 1. The activities have been obtained by extrapolation to 150°C of Arrhenius plots for measurements performed between 127 and 144°C. The last two columns indicate the calculated activation energies and the specific activities (i.e., per square meter) measured after the reaction. The catalytic activity (i.e., per gram of the solids) decreases during the first few hours.

For the 300°C prepared Sample 5, the activation energy and the surface area did not change during catalysis, but the activity per gram of catalyst decreased. This decrease can be attributed to an inhibition effect due to reactants and reaction products.

The oxides designated as Samples 1 and 6 prepared at 150°C have different carbonate and hydroxide contents. Their activation energies were similar at the beginning but differed at the end of the catalytic run. However, they had similar porosity (*1*). To answer the question expressed previously (*1*), the final specific activity of Samples 1 and 6 are different. Since the basic carbonate is not decomposed before 310°C (*1*), the variation of the activation energy for the two preparations can be reasonably related to the change of the surface of the solids during catalysis and perhaps to the decomposition of the surface hydroxide groups under the influence of isopropyl alcohol.

Thus we find no correlation between the catalytic measurements and the carbonate or hydroxide contents (Table 1), since the latter relate to the bulk of the solid but not its surface. So we must use simultaneously thermogravimetry and gas chromatography to understand the reaction mechanism in the presence of reactants and reaction products.

B. Reducing Power of Isopropyl Alcohol

Komarov and Burevova (*3*) have observed the reduction by isopropyl alcohol of a mixture of copper, cuprous and cupric oxides. Before beginning a more complete study, it was necessary to check this result. For this purpose, we used a Setaram MTB 10-8 electronic microbalance. In each test, the same mass of copper(II) hydroxide was decomposed *in situ* as for the preparation of Sample 6. The catalyst was then evacuated at 120°C and the weight loss was constantly monitored while admitting a gas flow through the balance. Finally the solid was analyzed by X-ray analysis.

The following results were obtained:

Isopropyl alcohol with nitrogen as carrier definitely reduced Sample 6 at 120°C into cuprous oxide and copper.

In the conditions used in catalysis, the solid was also slightly reduced.

The reducing power of the air–alcohol mixture towards solids depends on the composition of the gas.

In fact, reduced nuclei located on the defects of the solids (*4*) are probably present at the beginning of the catalytic test. They can be created by reduction by alcohol or previously during the evacuation process. This hypothesis can explain the good selectivity of the catalyst; this property is connected with a low coordination of the metallic ion (*5–7*).

C. Study of the Reaction Mechanism by Simultaneous Thermogravimetry and Gas Chromatography

To limit the carbonation, the samples were prepared *in situ* according to the procedures noted above. The starting material was a freshly prepared batch of copper(II) hydroxide kept in a desiccator containing sodium hydroxide.

1. Catalyst Sample 1 Prepared in situ

The experiment was performed at 133°C, and the results are given in Fig. 2. The rate is called V_{Ac} when referred to acetone (curve a) and V_{H_2O} when referred to water (curve b). The curve b′ is the difference between curves a and b and represents the removal of water from the solid.

Figure 2 shows that initially more water is evolved (curve b) than corresponds to the oxidation of isopropyl alcohol to acetone desorbing from the catalyst (curve a). When water set free by interaction of alcohol with a surface or by oxidation of the alcohol inhibits the reaction, it can do so only at the catalyst surface. Therefore, water should remain on the catalyst and should evolve less than the acetone produced by the oxidation. That is obviously not the case, since curve b lies above curve a. We can assume that the acetone produced by the oxidation is more strongly adsorbed than the generated water. Consequently more water is measured initially (part AB) until sites strongly adsorbing acetone are saturated (point C). Then, equal amounts of acetone and water are desorbed from the catalyst (part CD). The rapid increase in weight of the catalyst (curve c, part AB) is in keeping with this interpretation. Super-

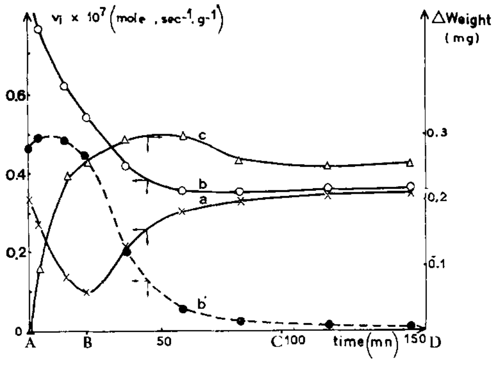

FIG. 2. Catalytic behavior of Sample 1. (a) = V_{Ac}, (b) = V_{H_2O}, (b′) = b − a, (c) variation of the catalyst weight.

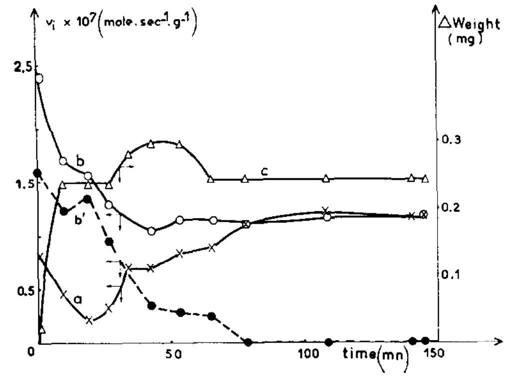

FIG. 3. Catalytic behavior of Sample 6; curve labels as for Fig. 2.

imposed on the increase in weight by adsorption of acetone is a decrease due to a slight reduction of the catalyst. The reduction proceeds more slowly, so this gives rise to the maximum in the weight curve. We can think that acetone is strongly adsorbed on cupric oxide at the beginning of the experiment. At the end, isopropyl alcohol reduces the solid and acetone is then weakly adsorbed on cuprous oxide nuclei.

2. Influence of the Reduction State of the Solid

a. Nonreduced solids. The catalytic behavior of a Sample 6 oxide has been studied at 133°C and the results are shown in Fig. 3. The shape of curves a, b and c are obviously the same as for Sample 1. They can be interpreted like those of Fig. 2. The initial value of the catalytic activity is 0.8×10^{-7} mole s^{-1} g^{-1}. It was equal to 0.35×10^{-7} for Sample 1. With the values of the specific areas of the two samples measured *in situ* before the experiment, the specific activity (i.e., activity per square meter) can be calculated and is found to be nearly identical in the two cases (0.9×10^{-9} and 1.02×10^{-9} moles s^{-1} m^{-2}).

The rates observed at 133°C after stabilization of the catalytic activity are 3.50×10^{-8} mole s^{-1} g^{-1} for Sample 1 and 1.23×10^{-8} for Sample 6. They are, respectively, equal to those extrapolated from the activation energies at equilibrium and the corresponding rates at 150°C indicated in Table 1 for samples stored in laboratory atmosphere. Therefore the final catalytic activity is reproducible.

b. Reduced solids. In order to study the influence of reducibility of the solids, Sample 6 was reduced by alcohol with nitrogen as carrier. We define the reduction percentage of the solids as the ratio $\alpha = \Delta m/\Delta m_0$; Δm is the observed weight loss and Δm_0 the weight loss corresponding to the complete theoretical reduction of cupric oxide to copper. The catalytic activity was

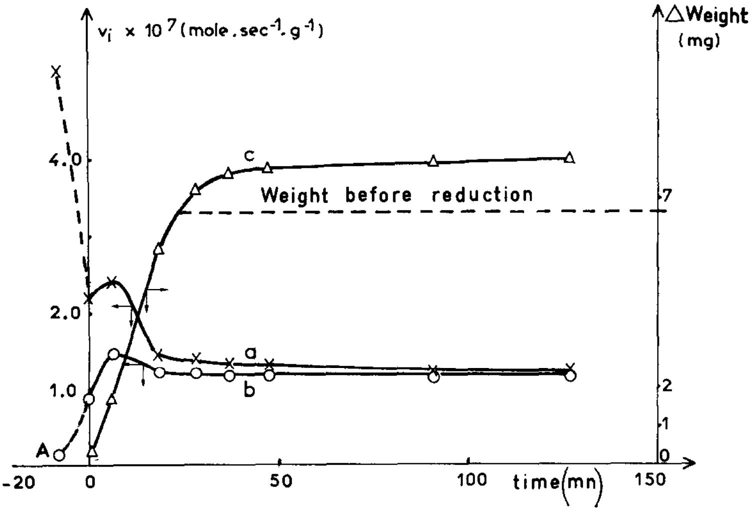

FIG. 4. Catalytic behavior of a 50% reduced Sample 6; $T = 133°C$; curve labels as for Fig. 2.

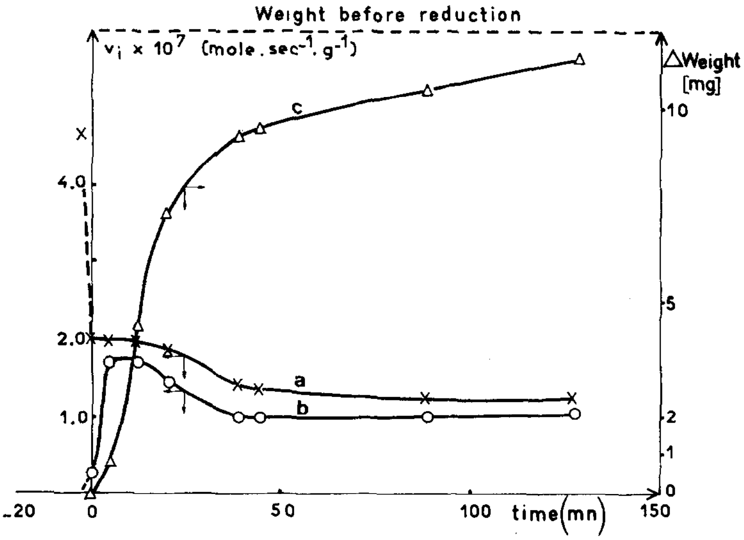

FIG. 5. Catalytic behavior of a 90% reduced Sample 6; $T = 133°C$; curve labels as for Fig. 2.

measured at 133°C, i.e., at time $t = 0$, nitrogen was replaced by air. Two experiments were performed on two solids which were, respectively, 50 and 90% reduced. The results are shown in Figs. 4 and 5. Compared to Fig. 3, curves a and b are reversed. The plateau attained in curve a corresponds to the same rate as for the nonreduced catalyst (1.23×10^{-7}). Thus, the mean surface oxidation degree and the final activity are both controlled by the gas phase composition. It is well known that copper is a good alcohol dehydrogenation catalyst (*8*). The reaction products are hydrogen and ketone. Therefore, the dehydrogenation should proceed on the reduced catalysts, and this appears to be the case from the relatively high rate of acetone formation in the absence of oxygen (negative times on Figs. 4 and 5). The acetone is obtained with a weak production of water, as shown in Figs. 4 and 5. The curves suggest also a rather rapid decrease in the rate of dehydrogenation versus time. However, in Fig. 5 where the degree of reduction is about 90% there is at zero time a rate equal to that in Fig. 4 where the catalyst is only 50% reduced. This proves that the reduction state of the surface is the same for the two catalysts whatever reduction state may exist in the bulk. When nitrogen is replaced by air at time zero, dehydrogenation changes into oxidation. Simultaneously, the copper catalyst is reoxidized. The transient maximum in the rate of formation of water may be due to reaction of adsorbed hydrogen resulting from the dehydrogenation with oxygen of the air admitted at time zero. A transient temperature rise of the catalyst due to the reaction or to the reoxidation of copper may be responsible for the maximum in the acetone production shown in Fig. 4.

In Fig. 5, it is interesting to see that the plateau of the acetone rate, curve a, is attained while the solid is still in a reduced state. Therefore the reoxidation of the solid in the bulk proceeds more slowly than the formation of the active catalyst surface.

3. *Influence of Temperature*

Experiments were performed on a reduced batch of Sample 5 which consisted in increasing and decreasing the temperature of the catalytic run. In the first case (Fig. 6) where the solid was 50% reduced, an air–alcohol mixture was admitted at 120°C with the oxygen/alcohol ratio equal to 6. There was no production of acetone. Then the temperature was increased stepwise up to 245°C. At this temperature, there was more carbon dioxide than acetone in the reaction

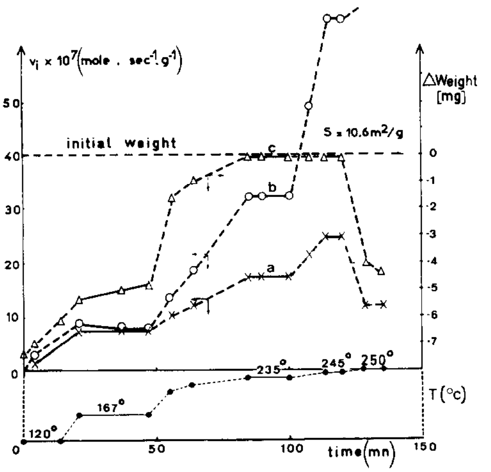

FIG. 6. Catalytic behavior of a reduced Sample 5. The temperature increases between each run.

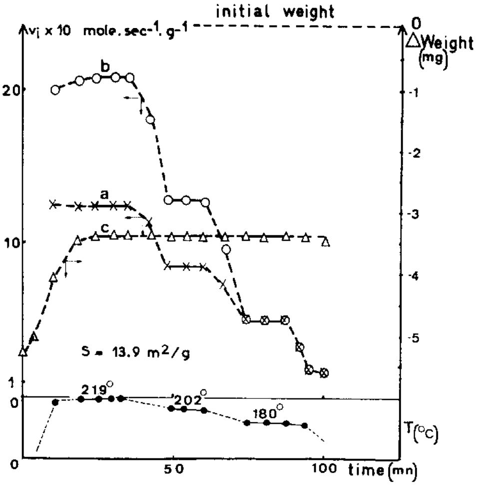

FIG. 7. Catalytic behavior of a reduced Sample 5. The temperature decreases between each run.

products and the solid was still 30% reduced. In the second case, (Fig. 7) the solid was 35% reduced, and the procedure was analogous except that temperature was decreased. We stopped the experiment at 150°C, when the solid was still 20% reduced. There was then no detectable carbon dioxide in the gaseous mixture. In both cases (Figs. 6 and 7), the observed difference between curves a and b grows with temperature. These results may be ascribed to oxidation of isopropyl alcohol to carbon dioxide and water. In Fig. 6, the complete oxidation starts above 167°C, carbon dioxide being detected in the gaseous flow. These perturbations occur at a temperature lower than in the case of Samples 1 and 6 for which this reaction is observed only at 300°C. Since much more oxygen is necessary for the oxidation of alcohol to carbon dioxide and water, a reducing atmosphere may result at temperature higher than 245°C where the conversion is important. This explains the decrease below the plateau (Fig. 6, curve c) and the corresponding

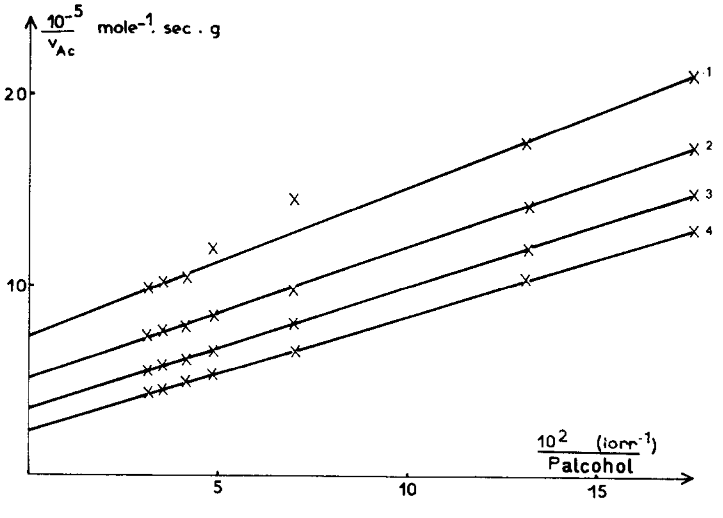

FIG. 8. $1/V_{Ac}$ versus $1/P_{Al}$; Sample 5; T = 200°C; P_{O_2} (Torr): (1) 19; (2) 38; (3) 76; (4) 152.

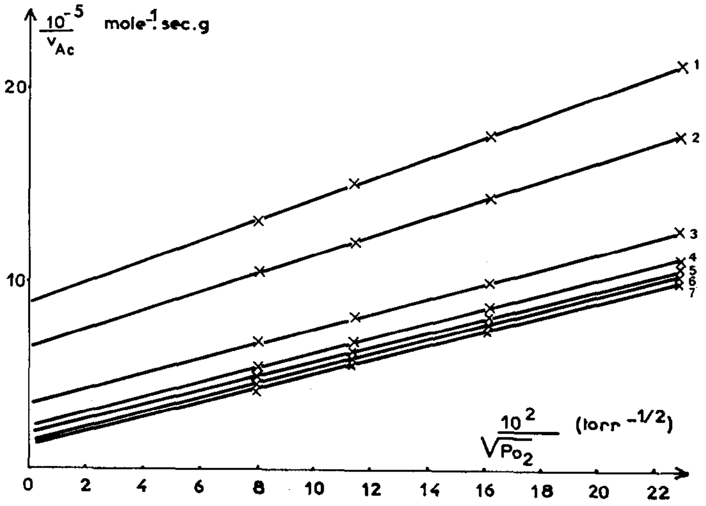

FIG. 9. $1/V_{Ac}$ versus $1/P_{O_2}$; Sample 5; T = 200°C; P_{Alc} (Torr): (1) 5.7; (2) 7.6; (3) 14.3; (4) 20.6; (5) 24.2; (6) 28.3; (7) 31.5.

decrease of the rate of formation of acetone, which is then completely oxidized. For decreasing temperature (Fig. 7), the complete oxidation is present from the beginning and stops at about 180°C where acetone and water are produced again at the same rate. The solid is still 20% reduced but this is in the bulk.

D. Kinetic Equation and Reaction Scheme for the Mild Oxidation of Isopropyl Alcohol

Using a Sample 5, the influence of the pressures of the two reactants was studied at 200°C. In Figs. 8 and 9, $1/V_{Ac}$ is plotted versus $1/P_{Al}$ for constant oxygen pressures and versus $1/(P_{O_2})^{1/2}$ for constant alcohol pressures.

The straight lines obtained are in agreement with the Mars and Van Krevelen mechanism (*9*):

$$\text{alcohol} + \text{oxidized catalyst} \xrightarrow{k_{red}} \text{acetone} + \text{reduced catalyst}, \quad (1)$$

$$\text{reduced catalyst} + \text{oxygen} \xrightarrow{k_{ox}} \text{oxidized catalyst}. \quad (2)$$

The kinetic equation is:

$$\frac{1}{V_{Ac}} = \frac{1}{k_{red}P_{Al}} + \frac{1}{k_{ox}P_{O2}{}^{n}},$$

with $n = 0.5$, which corresponds to a dissociative adsorption of oxygen.

The same equation would be obtained with the modified Hinshelwood mechanism. Mars and Van Krevelen (*9*) considered the departure of oxygen atoms from the lattice by a direct interaction with the reducing agent. Hinshelwood suggests that only adsorbed atomic or molecular oxygen can react with the molecules of alcohol. Garner, Stone and Tiley (*10*) have shown by studying oxygen chemisorption on cuprous and cupric oxide that this process occurs simultaneously with some incorporation of oxygen in the lattice. Margolis (*11*) proposed that during the oxidation, oxygen covers the whole solid surface. From the catalytic point of view, it is difficult to distinguish between surface oxygen and oxygen coming from the lattice. Nevertheless, the experimental results allow us to conclude that the Mars and Van Krevelen mechanism is the most probable in our case.

The mild oxidation of isopropyl alcohol to acetone can proceed by formation of a surface isopropylate group. Its oxidation leads to another surface hydroxyl group adsorbed on a copper atom of reduced valency. Desorption of water from a neighboring surface hydroxyl group leads to a site where oxygen can be incorporated. By the reaction with oxygen, the catalyst is reoxidized. In contrast with molybdenum-containing catalysts where the reoxidation proceeds rapidly (*12*), our copper catalysts are reoxidized slowly. For the copper-catalyzed oxidation of propylene to acrolein, it has been demonstrated (*13*) that the rate depended on oxygen partial pressure, as we observed. Since the reoxidation proceeds slowly, a number of oxygen vacancies at the surface but presumably also in the bulk is present during the reaction. The presence of oxygen vacancies implies that the catalyst is slightly reduced as we observed with the catalyst weight and the X-ray analysis of cuprous oxide. In the oxidation of propylene to acrolein on copper oxide catalyst, it is well known that the active phase is cuprous oxide (*13*, *14*). Moreover, Callahan and Grasselli assume that for selective oxidation there must be only a limited number of oxygen atoms in a reactive grouping on the catalyst (*15*). In our case, the actual oxidation catalyst is in fact active cupric oxide resulting from the oxidation of cuprous oxide nuclei. These conclusions are similar to those of Bielanski and Haber (*12*) who studied the oxidation of propylene on bismuth molybdates.

IV. CONCLUSIONS

Our study leads to information on the following points:

1. The mild oxidation of isopropyl alcohol on copper oxide catalysts shows the existence of two types of energetically different site where acetone is produced. We can attribute them to cupric and cuprous oxide sites.
2. During the catalytic process, a slight reduction of the solid occurs. The stationary catalytic activity is strongly dependent on operating conditions, viz, feed ratios, temperatures and reactant pressures.
3. The reoxidation of the catalysts proceeds more slowly than for molybdenum-containing catalysts.
4. After stabilization of the catalytic activity, the partial oxidation of isopropyl alcohol occurs according to the Mars and Van Krevelen mechanism.
5. At low temperatures, the copper oxide catalysts show a good selectivity towards acetone production. The actual catalyst is active cupric oxide resulting from the reoxidation of cuprous oxide nuclei.

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