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Catalytic Activity of Amorphous Aluminas for Oxidation of Carbon Monoxide

II. The Influence of Treatment in Oxidizing or Reducing Atmospheres on the Catalytic Activity of Amorphous Aluminas Activated *in Vacuo*

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The catalytic activity of amorphous alumina, activated *in vacuo*, for the oxidation of carbon monoxide, depends upon the nature of the surface defects (oxygen or aluminium ion vacancies) which predominate in the alumina. Treatment in oxygen following activation *in vacuo* fills the anionic vacancies and leads to decreased catalytic activity. Contrariwise, treatment with carbon monoxide further reduces chemically the surface of amorphous alumina previously activated *in vacuo* with consequent increase in the concentration of anionic vacancies and increase in the catalytic activity of the alumina. Thus, catalysts activated *in vacuo* and then in oxygen become almost inactive whereas those activated *in vacuo* and then in carbon monoxide become much more active. In the latter case, the reactants saturate the surface of the catalyst as is shown by the kinetic orders with respect to oxygen and carbon monoxide becoming nearly zero. The total observed order of 0.75 is an apparent one resulting from inhibition by the product, carbon dioxide. The connection between anionic defects and catalytic activity of amorphous aluminas for the oxidation of carbon monoxide seems well established.

INTRODUCTION

We have shown in a previous work (*1*) that catalytic activity for oxidation of carbon monoxide by amorphous alumina prepared in aqueous media and then activated *in vacuo* (10^{-6} torr) depends upon the type of defect, anionic or cationic, which predominates on the alumina.

Thus, *n*-type aluminas (*3*) prepared by activation *in vacuo* between 500 and 700°C decrease in catalytic activity as the deficit of oxygen ions decreases with increasing temperature of activation. Correspondingly, *p*-type aluminas (*3*) prepared by activation *in vacuo* between 730 and 800°C increase in catalytic activity as the deficit in aluminium ions increases.

Previous studies have shown (*3*) that exposure to oxygen at 500–700°C fills the surface oxygen vacancies in amorphous aluminas previously activated *in vacuo* at these temperatures. Above 700°C, amorphous alumina recrystallizes in the presence of oxygen (*2*). On the other hand, exposure to carbon monoxide at 450–800°C further chemically reduces the surface of amorphous aluminas and increases the deficit in oxygen above that resulting from mere activation *in vacuo* at the same temperature (*3*).

The purpose of the present study was to confirm the presence of a correlation between these surface defects and catalytic activity by studying aluminas with different types of surface defects prepared by activation *in vacuo* followed by exposure to oxygen or carbon monoxide.

Experimental techniques and procedures were those previously described (*1*): oxidation at 450°C of carbon monoxide was studied on the activated catalyst in a constant volume reactor.

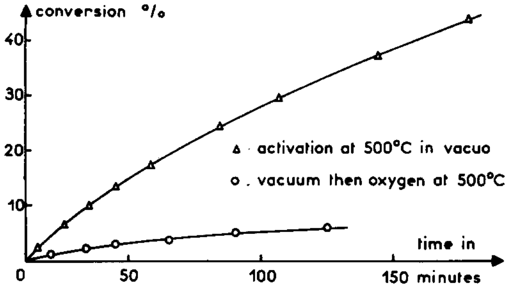

FIG. 1. Variation of conversion with time at 450°C for an amorphous alumina activated *in vacuo* at 500°C and then exposed to oxygen.

RESULTS AND DISCUSSION

I. *Treatment with Oxygen*

The catalyst was evacuated at 500, 600, 700, or 800°C for 14 hr, exposed to oxygen for a further 14 hr at the same temperature and then reevacuated for 1 hr at this temperature. The oxidation of carbon monoxide was then studied at 450°C under conditions identical to those previously employed (*1*). The specific area was unchanged by oxygen treatment (*2*).

In all instances, the catalytic activity of the samples exposed to oxygen was substantially less than that of samples which had only been evacuated. Figures 1 and 2 illustrate this phenomenon for samples activated at 500 and 600°C. Samples activated at 700 and 800°C were nearly devoid of catalytic activity after exposure to oxygen.

Thus, exposure to oxygen of *n*-type alumina formed by activation *in vacuo* at 500–700°C (*3*) fills the anionic vacancies formed during activation *in vacuo* and leads to an abrupt decline in catalytic activity. These results demonstrate that the catalytic activity of aluminas activated *in vacuo* at 500–700°C mainly derives from anionic defects. Above 700°C, amorphous alumina recrystallizes in the presence of oxygen (*2*) and its catalytic activity becomes negligible. It should be noted that exposure to air following evacuation *in vacuo* gives the same results as exposure to oxygen.

II. *Treatment with Carbon Monoxide*

Samples of amorphous alumina activated *in vacuo* were then exposed to carbon monoxide for 14 hr at 100 torr at the same temperature as during evacuation. During rapid introduction of carbon monoxide and oxygen to the catalyst so treated, a temperature rise of 10°C was observed. The temperature had returned to its original value, 450°C, before the end of the second minute. The period of introduction of reacting mixture was, therefore, fixed at 2 min and the oxidation of carbon monoxide was measured under the same conditions as formerly (*1*).

(*a*) *Effect of Conditions upon Catalytic Activity*

The experimental curves (solid lines) in Fig. 3 were obtained for samples activated *in vacuo* and then exposed to 100 torr of carbon monoxide at 500, 650, and 800°C; the broken lines represent samples activated at the same temperature *in vacuo* only. The sample activated at 800°C *in vacuo* and then exposed to carbon monoxide had recrystallized. The two sets of curves show that exposure to carbon monoxide considerably increases the catalytic activity of samples activated *in vacuo*.

The rate of carbon monoxide oxidation on alumina exposed to carbon monoxide is 0.75 order. Linear transforms representing

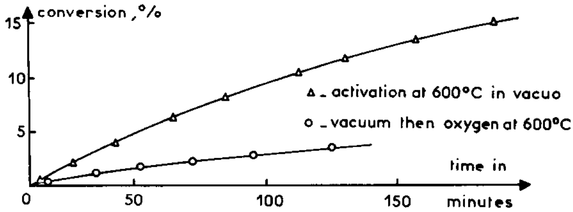

FIG. 2. Variation of conversion with time at 450°C for an amorphous alumina activated *in vacuo* at 600°C and then exposed to oxygen.

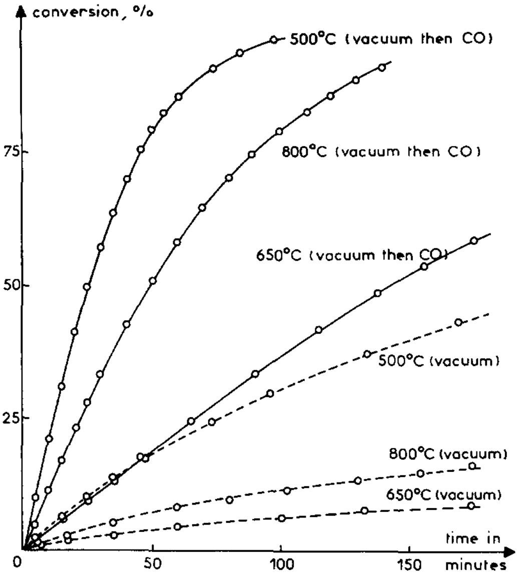

FIG. 3. Rate runs for amorphous aluminas activated *in vacuo* or *in vacuo* followed by exposure to carbon monoxide.

$(P_0^{1/4} - P^{1/4})$ as a function of time (Fig. 4) allow calculation of the rate constants. The rate constants are 8.1×10^{-4}, 3.1×10^{-4}, and 4.7×10^{-4} torr$^{1/4}$ min^{-1} m^{-2} per samples treated at 500, 650, and 800°C *in vacuo* and carbon monoxide.

The catalytic activity of amorphous aluminas, thus, appears linked, at least in part, to deficit in oxygen. The sample treated *in vacuo* and then in carbon monoxide at 800°C was an exception. It possessed the largest deficit in oxygen, 0.20% (*3*), but it had a catalytic activity less than the sample activated at 500°C, the deficit in oxygen of which was 0.16%. This anomaly was probably due to the recrystallization of the 800°C sample.

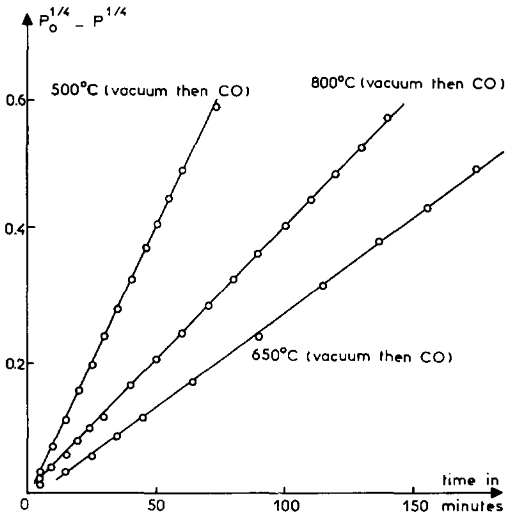

FIG. 4. Linear transforms for 0.75 order of the full lines of Fig. 3.

Since the total order for the oxidation was 2 for samples activated *in vacuo* only (*1*) and 0.75 per samples treated *in vacuo* and then in carbon monoxide, the reaction mechanisms must be different for the samples activated under the two conditions.

(*b*) *Determination of Individual Reaction Orders*

Orders with respect to the individual reactants were determined for samples which had been activated *in vacuo* and then in carbon monoxide at 500°C. This was done by measurement of initial rates in nonstoichiometric mixtures (excess of carbon monoxide or excess of oxygen) and in the reference stoichiometric mixture $(CO + \frac{1}{2}O_2)$. Figure 5 presents these data; Fig. 5 shows that the rates are nearly the same at $t = 0$ but that the rates of mixtures containing an excess of either carbon monoxide or of oxygen decrease with time a little more than the rates of the reference mixture.

Figure 6 presents the linear transforms for an order of 0.75, plots of $(P_0^{1/4} - P^{1/4})$ against time. The P_0 and P are the pressures at $t = 0$ and at t, respectively, of the reactant which is not in excess in the nonstoichiometric mixtures. For the stoichiometric mixture, P_0 and P represent total pressures.

As shown by Fig. 6, the order with respect to carbon monoxide is 0.75 in the mixture in which oxygen is in excess and the order with respect to oxygen is zero. In the mixture with an excess of carbon monoxide, the order with respect to oxygen is 0.75 and with respect to carbon monoxide, zero. On the other hand, a comparison of the rate curves of Fig. 5 shows that the rates are nearly independent of the partial pressures of CO or O_2, both initially and later. The most probable interpretation of these apparently contradictory results is that the global order 0.75 is but an ap-

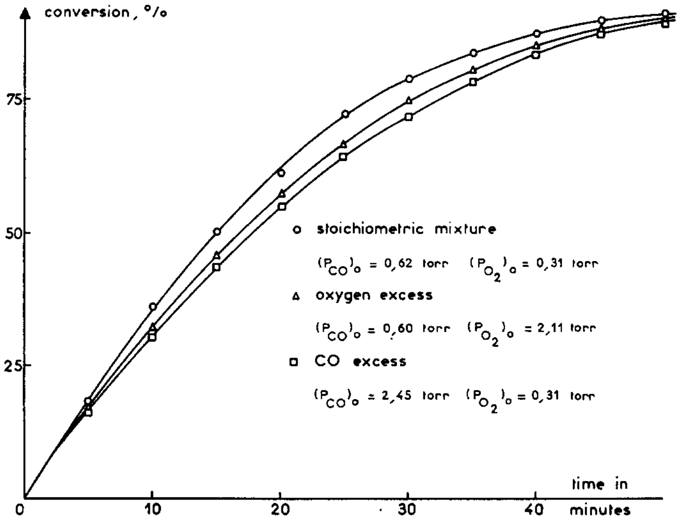

FIG. 5. Variation of conversion with time.

parent one, and that throughout a run the real order for each reactant is zero. The apparent order of 0.75 is probably due to an auto-inhibition effect of blocking of active sites on the catalyst by carbon dioxide formed during the reaction (*4–6*).

(*c*) *Auto-inhibition of the Reaction*

The interpretation just presented requires a determination of the initial total order and an analysis of the inhibition action of carbon dioxide. The initial rates for different initial pressures of a stoichiometric mixture were measured on samples activated at 500°C *in vacuo* and then in carbon monoxide. As shown in Fig. 7, the initial total order is about 0.2 as determined from the slope of the plot of the logarithm of initial rate versus the logarithm of initial pressure. Considering the low accuracy of this calculation, one can assume that the initial total order is near zero.

The slopes of the linear transforms for order 0.75 which are proportional to the rate constants differ with differing values of the initial pressure as shown in Fig. 8. The slopes increase as the initial pressure decreases. This anomaly is characteristic of reactions which exhibit an initial order different from that followed later in the reaction (*7*).

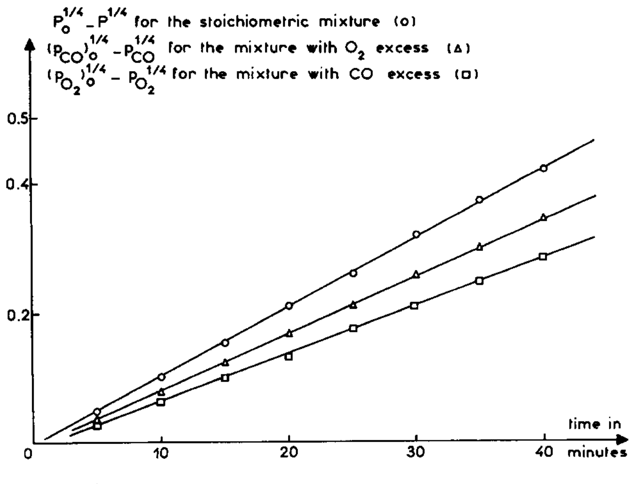

FIG. 6. Linear transforms for 0.75 order of the curves of Fig. 3.

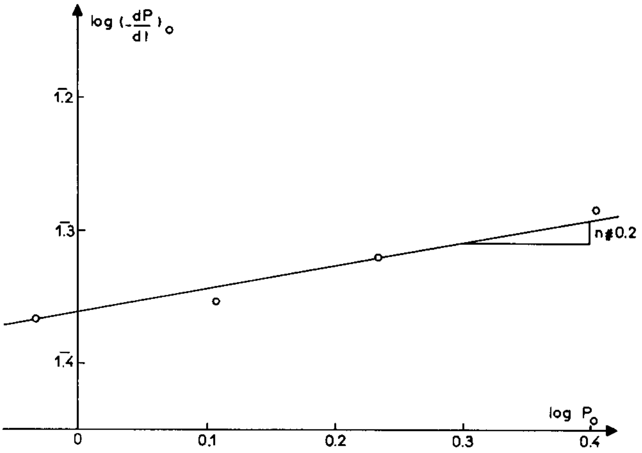

Fig. 7. Determination of initial order.

The curves of Fig. 9 provide evidence for auto-inhibition by carbon dioxide formed during the reaction. When the oxidation is run in the presence of a liquid nitrogen trap, the rate curve (1) follows 0.75 order. If the liquid nitrogen trap is replaced by a dry ice trap which permits the accumulation of carbon dioxide in the gas phase, the rate decreases with time even more rapidly [curve (2)] and the total order becomes about 2.

In sum, carbon dioxide inhibits the reaction, presumably by blocking active sites on the surface of the catalyst. The 0.75 order is an apparent one resulting from auto-inhibition. The true order with respect to reactants is zero.

Carbon dioxide, like oxygen, is ordinarily an electron acceptor. It seems reasonable that carbon dioxide should adsorb the more strongly on the catalyst surface as the number of anionic defects increases or as their degree of unsaturation increases. Thus, auto-inhibition is not observed on samples of alumina activated at 500°C *in vacuo* only. These samples are less active than those activated both *in vacuo* and in carbon monoxide at this temperature. These results accord with our former work (*4*) on the catalytic activity of anatase for carbon monoxide oxidation. We showed that pellets of compressed semiconducting *n*-type anatase powder, were highly nonstoichiometric with respect to oxygen, and

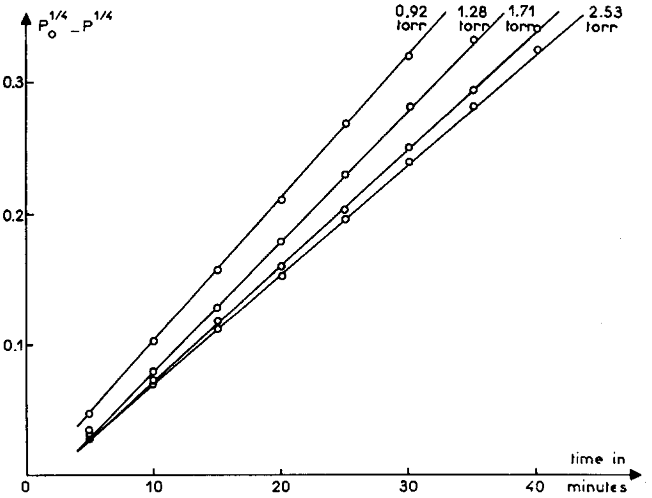

Fig. 8. Linear transforms for 0.75 order for various initial pressures, P_0.

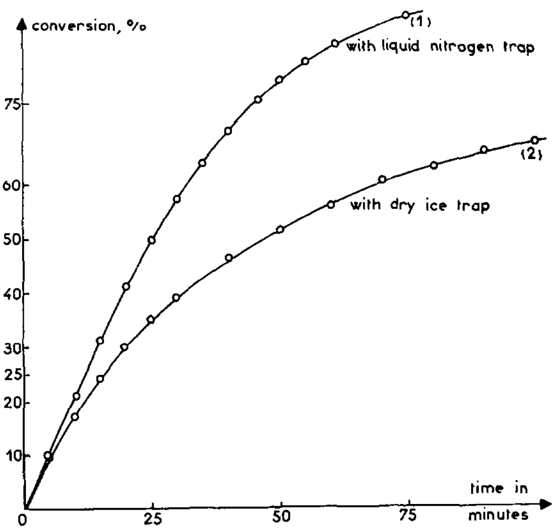

FIG. 9. Variation of conversion with time for an amorphous alumina activated *in vacuo* and then carbon monoxide at 500°C.

were at the same time the most active and gave the strongest inhibition by carbon dioxide. The less active anatase uncompressed powder with less nonstoichiometry exhibited no inhibition by carbon dioxide.

Thus, exposure to carbon monoxide increases the deficit of oxygen in amorphous alumina previously activated *in vacuo* (*3*) and makes it more active for the catalytic oxidation of carbon monoxide. The nature of the chemisorption of the reactants on the catalyst which must largely determine the catalytic activity of these materials is substantially modified by exposure to carbon monoxide. As indicated by the nearly zero order in each reactant during carbon monoxide oxidation, the reactants saturate now the surface of the catalyst. This result further implies that the two reactants adsorb on different sites noncompetitively. In addition, carbon dioxide formed in the reaction is also strongly adsorbed on the surface modified by exposure to carbon monoxide and this leads to auto-inhibition.

III. Conclusions

Activation of amorphous aluminas *in vacuo* at high temperatures forms at least two types of sites which are catalytically active for carbon monoxide oxidation. They are anionic and Al^{3+} defects. In activation *in vacuo* at 500–700°C, anionic defects predominate leading to *n*-type semiconductivity whereas at 730–800°C cationic defects are more numerous and lead to *p*-type semiconductivity (*3*). A study of the catalytic activity of amorphous aluminas activated *in vacuo* has shown the activity to be linked largely to the type of defect which predominates: of oxygen ions for activation at 500–700°C and of Al^{3+} ions for 730–800°C (*1*).

Exposure to oxygen fills the anionic defects formed by previous activation *in vacuo* at 500–700°C (*3*). Correspondingly, the catalytic activity of aluminas so exposed to oxygen diminishes considerably. Thus, the important role of anionic defects in aluminas activated *in vacuo* at 500–700°C for catalytic oxidation of carbon monoxide appears now to be well established. Unfortunately, exposure to oxygen above 700°C promotes the recrystallization of amorphous aluminas (*2*) and it is not possible to verify the role of cationic defects formed above 700°C *in vacuo* by study of the effect of exposure to oxygen.

Exposure to carbon monoxide increases the deficit in oxygen formed by activation *in vacuo* (*3*) and experiments with this material give further proof of the effect of anionic vacancies upon the catalytic activity of amorphous aluminas. Nevertheless, direct comparison of activities is made somewhat difficult by the fact that exposure to carbon monoxide generates surface properties not present in alumina activated *in vacuo*. Not only is the catalytic activity increased by the exposure but the mechanism of oxidation appears to be changed. Determination of the orders with respect to oxygen and carbon monoxide indicates that the reactants are adsorbed weakly (*1*) on the alumina merely activated *in vacuo* but adsorbed strongly and noncompetitively (on separate sites) on the alumina also exposed to carbon monoxide. Thus, exposure to carbon monoxide not only increases the number of oxygen vacancies formed on the surface by activation *in vacuo* but also forms new types of active sites or, at least, increases their number. Even if both types of active sites are present after activation *in vacuo,* exposure to carbon monoxide must increase their degree of unsaturation as shown by the strength of chemisorption of both reactants and of CO_2.

One cannot exclude the possibility that oxygen adsorbs on anionic defects and carbon monoxide on cationic. However, according to the rate studies, this hypothesis implies that any cationic defects formed by activation *in vacuo* must be considerably modified in energetic character and probably in number by exposure to carbon monoxide. This could result from carbon monoxide reducing the surface of alumina and decreasing the average coordination number of surface cations allowing them to distill out (*3*). Exposure to carbon monoxide could, thus, generate a surface in which the density and the degree of unsaturation of defects was increased over that of one merely activated *in vacuo*.

In summary, catalytic activity for oxidation of carbon monoxide by amorphous alumina activated *in vacuo* seems to depend mainly upon the defects, anionic or cationic, which predominate in the solid (*1*). Treatment with oxygen has confirmed the effect of anionic vacancies on the catalytic activity of these aluminas. Treatment with carbon monoxide has given kinetic results which confirm the role of oxygen vacancies and which may also be interpreted by assuming a creation of cationic defects as well as that of anionic ones.

We have developed a relation between catalytic activity and vacancies in oxygen or aluminium ion. However, no connection between modification of the electronic state of the alumina (in terms of the band theory of semiconductors) occasioned by the formation of these defects and the catalytic activity is established by our work. It is, however, possible that the modifications of the electronic state might be a simple consequence of a chemical structural alteration of the surface (*4*) and play no role in the catalytic reaction itself which should depend only upon the localized properties of the surface, that is upon surface defects (*8*).

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