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Catalytic Activity of Amorphous Aluminas for Oxidation of Carbon Monoxide

I. Activation by Evacuation *in Vacuo*

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The catalytic activity of amorphous aluminas in the oxidation of carbon monoxide was correlated with surface structural defects created in the course of evacuation *in vacuo* (10^{-6} torr) between 450 and 800°C. A kinetic study of the oxidation of carbon monoxide at 450°C showed that the catalytic activity of amorphous aluminas is determined by the type of surface defects, oxygen or aluminium ion vacancies which predominate and which can be created by appropriate treatments.

INTRODUCTION

Study of structural defects in pure amorphous aluminas prepared in aqueous media (*1, 2*) has shown that these aluminas can be made deficient in either oxygen or Al^{3+} and that they are then either *n*-type or *p*-type semiconductors. Such materials are of interest with respect to the relation of the defects to the catalytic activity of these materials.

As a test reaction, we have chosen the catalytic oxidation of carbon monoxide. The simplicity of this reaction makes it particularly interesting for fundamental investigations of catalytic oxidation. Further, this reaction has been widely studied in the presence of a variety of metallic oxides and these studies have led to several general conclusions (*3, 4*).

Semiconducting oxides of the *p*-type are the most active and lead to reaction at lower temperatures. Oxides of the *n*-type are active at intermediate temperatures while oxides which are insulators catalyse the reaction only at high temperatures.

The heterogeneous catalytic oxidation of carbon monoxide often follows one or the other of the following mechanisms: (a) At low temperatures, 150°C or less, oxygen and carbon monoxide chemisorb on the surface of the catalyst. Reaction occurs among adsorbed species without ensuing modification of the surface of the catalyst. Carbon dioxide is formed in an adsorbed state and desorption follows (*5–7*). (b) At higher temperatures, carbon monoxide tends to react with oxide ion of the solid to form carbon dioxide. The catalyst is, thus, first reduced and then reoxidized by gas-phase oxygen. Cyclic oxidation–reduction of the surface of the catalyst is, then, involved in the catalytic reaction (*4, 8*).

Kinetic studies show, in general, that the kinetic order with respect to oxygen decreases from unity to zero as the temperature is raised, whereas, that with respect to carbon monoxide increases from zero to unity (*9*). These general rules suffer numerous exceptions. As Winter (*10*) has shown, the mechanisms are often complex. In particular, as one of us has shown, the kinetic orders in oxidation over nickel oxide at room temperature are zero with respect both to oxygen and to carbon monoxide (*5, 7*).

Oxidation of carbon monoxide on alumina appears to have been little studied. However, alumina has been stated to follow titanium dioxide, thoria, and zirconia in the scale of decreasing catalytic activity (*4*).

EXPERIMENTAL TECHNIQUES

The catalytic oxidation of carbon monoxide was carried out in a constant volume apparatus (*5, 7, 11*) and the fall in pressure with time was used to determine the kinetics of the reaction. The previously described reactor (*7*) permitted the use of a small amount of catalyst and it permitted exact control of its temperature. The following conditions were employed:

(*a*) *Quantity of Catalyst*

The same amount of powdered amorphous alumina (510 mg) previously treated in air at 400°C for 20 hr was used in all experiments. The samples of alumina were prepared from solutions of aluminium chloride and ammonium carbonate (*1*), their properties have been described (*1, 2*).

(*b*) *Initial Pressure of Reactants*

Most experiments were carried out with a stoichiometric mixture ($O_2/CO = \frac{1}{2}$) at pressures between 2.5 and 2.7 torr. As it formed, carbon dioxide was condensed by a liquid nitrogen trap, the level of which was kept constant. The pressure fall resulting from the reaction was followed by a McLeod gauge. It was established that mass transport did not control reaction rates (*5*).

(*c*) *Temperatures*

The catalytic activity of the least active sample of alumina could not be measured below 450°C. It was, therefore, necessary to determine whether the reaction proceeded in the absence of a catalyst at these temperatures. It was often found that the walls of the reaction vessel exhibited catalytic activity.

A number of experiments at 450°C in the absence of catalyst showed that at initial pressures of 2.5 to 2.7 torr, the conversion was less than 4% in 3 hr. At 500°C, however, the conversion reached 17% in 3 hr in some experiments. Above 450°C, then, reaction does not occur only on the added catalyst. Below 450°C, on the other hand, the activity of the least active catalysts could not be measured. All rates were, therefore, measured at 450°C.

(*d*) *Rate of Introduction of Reactants*

No temperature rise of the catalyst could be detected even with rapid introduction of the reactant mixture. The reactants were, therefore, added during a period of 2 min.

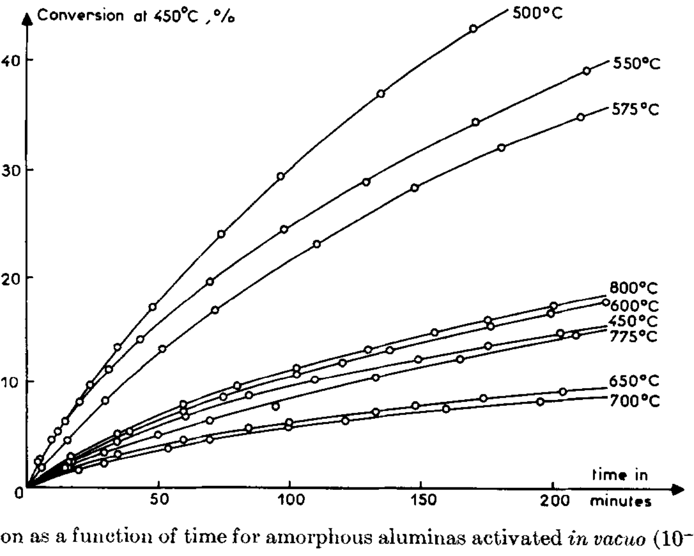

FIG. 1. Conversion as a function of time for amorphous aluminas activated *in vacuo* (10^{-6} torr) at different temperatures.

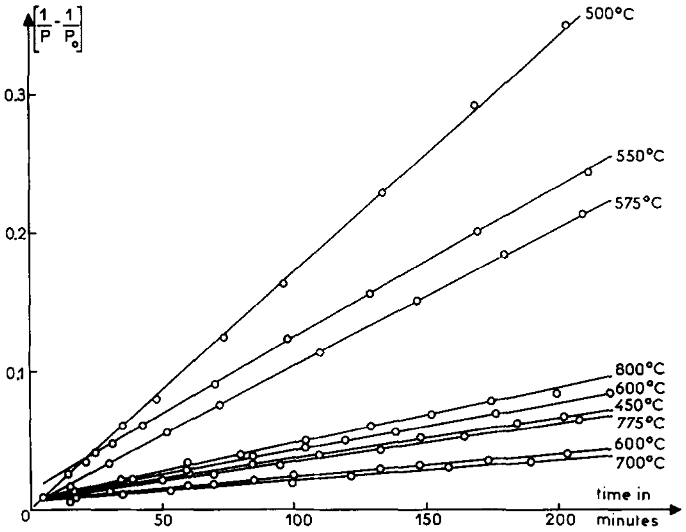

FIG. 2. Linear transformations of the curves of Fig. 1 according to the second-order rate law.

Zero time was taken as the end of the second minute.

(e) *Kinetic Analysis*

The oxidation of carbon monoxide was followed by recording the variation in total pressure, P, with time, t. Kinetic analysis proceeded from curves giving $P = f(t)$. At each value of P and t, there is a rate, $-dP/dt$, which is equal to the tangent at t. To compare the activities of samples activated under different conditions, the data are represented by the curves of degree of conversion as a function of time. If at time t, the pressure is P for an initial pressure of P_0 (at $t = 0$), then the conversion is given by $(P_0 - P)/P_0$.

Assuming that the reaction of a stoichiometric mixture follows the general kinetic law:

$$-\frac{dP}{dt} = kP^n,$$

where n is the total order of the reaction and k is the rate constant, n is determined from the integrated equation:

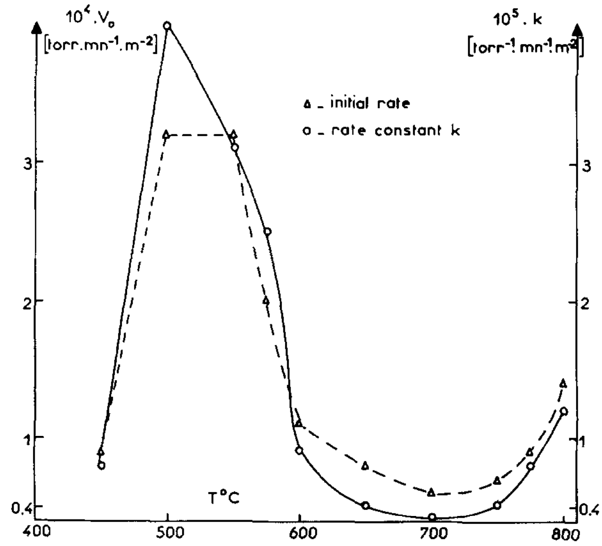

FIG. 3. Dependence of catalytic activity upon the temperature of activation *in vacuo*.

TABLE 1
VALUES OF k AND INITIAL RATES

Activation temp. (°C):	450	500	550	575	600	650	700	750	775	800
$10^5\ k$ (torr^{-1} min^{-1} m^{-2})	0.8	4	3.1	2.5	0.9	0.5	0.4	0.5	0.8	1.2
$10^4\ V_0$ (torr min^{-1} m^{-2})	0.9	3.2	3.2	2.1	1.1	0.8	0.6	0.7	0.9	1.4
Specific surface (m^2 g^{-1})	101	91	84	83	82	81	80	79	78	76

$$\frac{1}{1-n}\left(P_0^{1-n} - P^{1-n}\right) = kt. \qquad \text{(a)}$$

The orders with respect to each reactant follow the equations:

$$-\frac{dP}{dt} = kp_{\mathrm{CO}}{}^{x}p_{\mathrm{O_2}}{}^{y}, \qquad \text{(b)}$$

with $x + y = n$ if the reaction exhibits simple orders.

RESULTS AND DISCUSSION

I. *Development of Catalytic Activity*

Rate curves obtained for samples of alumina activated *in vacuo* (10^{-6} torr) for 14 hr at temperatures between 450 and 800°C appear in Fig. 1. The oxidation of carbon monoxide was carried out at 450°C in all cases.

Application of Eq. (a) to the experimental results showed that the total order was 2 for all samples. In Fig. 2, $[(1/P) - (1/P_0)]$ versus t are represented by lines from whose slopes one may calculate the rate constants, k. Table 1 presents values of k and the initial rates, both per 1 m^2 of alumina.

The curves in Fig. 3 present the dependence of initial rate and of the rate constants upon the temperature of activation *in vacuo*. These curves show that maximum activity results from activation at 500 to 550°C, that minimum activity occurs at about 700°C following which activity increases as the temperature of activation is further increased. However, the activity in this temperature region is always less than that at 500–550°C.

It should be noted that a maximum in the deficit of oxygen in alumina appears at about 500°C (*2*). As the temperature of activation *in vacuo* is increased from 500 to 700°C, the deficit in oxygen decreases although oxygen continues to be deficient (the catalyst is still an n-type semiconductor) (*2*). The catalytic activity also decreases distinctly as the temperature of activation is raised beyond 500–550°C and attains a minimum at about 700°C. Above

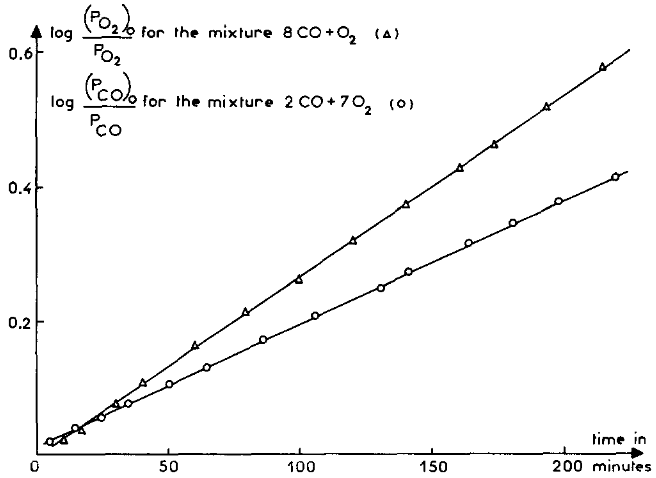

FIG. 4. Linear transformations according to the first-order rate law (nonstoichiometric mixtures).

700°C, the number of cation defects (distillation of aluminium) tends to become predominant and the solid becomes a *p*-type semiconductor at about 730°C (*2*). The increase in the deficit in aluminium which is uncompensated by the deficit in oxygen correlates closely with the increase in catalytic activity of alumina in the activation range of 700–800°C.

II. Determination of Individual Kinetic Orders

At 450°C, a total kinetic order of 2 was found for samples activated between 450 and 800°C (Fig. 2). The rate should, then, be expressable following Eq. (b):

$$\frac{dp_{CO_2}}{dt} = kp_{CO}{}^{x}p_{O_2}{}^{y},$$

since the reaction involves two reactant gases and the product, carbon dioxide, is continuously removed by a liquid nitrogen trap. Further, our experiments show that $x + y = 2$.

We have determined the individual kinetic orders for a sample activated at 500°C using the isolation method of Ostwald. In this we measured the rate of reaction of nonstoichiometric mixtures of reactants and determined the order of the reaction with respect to the partial pressure of the reactant in lowest concentration.

Thus, experiments with $2CO + 7O_2$ and $8CO + O_2$ showed that orders with respect to carbon monoxide and oxygen were both unity (Fig. 4).

These results show that $x = 1$ and $y = 1$ and that the oxidation of carbon monoxide on amorphous alumina activated at 500°C *in vacuo* follows the following rate law:

$$\frac{dp_{CO_2}}{dt} = kp_{CO}p_{O_2}.$$

III. Conclusions

The present data established a close correlation between the structural defects of alumina activated *in vacuo* and the catalytic activity of the alumina for oxidation of carbon monoxide.

The catalytic activity diminishes as the deficit in oxygen (anion defects) is reduced, in part, by the loss of aluminum (activation *in vacuo* rising from 500 to 700°C). Above 700°C, the amount of aluminium distilled from the alumina increases rapidly enough so that Al^{3+} defects predominate above about 730°C and the aluminium distilled from the alumina in-Correspondingly, the catalytic activity rises.

These results appear to be novel. Previous work seemed to show that catalytic activity for the hydrogenation of ethylene by nonstoichiometric alumina was not related to the degree of departure from exact stoichiometry (*12–14*). Moreover, studies of the oxidation of carbon monoxide on anatase (TiO_2) showed that catalytic activity depended upon defects only of oxygen (*15*). With alumina, catalytic activity seems to be linked to defects both in oxygen and in Al^{3+}.

Finally, the rate equation $dp_{CO_2}/dt = kp_{CO}p_{O_2}$ indicates that both oxygen and carbon monoxide are probably adsorbed rather weakly on alumina activated at 500°C *in vacuo*.

It would be desirable to confirm these conclusions as to the relation between catalytic activity and the nature and the degree of the departure from exact stoichiometry of the alumina catalyst (Fig. 3). A preliminary treatment of the catalyst in oxidizing or in reducing atmospheres would test our hypothesis as to the influence of structural defects of the two types upon the rate of catalytic oxidation of carbon monoxide. Results of such experiments will appear in a forthcoming publication.

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