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NOTE

A Study of the Catalysis of the Reaction $^{16}O_2 + {}^{18}O_2 = 2\ {}^{16}O^{18}O$ by α-$Cr_xAl_{2-x}O_3$ Solid Solutions

α-Chromia and α-alumina are isomorphous and form homogeneous solid solutions α-$Cr_xAl_{2-x}O_3$ with corundum structure over the whole range of x-values between 0 and 2. There have been many studies dealing with the physical properties of this system (*1–6*) and a number of researchers have pointed out the catalytic properties of α-chromia–alumina in relation to various gaseous reactions (*7–9*). A theoretical consideration of the dependence of the chromium ion distribution in the corundum matrix on the total chromium content can also be found (*10*). The aim of the present work was to investigate the dependence of the activity of the α-$Cr_xAl_{2-x}O_3$ solid solutions on composition in relation to homomolecular oxygen exchange.

EXPERIMENTAL METHODS

The solid solutions α-$Cr_xAl_{2-x}O_3$ were prepared by impregnating α-Al_2O_3 (spec. pure) with a solution of CrO_3 (reagent grade) in water. After drying at 120°C the samples were calcined in air in platinum crucibles at 1370°C for 32 hr with an intermediate cooling and regrinding after 16 hr. The specific surface areas of the samples were measured by means of krypton adsorption at -196°C and all coincided with that of pure α-Al_2O_3 treated in the same conditions (i.e., 2.0 ± 0.1 m^2/g). If the designation AC N, where N is the number of Cr atoms per 100 atoms of Al, is used to label the solid solutions (*6*) then the sample preparations correspond to AC 0.1, AC 0.5, AC 1.0, AC 4.4 and AC 10.0. The reaction $^{16}O_2 + {}^{18}O_2 = 2{}^{16}O^{18}O$ was studied in a static system connected to a mass spectrometer using oxygen pressures in the range 0.05–2 Torr. The concentration of ^{18}O in the nonequilibrium mixture varied but was about 18 atomic %. The samples were pretreated together at 830°C for 16 hr in vacuum (5×10^{-6} Torr). The catalysis of the reaction $^{16}O_2 + {}^{18}O_2 = 2\ {}^{16}O^{18}O$ in the low temperature region was studied immediately after the vacuum pretreatment. Before the high temperature experiments the samples were first equilibrated with the gas mixture so that they had the same ^{18}O content as the gas. The activities were expressed as the specific first order rate constants (min^{-1} cm^{-2}) which were reproducible to within ±10%.

RESULTS AND DISCUSSION

The main results for both the low and high temperature exchange reactions are summarized in Table 1 where K, E and n represent the specific rate constants, apparent activation energies and the orders of reaction, respectively. The subscripts l and h denote the low and high temperature cases. The activation energies (E_l) and orders with respect to oxygen pressure (n_l) are nearly the same for all the samples studied and the numerical values of E_l and n_l give evidence in favor of an associative mechanism of catalysis. The low temperature activity was unstable at temperatures above -100°C and this phenomenon was studied for the three samples AC 0.1, AC 1.0 and AC 10.0 in the temperature range -100 to -30°C. At selected temperatures, the reaction time ($t_{1/2}$) which corresponded to a decrease in activity to half the initial value was calculated. The activation energies for the deactivating processes could then be calculated and as shown in Fig. 1 they are

TABLE 1

KINETIC DATA FOR HIGH AND LOW TEMPERATURE REACTIONS

Sample	K_l at −100°C ($\text{min}^{-1}\ \text{m}^{-2}$)	K_h at 630°C ($\text{min}^{-1}\ \text{m}^{-2}$)	R_h at 630°C ($\text{min}^{-1}\ \text{m}^{-2}$)	E_l (kcal/mole)	E_h (kcal/mole)	n_l	n_h
α-Al_2O_3	0.02	Inactive	—	—	—	—	—
AC 0.1	0.06	0.29	0.17	2.1	26	0.4	1.1
AC 0.5	0.16	0.49	—	1.7	28	0.5	0.9
AC 1.0	0.16	0.24	0.10	2.2	29	0.5	0.8
AC 4.4	0.18	—	—	1.8	—	0.5	—
AC 10.0	0.23	0.67	0.26	1.8	29	0.4	0.9

approximately equal (1.5–2.0 kcal/mole). It can thus be concluded that the activity with regard to the low temperature reaction is generated on sites of a similar nature for the whole range of solid solutions studied. The differences observed in the reaction rates K_l over the different samples can be attributed to a change in the *number* of sites.

With regard to the high temperature experiments, it was found that where measurements were made the value obtained for the rate constant of heterogeneous exchange of ^{18}O between the oxide and the gas mixture (R_h) was approximately half the K_h value (see Table 1). This suggests that the catalysis of the homomolecular reaction at high temperatures proceeds mainly through a heterogeneous exchange process between the gas mixture and the surfaces of the samples. An analysis of the change in the relative amounts of the molecules $^{16}O^{16}O$, $^{16}O^{18}O$ and $^{18}O^{18}O$ in the course of the heterogeneous exchange showed that the predominant type of exchange involved the participation of only one atom of the oxygen molecule per elementary step (*11*, *12*). As in the low temperature case, the values obtained for E_h and n_h for the different solid solutions are nearly coincident suggesting similar mechanisms of homomolecular exchange catalysis.

When considered in terms of the rate constant per chromium ion, the activity decreases as the chromium content of the samples increases and this applies to both the high temperature and the low temperature reactions (see Fig. 2). Previous studies (*9*, *10*) have shown that at low chromium content, chromium is present in the corundum structure mainly in the form of isolated ions. As the chromium content increases, the *proportion* of chromium in the form of isolated ions decreases due to the

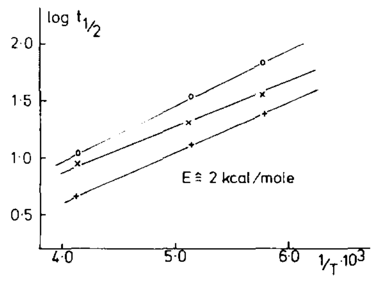

FIG. 1. Deactivating process for low temperature exchange reaction measured for (○) AC 10.0; (×) AC 1.0; (+) AC 0.1.

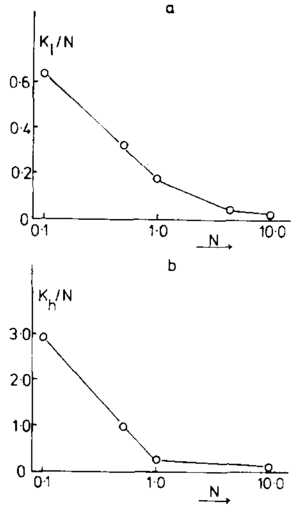

FIG. 2. Dependence of rate constant per chromium ion on the chromium content of the solid solution for (a) low temperature exchange (measured at −100°C) and (b) high temperature exchange (measured at 630°C).

higher probability of having Cr ions in adjacent positions. Therefore if it is assumed that the most active catalytic sites are connected with isolated Cr ions on the surface, the decrease in activity, which is evident for both the high and low temperature cases, can be attributed to the depletion in the number of active sites as the proportion of isolated Cr ions in the solid solution decreases. It is known from ESR studies that O^- species (*13–15*) arise when O_2 is admitted to a vacuum-reduced oxide surface. In the chromia–alumina system O^- ions adsorbed near to low-coordinate Cr^{3+} ions on the surface could provide suitable surface sites, active in the catalysis of homomolecular exchange. This exchange could then proceed through the formation of complexes of the O_3^- type (*13*). At high temperatures the oxygen ions which complete the coordination sphere of isolated surface Cr^{3+} ions will be most mobile and in this case the mechanism of exchange can be thought of as the breaking and reforming of the bonds in the coordination spheres of isolated surface Cr_3^+ ions.

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G. V. ANTOSHIN
M. F. O'CONNOR*

Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR
Moscow, U.S.S.R.

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* Present address: Du Pont de Nemours (Deutschland) GmbH, Konigsbergerstrasse 16, 636 Friedberg/Hessen 1, West Germany.