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NOTES

Exchangeable Oxygen on Alumina[1]

In our previous paper (*1*) we reported that oxygen atoms on the alumina surface are exchangeable with carbon dioxide and that the amount of exchangeable oxygen increases with the reaction temperature. It was also found that there are two sorts of exchangeable oxygen: One is exchanged readily at temperatures lower than 300°C, while the other becomes exchangeable at higher temperatures. The former was called reactive oxygen to distinguish it from the latter. The maximum surface density of the reactive oxygen as well as that of total exchangeable oxygen (N_{ex}) at various temperatures were measured in the previous study (*1*).

Bicarbonate ion and possibly carbonate ion as well were suggested as the intermediates of the exchange reaction. On the other hand, most results of infrared spectroscopy (*2–4*) show that carbon monoxide adsorbed on alumina gives absorption bands below 2000 cm^{-1} similar to those of carbon dioxide. Parkyns (*3*) concluded that those bands observed with carbon monoxide were mainly due to carbon dioxide formed by the surface oxidation. In our study, too, carbon monoxide adsorbed at room temperature on an η-alumina used for the exchange reaction gave absorption bands at 1830, 1630, 1470, 1230, and 1180 cm^{-1}, while carbon dioxide on the same sample showed bands at 1900–1750, 1636, 1484, 1235, and 1180 cm^{-1}, as previously reported (*1, 5*). Since these bands seem ascribable to bicarbonate and carbonate ions, we carried out the exchange reaction of oxygen between $\mathrm{C^{18}O}$ and the alumina used for the $\mathrm{CO_2}$ exchange.

The catalyst (0.501 g, 129 $\mathrm{m^2/g}$) and apparatus have been described previously (*1*). The isotopic purity of $\mathrm{C^{18}O}$ used was 99 atom%. The results of a reaction are shown in Fig. 1, where those with $\mathrm{C^{18}O_2}$ are also included for comparison. The exchange with carbon monoxide is much slower than that with carbon dioxide at 300°C. Note that ${}^{16}f$ for CO in Fig. 1 should be reduced to half to compare the net rate of exchange because about the same number of molecules of CO and $\mathrm{CO_2}$ was used in both reactions. Even at temperatures higher than 500°C it took 1 to 4 hr for the exchange with CO to be equilibrated, and the reaction was too slow to follow below 300°C. When the equilibrium (no change of ${}^{16}f$ with time) was reached, the number of exchangeable oxygen atoms, N_{ex}, was calculated from the equation

$$N_{\mathrm{ex}} = N({}^{16}f_{\mathrm{e}} - {}^{16}f_{\mathrm{o}})/({}^{16}f_{\mathrm{so}} - {}^{16}f_{\mathrm{e}}),$$

where N is the number of carbon monoxide molecules in the system, ${}^{16}f_{\mathrm{e}}$ is the atom fraction of $^{16}\mathrm{O}$ in the gas phase at equilibrium, and ${}^{16}f_0$ and ${}^{16}f_{\mathrm{so}}$ are the initial atom fractions of $^{16}\mathrm{O}$ in the gas phase and on the surface, respectively. The surface densities of N_{ex} measured at 500, 550, and 624°C were, respectively, 2.02, 3.81, and 5.09 $\times 10^{14}$ atoms/$\mathrm{cm^2}$ on the alumina de-

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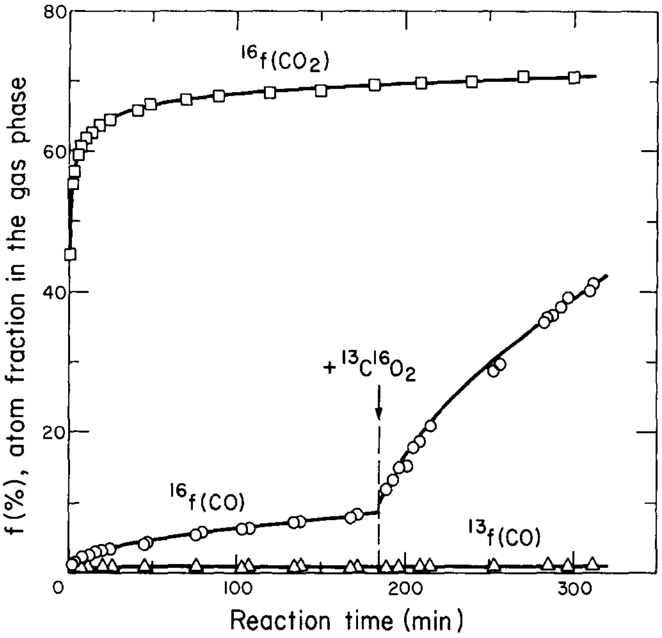


FIG. 1. Time course of oxygen exchange at 300°C: the upper curve with carbon dioxide, the lower curves with carbon monoxide. The pressures of CO_2, CO, and ^{13}CO added were all about 1 Torr.

hydrated at 650°C. These densities are all smaller than those obtained with carbon dioxide at corresponding temperatures, and the ratios are 0.48, 0.61, and 0.46, the average of which is 0.52.

As seen in Fig. 1, $^{13}C^{16}O_2$ was added to the system at 185 min and an increase in oxygen exchange was observed, while there was no appreciable increase in the atom fraction of ^{13}C in the carbon monoxide. The ^{13}C fraction did not change even after the reaction temperature was increased to 400°C later, indicating that the reaction $CO + {}^{13}CO_2 \rightleftharpoons CO_2 + {}^{13}CO$ did not take place at these temperatures. The exchange rate of oxygen atoms after the addition of carbon dioxide became about 15 times faster than the rate immediately before the addition. However, the former was found to be equal to the initial rate of exchange without CO_2 when it was measured from the slope on an expanded scale, as shown in Table 1.

It appears that the fast exchange by carbon dioxide replenishes the active oxide sites with ^{16}O, bringing them back to the initial concentration of ^{16}O; thus, the exchange with CO continues at its initial rate. Indeed, the actual number of exchanged oxygen atoms replotted from Fig. 1 became linear with time after CO_2 was added. Also, at high temperatures, where $^{16}f_e$ could be determined, the plot of $\log(^{16}f_e - {}^{16}f_t)$ against reaction time t was not linear, but deviated upward. Apparently, the surface oxide ions are heterogeneous for carbon monoxide and most of

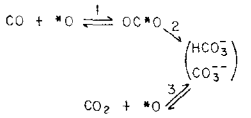
TABLE 1

Comparison of the Initial Rate of Exchange before and after the Addition of CO_2

Temperature (°C)	Initial rate (atoms/cm²·min)	
	V_1 (before)	V_2 (after)
300	1.55×10^{11}	1.56×10^{11}
420	2.01×10^{12}	1.98×10^{12}

the exchange at the initial stage takes place on the most active oxide sites.

Summarizing the results, the rate of oxygen exchange with carbon monoxide is much slower than that with carbon dioxide, and no exchange of carbon atoms between the two molecules takes place at least up to 400°C in spite of the fact that both molecules give similar absorption bands on alumina in infrared spectroscopy. The results leave two alternative mechanisms for the exchange: (1) CO and CO_2 have common intermediates, but step 2 is much slower than the others in the scheme



or (2) all steps are equilibrated but carbonate and bicarbonate ions from the respective molecules are formed on different sites.

In mechanism (1) a type of $\mathrm{O{-}\underset{|}{C}^*{-}O}$ is more likely as the precursor of carbonate groups than the dipole-type interaction of CO suggested by Amberg and Seanor (*6*) for weakly adsorbed carbon monoxide. Also the case where step 2 does not practically occur at high temperatures in particular is included in mechanism (1). Actually no absorption bands were observed in infrared spectroscopy at 300°C with CO up to 200 Torr, while with CO_2 all bands below 2000 cm^{-1} were observed at 400°C and the 1480-cm^{-1} band was still detectable at 600°C. Mechanism (2) seems less likely although the constant ratio of N_{ex} (0.5) between CO and CO_2 observed at high temperatures may be related to this mechanism.

The exchange of oxygen between $^{18}O_2$ and alumina was still found to be much slower. No exchange could be observed below 300°C, and at 520°C it took longer than 100 hr to reach equilibrium. However, the intermolecular equilibration in the gas phase, $^{16}O_2 + {}^{18}O_2 \rightleftharpoons 2{}^{16}O^{18}O$, was established much faster, for example, 3 hr at 520°C. Apparently, the exchange between the surface oxygen and adsorbed oxygen is the rate-determining step for the exchange reaction. In contrast with the case of carbon monoxide, the number of exchangeable oxygen atoms, N_{ex}, obtained with O_2 between 520 and 630°C was in good agreement with those obtained with CO_2 (5 to 10 $\times$ 10^{14} atoms/cm^2). Winter (*7*) also reported that the number of exchangeable oxygen atoms on γ- and δ-alumina measured by the exchange with $^{18}O_2$ exceeded 10^{15} atoms/cm^2 at temperatures between 480 and 720°C.

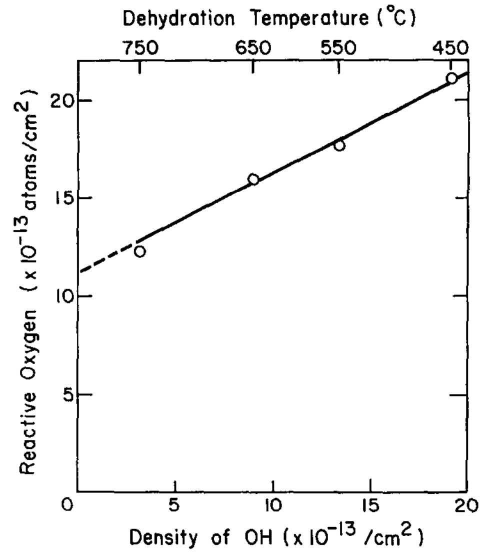


FIG. 2. Reactive oxygen versus hydroxyl groups.

It was assumed in the previous paper (*1*) that the reactive oxygen atoms are preferentially removed as water when alumina is dehydrated. If this is true, the number of reactive oxygen atoms should decrease linearly with the number of hydroxyl groups on the surface. After the measurements were made on the alumina dehydrated at 650 and 750°C, as reported previously (*1*), the surface was contacted with water vapor from 600°C to room temperature and then dehydrated by evacuating at 450 and 550°C, respectively. The density of hydroxyl groups was measured by exchange with deuterium gas, and N_{ex} measured with $C^{18}O_2$ at 300°C was taken as the number of reactive oxygen atoms because they are approximately equal, as reported earlier (*1*). The results plotted in Fig. 2 give a linear line and the slope shows that the decrease in reactive oxygen is half of the hydroxyl groups removed, supporting the above assumption.

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