JOURNAL OF CATALYSIS 48, 120–128 (1977)

Exchange of Oxygen between Carbon Dioxide and Alumina[1]

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Received October 22, 1976; revised January 31, 1977

Oxygen exchange between $C^{18}O_2$ and an η-alumina has been studied over a wide range of temperature between 27 and 700°C mainly by mass spectrometry. The amount of exchangeable oxygen increased with increasing temperature, and finally exceeded 10^{15} atoms/cm². However, the temperature dependence had an inflection point at about 300°C, and it became much steeper at higher temperatures. It was concluded that two different sorts of processes take place: unstable (reactive) oxygen atoms on alumina are exchanged readily at relatively low temperatures, while at higher temperatures all oxygen atoms on the surface and also those in the deeper layers are involved in exchange.

Strongly chemisorbed carbon dioxide which neither exchanged nor communicated with the gaseous molecules was detected by infrared spectroscopy, and the amounts of this irreversible adsorption were measured under the reaction conditions by using $^{13}CO_2$ as a tracer. The maximum surface density of the reactive oxygen atoms exchangeable at lower temperatures was also obtained as 1.32×10^{14} and 1.03×10^{14} atoms/cm² for the catalyst dehydrated at 650 and 750°C, respectively. A likely intermediate of the exchange reaction is bicarbonate ion which, in turn, blocks two to three adjacent oxygen atoms for the exchange when adsorbed irreversibly. Below 300°C, the increase in the exchangeable oxygen with temperature seems to result from the decreasing amount of the irreversible adsorption.

INTRODUCTION

Carbon dioxide is an interesting poison for various reactions catalyzed by alumina. Generally it poisons alumina for reactions involving hydrogen but has little effect on the isomerization reaction of olefins (*1–6*). The adsorption of carbon dioxide on alumina has been studied extensively mainly by infrared spectroscopy (*1, 7–11*), but the assignment of some absorption bands is still controversial. Consequently, the mechanism of CO_2 poisoning is not yet clear.

In general, three kinds of ions, Al^{3+}, OH^- and O^{2-}, are exposed on the surface of alumina. The ions themselves, or more likely, various combinations of them constitute active sites as suggested by Peri (*12*) by a model of alumina surface. The oxide ions, however, have not been studied extensively compared to the other ions. In view of this, we started an investigation of the oxygen atoms on alumina surface by the exchange reaction of oxygen between $C^{18}O_2$ and an η-alumina.

Recently, Peri (*13*) published interesting results of similar exchange reaction between $C^{18}O_2$ and oxide catalysts including alumina. He detected very reactive oxide ions on the catalysts which were exchangeable at relatively low temperatures. Nevertheless, we felt it worthy to report our results for a few reasons. While Peri measured the exchangeable oxygen from

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ISSN 0021-9517

the relative intensities of the infrared bands of CO_2 physically adsorbed, we used a mass spectrometer although the results were supplemented by infrared spectroscopy. The reaction temperature was extended to 700°C in our study, and as a result of that, we found two different types of exchange reaction. We also found that a certain portion of adsorbed gas did not participate in exchange and its amount was measured.

This paper reports the results obtained and a possible mechanism is suggested.

EXPERIMENTAL METHODS

Materials

Alumina sample used in this study was an η-alumina which was described previously (*14*). The alumina was ground into fine powder which was pressed into disks under a pressure of 2 tons/cm^2. One was thin (9.8 mg/cm^2) and used for infrared spectroscopy, while the others (about 100 mg/cm^2) were cut into fragments of about 4 mm^2 for the exchange reaction. An amount of 0.501 g of the fragments was loaded in the reactor and used throughout the present study. The catalyst was calcined with air in the reactor for 3 hr at 650°C and evacuated for 3 hr at the same temperature. The surface area after this treatment was 129 m^2/g as measured by BET with krypton at liquid nitrogen temperature. The catalyst was evacuated at 627°C prior to each run until the pressure became less than 1×10^{-7} Torr (1 Torr = 133.3 N m^{-2}).

^{18}O enriched carbon dioxide ($^{12}C^{18}O_2$) and ^{13}C enriched one ($^{13}C^{16}O_2$) were both purchased from Bio-Rad Laboratories, California, and their isotopic concentrations at the time of use were 94 and 84 atom%, respectively. All carbon dioxide including $^{12}C^{16}O_2$ (Matheson's research grade) was thoroughly degassed at liquid nitrogen temperature and evaporated at dry ice–methanol temperature into reservoirs. Argon used as diluent was taken from a Metheson's ultrahigh purity cylinder and dried through a trap by dry ice–methanol bath.

Apparatus

The apparatus was a closed recirculation system made of glass with metal valves and equipped with a capacitance pressure transducer whose range was 10^{-5} to 10 Torr. The quartz reactor was in the shape of trap, and the catalyst was held on a perforated disk fused to the bottom of the inner tube. The total volume of the system was 620 cm^3 including the reactor (53 cm^3). The gas was circulated during the reaction by a all glass circulation pump, and the isotopic composition was analyzed continuously or at proper intervals of time by a mass spectrometer (Model 610-611, Aero Vac Co., New York) which was connected to the reaction system through a variable leak valve. The reaction system could be easily evacuated to 5×10^{-8} Torr or less after a bake out at 150°C, while the basic pressure in the mass spectrometer was kept lower than 1×10^{-9} Torr so that no correction for the background was necessary. It was found that a considerable exchange occurred at first between carbon dioxide and the walls of the system, but it was reduced after an extensive bake out of the whole system at 150°C to a rate of 1.6×10^{15} atoms/min which was much lower than the rates observed with the catalyst.

The apparatus for infrared spectroscopy has been described previously (*14, 15*). The alumina wafer was treated in the infrared cell similarly to the case of exchange reaction.

Procedure

Most of the reactions were carried out under a partial pressure of $C^{18}O_2$ of less than 3 Torr. The amount of carbon dioxide was measured in the system (excluding the

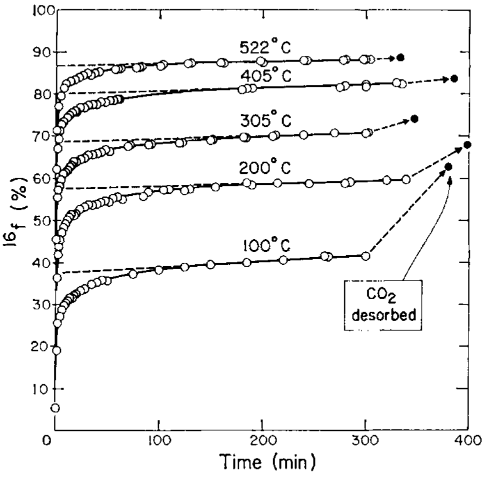

FIG. 1. Time course of exchange reaction with $C^{18}O_2$. The reaction temperature is indicated on each curve. (●) The isotopic concentration of the gas removed from the surface at temperatures higher than 350°C after reaction.

reactor) manometrically, and condensed into a trap. Argon was then added to the system so that the total pressure became about 10 Torr at the time of reaction in order to increase the thermal conductivity in the reactor and the efficiency of the circulation pump. Carbon dioxide was mixed thoroughly with argon by evaporating it and circulating through the system for about 10 min before reaction. After the initial isotopic composition of the gas was analyzed, the reaction was started by diverting the gas to circulate through the reactor. The amount of carbon dioxide consumed for the mass spectrometric analysis during a run was less than 0.5% of the total carbon dioxide in the system, and was neglected in the calculation. The surface enriched by ^{18}O as a result of reaction was exchanged back by treating it with $C^{16}O_2$ at 627°C several times, and the isotopic composition in the gas at the final treatment was regarded as the initial surface composition for the next run.

The amount of oxygen atoms exchangeable under the reaction conditions was calculated from the material balance for ^{16}O. When the fraction of ^{16}O atoms in the gas phase increases from its initial value, $^{16}f_0$, to $^{16}f_e$ as a result of isotopic equilibration, the number of exchangeable oxygen atoms on the surface, N_{ex}, is given by the equation,

$$N_{ex} = 2N(^{16}f_e - {}^{16}f_0)/(^{16}f_{s0} - {}^{16}f_e), \quad (1)$$

where N is the number of carbon dioxide molecules in the system and $^{16}f_{s0}$ the initial fraction of ^{16}O atoms on the surface. In this paper, the equilibration of oxygen atoms between the gas phase and the exchangeable oxygen on the surface was assumed. Equation (1) is valid as long as the fraction of ^{16}O is homogeneous throughout the carbon dioxide in the system. Cases where this condition is not met are discussed below.

The number of hydroxyl groups on the surface was also measured by exchange with deuterium. Deuterium at a pressure of about 10 Torr was circulated through the catalyst at 627°C and the isotopic composition in the gas phase was analyzed gas chromatographically. The protium concentration in the gas phase did not change appreciably after 1 hr, and the surface density of hydroxyl groups was determined from the flat portion after 1 hr. Peri and Hannan (*16*) also reported that all the hydrogen of hydroxyl groups on γ-alumina exchanged readily with deuterium when the temperature was higher than 500°C.

RESULTS

1. *Exchange Reaction with $C^{18}O_2$*

Results of exchange reaction obtained with $C^{18}O_2$ at various temperatures are shown in Fig. 1 where the fraction of ^{16}O atoms in the gas phase calculated from the mass spectra was plotted against the reaction time. At all temperatures, the fraction of ^{16}O increased rapidly in the initial stage followed by a slow and almost linear increase. The intermolecular equilibration was fast and the statistical equilibrium ($[C^{16}O^{18}O]^2/[C^{16}O_2][C^{18}O_2] = 4$) was attained within 10 min even at the lowest temperature employed. The slow reaction in the later stages took place at a rate of 2.8×10^{16} and 1.8×10^{17} atoms/min, respectively, at 100 and 522°C, which were still much faster than the rate of exchange with the walls of the system (1.6×10^{15} atoms/min). It was therefore concluded that this slow process is also an exchange reaction of oxygen atoms of the catalyst but occurs by a different mechanism from that of the initial process.

The initial rapid exchange was so fast that the real rates could not be measured. The linear portion of the slow process was extrapolated to time 0 at each temperature as shown in Fig. 1, and the intercept was taken as ${}^{16}f_e$ in Eq. (1) to calculate N_{ex}, the number of readily exchangeable oxygen atoms on the surface. Although the actual values of N_{ex} are discussed below in more detail, Fig. 1 shows clearly that the exchangeable oxygen atoms on the surface increase with temperature in agreement with the results of Peri (*13*).

In the experiments shown in Fig. 1, the amount of carbon dioxide used was so adjusted that it gave about 1 Torr of the partial pressure at all temperatures. For example, the experiment at 522°C was done with 32.7 μmol of $C^{18}O_2$. Two other reactions were carried out at 522°C but with 18.2 and 77.2 μmol of $C^{18}O_2$, respectively. N_{ex} thus obtained agreed within 10% with that calculated from the curve in Fig. 1, indicating that N_{ex} could be measured independent of the amount of the gas used. A deviation of 10% was not thought to be serious from the difficulties of the experiments and the reproducibility of the surface state in particular. In fact, larger amounts of carbon dioxide (about 77 μmol) were used to obtain the reliable values of N_{ex} at high temperatures, which otherwise became erroneous due to a small numerical value of the denominator in Eq. (1).

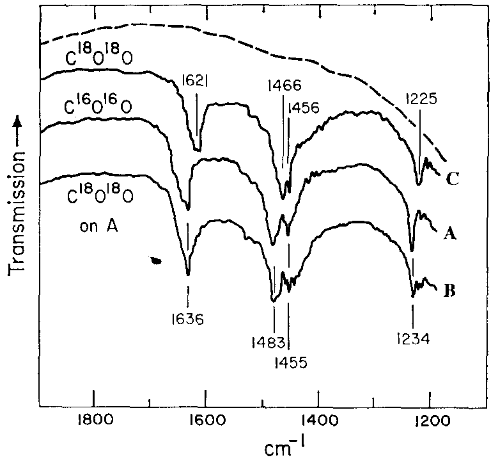

FIG. 2. Infrared spectra of carbon dioxide remaining on alumina after evacuation at 100°C. In all cases, the gas was adsorbed at 100°C and about 1 Torr, and evacuated at 100°C before taking spectrum at 27°C. (— —) The absorption with the catalyst only. The spectra were displaced vertically for clarity.

2. Irreversible Chemisorption

After the time course in Fig. 1 was observed at each temperature, the gas was removed from the surface by heating the catalyst up to 627°C continuously while pumping. A portion of the gas removed was collected in a trap between 350 and 627°C and its isotopic concentration was analyzed, as shown by filled circles in Fig. 1. As shown in Fig. 1, the ${}^{16}O$ fraction of the gas removed was greater than that at the end of the reaction, and the difference increased with decreasing reaction temperature. The facts suggest that there is a certain amount of carbon dioxide irreversibly chemisorbed and not equilibrated with the gaseous molecules during the reaction and that on the removal at higher temperature the exchange with the surface went on more extensively. Strongly adsorbed carbon dioxide has been observed on alumina also by other investigators (*2*, *4*, *17*).

In order to obtain more information on the irreversible chemisorption, some experiments were carried out by infrared spectroscopy, the results of which were shown in Fig. 2. Spectrum A in Fig. 2 was obtained by adsorbing $C^{16}O_2$ on alumina at 100°C and 1 Torr and subsequently evacuating for 45 min at the same temperature, while spectrum C was taken under similar conditions but with $C^{18}O_2$ on the ^{18}O enriched alumina obtained by repeated exchange. Therefore, these spectra are those of carbon dioxide strongly chemisorbed and remaining on the surface after evacuation at this particular temperature. The temperature and pressure employed here were similar to those used for the 100°C exchange in Fig. 1.

The present results were in good agreement with the previous results (*15*) except for a band at 1455 cm^{-1} whose origin was not known yet. In the previous report (*15*), we have assigned the bands at 1636, 1483 and 1234 cm^{-1} to a bicarbonate ion on the surface. The previous paper also showed that the frequency of the asymmetric and symmetric CO vibrations, namely 1636 and 1483 cm^{-1}, shifted smoothly as a function of the isotopic concentration of oxygen of the carbon dioxide. After taking the spectrum A in Fig. 2, $C^{18}O_2$ was admitted in the cell at 100°C and 1 Torr for 2 hr, and finally pumped out at the same temperature before taking a spectrum (spectrum B). An extensive exchange of oxygen was observed with the gas removed by a mass spectrometer attached. Nevertheless, the spectrum B shows no frequency shifts at all indicating that the majority of bicarbonate ions strongly adsorbed did neither exchange its oxygen nor communicate with the gaseous molecules at the reaction temperature. The solid circles in Fig. 1 apparently resulted from further exchange with the gas desorbed from the surface at higher temperatures during evacuation.

It should be noted here that the absorption bands shown in Fig. 2 are not representing the whole surface species remaining on the surface. A weak but clear absorption was observed in the 2330–2370 cm^{-1} region even after evacuation at 100°C. Also in the presence of carbon dioxide in the gas phase at 1 Torr, the absorption of the bands shown in Fig. 2 was stronger with some other bands appearing at 2330–2370, 1900–1750 and at 1180 cm^{-1}. Therefore, some bicarbonate ions as well as most of the physically adsorbed molecules and probably bridged carbonate ions are easily removed by pumping, while a part of bicarbonate ions is chemisorbed irreversibly at the reaction temperature probably due to an energetic heterogeneity of the sites.

Since some carbon dioxide did not exchange as found above, we can no longer use the total amount of carbon dioxide in the system as N in Eq. (1) for the accurate calculation of N_{ex} particularly at low temperatures. The results of ir could not be used to evaluate the amount of irreversible chemisorption, because the reliable extinction coefficient of bicarbonate bands on this particular alumina was not available, and moreover, the amount of irreversible chemisorption varied with the reaction conditions. The irreversible chemisorption was measured simultaneously with the exchange reaction by the displacement of preadsorbed $^{13}C^{16}O_2$ by the gaseous molecules similarly to a method used by Morikawa and Ozaki (*18*) for the study of nitrogen displacement on iron catalysts.

First, $^{13}CO_2$ was allowed to adsorb for 300 min at about 1 Torr and at the temperature of reaction to be studied. The adsorption actually continued longer, but the increase in the adsorbed amount after 300 min was so small that the adsorption equilibrium was assumed to have established practically. The reactor was isolated and the rest of the gas was pumped out. At this stage, the total amount of the gas in the reactor, the total amount adsorbed and, therefore, the amount in the gas phase were all known and the fractions of carbon and oxygen isotopes were analyzed just before the isolation of the reactor. $C^{18}O_2$ was then admitted to the rest of the system carefully adjusting its pressure to that of $^{13}CO_2$ remaining in the reactor, so that, when the exchange reaction took place by circulating the whole gas through the reactor, the adsorbed amount of carbon dioxide was not disturbed. One of the results thus obtained is shown in Fig. 3 which was carried out at 100°C. The fractions of ^{13}C and ^{16}O atoms in the gas phase were plotted in the figure against time, as indicated by ^{13}f and ^{16}f, respectively. Also included in Fig. 3 are two broken lines which were calculated by assuming, respectively, that the total $^{13}CO_2$ in the reactor was equilibrated with $C^{18}O_2$ [$^{13}f_e$(total)] or the only $^{13}CO_2$ present in the gas phase in the reactor participated in the equilibration [$^{13}f_e$(gas)]. In Fig. 3, the fraction of ^{13}C increased very rapidly well beyond $^{13}f_e$(gas) to a value closer to $^{13}f_e$(total), but was always lower than that. Apparently, a large fraction of preadsorbed molecules was readily replaced by gaseous molecules but, as expected, some remained adsorbed irreversibly without communicating with the gas phase. In the gas phase, an equilibrium was attained in 40 min among all molecular species of carbon dioxide, that is,

$$[C^{18}O^{16}O]^2/[C^{18}O_2][C^{16}O_2] = [^{13}C^{18}O^{16}O]^2/[^{13}C^{18}O_2][^{13}C^{16}O_2] = 4.$$

The material balance for ^{13}C leads us to the equation,

$$N_{\text{rev}} + N_G = N(^{13}f_e - {}^{13}f_0)/(^{13}f_r - {}^{13}f_e), \quad (2)$$

where N_{rev} and N_G are the numbers of $^{13}CO_2$ molecules reversibly adsorbed and present in the gas phase of the reactor before the mixing, respectively, and N is the number of $C^{18}O_2$ molecules added. $^{13}f_r$ and $^{13}f_0$ are, respectively, the fractions of ^{13}C of $^{13}CO_2$ in the reactor and of $C^{18}O_2$ used (natural abundance) before the mixing, while $^{13}f_e$ is the fraction at equilibrium.

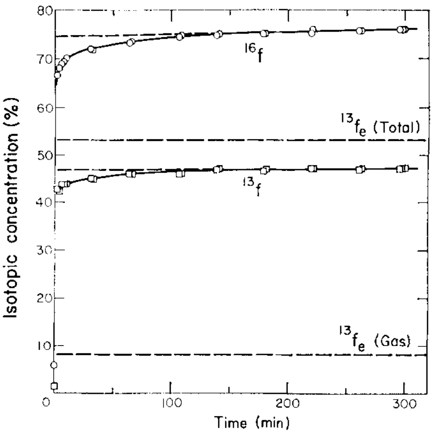

FIG. 3. Time courses of ^{16}O and ^{13}C concentration in the gas phase at 100°C. $^{13}f_e$(total) and $^{13}f_e$(gas) are the calculated fractions assuming the complete mixing of total and gaseous $^{13}CO_2$ in the reactor, respectively.

As was done in Fig. 1, the intercept obtained by extrapolating the later linear portion of ^{13}f was taken as $^{13}f_e$ for calculation. Thus the amount of carbon dioxide reversibly adsorbed, N_{rev}, was first calculated by Eq. (2), and the amount of irreversible adsorption, N_{irr}, was obtained by subtracting N_{rev} from the total adsorption which had been measured at the preadsorption of $^{13}CO_2$. The preadsorption was measured in much smaller volume than the reaction system for better accuracy.

The number of exchangeable oxygen atoms on the surface, N_{ex}, was also calculated from the fraction of ^{16}O at equilibrium, $^{16}f_e$ (extrapolation of ^{16}f in Fig. 3 to time 0), by the equation

$$N_{\text{ex}} + 2(N_{\text{rev}} + N_G) = 2N(^{16}f_e - {}^{16}f_0)/(^{16}f_{s0} - {}^{16}f_e). \quad (3)$$

In the above equation, the initial fraction of ^{16}O in the $^{13}CO_2$ was assumed to be equal to that of the surface, $^{16}f_{s0}$, because the catalyst was treated with $^{13}CO_2$ for 5 hr at 627°C before the preadsorption and the same $^{13}CO_2$ was preadsorbed.

Results thus calculated were summarized in Table 1 where N_{rev}, N_{irr} and N_{ex} were calculated from Eqs. (2) and (3) at lower

TABLE 1

Results of Exchange Reaction on Alumina Dehydrated at 650°C[a]

Temp (°C)	P (Torr)	$N_{rev} \times 10^{-13}$ (molecules/cm²)	$N_{irr} \times 10^{-13}$ (molecules/cm²)	$N_{ex} \times 10^{-13}$ (atoms/cm²)
50	1.09	3.62	2.02	6.72
100	0.91	3.03	1.22	8.59
200	0.89	1.68	0.45	11.91
305	1.00	0.71	0.19	15.99
405	1.13[b]			27.96
522	1.00[b]			47.21
627	2.36[b]			105.52

[a] Surface density of OH: 9.0×10^{13} OH/cm², surface area: 129 m²/g.

[b] Pressure was calculated from the amount of $C^{18}O_2$ admitted.

temperatures, while Eq. (1) was used for the simple exchange reaction at high temperatures because of negligible amounts of irreversible adsorption. Results obtained by similar experiments on the same catalyst but dehydrated at 750°C are shown in Table 2. The dehydration at 750°C did not change the surface area within experimental error. The number of hydroxyl groups measured was also added to the tables.

DISCUSSION

The amount of irreversibly adsorbed molecules in Tables 1 and 2 decreases with increasing temperature as expected from the results of Fig. 1. Larson and Hall (*2*), Van Cauwelaert and Hall (*4*) and recently Rosynek (*17*) also measured strongly adsorbed carbon dioxide on alumina as the amount of gas retained on the surface after evacuation at various temperatures. The amounts obtained by Van Cauwelaert and Hall (*4*) were about twice larger than N_{irr} measured in the present study at corresponding temperatures between 100 and 300°C, and those obtained by Rosynek (*17*) were still larger. We also made similar measurements and found a good agreement with the results of Van Cauwelaert and Hall between 50 and 305°C. Apparently, a part of the carbon dioxide is adsorbed very strongly without undergoing the exchange, while some other molecules do not desorb on evacuation but in the presence of gaseous molecules do communicate with them probably due to an induced heterogeneity. Indeed, in addition to the bicarbonate ions not exchanged other adsorbed species were also found on infrared spectra after evacuation as already pointed out.

A high mobility of carbon dioxide on alumina was indicated above 150°C by Rosynek (*17*) from the calculation of entropy. The irreversibly adsorbed carbon dioxide observed here should remain immobile up to 300°C because it was not displaced. The amount is, however, very small above 100°C.

Although the present results are generally consistent with those of Peri (*13*), N_{ex} in Table 1 differ from those measured by Peri by a factor of up to 2.8 between 200 and 400°C. Also, he observed no exchange at 40°C, while an exchange was easily detected in the present study at as low as 27°C (Table 2). The two works were, of course, different in alumina used and the method of analysis, and Peri assumed the isotopic equilibration of the all carbon dioxide in the system.

The results of Tables 1 and 2 were plotted in Fig. 4 as a function of the reciprocal of reaction temperature. N_{ex}

TABLE 2

Results of Exchange Reaction on Alumnia Dehydrated at 750°[a]

Temp (°C)	P (Torr)	$N_{rev} \times 10^{-13}$ (molecules/cm²)	$N_{irr} \times 10^{-13}$ (molecules/cm²)	$N_{ex} \times 10^{-13}$ (atoms/cm²)
27	1.06	3.46	1.65	5.02
50	1.10	3.10	1.22	5.14
100	0.91	2.40	0.78	6.85
200	1.00	1.14	0.28	9.35
305				12.28
405				19.26
522				41.21
627				91.56
700				156.81

[a] Surface density of OH: 3.2×10^{13} OH/cm², surface area: 129 m²/g.

[b] Equal amount of $C^{18}O_2$ (about 76 μmol) was used. The pressure was about 2 Torr.

increases with temperature but more steeply when the temperature becomes higher than 300°C, and finally exceeds 10^{15} atoms/cm^2. Two sorts of oxygen exchange seem to take place: one occurs readily at relatively low temperatures and the other takes place only at high temperature involving not only the oxygen atoms on the surface but those in the second layer or even in the bulk of alumina. Our previous results of infrared spectroscopy on a deuterated alumina (*15*) showed that, of the three deuteroxyl groups observed, the two OD groups giving lower frequencies did not change until 180°C on the exposure to $C^{18}O_2$ but were converted to ^{18}OD at 475°C. Protons on alumina will become mobile at high temperatures thus exposing more oxide ions for exchange. Rearrangement of the surface oxide ions would also occur at extremely high temperature.

The oxygen atoms exchangeable at low temperatures are certainly of greater interest because the active sites of alumina for some hydrocarbon reactions could be associated with them as pointed out by Peri (*13*). These unstable oxygen atoms will be called the reactive oxygen atoms in the following discussion to distinguish them from those exchanged at high temperatures. The maximum density of the reactive oxygen could be roughly estimated from Fig. 4 as the intersection of the extrapolations of N_{ex} from the two temperature regions. It gave a density of 1–2 × 10^{14} atoms/cm^2 for both 650 and 750°C dehydrated surfaces.

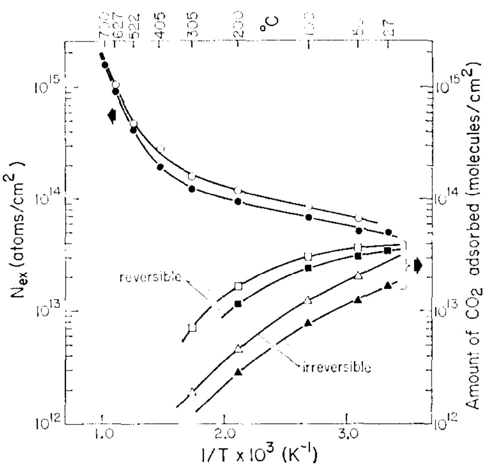

FIG. 4. Temperature dependence of N_{ex}, N_{rev} and N_{irr}. Open symbols for the results on the 650°C dehydrated surface, and filled symbols for those on the 750°C dehydrated surface.

The two curves of N_{ex} in Fig. 4 are almost parallel in the lower temperature range. In fact, the ratios of N_{ex} and of $N_{rev} + N_{irr}$ in Table 2 to those in Table 1 were approximately constant and the average was 0.78. Therefore, the maximum density of the reactive oxygen, n, will have the same ratio:

$$n(750°\text{C})/n(650°\text{C}) = 0.78. \quad (4)$$

If it is also assumed on dehydration that the reactive oxygen atoms are preferentially removed as water, and that this is the only process to reduce the reactive oxygen, the decrease in n by dehydration is then half of the difference in hydroxyl groups shown in Tables 1 and 2:

$$n(650°\text{C}) - n(750°\text{C}) = (9.0 - 3.2) \times 10^{13}/2. \quad (5)$$

From Eqs. (4) and (5), the maximum densities of the reactive oxygen were obtained as $n(650°\text{C}) = 1.32 \times 10^{14}$ and $n(750°\text{C}) = 1.03 \times 10^{14}$ atoms/cm^2, both of which were in a reasonable range of the rough estimation given above.

Although the reactive oxygen is preferentially removed on dehydration, the high mobility of protons at this high temperature would redistribute protons, so that on cooling the catalyst the energy distribution on the surface will be restored. The uniform factor of 0.78 for both N_{ex} and the adsorptive sites supports the above view, and the infrared spectroscopy of the alumina confirmed roughly the same distribution of the three hydroxyl bands before and after dehydration at 750°C. Borello *et al.* (*19*) also reported a reproducibility of surface energy distribution on an alumina independent of dehydration temperature.

The maximum densities of the reactive oxygen calculated above are both slightly smaller than the N_{ex} measured at 305°C on each surface. It may imply the participation of stable oxygen in the reaction to some extent already at 300°C. An interesting fact is that, below 300°C, the value $(n - N_{ex})/N_{irr}$ is fairly constant between 3 and 4 on both surfaces independent of temperature. A molecule irreversibly adsorbed apparently blocks 3 to 4 reactive oxygen atoms. The temperature dependence of N_{ex} in the lower temperature region seems to result from the decreasing amount of irreversible adsorption with temperature. If the above blocking factor is applied to the total n(650°C), we have $3.3–4.4 \times 10^{13}/\mathrm{cm}^2$ as a site density for the chemisorption of carbon dioxide, which agrees well with the saturated amount of CO_2 (3.8×10^{13} molecules/cm^2) obtained on a similar alumina by a conventional temperature-programmed desorption.

The above site density and N_{irr} are, however, much larger than the site densities previously found on alumina by CO_2 poisoning for $C_6H_6–D_2$ (*1, 6*), $CH_4–CD_4$ (*2*), cyclopentene-D_2 (*3*) and $H_2–D_2$ (*4*) exchange reactions. Those sites seem to involve only a fraction of the reactive oxygen atoms found here. Although the sites for butene isomerization may be associated with the reactive oxygen, a direct correlation is impossible at this stage because carbon dioxide has very little effect on the isomerization reaction (*1, 6, 14*).

From the present and previous results (*15*), bicarbonate ion is a likely intermediate of the exchange reaction. At the same time, some bicarbonate ions are so strongly adsorbed that the hydroxyl group in the ion is frozen, thus a couple of adjacent oxygen atoms become ineligible for exchange. However, Hightower (*1*) showed some strong evidence that the 1480 cm^{-1} band was not due to bicarbonate ion but probably due to a carbonate ion. Also we found that the bands between 1900 and 1750 cm^{-1} shifted with the exchange (*15*), so that other surface species might also be involved in the reaction. Certainly further information on those surface species is necessary to decide a definite mechanism.

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