

Alkali-Promoted Alumina Catalysts

I. Chemisorption and Oxygen Exchange of Carbon Monoxide and Carbon Dioxide on Potassium-Promoted Alumina Catalysts¹

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Some potassium-promoted alumina catalysts were prepared by impregnating alumina with K_2CO_3 solutions. The catalysts were calcined at 620°C before use. K_2CO_3 decomposed completely during calcination, but no potassium oxides or aluminates were formed on the surface. Oxygen exchange between those catalysts and $C^{18}O_2$ and $C^{18}O$ was measured over a wide temperature range between 50 and 600°C and compared with results obtained with alumina used as the support. It was found that potassium not only increased the number of exchangeable oxygens on the surface but also weakened the bond between these oxygens and the surface. The chemisorption of carbon monoxide and carbon dioxide was also investigated mainly by infrared spectroscopy. On the present K_2CO_3/Al_2O_3 catalysts both gases showed distinctive ir bands, a pair of bands at 1590 and 1320 cm^{-1} and another pair of bands at 1570 and 1320 cm^{-1} depending on the temperature. The former pair was assigned to a CO_2^- ion and the latter pair to a bidentate carbonate both attached on the potassium ion. The present results of oxygen exchange on K_2CO_3/Al_2O_3 were successfully explained by assuming that the surface species assigned above are the intermediates of the exchange reaction with carbon monoxide and carbon dioxide, respectively.

INTRODUCTION

Alkali salts are widely used as a promoter in industrial catalysts such as those for the synthesis of ammonia and the Fischer-Tropsch reaction. When added to supported metal catalysts, the salts increase the selectivity of catalysts or suppress undesirable side reactions. Yet the mechanism of promotion is not fully understood. In view of this, we have investigated the catalytic properties of alkali salts supported on γ -alumina. In this paper we report the results of the chemisorption of carbon monoxide and carbon dioxide on some potassium carbonate/ γ -alumina catalysts and also the results of the exchange of oxygen between these gases and one of the catalysts. Potassium and alumina are often used

in practical catalysts as promoter and support, respectively. Results were compared with those obtained with alumina used as the support to examine the influence of potassium on the surface of alumina.

Unstable oxygen atoms exchangeable with carbon dioxide were found on alumina by Peri (1) and Amenomiya *et al.* (2), and the surface density of those oxygens on an η -alumina was measured over a wide temperature range (3). It was also found that the oxygen exchange of η -alumina with carbon monoxide was much slower than that with carbon dioxide and required higher temperatures (4). In the present study, the oxygen exchange between the K_2CO_3/Al_2O_3 and $C^{18}O_2$ was measured between 50 and 600°C, and the rate of oxygen exchange with $C^{18}O$ was compared at 300 and 400°C. While the amounts of reversible and irreversible adsorption of carbon dioxide were measured during the exchange reaction in a manner similar to that of the previous work (3), the molecular structure

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of adsorbed species was investigated mainly by infrared spectroscopy.

EXPERIMENTAL METHODS

Apparatus and Procedure

The apparatus and procedure used for the exchange reaction were described in detail previously (3). The apparatus was a closed recirculation system equipped with a sector-type mass spectrometer. $C^{18}O_2$ at a pressure of about 3 Torr (1 Torr = 133.3 Nm^{-2}) was mixed with argon (total pressure about 10 Torr) and circulated through the catalyst while the isotopic composition of carbon dioxide was monitored by the mass spectrometer. When the initial atom fraction of ^{16}O in the $C^{18}O_2$, $^{16}f_0$, increased to $^{16}f_e$ as a result of isotopic equilibration with the catalyst, the number of exchangeable oxygens of the catalyst, N_{ex} , was calculated 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 on the surface. $^{16}f_{s0}$ was obtained from the final atom fraction of ^{16}O in $C^{16}O_2$, with which the catalyst was treated at 600°C before each run to exchange back the surface.

Equation (1) was derived under the conditions that the equilibration of oxygen atoms between the gas phase and the surface of the catalyst be established and that all the carbon dioxide in the system be involved in the exchange. The former condition was assumed throughout this paper, but the latter condition was not met at low temperatures, where an appreciable amount of carbon dioxide was adsorbed irreversibly without exchange as found in the previous paper (3). In that case $^{13}CO_2$ was preadsorbed under the reaction conditions before $C^{18}O_2$ was introduced. The amounts of carbon dioxide adsorbed reversibly and irreversibly during the exchange reaction were calculated from the material balance of ^{13}C , and N_{ex} was calcu-

lated by taking the amount of irreversible adsorption into account. The detailed procedure and calculations were described previously (3).

Infrared spectra of adsorbed molecules were obtained either with a Beckman IR4230 or with a Perkin-Elmer 281B spectrophotometer. Both spectrophotometers were operated with a presample chopper to minimize the temperature effect. Also two cells were used, both of which consisted of dual cells to cancel the absorption by gaseous molecules. One of the cells was connected to a quadrupole mass spectrometer so that a temperature-programmed desorption could be carried out in the infrared cell to supplement information on the state of adsorption (5).

Materials

Alon alumina (Cabot Corp., Boston, Mass.) was used as the support of potassium in the present investigation. The alumina powder was mixed with water, heated for 3 hr at 600°C , crushed, and sieved to particles of 1 to 2 mm. A 5 wt% (actually 4.9%) K_2CO_3/Al_2O_3 catalyst was prepared by impregnating the alumina particles with a potassium carbonate solution. The catalyst was dried and finally calcined with air for 3 hr at 620°C . A sample of alumina was taken from the above batch of the particles, soaked with the same volume of water as that used for the K_2CO_3 solution, dried, and calcined similarly. This was used as control alumina. Another catalyst with a higher concentration of K_2CO_3 at 9 wt% (actually 9.1%) was prepared by directly mixing the Alon powder with a K_2CO_3 solution. Drying and calcination were done in the same manner. This catalyst was used mainly for infrared spectroscopy. Catalyst samples for spectroscopy were pressed into a disk of 19-mm diameter, the weight of which was about 0.14 g.

The surface area of the catalysts was $92.3 \text{ m}^2/\text{g}$ (control alumina), $83.9 \text{ m}^2/\text{g}$ (5% K_2CO_3/Al_2O_3), and $102.1 \text{ m}^2/\text{g}$ (9% K_2CO_3/Al_2O_3). The surface density of hy-

droxyl groups measured by exchange with deuterium (3) was 4.8×10^{13} OH/cm² on the control alumina and 6.6×10^{13} OH/cm² on the 5% K₂CO₃/Al₂O₃. The gases used and their purification were also described previously (3).

RESULTS

1. State of Potassium on the Surface

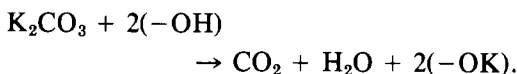
During the course of the preparation of the 5% K₂CO₃/Al₂O₃, a part of the catalyst was put into a quartz reactor after impregnation with K₂CO₃ and thorough drying at 110°C but before calcination. The catalyst sample was then evacuated for 2 hr at 600°C through two traps in series, the first cooled at -75°C and the second at -195°C. The amount of carbon dioxide in moles collected in the second trap agreed within 2% with that of K₂CO₃ added to alumina. Potassium carbonate on alumina, therefore, decomposed completely at 600°C, although the results did not necessarily indicate the formation of K₂O on the surface. The dissociation pressure of pure K₂CO₃ is negligible below 900°C, but the rate of decomposition is known to be promoted by alumina in the presence of water vapor in particular (6).

The structures of alkali carbonates on γ -alumina were studied by Stork and Pott (7) by both X-ray diffraction and phosphorescence spectroscopy. Their results also showed that K₂CO₃ decomposed at about 550°C but no reaction took place between the carbonate and the γ -alumina lattice below 900°C. Although their data did not specify any definite state of potassium, they concluded that at calcination temperatures up to 900°C the surface hydroxyl groups reacted with the carbonate to form OK groups.

The X-ray analysis of the present 9% K₂CO₃/Al₂O₃ after calcination at 620°C did not detect any potassium oxides or aluminates including K₂O, KO₂, KO₃⁻, KAlO₂, K₃AlO₃, KAl₅O₈, and KAl₁₁O₁₇. While isolated hydroxyl groups on the Alon alumina gave four infrared absorption bands appear-

ing at 3804, 3786, 3738, and 3685 cm⁻¹ (8), the potassium-promoted aluminas showed, after evacuation at 600°C, only one sharp band (3740 cm⁻¹ on 5% and 3710 cm⁻¹ on 9% K₂CO₃/Al₂O₃) together with a broad band centered at 3520 cm⁻¹. The latter is probably due to hydrogen-bonded hydroxyl groups instead of KOH, whose hydroxyl ion usually gives a sharp band at 3600 cm⁻¹ (9). In fact, the 3520-cm⁻¹ band was reduced by prolonged evacuation at 600°C.

Since the present results did not reveal the definite state of surface potassium, the exact amount of K⁺ ion in the catalyst samples taken in the reactor could not be calculated. The catalysts are, therefore, designated by the weight percentage of the K₂CO₃ added originally. Assuming K₂O for an approximation, however, the concentration of K⁺ was calculated as 4.4×10^{20} ions/g or 5.2×10^{14} ions/cm² for 5% K₂CO₃/Al₂O₃ and 8.2×10^{20} ions/g or 8.0×10^{14} ions/cm² for 9% K₂CO₃/Al₂O₃. The surface concentration was calculated by assuming that all ions were held on the surface. From the results of X-ray and infrared spectroscopy, however, it is more likely that K⁺ ions replace the protons of hydroxyl groups on the surface as suggested by Stork and Pott (7),



The OK groups thus formed would be hydrogen bonded to the neighboring hydroxyl groups.

2. Exchange of Oxygen

Exchange of oxygen with C¹⁸O₂ and C¹⁸O was measured on the control alumina and 5% K₂CO₃/Al₂O₃ catalyst. All catalysts were evacuated at 640°C before the exchange reactions.

At all temperatures, a rapid exchange of oxygen between the catalysts and C¹⁸O₂ occurred in the initial stage of the reaction followed by a slow exchange as observed on η -alumina previously (3). The number of

exchangeable oxygens, N_{ex} , was calculated either by Eq. (1) or with $^{13}CO_2$ as already explained under Experimental Methods, and was plotted in Fig. 1 as a function of temperature. Plotted also are the amounts of reversible (N_{rev}) and irreversible adsorption (N_{irr}) measured during the exchange reaction with $^{13}CO_2$. It is clear in Fig. 1 that the potassium promoter increased the exchangeable oxygen at all temperatures. It also increased the adsorption of carbon dioxide but the effect was greater on the reversible adsorption.

The number of exchangeable oxygens on the Alon alumina shown in Fig. 1 was very close to that obtained on η -alumina (3) at all temperatures in spite of the fact that the two aluminas differed in crystal form. In both cases, the slope of the N_{ex} curve became steeper at higher temperatures. It was concluded that very reactive oxygen on the surface of η -alumina, which amounts to 1.3×10^{14} atoms/cm², exchanges with carbon dioxide readily at temperatures below 300°C while, above 300°C, other oxygen atoms including those in the bulk are involved in the exchange (3). As shown in

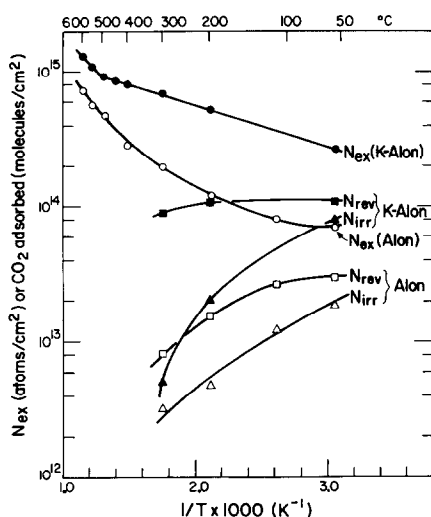


FIG. 1. Number of exchangeable oxygens, N_{ex} , on control alumina (Alon) and 5% K_2CO_3/Al_2O_3 (K-Alon). Amounts of reversible adsorption (N_{rev}) and irreversible adsorption (N_{irr}) were measured during the exchange reaction with $^{13}CO_2$.

TABLE 1

Temperature (°C)	Initial Rate of Oxygen Exchange with $C^{18}O$	
	Initial rate ($\times 10^{-10}$ atoms \cdot cm ⁻² sec ⁻¹)	
	Alumina (Alon)	5% K_2CO_3/Al_2O_3
304	0.37	7.45
402	1.73	58.9

Fig. 1, N_{ex} on 5% K_2CO_3/Al_2O_3 increased linearly with $1/T$ up to 480°C after which it increased more steeply beyond 10^{15} atoms/cm². The results may suggest that only surface oxygen atoms are involved in the exchange below 480°C as the break in linearity at 480°C is close to 10^{15} atoms/cm².

Exchange with $C^{18}O$ was much slower than that with $C^{18}O_2$ on all catalysts as observed on η -alumina (4). The oxygen exchange between $C^{18}O$ and 5% K_2CO_3/Al_2O_3 was not observed below 70°C, but it became measurable above 300°C. The initial rate of the exchange with the 5% K_2CO_3 catalyst was found to be 20 to 35 times faster than that with the Alon alumina at 300–400°C, as compared in Table 1. Apparently, potassium on alumina not only increases the number of exchangeable oxygens but also weakens the bond between the oxygen and the surface.

3. Chemisorption of CO and CO_2

The adsorption of carbon monoxide on the present Alon alumina was almost negligible at room temperature, and when heated at 300°C, it gave very weak infrared absorption bands at frequencies similar to those found with carbon dioxide as reported on η -alumina previously (4). The adsorption of CO on 9% K_2CO_3/Al_2O_3 at 80 Torr also did not show any appreciable ir bands at 30°C. At about 150°C, however, bands started appearing at 1590 and 1320 cm^{-1} , and these bands developed fully at 300°C as shown by the solid line (lower spectrum) in Fig. 2. When the temperature

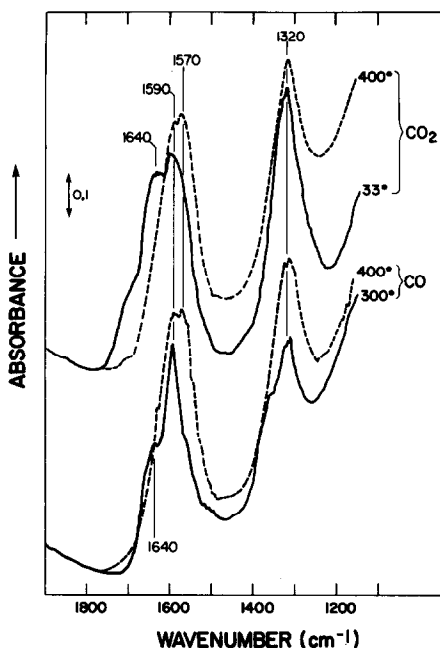


FIG. 2. Infrared spectra of CO and CO₂ on 9% K₂CO₃/Al₂O₃. Lower spectra with CO; upper spectra with CO₂ were displaced vertically for clarity.

was increased to 400°C or higher, a new band appeared at 1570 cm⁻¹ in addition to the 1590-cm⁻¹ band and the intensity of the 1320-cm⁻¹ band increased (lower broken line in Fig. 2). A brief evacuation at 300°C removed a shoulder at 1640 cm⁻¹ but removed only a part of the 1590- and 1320-cm⁻¹ bands. The 1590-cm⁻¹ band was virtually removed by evacuation at 400°C while the 1570-cm⁻¹ band remained almost unchanged and the absorbance of the 1320-cm⁻¹ band was reduced to about half. Apparently the 1590- and 1570-cm⁻¹ bands are both accompanied by a 1320-cm⁻¹ band.

In contrast with carbon monoxide, carbon dioxide adsorbed strongly on the 9% K₂CO₃/Al₂O₃ sample even at room temperature and gave ir bands at 1640, 1590, and 1320 cm⁻¹ as represented by the upper solid line in Fig. 2 which was obtained with an adsorbed amount of 3.1×10^{19} molecules of CO₂/g without the gaseous pressure. The lower-frequency side of the 1590-cm⁻¹ band extended over 1570 cm⁻¹ and a band was

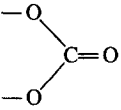
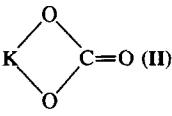
shaped clearly at this frequency when the temperature was increased to 150°C or higher. At 300°C or higher, the 1570-cm⁻¹ band developed fully and the spectrum (upper broken line in Fig. 2) became identical with that of carbon monoxide at 400°C, that is, the bands appearing at 1590, 1570, and 1320 cm⁻¹. The amount of CO₂ adsorbed at 400°C for this particular spectrum was 2.6×10^{19} molecules/g still without appreciable pressure of CO₂.

The ir bands observed in the present investigation are summarized in Table 2, in which most of the assignment of the bands of CO₂ on alumina was reported in a previous work (2) and that for the bands on K₂CO₃/Al₂O₃ is discussed later under Discussion. Spectra similar to those in Fig. 2 were also observed on 5% K₂CO₃/Al₂O₃ but with enhanced shoulders at 1700 and 1640 cm⁻¹. From this fact and Table 2, it is obvious that the bands appearing at 1700–1640 cm⁻¹ with K₂CO₃/Al₂O₃ are due to the adsorption on the free alumina surface. These bands could be removed easily by evacuation, as already pointed out. Judging roughly from the intensity of ir bands, the adsorption of CO₂ on the free alumina surface did not seem to be affected by the addition of potassium up to 5%. However, the 1480-cm⁻¹ band which persisted on alumina at high temperatures was missing on K₂CO₃/Al₂O₃ catalysts.

The temperature-programmed desorption (TPD) of CO and CO₂ on 5% K₂CO₃/Al₂O₃ gave interesting results in connection with those of infrared spectroscopy. Figure 3 shows some typical spectra of TPD which was carried out at a heating rate of 20°C/min in an infrared cell by pumping the desorbed gas through the mass spectrometer as already described. The mass spectrometer was scanned repeatedly during TPD between $m/e = 28$ and 44.

TPD spectrum a in Fig. 3 was obtained with carbon dioxide adsorbed on the alumina (Alon) from 500°C to room temperature. Infrared spectrum taken before the TPD showed all absorption bands due to

TABLE 2
 Infrared Bands (cm^{-1}) of CO and CO_2

Alumina (Alon)	5 and 9% K_2CO_3/Al_2O_3				Assignment
	CO_2		CO		
	30°C	150–500°C	150–300°C	400–500°C	
3614					HCO_3^- 
1750 ^a	1700				
1640	1640 1590	1590	1640 1590	1590	HCO_3^- $K^+ - CO_2^-$ (I) 
	(1570) ^b	1570		1570	
1480 ^c					CO_3^{2-}
1235	1320	1320	1320	1320	I + II HCO_3^-

^a Broadband.^b Present in a small amount.^c Only band observed at 400–500°C.

adsorbed CO_2 as listed in Table 2. These surface species are desorbed in one peak in TPD at relatively low temperatures as seen by spectrum a. Carbon dioxide which was adsorbed on 5% K_2CO_3/Al_2O_3 at room temperature and gave an ir spectrum similar to the upper solid line in Fig. 2 was desorbed over a wide temperature range as shown by spectrum b in Fig. 3. When CO_2 was adsorbed on the same sample at 400°C, however, it was desorbed at temperatures higher than 500°C (spectrum c). The heating in TPD was stopped at 600°C so that the real temperature of these high-temperature peaks was not known. Before TPD spectrum c was taken, the catalyst was evacuated at 400°C and only two ir bands were observed at 1570 and 1320 cm^{-1} . The low-temperature peak of spectrum b appearing at about 270°C coincides with spectrum a and is apparently due to carbon dioxide

adsorbed on the free alumina surface. The high-temperature peak of spectrum b appearing above 600°C corresponds to spectrum c and is due to the surface species which gives the 1570- and 1320- cm^{-1} bands in ir. Carbon dioxide desorbed in spectrum b also contained surface species which showed ir bands at 1590 and 1320 cm^{-1} . This surface species would probably be desorbed between the two peaks of spectrum b thus raised the valley to a level almost comparable with the two peaks.

Carbon monoxide adsorbed on 5% K_2CO_3/Al_2O_3 at 300°C desorbed as CO in a sharp peak in TPD (spectrum d in Fig. 3). The ir spectrum observed before the TPD was similar to the lower solid line in Fig. 2, namely, the bands at 1590 and 1320 cm^{-1} with a shoulder at 1640 cm^{-1} . Only a trace of CO_2 was detected at high temperatures. However, CO adsorbed on the same sam-

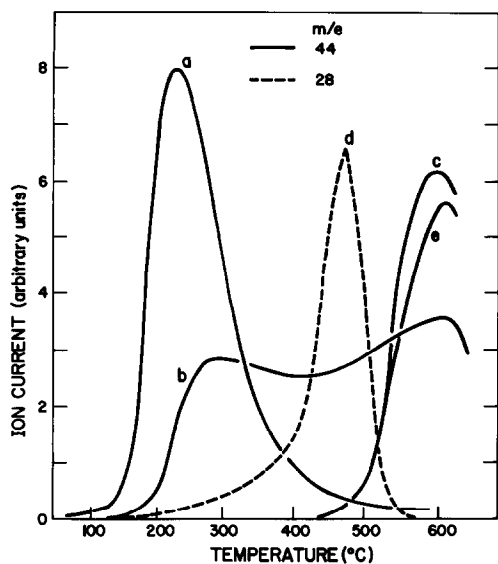


FIG. 3. TPD spectra of CO and CO₂: (a) on Alon alumina and (b) to (e) on 5% K₂CO₃/Al₂O₃. Gas and the temperature of adsorption and evacuation before TPD were: (a) CO₂, ads. 500 to 25°C, evac. 25°C; (b) CO₂, ads. 25°C, evac. 25°C; (c) CO₂, ads. 400°C, evac. 400°C; (d) CO, ads. 300°C, evac. 25°C; (e) CO, ads. 400°C, evac. 400°C.

ple at 400°C whose ir spectrum consisted of the 1570- and 1320-cm⁻¹ bands desorbed as CO₂ at high temperatures (spectrum e).

It should be noted here that, in TPD, the catalyst disk of 19-mm diameter was heated *in vacua* by an outer furnace whose temperature is shown in Fig. 3. Therefore, the peaks would be broader than those taken under ideal conditions and the real peak temperatures could be considerably lower.

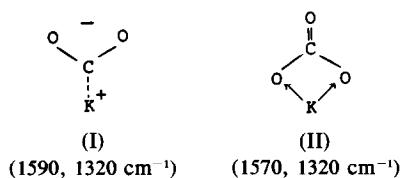
In summary, of the surface species formed by the adsorption of CO and CO₂ on K₂CO₃/Al₂O₃, those characterized by the 1570- and 1320-cm⁻¹ ir bands desorb as CO₂ at high temperatures, while those characterized by the 1590- and 1320-cm⁻¹ bands desorb in TPD at lower temperatures as different molecules depending on the gas adsorbed.

DISCUSSION

Potassium carbonate added to alumina decomposed rather readily by calcination at 600°C but the resulting compound was not

potassium oxides or aluminates as discussed in the preceding sections. The results of infrared spectroscopy and TPD clearly indicate that the adsorption of CO and CO₂ on potassium-promoted alumina produced surface species entirely different from those adsorbed on alumina. None of the surface species thus formed is K₂CO₃ which is usually characterized by a carbonate band appearing at 1500–1410 cm⁻¹ (10).

We assign the 1590- and 1320-cm⁻¹ bands found in the infrared spectroscopy on the K₂CO₃/Al₂O₃ catalysts to a CO₂⁻ ion chemisorbed on K⁺ and those found at 1570 and 1320 cm⁻¹ to a bidentate carbonate.



The observed difference in frequency between the two bands for species II was 250 cm⁻¹, which was too large as the splitting of ν₃ vibration for a monodentate carbonate (9). Because of the cationic nature of potassium, the K–O bond would have a considerable fraction of ionic character. This may give a splitting of 250 cm⁻¹ while that of the carbonate in bidentate complexes is somewhat greater than 300 cm⁻¹ (11). It is impossible, however, to decide at this stage whether species II is bonded to a single metal ion as shown above or bonded to two K ions in a bridged form.

The results of exchange reactions clearly showed that potassium added onto alumina not only increased the number of exchangeable oxygens but weakened the bonding of these oxygens as already pointed out. These oxygens would be picked up by carbon monoxide at 150 to 300°C to form CO₂⁻ (species I). In the case of carbon dioxide, there is no need for the addition of oxygen so that species I is formed at room temperature as seen in Fig. 2. In desorption, however, this surface species, if formed from CO, returns an oxygen atom

to the deficient site created at adsorption and desorbs as CO. At 400°C or higher, species I from CO is combined with another oxygen to form species II. This process is irreversible and species II desorbs as CO_2 at high temperatures. On the other hand, it requires only one surface oxygen for carbon dioxide to form species II. Some species II are therefore formed even at room temperature as observed by infrared spectroscopy (Fig. 2).

As described in the preceding section, the oxygen exchange between K_2CO_3/Al_2O_3 and $C^{18}O$ took place at measurable rates at temperatures higher than 300°C, although it was not as fast as the exchange with $C^{18}O_2$. The exchange would occur through species I as an intermediate. The reaction, therefore, requires higher temperatures compared to the exchange with carbon dioxide, and did not take place below 70°C as already pointed out. Species I from CO was observed clearly by infrared spectroscopy only at temperatures above 150°C as mentioned earlier. However, this surface species is not formed on alumina so that the rate of exchange of CO with alumina is much slower than that with the promoted alumina (Table 1).

The oxygen exchange between alumina and carbon dioxide was explained by considering surface carbonate and/or bicarbonate ions as possible intermediates (4). The present exchange between K_2CO_3/Al_2O_3 and $C^{18}O_2$ can be explained by considering the bidentate carbonate (species II) as an intermediate. Some of these surface species are formed readily even at room temperature and the amount increases with temperature up to about 300°C as observed spectroscopically. N_{ex} , the number of exchangeable oxygens, was also observed even at 50°C and increased with temperature as shown in Fig. 1. For N_{ex} , however, the amount of irreversible adsorption, as well as species II, has to be taken into consideration.

The results of infrared spectroscopy and TPD both indicated that the surface of the

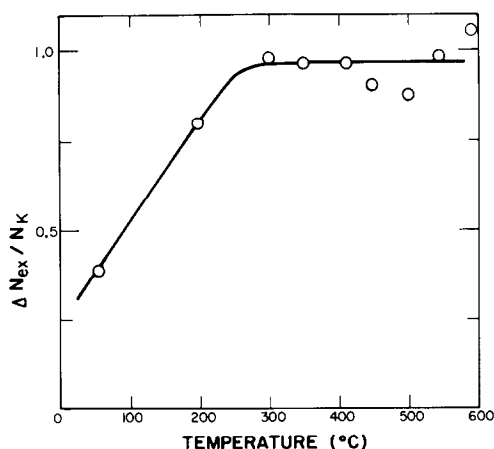


FIG. 4. $\Delta N_{ex}/N_K$ on 5% K_2CO_3/Al_2O_3 versus temperature.

present K_2CO_3/Al_2O_3 catalysts consists of two parts, the free and the alkalinized alumina. It was also pointed out that the chemisorption of CO_2 on the free alumina surface on 5% K_2CO_3/Al_2O_3 was not affected too much by potassium. Assuming then that N_{ex} (K-Alon) plotted in Fig. 1 simply resulted from the sum of the two parts of the K_2CO_3/Al_2O_3 surface, $\Delta N_{ex} = N_{ex}(\text{K-Alon}) - N_{ex}(\text{Alon})$ was calculated to estimate the exchange on the alkalinized surface. The results are plotted in Fig. 4 as $\Delta N_{ex}/N_K$, where N_K is the surface concentration of K^+ ions (5.2×10^{14} ions/cm²). As seen in Fig. 4, the number of exchangeable oxygen atoms on the alkalinized surface is less than the number of potassium ions at 50°C but increases with temperature and finally reaches a plateau at about 300°C, where each K^+ ion is associated with one exchangeable oxygen. The curve of Fig. 4 again reflects the spectroscopic observation that the 1570- and 1320-cm⁻¹ bands increased with temperature up to about 300°C. All hydroxyl groups on alumina were found to be involved in the exchange reaction with carbon dioxide (2-4). OK groups formed on the promoted catalysts by calcination may behave similarly so that $\Delta N_{ex}/N_K$ becomes unity at high temperatures.

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