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Alkali-Promoted Alumina Catalysts

II. Water-Gas Shift Reaction[1]

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The water-gas shift reaction was investigated on alkali-promoted alumina catalysts prepared by mixing alumina with various alkali metal salts. Results showed that the activity for the $CO + H_2O$ reaction increased with the concentration of promoter until the surface was almost saturated by the alkali metal ions. At the same concentration of metal ions, the efficiency of promotion was in the order $Cs > K > Na > Li$. The addition of alkali salts also increased the catalyst activity for the $CO_2 + H_2$ reaction at high temperatures. Although the promoters showed similar effect of concentration and tendency for the efficiency, the results were not as clear as those for the $CO + H_2O$ reaction. The kinetics of the water-gas shift reaction was studied on a potassium-promoted alumina in an infrared cell used as a flow-type reactor with the simultaneous spectroscopy of surface species. It was thus found that formate ion was formed during the $CO + H_2O$ reaction and that the reaction rate was proportional to the surface concentration of the formate ions. A reaction mechanism through formate was proposed and physical and chemical factors contributing to the promotion were discussed based on this mechanism.

INTRODUCTION

In Part I of this series (*1*), we investigated the exchange of oxygen between some potassium-promoted alumina catalysts and carbon dioxide and carbon monoxide in an attempt to clarify the catalytic properties of alkali salts widely used in industrial catalysts as a promoter. Some oxygen atoms on the alumina surface are very reactive and readily exchanged with the oxygen of carbon dioxide (*2*), while the exchange with carbon monoxide is much slower and requires higher temperatures (*3*). The results of Part I (*1*) clearly showed that the presence of potassium not only increased the number of exchangeable oxygens but also increased their reactivity for the exchange with carbon monoxide. Results of infrared spectroscopy and temperature-programmed desorption also indicated that these exchangeable oxygens participate in the chemisorption of CO and CO_2 forming a carboxylate and/or a bidentate carbonate species on the surface depending on temperature (*1*).

One of our recent studies also showed that alumina was an active catalyst for the water-gas shift reaction (*4*). Further investigation by infrared spectroscopy revealed that the water-gas shift reaction proceeds through formate ion formed on the alumina surface (*5*). Since the addition of potassium activated the alumina surface as reported in Part I (*1*), we have investigated the water-gas shift (WGS) reaction on alkali-promoted alumina catalysts to give a deeper insight into the mechanism of promotion. The rate of the WGS reaction was measured for comparison on aluminas promoted by potassium carbonate at various concentrations, by other potassium salts, and also by the carbonates of other alkali metals. In addition, the kinetics of the reaction was investigated on a potassium-promoted alumina simultaneously with the infrared spectroscopy of surface species in

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order to obtain more information on the mechanism of the WGS reaction.

EXPERIMENTAL METHODS

Materials

All catalysts were prepared by mixing Alon alumina (Cabot Corp., Boston, Mass.) with the solutions of alkali salts. The resulting slurry was dried, crushed, screened, and finally calcined in air for 3 hr at 600–620°C. The alkali salts used and their concentration are listed in Table 1 together with some results which will be explained later. As reported in the previous paper (*1*), potassium carbonate mixed with alumina decomposed on heating at 600°C producing the stoichiometric amount of carbon dioxide, but no potassium oxides or aluminates were detected by X-ray analysis. Although the results suggested the formation of OK groups on the surface (*1*), the state of alkali metals after the calcination is not yet known definitely. Therefore, the concentration of the promoters was expressed in Table 1 as the weight percentage of the salts initially added, while the concentration of alkali ions was calculated by using monoxide (M_2O) as an approximation. All promoted catalysts except for 9K/A and 20K/A were prepared so that the ion concentration became about the same.

Ultrahigh-purity hydrogen and helium (99.999%), research-purity carbon monoxide (99.99%), and Coleman-grade carbon dioxide (99.99%), were all purchased from Matheson of Canada and used without further purification.

Apparatus and Procedure

For the comparison of catalytic activity, the rate of reaction was measured between 400 and 600°C in a greaseless closed circulation system used previously for the water-gas reaction on alumina (*4*). The $CO + H_2O$ reaction was carried out under an initial pressure of carbon monoxide of 100 Torr (1 Torr = 133.3 N m^{-2}) and a constant vapor pressure of water of 18 Torr for all catalysts, while the $CO_2 + H_2$ reaction was carried out with an initial pressure of 94 Torr of each reactant with a trap cooled by a dry ice–alcohol bath. The amount of catalyst used was between 0.3 and 0.8 g depending on the activity. The detailed experimental procedures and the methods of calculation of the rates have been described previously (*1*).

TABLE 1

Catalysts

Catalyst	Promoter			Surface area (m^2/g)	Activation energy (kcal/mole)	
	Salt	Concentration			$CO + H_2O$	$CO_2 + H_2$
		(wt%)[a]	($\times 10^{-20}$ ions/g)[b]			
A (Alon)	—	—	—	90	20	16
5K/A	K_2CO_3	4.8	4.2	107	19	23
9K/A	K_2CO_3	9.1	8.2	102	17	26
20K/A	K_2CO_3	20.0	18.6	68	(17)[c]	(26)[c]
KOH/A	KOH	3.9	4.3	88		
KCl/A	KCl	5.1	4.2	102		
Li/A	Li_2CO_3	2.6	4.4	107	26	18
Na/A	Na_2CO_3	3.7	4.3	100	28	20
Cs/A	Cs_2CO_3	10.6	3.9	89	18	18

[a] Weight percentage of salt added.

[b] The concentration of alkali metal ions calculated as monoxide.

[c] Estimated from 2 points.

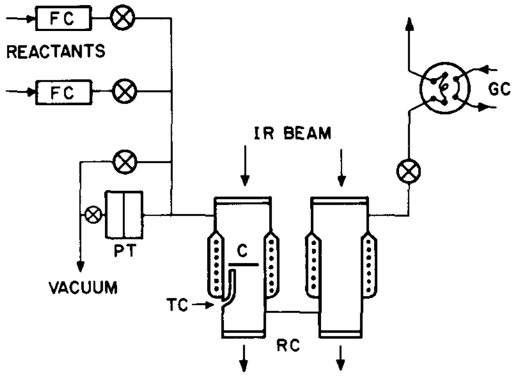


FIG. 1. Schematic diagram of the infrared apparatus. FC, electronic mass flow controller; PT, pressure transducer; RC, reactor cell; C, catalyst disk; TC, thermocouple; GC, gas sampling valve of gas chromatograph.

The infrared spectroscopy of the surface species and the kinetic study were made simultaneously in an infrared cell with a disk of 9 K/A catalyst (0.144 g). The infrared system constructed with metal valves and stainless-steel tubing is shown schematically in Fig. 1. Spectra were recorded with a Perkin–Elmer model 281B infrared spectrophotometer equipped with a presample chopper. The cell which was made of quartz with calcium fluoride windows was used as a flow-type reactor and the flow rates of the reactant gases were controlled by a pair of electronic mass flow controllers. In the case of $CO + H_2O$ reaction, the flows of helium and carbon monoxide were individually controlled by the flow controllers, and the mixture of the gases was then passed through a series of saturators filled with doubly distilled water. All reactions were carried out at 1 atm pressure, but the partial pressures of the reactants were varied by varying the flow rates of the reactants and/or the temperature of the saturators. The effluents were analyzed by a gas chromatograph through a gas sampling valve located downstream. Since no side reactions were found, the conversion was calculated from the ratio of CO to CO_2. The specific rates thus obtained were in good agreement with those measured in the circulation system under the same conditions. The kinetics was investigated within a range where the conversion was linear against the contact time (the reciprocal of the total flow rate). All ir spectra reported in this paper were taken after the reaction reached steady state under each set of reaction conditions usually within several minutes.

The catalysts in the circulation system were evacuated for 1 hr at 600°C between runs while the evacuation temperature was limited to 500°C in the infrared cell. However, these treatments were adequate to obtain reproducible results.

RESULTS

1. *Effect of Alkali Salts*

(*a*) *$CO + H_2O$*. The Arrhenius plots of the rates measured on various catalysts are shown in Fig. 2 where the catalyst symbols listed in Table 1 are used to identify each line. It is clear that all alkali salts added increased the activity compared to alumina (line A). For example, the rate on 9 K/A catalyst was about 20 times greater than that

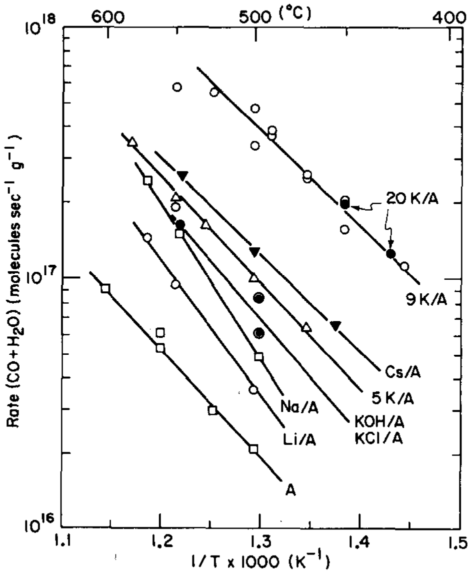


FIG. 2. Arrhenius plots for $CO + H_2O$ reaction. Catalyst designations appear in Table 1. The partial pressures of carbon monoxide and water vapor were 100 and 18 Torr, respectively.

on alumina over a temperature range used in this study. The activity increased when the concentration of potassium carbonate was increased from 5 to 9%, but no further promotion was observed at 20% as seen in Fig. 2. As reported in the previous paper (*1*), potassium carbonate in 9K/A catalyst decomposed completely by calcination and probably the surface hydroxyl groups were replaced by OK groups. If all the potassium ions exist on the surface, 9K/A catalyst has a surface concentration of 8.0×10^{14} K^+/cm^2 which is close to saturation for a monolayer. It appears that potassium carbonate added beyond this level did not decompose to form the OK groups. It was also observed that the surface area did not decrease with up to 9% of K_2CO_3 but a serious loss of area occurred with 20% of the salt (Table 1).

Figure 2 also indicates that the efficiency of alkali metal ions for the promotion is in the order Cs > K > Na > Li when compared at the same ion concentration. The activation energy, the value of which is listed in Table 1, increases also in the same order except for lithium. Results obtained with KOH- and KCl-promoted catalysts were not as reproducible as those obtained with catalysts promoted by carbonates. The reason is not yet known. However, the activity of these two catalysts does not seem to be much different from that of alumina promoted by potassium carbonate at the same concentration.

(*b*) $CO_2 + H_2$. Results are shown in Fig. 3. Although the Arrhenius plots for some catalysts were omitted from Fig. 3 for clarity, all other lines fell between lines A and 9K/A converging at about 400°C. As seen in Fig. 3, the activity of all promoted catalysts was higher than that of alumina above 450°C except for the $LiCO_3$-promoted catalyst whose activity was about the same as that of alumina. Generally speaking, the efficiency of the metals was in the same order as that observed for the $CO + H_2O$ reaction, namely, cesium was the best. However, the differences were not very clear compared to Fig. 2 and they strongly depended on temperature. Again no further change in activity was found over 9% of K_2CO_3 added.

2. *Kinetics*

As already described, the kinetics was investigated with a disk of 9% K_2CO_3-promoted alumina (9K/A) in the cell of the infrared system. Some typical results are shown in Figs. 4 and 5. As shown in Fig. 4, the $CO + H_2O$ reaction is of first order with respect to carbon monoxide, but the reaction order for water vapor is much less than unity indicating a strong adsorption of water. The reaction rate, r (molecules sec^{-1} g^{-1}), can be expressed by an empirical equation,

$$r(CO + H_2O) = k_1 p_m p_w / (1 + K_w p_w), \quad (1)$$

where p_m and p_w are the partial pressures (Torr) of carbon monoxide and water vapor, respectively, and k_1 and K_w are constants ($k_1 = 9.47 \times 10^{14}$ molecules sec^{-1} g^{-1} $Torr^{-2}$ and $K_w = 0.317$ $Torr^{-1}$ at 400°C).

Unfortunately, the partial pressure of each reactant could not be varied indepen-

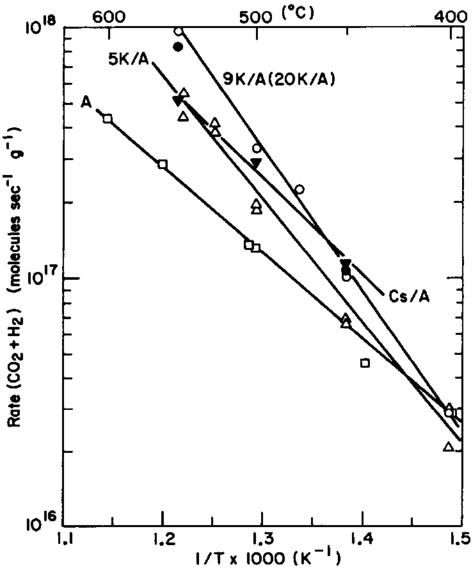


FIG. 3. Arrhenius plots for $CO_2 + H_2$ reaction. Reactions were carried out with 94 Torr of CO_2 + 94 Torr of H_2.

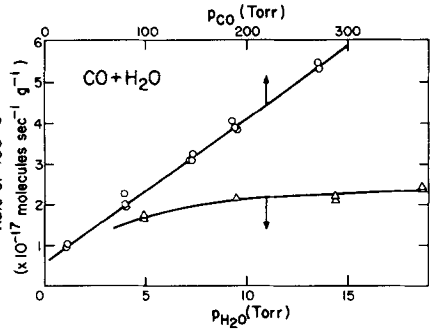


FIG. 4. Pressure dependence of CO + H_2O reaction on 9K/A catalyst. Reactions were carried out at 400°C under a constant pressure of water (20 Torr) for the upper line or carbon monoxide (93 Torr) for the lower curve.

dently in the case of CO_2 + H_2 reaction. However, results obtained by varying the ratio of the reactants (Fig. 5) could be approximated by a similar Langmuir-type equation,

$$r(CO_2 + H_2) = k_2p_hp_d/(1 + K_dp_d), \quad (2)$$

where p_h and p_d are, respectively, the partial pressures of hydrogen and carbon dioxide, and k_2 and K_d are constants. The values of the constants were obtained by the method of least squares as $k_2 = 3.14 \times 10^{13}$ molecules sec^{-1} g^{-1} Torr^{-2} and $K_d = 0.0115$ Torr^{-1}, respectively. The rate calculated with these values is shown in Fig. 5 by a broken line which fits reasonably well with those observed.

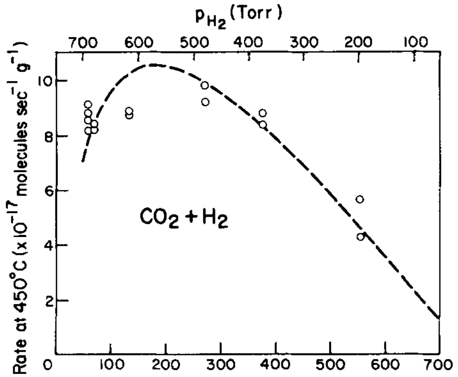


FIG. 5. Pressure dependence of CO_2 + H_2 reaction on 9K/A catalyst. Reactions were carried out at 450°C at 1 atm pressure with varying ratio of CO_2/H_2.

3. *Infrared Spectroscopy*

(*a*) *CO* + H_2O. Infrared spectra were recorded while the water-gas shift reaction was proceeding on 9K/A catalyst at steady state as already described. Some typical spectra taken during the CO + H_2O reaction are shown in Fig. 6. Besides the absorption bands shown in the figure, a broad band due to hydrogen-bonded water was observed at 3500 cm^{-1}.

When the reaction was carried out at a CO pressure lower than 100 Torr and at a temperature above 400°C (spectrum a in Fig. 6), two strong bands appeared at 1570 and 1320 cm^{-1} with a shoulder at 1600 cm^{-1}. The 1570- and 1320-cm^{-1} bands had been observed in the previous report on the same catalyst with carbon monoxide chemisorbed at 400°C or higher and assigned to a bidentate carbonate (*1*). When the CO pressure was varied from 20 to 270 Torr, however, the absorbance of these bands increased only by 30% while the reaction rate increased linearly with the CO pressure as

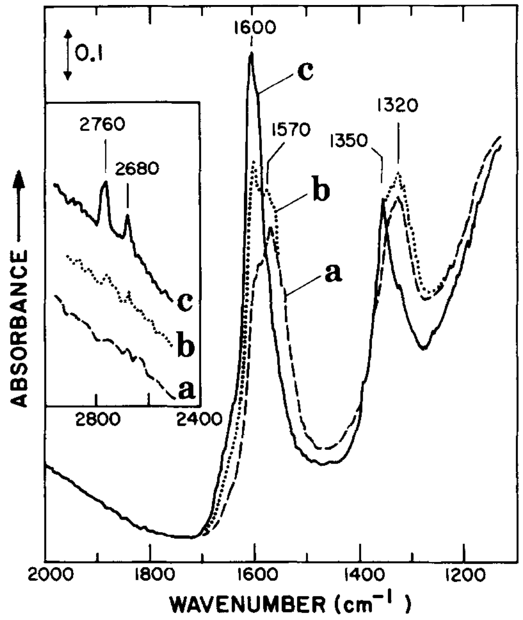


FIG. 6. Infrared spectra taken during the CO + H_2O reaction on 9K/A catalyst: (a) at 400°C, 90 Torr CO + 19 Torr H_2O; (b) at 400°C, 268 Torr CO + 20 Torr H_2O; (c) at 300°C, 90 Torr CO + 19 Torr H_2O.

already shown in Fig. 4. Therefore, the bidentate carbonate (1570- and 1320-cm^{-1} bands) is not directly responsible for the reaction.

As the pressure of carbon monoxide was increased at 400°C (spectrum b in Fig. 6), the band at 1600 cm^{-1} became clearer and a new shoulder developed at 1350 cm^{-1}. Also, two weak bands became detectable at 2760 and 2680 cm^{-1} as shown in the inset in Fig. 6. When the CO + H_2O reaction was carried out at low temperatures between 200 and 300°C, the 1570- and 1320-cm^{-1} bands almost disappeared and the four bands were clearly observed at 2760, 2680, 1600, and 1350 cm^{-1} as represented by spectrum c in Fig. 6. The intensities of these four bands varied in a constant ratio indicating that all the bands belonged to the same species. The frequencies of the four bands are close to those observed with potassium formate by other investigators (*6–8*) but different from those found with aluminum formate (*7*) or with formate ions formed on alumina during the WGS reaction (*5*). Apparently, formate ions were formed on potassium ions on the promoted catalyst by the CO + H_2O reaction. We assign the 1600- and 1350-cm^{-1} bands, respectively, to the antisymmetric (ν_4) and symmetric (ν_2) stretching vibrations of O–C–O, and the 2760-cm^{-1} band to the CH stretching vibration (ν_1). The frequency shifts observed with the CO + D_2O reaction ($\Delta\nu_1 = 710\ cm^{-1}$, $\Delta\nu_2 = 24\ cm^{-1}$, and $\Delta\nu_4 = 7\ cm^{-1}$) were all in good agreement with similar shifts observed with sodium formate (*6*) or formate ions on alumina ($\Delta\nu_1 = 706\ cm^{-1}$, $\Delta\nu_2 = 23\ cm^{-1}$, and $\Delta\nu_4 = 5\ cm^{-1}$).

As reported previously (*1*), carbon monoxide chemisorbed on the potassium-promoted alumina at 300°C forms a carboxylate ion giving rise to a pair of bands at 1590 and 1320 cm^{-1}, while, at 400°C or higher, another pair of bands due to a bidentate carbonate appears at 1570 and 1320 cm^{-1} in addition to the former pair. Spectrum c in Fig. 6 is almost free of the 1570- and 1320-cm^{-1} bands so that the surface species formed below 300°C are mainly formate ions. With spectrum a, however, it might be feared that carboxylate ions instead of formate ions are formed together with carbonate ions. When carboxylate and carbonate ions are both present on 9K/A catalyst at maximum concentrations at 400°C, a similar shoulder appears at 1590–1600 cm^{-1} (*1*), and the ratio of peak absorbances, A_{1320}/A_{1570}, is about 0.8. The same ratio for spectrum a in Fig. 6 is 0.6 which is very close to the ratio obtained with the carbonate ions alone. Therefore, the surface species formed during the CO + H_2O reaction at 400°C are mainly formate and bidentate carbonate but the amount of carboxylate ion, if any, should be very small.

The surface formate seems to be in equilibrium with the reactants since the intensity of the bands due to formate responded quickly to the changes in the reactant pressures and temperature. It was difficult, however, to correlate the surface concentration of formate and the reaction rate because the 1600- and 1350-cm^{-1} bands overlapped strongly with those of carbonate at 400°C or higher, while, below 300°C, the reaction rate was too slow to be measured. Therefore, the integrated intensity of the 2760-cm^{-1} band observed at 350°C under various pressures of carbon monoxide between 70 and 260 Torr was plotted in Fig. 7 against the reaction rate measured simultaneously. The 1600- and 1350-cm^{-1} bands were much stronger but they were not used to avoid possible errors due to the overlaps. As seen in Fig. 7, the rate is proportional to the surface concentration of formate suggesting that the CO + H_2O reaction takes place through formate formed on potassium ions on the surface.

It is not clear at this stage whether carbonate species observed at high temperatures results from the direct adsorption of carbon monoxide or from the adsorption of carbon dioxide produced by the reaction because the same carbonate species is formed in both cases (*1*). If it is the latter case, however, we can exclude the possibil-

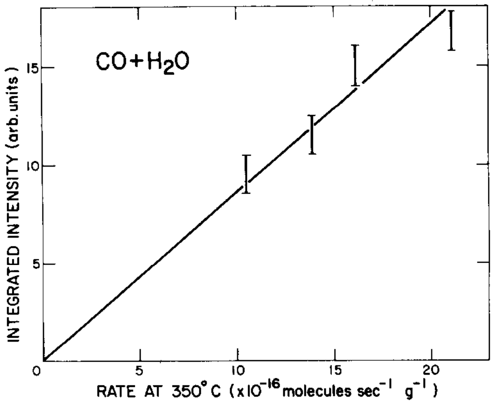


FIG. 7. Integrated intensity of the 2760-cm^{-1} band vs the reaction rate of $CO + H_2O$ on 9K/A catalyst at 350°C.

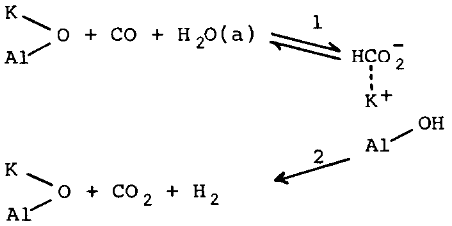
ity that the desorption of CO_2 is the rate-determining step. The removal of the surface carbonate in a flow of helium was examined and it was found to be much faster when water vapor was present in the helium flow. However, the rate of removal of the carbonate at 400°C in the helium flow with 19 Torr of water vapor was 3.9×10^{16} molecules sec^{-1} g^{-1} at the same surface concentration of carbonate as that of spectrum a in Fig. 6, while the reaction rate measured with spectrum a was 2.5×10^{17} molecules sec^{-1} g^{-1} which was almost an order of magnitude faster than the desorption rate. Therefore, the carbonate species observed in spectra a and b in Fig. 6 is not in the direct path of the reaction, but is formed by a side reaction.

(*b*) $CO_2 + H_2$. During the $CO_2 + H_2$ reaction, strong bands due to chemisorbed carbon dioxide obscured all bands in the region of CO stretching vibrations. However, no 2760- and 2680-cm^{-1} bands were observed at all temperatures so that the surface concentration of formate, if any, should be very low.

DISCUSSION

The present results clearly demonstrated that alkali salts added on alumina promoted the WGS reaction. The activity of catalyst increased with the concentration of promoter until it almost saturated the surface of alumina. While the surface of 9K/A catalyst was almost fully covered by potassium, results obtained by infrared spectroscopy and temperature-programmed desorption indicated that a considerable fraction of the surface of 5K/A catalyst was free of potassium as reported in Part I (*1*). Therefore, the activity measured on 5K/A and other catalysts with similar concentration of alkali metal ions should be the sum of those on free and alkalized alumina surfaces. Actually, the activation energies found on 5K/A were in between those on alumina and 9K/A catalysts as seen in Table 1.

In the case of unpromoted alumina, a good agreement was found between the decomposition rate of surface formate and the overall rate of the WGS reaction as reported previously (*5*). Although such a direct comparison could not be made in the present work, the results of Fig. 7 indicate that formate formed on alkali metal ions is an intermediate of the WGS reaction on the promoted aluminas. The $CO + H_2O$ reaction may be written as follows:



As already discussed, the surface formate was equilibrated with the reactants (step 1) and the rate was proportional to the concentration of formate while the possibility of the control of the reaction by the desorption of carbon dioxide was excluded. Therefore, the rate-determining step should be step 2 in the above reaction scheme, the dehydrogenation of surface formate. The rate is then expressed by the surface concentration of formate, $\theta_{HCO_2^-}$, as

$$r(CO + H_2O) = k\theta_{HCO_2^-}. \qquad (3)$$

Since the surface formate is in equilibrium with the reactants, $\theta_{HCO_2^-}$ may be proportional to the product of the surface concentration of adsorbed water and the pressure of carbon monoxide. This leads to Eq. (1) as the overall rate equation. In the case of $CO_2 + H_2$ reaction, on the other hand, only bands due to chemisorbed carbon dioxide were observed without any signs of formate species as described earlier. The rate-determining step of the $CO_2 + H_2$ reaction would probably be the formation of formate (step 2) so that the surface formate is dehydrated as soon as it is formed.

The rate-determining step of the $CO + H_2O$ reaction on unpromoted alumina is also the dehydrogenation of surface formate (*5*) so that the rate of that elementary step is expressed by Eq. (3). Having the same rate expression on the promoted and unpromoted catalysts, the promotion by alkali metal ions should result either from a greater rate constant or from a larger concentration of surface formate or both. Alkali metal ions added, of course, serve as sites to accommodate formate thus increasing the surface concentration of the intermediate. At the same concentration of metal ions, on the other hand, the efficiency of promotion depends on the alkali metal used as already pointed out. This would probably result from different values of the rate constant of Eq. (3) due to the difference in chemical nature of the promoters. The order of the promotion effect (Cs > K > Na >Li) found in this study is in reverse order for the ionization potential. This may indicate that formate on the surface becomes unstable due to the electron-donating character of alkali metals. Formate on alumina would be more stable. In fact, we could follow the decomposition of surface formate on alumina (*5*).

As described in the Introduction, there are some reactive oxygen atoms on the alumina surface which are exchangeable with carbon dioxide (*2*). The previous report (*1*) showed that the addition of potassium increases the number of these reactive oxygens and that each potassium ion added is associated with one reactive oxygen at 300°C or higher. The promoted alumina also showed much higher activity for the oxygen exchange with carbon monoxide (*1*), while, on unpromoted alumina, the exchange with CO was much slower and almost unmeasurable below 300°C (*3*). The results of temperature-programmed desorption and infrared spectroscopy carried out in the previous work have indicated that carbon monoxide chemisorbed on the promoted alumina at 150°C or higher picks up a reactive oxygen to form a carboxylate ion while, above 400°C, another oxygen participates in the chemisorption forming a carbonate species (*1*). These reactive oxygens on the surface might be involved in the formation of formate on the promoted catalysts thus becoming an important factor in the promotion although the participation of catalyst oxygen is not necessary stoichiometrically for the reaction mechanism proposed in this paper. The formation of surface formate in the WGS reaction became visible spectroscopically at temperatures between 150 and 200°C, the same temperature range for the formation of carboxylate species in the CO chemisorption as described above. When formate is formed, very few carboxylate ions are present as discussed in section 3(a) under Results indicating that most of the reactive oxygens are used up in producing formate. Carboxylate ion may be a precursor of formate. These surface oxygens could also be involved in the WGS reaction on alumina, but their number is smaller and the activity particularly toward carbon monoxide is much lower. It is difficult, however, to prove directly the involvement of catalyst oxygen, say, by using an isotope ($C^{18}O$) because these reactive oxygens are readily exchanged with carbon monoxide and carbon dioxide in particular (*1*, *2*).

Grenoble *et al.* (*9*) have recently studied the water-gas shift reaction on supported metal catalysts and assumed that carbon monoxide is first activated by adsorbing on metal sites for the subsequent formation of formic acid on an adjacent alumina surface. For the present catalysts, however, the chemisorption of CO on alkali metal sites is not thought to be an essential factor for the promotion. Absorption bands due to carbon monoxide chemisorbed on metal sites usually appear between 2080 and 1850 cm^{-1}, but no bands in this region were observed either in the CO chemisorption or during the WGS reaction in the present study. Alkali metal ions probably stay on the surface as –OM groups as discussed in Part I (*1*) and are not reduced to metal under reaction conditions. Oxidation of the promoted catalysts with air at 600°C or reduction with CO at 500°C did not show any difference in both the chemisorption of CO and the activity for the water-gas shift reaction.

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