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Active Sites of Solid Acidic Catalysts

II. Water–Gas Conversion on Alumina and Some Other Catalysts[1]

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The water–gas conversion reaction ($CO_2 + H_2 \rightleftarrows CO + H_2O$) on alumina was studied in an attempt to obtain further information on the redox properties of alumina. The kinetics of the forward and backward reactions were investigated separately over a temperature range between 400 and 600°C: The rate of $CO_2 + H_2$ is proportional to the square root of both carbon dioxide and hydrogen pressures while the rate of $CO + H_2O$ is of first order with respect to carbon monoxide but almost independent of the water pressure. The apparent activation energies obtained were 16.1 and 22.9 kcal/mole for the respective reactions. A possible nature of active sites is discussed. The activity of some other catalysts including a commercial iron oxide catalyst was also measured. The catalysts studied could be classified in terms of compensation effect into three groups in the following order: catalysts with variable valency; catalysts with Lewis acidity; and catalysts with Brønsted acidity with decreasing activity.

INTRODUCTION

In the preceding paper of this series (*1*), the acid centers of alumina were studied by the isomerization of butenes and the nature of the sites was discussed in connection with the chemisorption of ammonia. In addition to the acid properties, the redox properties of alumina was reported particularly from the capability of electron transfer (*2*, *3*). More recently, some oxide ions on the alumina surface have been found to be very reactive and exchanged readily with carbon dioxide (*4*, *5*). Therefore, we studied the water-gas conversion reaction on alumina as a typical redox reaction. The kinetics and mechanism of water–gas reaction have been studied extensively but mostly on iron oxide catalysts (*6*).

This paper reports the results obtained mainly on alumina, but the work was extended to some other acidic catalysts and to an iron-based commerical catalyst for comparison.

EXPERIMENTAL METHODS

Materials

Most of the experiments were done in a closed circulation system with a γ-alumina which was Alon alumina of Cabot Corporation, Boston, Massachusetts. Alon powder was ground with water, dried at 100°C, and crushed. An amount of 1.16 g of a 9- to 16-mesh portion was taken into the reactor, calcined with dry air for 2 hr at 600°C, and finally evacuated for 3 hr at the same temperature before use. The surface area was 92.5 m^2/g after the above treatment,

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but decreased by 5% during the experiments (90 runs).

The activity of some other catalysts was compared in a flow-type reactor. They were γ-alumina prepared from aluminum isopropoxide (7), η-alumina (*1*), sodium carbonate-impregnated η-alumina (3% as Na_2O), silica–alumina (74% Al_2O) (7), Houdry M-46 silica–alumina, Davison silica–magnesia (30% MgO), alumina–boria (15% B_2O_3), silica (7), chromia–alumina (40% Cr_2O_3), and Girdler G-3 conversion catalyst (chromia-promoted iron oxide). All compositions are in weight percentage. The preparation of some catalysts has been described in previous papers as cited above.

All gases were taken from Matheson's cylinders: research purity carbon dioxide (99.995%), carbon monoxide (99.99%), and ultrahigh purity hydrogen (99.999%). Before being stored in reservoirs, hydrogen and carbon monoxide were passed through a trap at liquid nitrogen temperature, and carbon dioxide was degassed at the same temperature. For the flow-type reactor, ultrahigh purity hydrogen and Coleman instrument-grade carbon dioxide (99.99%) were used without further purification.

Apparatus

The closed circulation system used for the study is shown in Fig. 1; it was a greaseless apparatus constructed with stainless-steel bellows valves and a bellows pump. The reactor was made of quartz. The whole system except for the reactor and trap was in an oven thermostatted at 100°C. The cylinders V_1 and V_2 were used with a capacitance-type pressure transducer (P_2) to mix gases (CO_2 and H_2) quantitatively, but only V_2 was used for reaction. Also, the pressure during the reaction was measured by a bonded strain gauge (P_1) which was not affected by water vapor. When necessary, a small amount of sample (about 1% of the total amount in the system) was taken into a gas-sampling valve (S) and sent to a gas chromatograph for analysis. The samples were taken through a three-way valve to the preevacuated loop of S so that no helium was back fed to the reaction system.

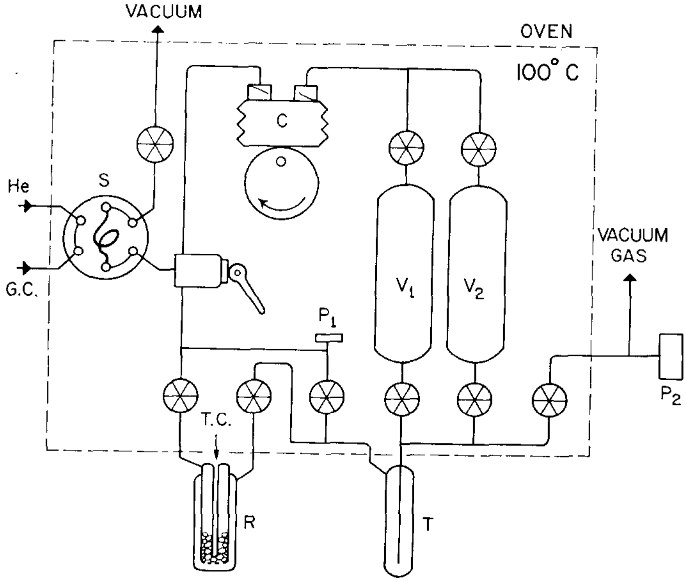

FIG. 1. Schematic diagram of the apparatus: S, sampling valve of gas chromatograph; C, bellows circulation pump; R, reactor; T.C., thermocouple; T, trap; P_1, P_2, pressure transducers.

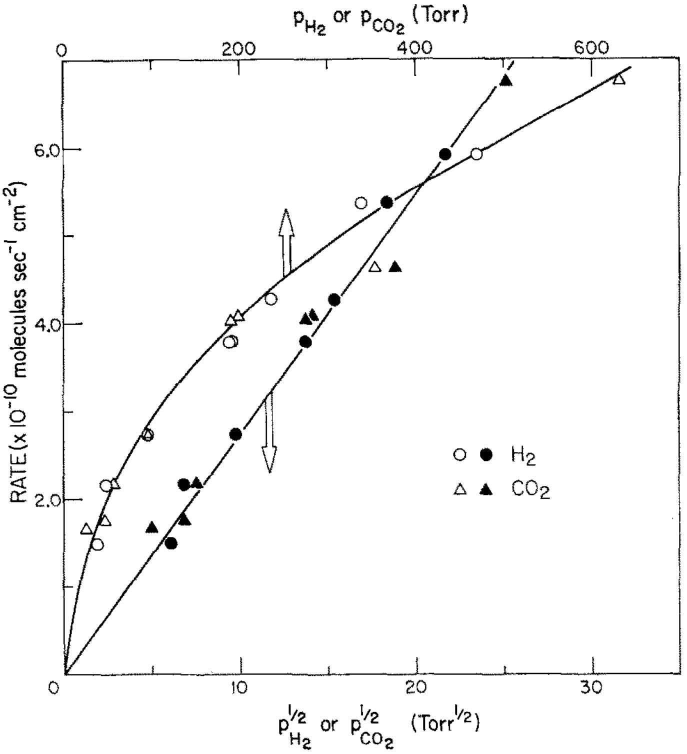

FIG. 2. Pressure dependence of $CO_2 + H_2$. Reactions were carried out at 400°C at a constant pressure (95 Torr) of hydrogen or carbon dioxide.

The flow reactor used was a quartz tube (10 mm in diameter) which was connected to a gas chromatograph through a stainless-steel gas-sampling valve.

Procedure

The forward and backward reactions of $CO_2 + H_2 \rightleftarrows CO + H_2O$ were studied separately. For the $CO_2 + H_2$ reaction, the mixture of the reactants was circulated through the reactor, the circulation pump, V_2, and the trap cooled by the dry ice–alcohol bath. The pump was operated at a high speed so that the reaction rate was not affected by the circulation speed. The total pressure was recorded through P_1, and the rate of reaction was calculated from the pressure–time curve. In some experiments, however, the amount of carbon monoxide was also followed by the gas chromatograph, and the results agreed with the pressure change within an error of 5%.

In the case of $CO + H_2O$, carbon monoxide was circulated through the trap in which triple-distilled water was kept at desired temperatures. The vapor pressures measured by the strain gauge were in good agreement with the table values at the trap temperatures, and blank tests showed that the water vapor saturated the gas quickly. The composition of the gas phase was analyzed by the gas chromatograph at proper intervals of time, and the reaction rate was obtained from the increase in carbon dioxide, as will be described later.

No side reactions were observed in both reactions within the detection limit of analysis. After each run, the catalyst was evacuated for 2 hr at 600°C. This treatment was adequate to obtain reproducible results. Indeed, the regeneration of catalyst with dry air at 600°C after several runs did not change the activity.

The amount of catalysts in the flow reactor was adjusted to between 0.2 and 0.5 g to give conversions of less than 5%. It was therefore treated as a differential reactor.

RESULTS

$CO_2 + H_2$

The total pressure decreased almost linearly in the first 10 to 30 min depending on temperature. At 600°C which was the highest temperature used, the reaction was completed in 80 min with the stoichiometric pressure drop. Since the water formed was trapped during the reaction, no backward reaction took place, and the reaction rate was calculated from the initial pressure decrease as already described. The pressure dependence at 400°C is shown in Fig. 2 where the partial pressure of CO_2 (or H_2) was varied at a constant pressure (95 Torr $= 1.266 \times 10^4$ N m^{-2}) of H_2 (or CO_2). Both reactants have almost identical effects on the rate and the rate is proportional to the square root of each pressure as shown by filled points in Fig. 2.

The Arrhenius plot of the rate between 350 and 600°C is shown in Fig. 3, from which the activation energy was obtained as 16.1 kcal/mole (1 kcal = 4.18 kJ). From the above results the rate, r_1, is expressed by the equation

$$r_1(\text{molecules sec}^{-1}\text{ cm}^{-2}) = 5.07 \times 10^{13} \exp(-16{,}100/RT)p_d^{\frac{1}{2}}p_h^{\frac{1}{2}}, \quad (1)$$

in which p_d and p_h are the pressures (Torr) of carbon dioxide and hydrogen, respectively.

Some reactions were preceded by the adsorption of carbon dioxide or hydrogen for 1 hr at the reaction temperature and pressure, but no effect of the preadsorption of either reactant on the reaction rate was observed at 400 and 560°C. Also, the presence of carbon monoxide at least up to 20 Torr did not change the rate at both temperatures. The presence of water vapor,

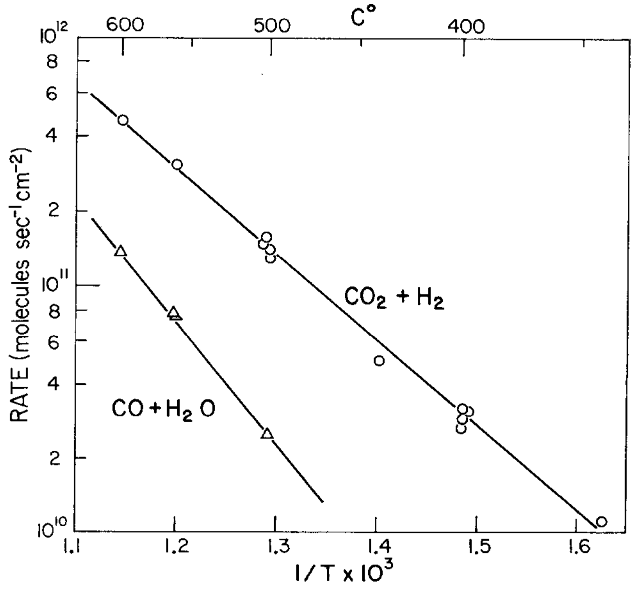

FIG. 3. Arrhenius plot. Rates were measured with 95 Torr of CO_2 + 95 Torr of H_2 (○) and with 100 Torr of CO + 24 Torr of H_2O (△).

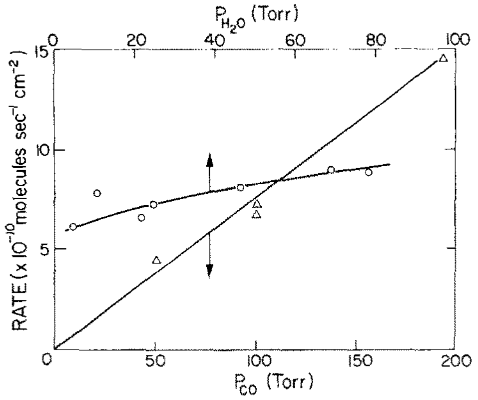

FIG. 4. Pressure dependence of $CO + H_2O$. Reactions were carried out at a constant pressure of carbon monoxide (100 Torr) or water vapor (24 Torr) at 560°C.

however, retarded the reaction seriously: At 22 Torr of water vapor, for example, the reaction was stopped completely at 400°C and the rate was reduced to 23% at 560°C. As soon as the vapor was trapped by dry ice–alcohol trap, the activity of the catalyst was recovered to about 80% of the original activity at both temperatures.

The results of reactions with deuterium and carbon dioxide showed no isotope effect of hydrogen within the experimental error.

$CO + H_2O$

The reaction was too slow to follow at 400°C. Therefore, most experiments were carried out between 500 and 600°C at a constant vapor pressure of water. The total pressure decreased slightly for about a minute due to the adsorption of water, but it increased monotonously after that and finally reached a plateau. For example, the pressure in a reaction (101 Torr of CO + 23 Torr of H_2O) at 600°C dropped by 4.5 Torr in the first 45 sec, then increased until it became constant at 170 Torr at 150 min. The final analysis by the gas chromatograph gave $[CO_2][H_2]/[CO][H_2O] = 2.52$ which was close to the 2.69 calculated as the equilibrium constant from a thermochemical table (*8*).

Since the pressure was disturbed by the water adsorption, the total pressure was not used for measuring the rate. Instead, the partial pressure of carbon dioxide formed was plotted against time, and the initial rate was calculated from the slope of the curve. These initial rates were plotted in Fig. 4 with the pressures of carbon monoxide and water. The reaction is of first order with respect to carbon monoxide, but

TABLE 1

Comparison of Catalysts[a]

Catalyst	Symbol (in Fig. 5)	Surface area (m^2/g)	Activation energy (kcal/mole)	r_1 at 500°C (molecules cm^{-2} sec^{-1})
γ-Alumina (Alon)	A	93	19	3.2×10^{11}
γ-Alumina (from Al-isopropoxide)	B	91	13	2.2×10^{11}
η-Alumina	C	151	26	7.1×10^{11}
Na_2O–η-alumina (3%)	D	270	28	4.6×10^{11}
Silica–alumina (74%)	E	263	36	1.4×10^{11}
Silica–alumina (Houdry M-46)	F	240	24	4.5×10^{9}
Silica–magnesia (Davison)	G	426	25	5.3×10^{9}
Alumina–boria (15%)	H	228	34	8.9×10^{9}
Silica	I	630	28	2.8×10^{8}
Iron oxide–chromia (Girdler G-3)	J	56	33	6.7×10^{14}[b]
Chromia (40%)–alumina (oxidized)	K	176	31	3.1×10^{13}[c]
Chromia (40%)–alumina (reduced)	L	176	24	9.6×10^{12}[c]

[a] All reactions were carried out under atmospheric pressure with about 65% of CO_2.

[b] Rate calculated from the reaction at 316°C.

[c] Rate caluclated from the reaction at 346°C.

the reaction order in water is much less than unity. Apparently water is chemisorbed strongly and almost saturates the active sites under small pressures. The best fit for a simple Langmuir formula was obtained by the equation,

$$r_2(\text{molecules sec}^{-1}\text{ cm}^{-2}) = 1.01 \times 10^9 K_w p_w p_m/(1 + K_w p_w), \quad (2)$$

where p_m and p_w are, respectively, the partial pressures (Torr) of carbon monoxide and water, and K_w is the equilibrium constant of adsorption of water ($K_w = 0.109$ Torr^{-1} at 560°C). The Arrhenius plot for this reaction is included in Fig. 3 from which the activation energy was obtained as 22.9 kcal/mole. The preadsorption of either reactant did not change the initial rate.

Comparison of Catalysts

As already described, the activity of some other catalysts was compared in the flow-type reactor. Only the forward reaction, $CO_2 + H_2$, was examined. All catalysts except chromia–alumina and iron oxide catalysts were treated in the air flow for 2 hr at 600°C, and the reaction rate was measured at 500°C. The chromia–alumina was treated at 600°C with air (oxidized) or hydrogen (reduced) and the reaction was carried out at 346°C. The iron oxide (Girdler G-3) was first treated with air at increasing temperature (2°C/min) up to 200°C where the air was switched to helium and the heating was continued to 390°C. The helium was then replaced gradually by the mixture of the reactants while the temperature was decreased to the reaction temperature (316°C).

The results are listed in Table 1. Although the rate of Alon alumina measured in the flow-type reactor was in the same order of magnitude as that obtained in the circulation system, the activation energy was somewhat larger. It should be pointed out, however, that the measurement of activation energy in the flow-type reactor was not as accurate as in the circulation system. η-Alumina was two to three times more active than γ-aluminas. This was confirmed also in the circulation system.

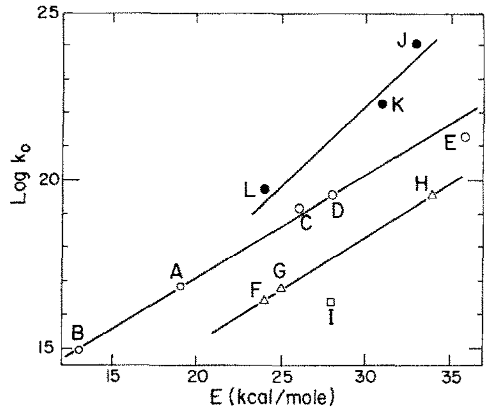

FIG. 5. Compensation effect. Symbols in the figure appear in Table 1.

It is of interest that all catalysts studied here with the exception of silica are classified in terms of the compensation effect into three groups as shown in Fig. 5. The most active group is the redox catalysts with variable valency (iron oxide and chromia), the second group is aluminas characterized by Lewis acidity, and the least active group is catalysts with Brønsted acidity (*9*). The above characterization of catalysts is rather conventional, since some Brønsted acid centers are recently reported on alumina (*10, 11*), and silica–alumina possesses Lewis acidity to some extent as well as Brønsted centers. Moreover, no definite correlation has yet been found between the acidity and the water–gas reaction. Nevertheless, aluminas are much more active than other acidic catalysts and one of the silica–aluminas (70% alumina, E in Fig. 5) which was characterized between a pure alumina and the most active silica–alumina for olefin reactions (*7*) lies also between the lower two lines in Fig. 5.

DISCUSSION

The rate equations obtained in the preceding sections are valid over a wide

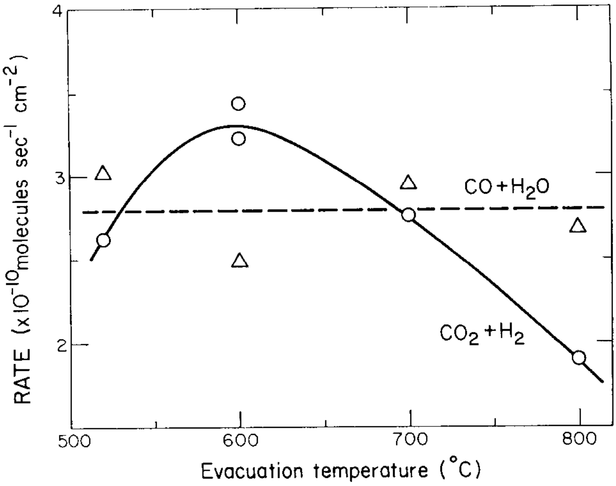

FIG. 6. Effect of the evacuation temperature of catalyst on the activity. Rates were measured at 400°C for $CO_2 + H_2$ and at 500°C for $CO + H_2O$.

range of reaction conditions employed in the present study. However, the reaction mechanism cannot be deduced directly from these equations, Eq. (1) in particular. Indeed, the pressure dependence of r_1 could also be approximated by the first order Langmuir equation, $K_p/(1 + K_p)$, for both carbon dioxide and hydrogen. When the strength of adsorption is moderate, the order of the Langmuir equation falls between 0 and 1 and may be expressed as $r_1 \propto (p)^{\frac{1}{2}}$. Also, Eq. (1) was obtained by neglecting the effect of water vapor. r_1 and r_2 calculated from Eqs. (1) and (2) at an equilibrium composition are different: r_1 is much larger than r_2. As already pointed out, however, the presence of water vapor reduces r_1 greatly while r_2 varies little with the vapor pressure. Therefore, the actual rate of the $CO_2 + H_2$ reaction at equilibrium would be much smaller than calculated from Eq. (1) and equalized with r_2. Although the rates in Fig. 2 were measured by circulating the gas at high speed to avoid the diffusion control and removing the water continuously by the trap, it is possible that water exists on the catalyst at a concentration established by the balance between the rates of formation and desorption.

The apparent activation energy of r_1 obtained from Fig. 3 could include the heat of adsorption of the reactants to some extent depending on the true form of the rate equation. In any case the activation energy of the rate-determining step would be higher than observed. On the other hand, the participation of the adsorption heat of water in r_2 would be much less since the adsorption of water is near saturation. When the rate r_2 is treated approximately as the zeroth order in the water pressure, it is expressed as

$$r_2(\text{molecules sec}^{-1}\text{ cm}^{-2}) = 7.51 \times 10^{14} \exp(-22{,}900/RT)p_m. \quad (3)$$

The nature of active sites for this redox reaction is not clear yet. All curves in Figs. 2 and 4 increase monotonously with the pressures without showing a maximum. It probably indicates that the sites are not shared by the reactants. Although the study of this reaction by infrared spectroscopy is still under way, formate ion was detected during the reaction in either direction (*12*). The formate ions would probably be held on aluminum ions exposed on the surface. At the same time, the activity of the catalyst for the $CO_2 + H_2$

reaction showed a maximum against the temperature of evacuation of catalyst as shown in Fig. 6. It is, therefore, likely that the active sites are dual sites, for example, aluminum ions associated with either oxide ions or hydroxyl groups. As already pointed out, very reactive oxide ions have been found on alumina recently and the density of these oxide ions decreases in parallel with hydroxyl groups when alumina is evacuated at increasing temperatures (*5*, *13*). The activity of the $CO + H_2O$ reaction in Fig. 6 did not vary with the evacuation temperature because the presence of water vapor reconditioned the surface.

It has been reported that carbon dioxide catalyzes the exchange reaction between deuterium gas and the hydroxyl groups of zeolites (*14*). We also observed that the exchange on alumina was promoted by a small amount of carbon dioxide. This promotion by carbon dioxide would result from water formed by the water–gas conversion between deuterium and carbon dioxide.

The compensation effect observed in Fig. 5 could be due to a parallel increase in both activation entropy and enthalpy although a definite explanation is impossible at this stage. In any case, however, the three different lines seem to suggest different mechanisms.

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