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TRAPPING ADSORPTION OF CARBON MONOXIDE LOCATED BETWEEN CARBON DIOXIDE ADSORBED ON MAGNESIUM OXIDE

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Carbon monoxide adsorbed on MgO is strongly trapped by the adsorbed carbon dioxide, increasing the heat of adsorption from 85.4 to 184.1 kJ/mol. The trapped CO is thought to be captured by two or three adsorbed CO_2 and becomes less active to react with oxygen.

Монооκись углерода, адсорбированная на MgO, сильно связана адсорбированной двуокисью углерода, что приводит к увеличению теплоты адсорбции с 85,4 до 184,1 кДж/моль. Полагают, что одна молекула CO захватывается двумя или тремя адсорбированными молекулами CO_2 и тем самым становится менее активной к реакции с кислородом.

The interaction between CO species adsorbed on MgO has been studied in detail by Zecchina et al. [1], who illustrate the formation of CO clusters and carbonate like species. In the present study, our further interest is focused on the interaction of CO with CO_2 coadsorbed on MgO at 290-320 °C. An anomalously coinfluenced adsorption behavior of CO and CO_2 has been studied by the transient response method [2,3] and the temperature programmed desorption technique in a flow system.

The sample used in this study was prepared from Wako Pure Chemicals, guaranteed reagent. MgO (20-30 mesh, BET surface area is 27.5 m^2/g) was packed into a Pyrex glass tubular flow reactor and pretreated in a He stream at 300 °C for 20 h prior to use.

Figure 1 shows the transient desorption behavior of CO

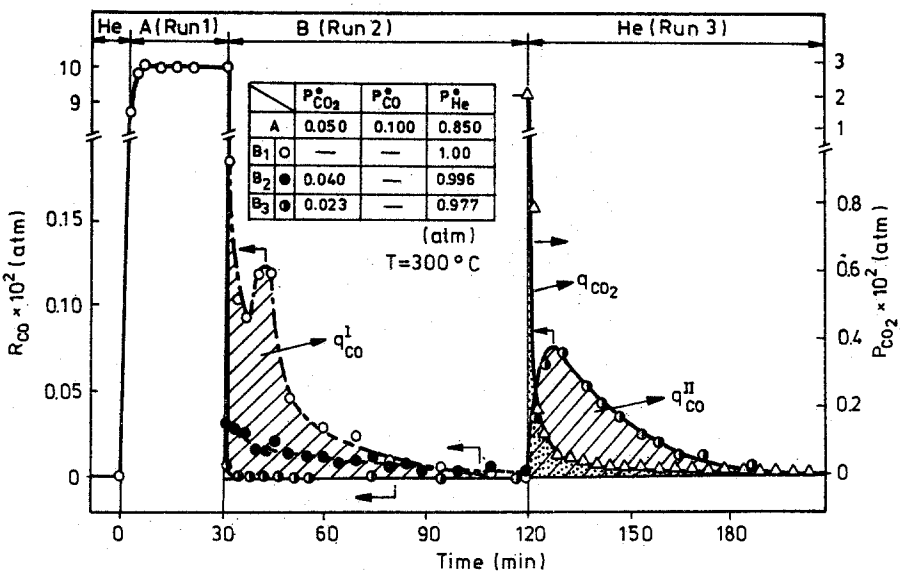

Fig. 1. Desorption of adsorbed CO retained on the surface into the CO_2–He stream

affected by the adsorption of CO_2. In Run 1, the catalyst is exposed to a mixture of CO (10%) – CO_2 (5%) – He (A-gas stream) for 30 min at 300 °C to perform the co-adsorption of CO and CO_2, and then the gas mixture is separately switched over to three different gas streams (Run 2), a pure He (gas-B_1), a CO_2 (0.4%) – He (gas-B_2) and a CO_2 (2.3%) – He (gas-B_3) streams. In Run 2, the desorption response of CO is sensitively affected by the concentration of CO_2 coexisting.

The graphical integration of the three response curves in Run 2 of Fig. 1 shows the amount of desorbed CO, which is decreased with increasing concentration of CO_2 in the gas phase. One may recognize the critical concentration of CO_2 for completely trapping CO to be $P^{C}_{CO_2}$ = 0.023 atm. When the gas mixture at the critical CO_2 (designated as $P^{C}_{CO_2}$, is successively switched over to the pure He stream, an appreciable amount of CO is desorbed as shown in Run 3. The desorbed amount q^{II}_{CO} =

= 2.5×10^{-6} mol/g) is in good agreement with that (q^{I}_{CO} = = 2.65×10^{-6} mol/g) obtained in the pure He stream (gas-B_1) at Run 2. These results clearly show that the CO trapped on the surface in the CO_2–He mixture is desorbed with the desorption of CO_2 in He.

The amount of CO_2 desorbed in Run 3 of Fig. 1 is estimated to be $q_{CO_2} = 6.3\times10^{-6}$ mol/g from graphical integration: the ratio of q_{CO_2} to q^{II}_{CO} is therefore about 2.5. This means that 2.5 adsorbed CO_2 is necessary to trap one adsorbed CO. $P^{C}_{CO_2}$ corresponds to the critical concentration of CO_2 to completely trap the adsorbed CO on the surface, and it depends on the concentration of gaseous CO. Figure 2 illustrates the amounts of CO desorbed in Run 2 of Fig. 1 as functions of P_{CO_2} in Run 2 and P_{CO_2} in Run 1. $P^{C}_{CO_2}$ equals 7×10^{-3} atm at P_{CO} = 0.05 atm and 2.3×10^{-2} atm at P_{CO} = 0.10 atm. A large number of calculations

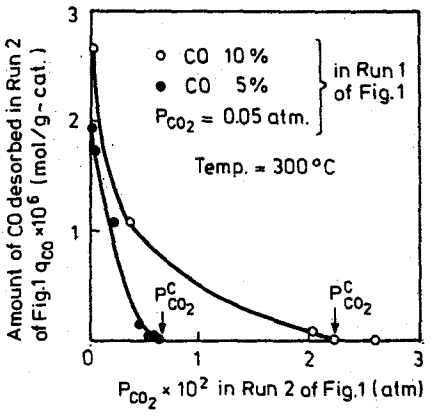

Fig. 2. Plots of q_{CO} as a function of P_{CO_2} in Run 2 of Fig.1

for the amounts of adsorbed CO and CO_2 obtained at $P^{C}_{CO_2}$ falls between two and three adsorbed CO_2 species to trap one adsorbed CO species.

The adsorption isotherm of CO obtained from the transient response method in the He stream, in which there is no trapping

effect by CO_2, obeys the Langmuir equation and the heat of adsorption is estimated to be 85.4 kJ/mol. The temperature programmed desorption spectra of CO, on the other hand, are obtained in the CO_2 coexisting stream, and the peak analysis of the spectra obtained by changing the rate of temperature increase estimates the activation energy of desorption to be 184 kJ/mol. This much higher energy compared to the adsorption heat in He should result from the strong trapping effect of CO_2 on the adsorbed CO.

On the contrary, the desorption behavior of CO_2 is not affected by the CO coexisting in the stream with no appreciable change in its adsorption heat and in its adsorbed amount. In addition, the separate transient experiments clearly demonstrate that no CO adsorbs on the surface fully occupied by the adsorbed CO_2. From these results, one may exactly recognize that CO_2 is competitively adsorbed on the same active sites stronger than CO, and CO is strongly trapped by CO_2 adsorbed on the neighboring sites. For the detailed mechanism for the trapping effect of CO_2, although it is difficult to clear in this study, one may propose a possible explanation: the base sites which are O^{2-} with lower coordinative unsaturation may be considered as the active sites [4], and the CO will be trapped on the vacant O^{2-} located between two or three neighboring CO_2.

For the reactivity of the trapped CO, it has been confirmed that the CO has no activity to react with oxygen, whereas, if freed from the trapping effect of CO_2, it can easily react with adsorbed oxygen to produce CO_2. Further study of the detailed structure of the trapped CO is under way using the FT-IR technique and will be reported later.

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