The Formation of Adsorbed Formaldehyde by the Reaction of Adsorbed Carbon Monoxide with Hydrogen on Magnesium Oxide

Gong-Wei Wang, Hideshi Hattori,* Hidenobu Itoh, and Kozo Tanabe

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Carbon monoxide adsorbed on a well-degassed MgO surface reacts with H_2 to form adsorbed formaldehyde in the temperature range 343—583 K, which was observed by temperature-programmed desorption and by i.r. spectroscopy.

The nature of adsorbed CO on MgO has been investigated by several groups by using various methods such as e.s.r.,[1,2] i.r.,[2–4] and u.v.[5] spectroscopy, and different types of adsorbed CO were observed. The reactivities of these adsorbed species, however, have not yet been fully studied. In this communication, we report the formation of formaldehyde on an MgO surface by the reaction of adsorbed CO with H_2, revealing a novel reaction system including CO, H_2, and metal oxide catalysts.

In the temperature-programmed desorption procedure magnesium hydroxide (0.50 g) was decomposed to give MgO by outgassing at 1273 K for 2 h. After cooling to 273 K, the MgO was exposed to 2660 Pa of CO for 30 min, followed by outgassing for 30 min at 273 K. The sample was then exposed to about 4000 Pa of H_2 and was heated at different temperatures for 30 min. The sample was cooled to 273 K, outgassed for 30 min, and subjected to temperature-programmed desorption. To normalize the sensitivity of the spectrometer, a small amount of Ar was constantly leaked into the system. The relative amounts of desorbed gases were determined as peak heights relative to that of Ar ($m/z = 40$).

Figure 1 shows the temperature-programmed desorption profiles obtained when adsorbed CO was exposed to H_2 at different temperatures. Without addition of H_2, the profiles contained two peaks for CO at 438 and 568 K. On exposure to H_2, these two peaks decreased, and a new peak for CO

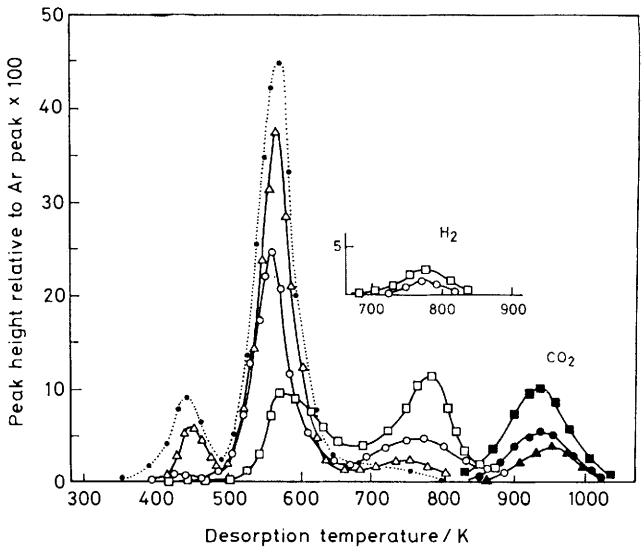

Figure 1. Temperature-programmed desorption profiles of the surface species formed on MgO by the reaction of adsorbed CO with H_2 at different temperatures: CO △(343 K), ○(423 K), □(483 K); CO_2 ▲(343 K), ●(423 K), ■(483 K); H_2 (shown in the inset) ○(423 K), □(483 K). The dotted line denotes the evolution of CO when H_2 was not admitted.

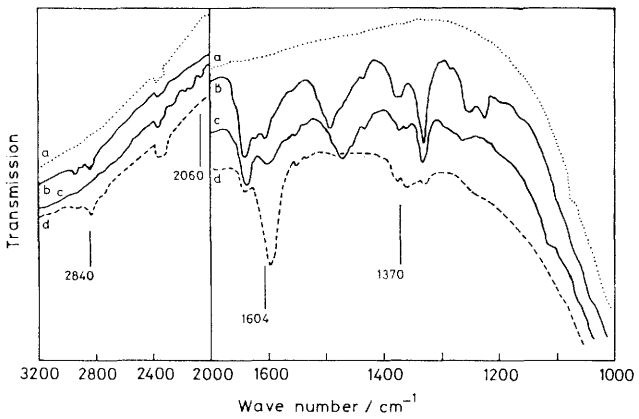

Figure 2. I.r. spectra of surface species on MgO: a, background; b, after reaction of adsorbed CO with H_2 at 458 K; c, after reaction of adsorbed CO with D_2 at 458 K; d, HCHO adsorbed on MgO.

appeared at about 773 K. The new peak for CO was accompanied by the H_2 peak. In addition a peak for CO_2 appeared at about 943 K.

It is apparent that the adsorbed CO reacted with H_2 to form a surface species from which CO and H_2 evolved at about 773 K. This surface species might be adsorbed formaldehyde. The temperature-programmed desorption profile for adsorbed formaldehyde gave three peaks for CO at 383, 573, and 788 K. Evolution of CO at 788 K was accompanied by evolution of H_2. Therefore, it is suggested that the peaks for CO and H_2 which appeared at about 773 K in Figure 1 originated from adsorbed formaldehyde. Thus, we propose that the adsorbed formaldehyde decomposed into CO and H_2 at about 773 K, and then CO and H_2 were desorbed.

To confirm the formation of adsorbed formaldehyde on the surface, the i.r. spectra of the surface species which resulted from the reaction of adsorbed CO with H_2 or with D_2 were obtained, and compared with that of formaldehyde adsorbed on MgO as shown in Figure 2. An $Mg(OH)_2$ sample was pressed into a disc and outgassed at 1272 K in a quartz i.r. cell with CaF_2 windows. The adsorption procedures were the same as those for the temperature-programmed desorption method, except that the adsorption and outgassing of CO were performed at room temperature instead of at 273 K. The bands at 1640 and 1332 cm^{-1} in Figure 2 were attributed to bidentate carbonate, and the band at 1496 (1470 for D_2) cm^{-1} to bicarbonate. These would be desorbed at about 943 K in the temperature-programmed desorption. The bands at 2840 (2060 for D_2), 1604, and 1370 cm^{-1} appeared both when formaldehyde was adsorbed and when adsorbed CO was exposed to H_2. The band at 2840 cm^{-1} was assigned to the C–H stretching vibration. Appearance of two bands at 1604 and 1370 cm^{-1} suggested that the adsorbed species was in a formate HC(:O)O– form rather than in the more simple formyl HC(:O)– form. Probably, formyl groups were adsorbed on surface O atoms to form formate. Therefore, we concluded that the CO adsorbed on MgO reacts with H_2 to form adsorbed formaldehyde.

This work was supported by a Grant-in-Aid for Scientific Research of the Ministry of Education, Science and Culture, Japan.

Received, 5th July 1982; Com. 768

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