INTERACTION OF CO AND HYDROGEN ON COBALT SURFACES: A TEMPERATURE-PROGRAMMED DESORPTION STUDY

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(Received November 23, 1983)

Summary

The nature of adsorption of CO and hydrogen and their interaction on a polycrystalline cobalt surface were elucidated by temperature-programmed desorption spectroscopy. It was found that CO dissociates to give CO_2 on the surface at around 440 K and there is no interaction between adsorbed CO and hydrogen on the surface under the experimental conditions employed.

Numerous studies [1 - 10] on the coadsorption of CO and hydrogen on group VIII metals have been carried out because of the relevance of co-adsorption to the understanding of the mechanism of the Fischer–Tropsch synthesis and methanation reaction. Evidence for the formation of surface complex species are available on Ni(100) [1, 2], W(100) [3], Fe(100) [4] and Ru(110) [5] surfaces. However, there are only limited reports [10] of similar studies on the cobalt surface, an efficient Fischer–Tropsch catalyst. The observation by Bridge *et al.* [10] that there is no interaction between adsorbed CO and hydrogen under their experimental conditions formed the basis for the present temperature-programmed desorption (TPD) investigation on polycrystalline cobalt surfaces.

A polycrystalline powdered cobalt metal catalyst was prepared by *in situ* reduction of cobalt oxide. The experiments were carried out in an all-glass static reactor with provisions for measuring the total pressure changes during the TPD. All the adsorption studies were carried out at pressures up to 200 Torr at room temperature for about 12 h. The desorption experiments were made using a heating range of 5 °C min⁻¹. The desorbed products were analysed using a Fisher–Hamilton gas partitioner. Between subsequent experiments the surface was regenerated by soaking it in hydrogen 4 - 5 times at 1 atm pressure and at 300 °C for about 15 h followed by evacuation at 10^{-6} Torr and at 360 - 400 °C for 5 h. The surface regeneration procedure employed was found to give reproducible results. IR spectra were recorded on self-supporting discs.

The adsorption isotherms obtained for individual and sequential adsorption of CO and hydrogen are given in Fig. 1. Preadsorbed hydrogen enhances
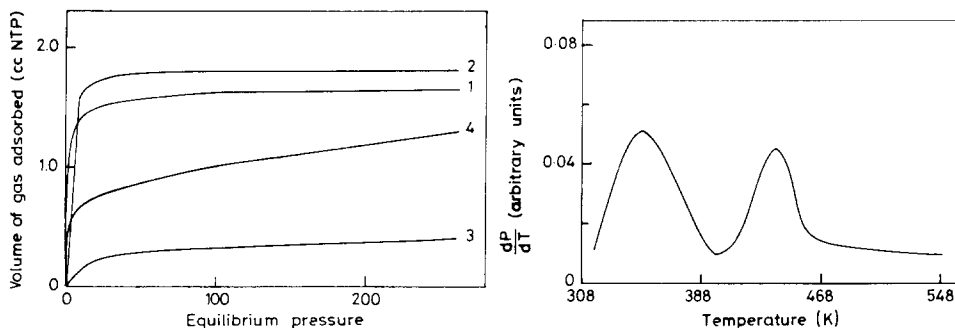
Fig. 1. Adsorption isotherms: curve 1, CO on a bare surface; curve 2, CO on a hydrogen-preadsorbed surface; curve 3, hydrogen on a CO-preadsorbed surface; curve 4, hydrogen on a bare surface.

Fig. 2. TPD spectrum of CO from a cobalt surface.

CO adsorption while presorbed CO inhibits subsequent hydrogen adsorption. Similar observations have been recorded on Ni(100) by Koel *et al.* [2]. The TPD trace of chemisorbed CO at 300 K on a cobalt surface shows two peaks (Fig. 2), one peak at around 350 K and a second peak due to desorption as CO_2, at 440 K. The value of the energy of activation for the first peak, calculated using first-order desorption kinetics, is 23 kcal mol^{-1}. The formation of CO_2 indicates dissociation of CO on a cobalt surface under the experimental conditions employed. Two IR absorption bands were observed at 1990 and 1800 cm^{-1} for the room temperature adsorption on the cobalt surface. These two bands can be assigned to linear and bridged carbonyl-type species. When the system was evacuated at 350 K for about 15 - 20 min the IR spectrum of the resulting system showed only one peak at 1800 cm^{-1}, indicating that the adsorbed linear CO species are desorbed at 350 K. However, no IR absorption due to adsorbed CO could be observed when the evacuation was carried out at 440 K. It is therefore deduced that the CO_2 desorption at 440 K probably arises from the CO adsorbed in the bridged structure.

The adsorption of hydrogen is found to be dissociative at room temperature. The TPD trace of adsorbed hydrogen contains two peaks (Fig. 3), one at around 350 K and the other at around 470 K. The separation of these two peaks may indicate the existence of two different adsorbed states.

Apart from the enhancement in CO adsorption on the hydrogen-covered surface, it is observed that when the amount of presorbed hydrogen increases the second desorption peak is shifted to lower temperatures (Fig. 4).

Dus and Lisowski [11] have shown that hydrogen adsorption on cobalt films at 195 and 273 K results in the formation of a negatively charged adsorbed species. This type of adsorption can cause a favourable situation for CO adsorption with donation of electrons at the metal sites depleted of charge density by prior hydrogen adsorption. The CO adsorbed could also be expected to be strongly bound as a result of this kind of charge transfer.
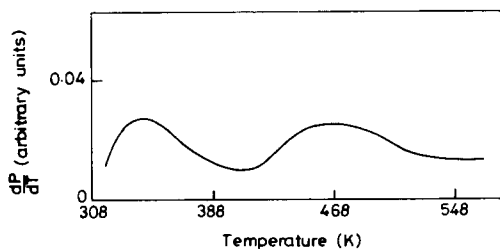
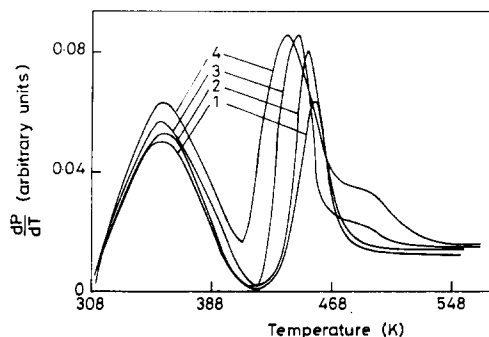Fig. 3. TPD spectrum of hydrogen from a cobalt surface.

Fig. 4. TPD spectra of CO adsorbed on hydrogen-preadsorbed cobalt surfaces: spectrum 1, θ_{H_2} = 0.32; spectrum 2, θ_{H_2} = 0.46; spectrum 3, θ_{H_2} = 0.57; spectrum 4, θ_{H_2} = 0.83.

However, at higher coverages of adsorbed CO, lateral and dipole interactions among the adsorbed species shift the desorption peak to lower temperatures.

A decrease in the hydrogen adsorption on CO-covered surfaces was observed (Fig. 1). Prior CO adsorption effectively decreases the net local electron density at the metal site as a result of the d level participation in the back-donation process and hence results in a decrease for subsequent hydrogen adsorption as adsorbed hydrogen cannot function as an accepting species on the cobalt surface [11]. The increase in the height of the second peak with increases in the CO coverage as revealed from Fig. 5 indicates that the desorption kinetics are dependent on the CO coverage. Admission of hydrogen to a CO-presorbed system not only increases the concentration of the species responsible for the second peak but also decreases the concentration of the species responsible for the first peak. This indicates that hydrogen transforms some of the adsorbed CO species to surface species responsible for the second peak. This could arise from the interaction between adsorbed hydrogen and CO through metal atoms, since direct participation would have given rise to a different type of surface species. The activation of CO on a site which already has an adsorbed hydrogen species can result in the subsequent elimination of hydrogen on the basis of net charge transfer in the adsorbed state.

The TPD traces for the simultaneous adsorption of CO and hydrogen are shown in Fig. 6 and are similar to the traces obtained for the hydrogen adsorption of CO-presorbed surfaces. This could be due to CO chemisorption
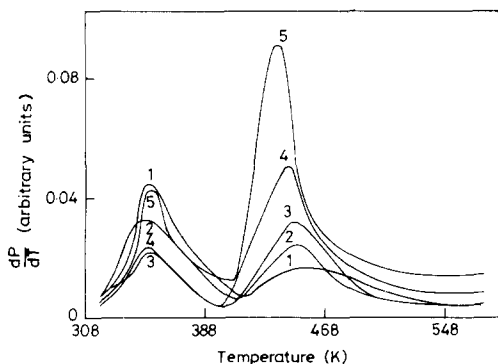
Fig. 5. TPD spectra of hydrogen adsorbed on CO-preadsorbed cobalt surfaces: spectrum 1, $\theta_{CO} = 0.17$; spectrum 2, $\theta_{CO} = 0.34$; spectrum 3, $\theta_{CO} = 0.47$; spectrum 4, $\theta_{CO} = 0.70$; spectrum 5, $\theta_{CO} = 0.94$.
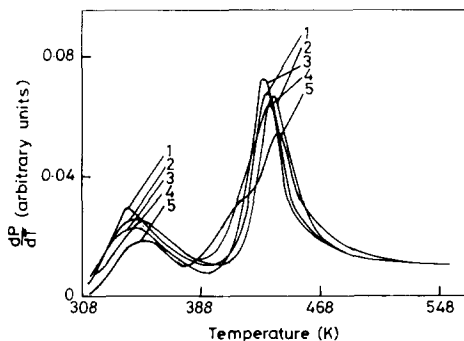

Fig. 6. TPD spectra of simultaneously adsorbed CO and hydrogen on cobalt surfaces for the following CO:H$_2$ ratios: spectrum 1, 3:1; spectrum 2, 2:1; spectrum 3, 1:1; spectrum 4; 1:2, spectrum 5, 1:3.

being stronger ($\Delta H_{ads} = 47$ kcal mol^{-1}) than hydrogen chemisorption ($\Delta H_{ads} = 24$ kcal mol^{-1}) [12].

In all three series of coadsorption experiments it was observed that the first peak is due to pure CO and the second peak is mostly due to CO$_2$. The absence of a considerable amount of hydrocarbon during coadsorption could be due to the lack of interaction between hydrogen and CO on the surface caused by the displacement of adsorbed hydrogen by CO adsorption. However, hydrogen may be able to interact with adsorbed carbon on the cobalt surface. Therefore, the absence of hydrocarbon formation could be due to the non-dissociative nature of the adsorption of CO at 300 K. Bridge et al. [10] have shown by their low energy electron diffraction studies that a $(3\frac{1}{2} \times 3\frac{1}{2})$ R30° pattern for adsorbed CO is not affected by subsequent hydrogen adsorption, indicating a lack of interaction between hydrogen and CO on a cobalt surface.

Acknowledgment

References

1 D. W. Goodman, J. T. Yates, Jr., and T. E. Madey, *Surf. Sci.*, *93* (1980) L135.
2 B. E. Koel, D. E. Peebles and J. M. White, *Surf. Sci.*, *107* (1981) L367.
3 J. C. Bertolin and B. Imelick, *Surf. Sci.*, *80* (1979) 586.
4 J. B. Benziger and R. J. Madix, *Surf. Sci.*, *77* (1978) 379.
5 D. W. Goodman, T. E. Madey and J. T. Yates, Jr., *J. Catal.*, *50* (1977) 279.
6 J. B. Benziger and R. J. Madix, *Surf. Sci.*, *115* (1982) 279.
7 V. H. Baldwin and J. B. Hudson, *J. Vac. Sci. Technol.*, *8* (1971) 49.
8 J. H. Craig, Jr., *Appl. Surf. Sci.*, *10* (1982) 315.
9 J. H. Craig, Jr., *Surf. Sci.*, *111* (1981) L695.
10 M. E. Bridge, C. M. Comrie and R. M. Lambert, *J. Catal.*, *58* (1979) 28.
11 R. Dus and W. Lisowski, *Surf. Sci.*, *61* (1976) 635.
12 I. Toyoshima and G. A. Somarjai, *Catal. Rev., Sci. Eng.*, *19* (1979) 190.