Temperature-Programmed Desorption and Infrared Studies on the Activation of Carbon Monoxide on Cobalt Surfaces

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Temperature-programmed desorption (TPD) and infrared (IR) spectroscopic studies have been used to identify the nature of adsorbed CO on polycrystalline cobalt surface at room temperature. Linear and bridged molecularly adsorbed CO surface species have been identified by their stretching frequencies at 1990 and 1800 cm^{-1}. Linear-type CO desorbs without dissociation to give desorption peak maximum at 350°K while bridge-type CO dissociates to produce CO_2 at the desorption maximum temperature 440°K. © 1984 Academic Press, Inc.

INTRODUCTION

The mode and nature of activation of CO on metals control the subsequent reduction by hydrogen thus leading to a distribution of products like hydrocarbons with varying numbers of carbon atoms and oxygenates. Studies relating to structure and reactivity of adsorbed CO on transition metals, especially on Group VIII metals active for Fischer–Tropsch (FT) reaction have been pursued in recent times. Under the experimental conditions, the mode and structure of adsorbed species depend on the surface coverage (θ) as deduced by LEED and vibrational spectroscopic techniques (1). The present investigation deals with the interaction of CO with polycrystalline cobalt as studied by temperature-programmed desorption (TPD) and infrared (IR) spectroscopic techniques, as extensive studies of this nature are not immediately available for cobalt surfaces.

MATERIALS AND METHODS

Polycrystalline cobalt metal catalyst was prepared by *in situ* reduction of cobalt oxide (Co_3O_4) in a stream of hydrogen at 573°K for about 48 hr. CO was prepared by the reaction of $CaCO_3$ with zinc metal powder at 973–1023°K. H_2 and He were used after purification by standard procedures.

The adsorption and desorption experiments were carried out in an all glass static reactor with facility for monitoring pressure changes during desorption. About 3.7 g of the sample was used for experiments. The adsorption studies were carried out up to 200 Torr for about 12 hr and the desorption was followed after evacuation of the gas phase components, using a heating rate (β) of 5°K/min. The desorbed products were analyzed in a Fisher–Hamilton gas partitioner. Between subsequent experiments, the surface was soaked with H_2 at 1 atm and at 573°K for 3 hr, the gas-phase components were pumped out and again the surface was soaked with H_2. This procedure was repeated 4 or 5 times for the total period of 15 hr. Finally, the surface was evacuated at 673°K and at 10^{-6} Torr for 4 hr. This surface regeneration procedure was found to give reproducible room-temperature hydrogen adsorption results with that of freshly reduced sample.

RESULTS

The extent of reduction of Co_3O_4 was estimated to be >99.5% by thermogravimetric method and the completion of reduction was

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checked by repeated volumetric hydrogen adsorption experiments at the reduction temperature (573°K). The surface area of the reduced sample was measured by nitrogen adsorption at liquid-nitrogen temperature (BET method) and also by CO adsorption at liquid-nitrogen temperature. The surface area was found to be 2 m^2/g in both experiments. The total amount of CO adsorbed at room temperature was found to be 1.60 ml.

The TPD trace of adsorbed CO obtained after adsorption at 300°K (Fig. 1) shows two peaks: one at 350°K (T_{M1}) and another at 440°K (T_{M2}). The desorption of CO is found to be responsible for the first peak, however, the desorbed species is CO_2 which is responsible for the second peak.

The IR spectrum of CO adsorbed on cobalt at room temperature shows two absorption bands at 1990 and 1800 cm^{-1}. This is in agreement with the IR data of CO adsorption on cobalt film reported by Cho and Schulman (2).

DISCUSSION

The observation that there are two desorption maxima in the TPD spectrum of adsorbed CO from cobalt surface indicates that there are two different adsorbed CO species. The desorption of CO_2 which is responsible for the second peak reveals that CO dissociates on the surface under the experimental conditions employed. CO can dissociate during adsorption at room temperature so that the surface C and O species can interact at higher temperatures to produce CO_2 or associatively adsorbed CO species can interact at higher temperatures to produce CO_2.

$$2CO(ads) \rightarrow CO_2(g) + C(ads)$$

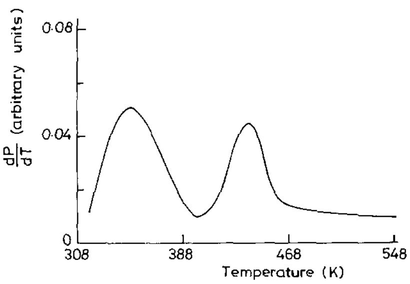

FIG. 1. TPD trace for CO desorption from cobalt surface (adsorption at room temperature).

The carbon-deposited cobalt surface, after the TPD experiment, was evacuated for a few minutes, cooled to room temperature, and He was admitted to 1 atm pressure. The glass reactor, with two stopcocks at both ends, was cut down from the system, heated slowly to 573°K, while pure oxygen was passed to oxidize the whole sample, and the CO_2 formed was trapped in baryta solution. The amount of CO_2 trapped in the baryta solution was not found to be equal to CO_2 desorbed under peak-2 of the TPD spectrum. Now the total amount of CO removed from the surface was calculated as the sum of all the forms (CO desorbed under peak-1, CO_2 formed under peak-2, and CO_2 produced from the C deposits) and it was found to be equal to the amount of CO adsorbed at room temperature on bare surface. Hence it is deduced that CO can adsorb on cobalt surface at 300°K in two forms.

The IR spectrum (Fig. 2) of CO adsorbed on cobalt surface shows two absorption bands at 1990 and 1800 cm^{-1}, which are assignable to linear- and bridged-type carbonyl species, respectively, as described by Eischens and Pliskin (3). After evacuation at 350°K (T_{M1}) the IR spectrum contains only one absorption band at 1800 cm^{-1} indicating that the linear CO species are desorbable at or below 350°K. The IR spectrum after evacuation at 440°K (T_{M2}) resembles that of pure cobalt surface. Hence the bridged CO species are responsible for CO_2 formation at 440°K. The formation of CO_2 at higher temperatures from bridged CO species indicates that the CO dissociation on cobalt surface is an activated process as it has been reported for nickel (4).

The fact that the temperature of formation of CO_2 (440°K) coincides with the temperature above which cobalt is reported to be active for methanation and other FT type reactions shows that CO dissociation may be

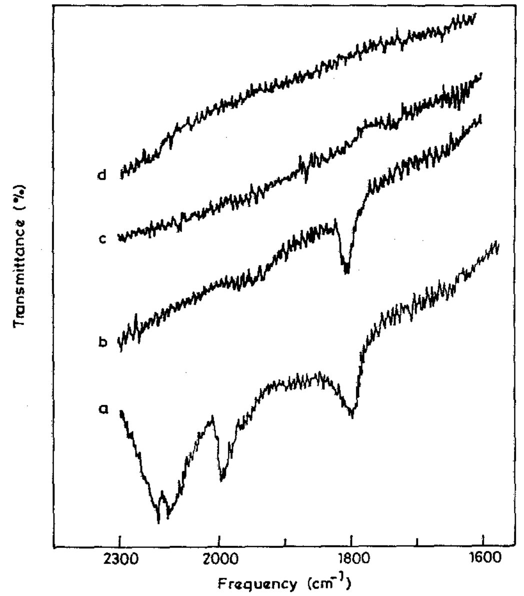

FIG. 2. IR spectra of cobalt surfaces in different conditions. (a) CO adsorbed cobalt surface at a pressure of 20 Torr, (b) surface "a" after evacuation at 350°K for a few minutes, (c) surface "b" after evacuation at 440°K for a few minutes, (d) pure cobalt surface.

a primary step in methanation and FT reactions. This supports the postulate: "metals which dissociate CO at the temperature of methanation and form surface oxides reducible under reaction conditions, namely Fe, Co, Ni, Ru, and Rh are the most active in the methanation reaction" (5).

The previously reported (6) third peak in the TPD spectrum of CO adsorbed on cobalt observed at 640°K is due to CO adsorption on oxide impurities as shown by Bridge *et al.* (7).

SUMMARY

1. At room temperature, the probable modes of adsorption of CO on polycrystalline cobalt are only linear and bridged forms as deduced from combined TPD and IR studies.
2. CO dissociation is an activated process on cobalt surface and this dissociation is a primary step in the methanation and FT reaction.

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