COADSORPTION OF CARBON MONOXIDE AND HYDROGEN ON COBALT FISCHER-TROPSCH CATALYSTS

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ABSTRACT

Studies of coadsorption of CO and hydrogen on typical cobalt FT catalysts with kieselguhr as support and thoria as promoter, using TPD and IR spectroscopy, showed the presence of metal support interaction. The number of surface cobalt atoms is increased in presence of thoria.

INTRODUCTION

In recent years, coadsorption of CO and hydrogen on many metal surfaces has been reported with the view to establish the nature of precursors formed on the surface. In Fischer-Tropsch (FT) synthesis, the stability of these precursors controls the distribution of products. The reported literature studies are mainly concerned with pure metals (1,2) (single crystal and polycrystalline), though the practical systems are usually supported ones. The present report therefore addresses to this question with the studies on supported cobalt catalysts especially with emphasis on the effect of kieselguhr (support) and thorium dioxide (promoter) on the coadsorption of CO and hydrogen.

EXPERIMENTAL

Two cobalt catalysts A and B of the composition Co:kieselguhr = 100:200(A) and Co:ThO_2:kieselguhr=100:18:200(B) were prepared by precipitating the respective metal (cobalt alone for A and cobalt and thorium for B) as carbonate on kieselguhr at constant stirring followed by decomposition and reduction at 600 K for 48 h. The completion of reduction was checked by the reproducibility of the hydrogen adsorption at the reduction temperature.

Adsorption and Temperature Programmed Desorption (TPD) experiments were carried out in an all glass reactor where a high vacuum of 10^{-6} torr was routinely available. Adsorption was carried out upto 200 torr for 12 h and after careful evacuation of the gas phase components TPD was followed using the heating rate (β) of 5 K/min. upto 600 K. Between subsequent experiments the surface was regenerated by soaking it in H_2 at 1 atm. pressure and at 570 K for about 12 h followed by evacuation of the surface at 650 K for 4 h.

Hydrogen chemisorption was carried out at 570 K and cooled very slowly to room temperature in hydrogen atmosphere to calculate the active metal atoms exposed at the surface and to evaluate the metal particle size. Extent of reduction of the catalysts was determined by reoxidising the catalyst in oxygen atmosphere at 670 K for about 4 h. The oxygen uptake under this condition was measured for the conversion of cobalt to Co_3O_4. The results are given in table 1.

RESULTS AND DISCUSSION

The TPD trace of CO adsorbed at room temperature was found to contain two desorption maxima one around 350 K and the other around 420 K (fig. 1 a and c) indicating two types of adsorbed forms of CO on catalysts A and B.

Two IR absorption bands were observed around 1987 and 1779 cm^{-1}. This is in agreement with the observations made on polycrystalline cobalt (3) and cobalt film (4). Detailed investigation on polycrystalline cobalt (3) reveals that linear type surface CO species are desorbable around 350 K and bridged type surface CO species dissociate to produce CO_2 around 440 K. The second desorption peak observed in this study at 420 K is found to be due to CO_2 formation. Hence it is concluded that linear carbonyls with IR absorption at 1987 cm^{-1} are desorbable as CO which is responsible for first desorption at 350 K and bridged carbonyls with IR absorption at 1779 cm^{-1} produce CO_2 at 420 K.

The TPD trace of hydrogen from catalysts A and B shows two peaks at 350 K and 460 K (Fig. 1 b and d).

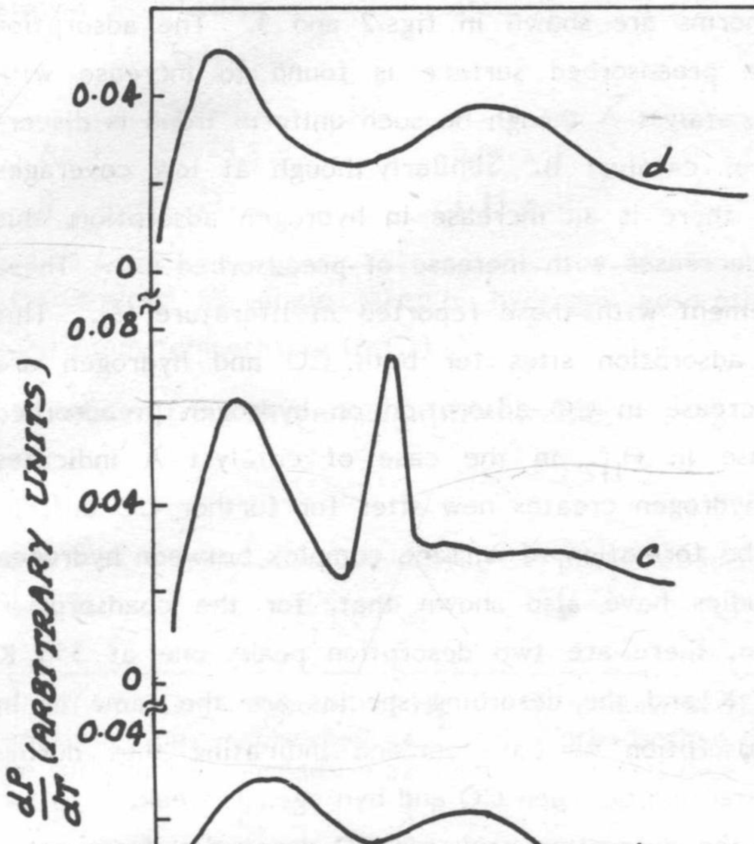

Fig.1 TPD traces for CO and hydrogen adsorption on catalysts A and B.
a) CO adsorbed on catalyst A
b) hydrogen adsorbed on catalyst A
c) CO adsorbed on catalyst B
d) hydrogen adsorbed on catalyst B

Coadsorption measurements were carried out by exposing one of the gases to the surface covered with the other gas. A series of adsorption experiments were carried out by varying the surface coverage of preadsorbed gas. The results are summarised in table 2 and the adsorption isotherms are shown in figs.2 and 3. The adsorption of CO on hydrogen preadsorbed surface is found to increase with increase in Θ_{H_2}, for catalyst A though no such uniform trend is discernable in the case of catalyst B. Similarly though at low coverages of CO preadsorbed, there is an increase in hydrogen adsorption, this quantity, however, decreases with increase of preadsorbed CO. These trends are in agreement with those reported in literature (6). This indicates that the adsorption sites for both CO and hydrogen are the same. The increase in CO adsorption on hydrogen preadsorbed surface with increase in Θ_{H2} in the case of catalyst A indicates either preadsorbed hydrogen creates new sites for further CO adsorption or there could be formation of surface complex between hydrogen and CO. TPD studies have also shown that, for the coadsorption of CO and hydrogen, there are two desorption peaks one at 350 K and another at 470 K and the desorbing species are the same as in the case of CO adsorption on bare surface indicating that during coadsorption the interaction between CO and hydrogen is weak.

The shape of second desorption peak for CO desorption from catalysts A and B (Figs.1 a and c) are different indicating that the nature of dispersion of cobalt particles on the surface is different in two catalysts. The particle size has been determined by the hydrogen chemisorption measurements and the extent of reduction by oxygen titration according to the procedures of Bartholomew and coworkers (7,8). Probably majority of cobalt oxide particles could have been encapsulated by kieselguhr, thus resisting the reduction and the interaction can be electronic in nature (9).

Adsorption of hydrogen follows the formation of hydride type species (10) thus enabling further CO adsorption on electron deficient site.

TABLE 1

Uptake of hydrogen, surface cobalt atoms and extent of reduction.

Catalyst	maximum amount of hydrogen adsorbed[a)] µmol/g	number of surface cobalt atoms/g	extent of reduction[b)] %
A	75.8	0.91×10^{20}	39
B	112.4	1.35×10^{20}	75

a) Determined by single stretch hydrogen adsorption between 570 K and room temperature (ref.7)

b) Estimated from oxygen adsorption (ref.8)

TABLE 2

Amount of CO/H_2 adsorbed on H_2/CO preadsorbed surface of catalysts A and B.

Amount of CO preadsorbed on bare surface µmol/g.	Amount of H_2 adsorbed on CO preadsorbed surface µmol/g	Amount of H_2 preadsorbed on bare surface µmol/g.	Amount of CO adsorbed on H_2 preadsorbed surface, µmol/g.
	CATALYST A		
0.0	69.4	0.0	106.9
19.0 (0.17)	57.1	14.7 (0.20)	102.6
36.9 (0.34)	45.4	30.7(0.41)	105.0
49.8 (0.45)	36.9	44.2 (0.59)	125.6
106.9 (0.97)	30.1	69.4 (0.93)	133.9
	CATALYST B		
0.0	76.1	0.0	122.0
19.5 (0.16)	98.9	18.9 (0.23)	113.5
35.4 (0.28)	88.5	36.0 (0.43)	102.5
54.3 (0.43)	78.1	48.8 (0.59)	95.8
73.2 (0.59)	54.3	56.7 (0.68)	103.1
122.0 (0.98)	50.0	76.1 (0.92)	100.1

Values in the paranthesis are the fraction of surface coverage (θ) of preadsorbed gas.

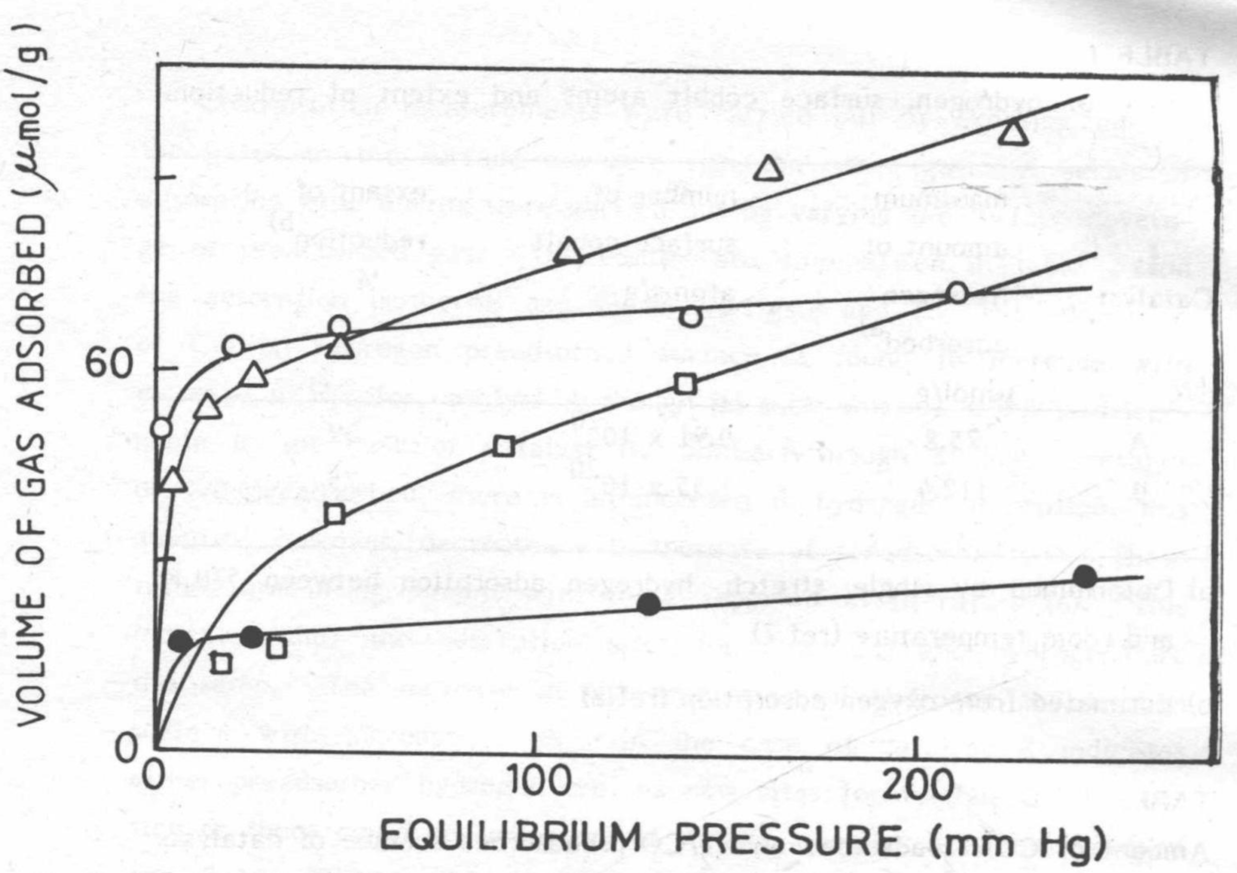

Fig.2 Adsorption isotherms (at room temperature) on catalyst A.
○ H_2 adsorption △ CO adsorption on H_2 covered surface
□ CO adsorption ● H_2 on CO covered surface

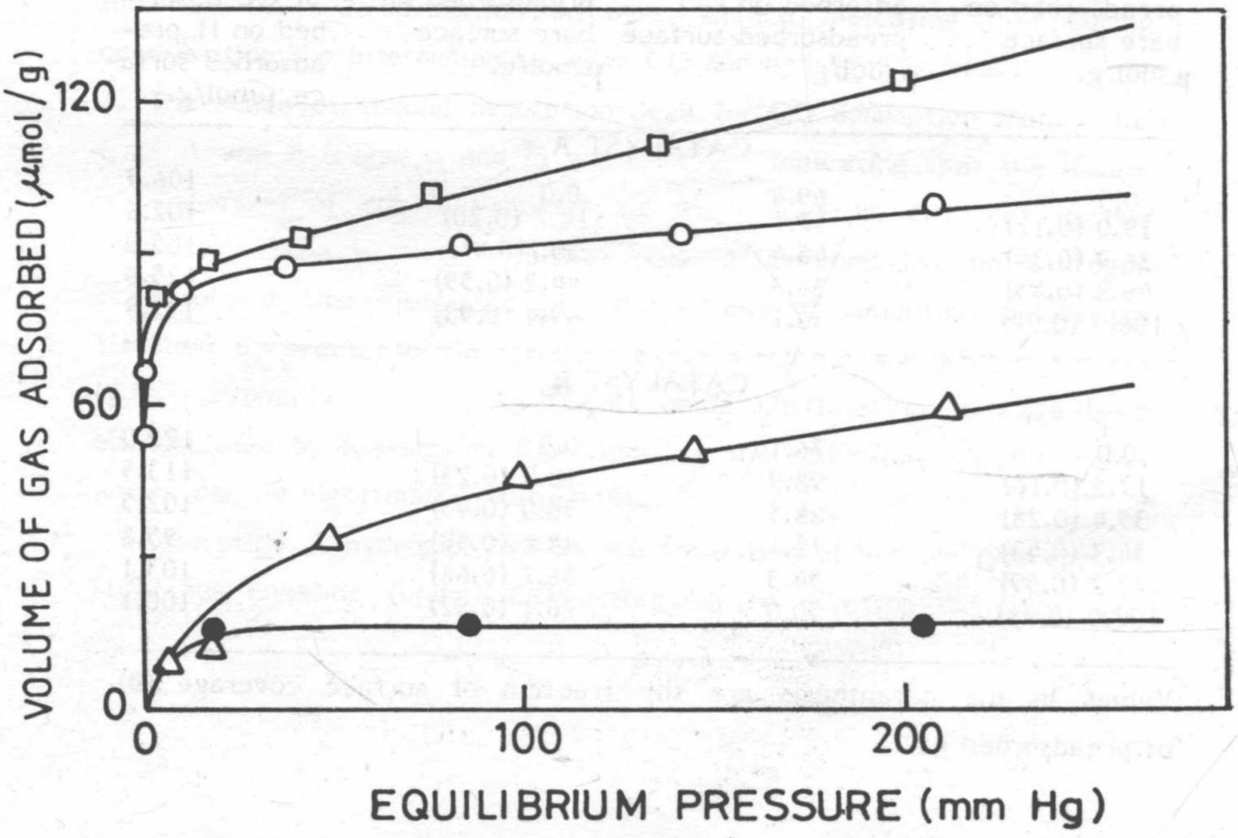

Fig.3 Adsorption isotherms (at room temperature) on catalyst B.
○ H_2 adsorption △ CO adsorption on H_2 covered surface
□ CO adsorption ● H_2 on CO covered surface

On the other hand, CO adsorption would increase the electronic charge at the metal site by the donation of a pair of electrons during chemisorption. On the electron rich metal sites, the hydrogen adsorption is less feasible.

REFERENCES

1. M.E. Bridge, C.M. Comrie and R.M. Lambert, J. Catal., 58,28(1979)
2. R. Gopalakrishnan and B. Viswanathan, Surface Technol., 23,173 (1984).
3. R. Gopalakrishnan and B. Viswanathan, J. Colloid Interface Sci., (in press).
4. F.S. Baker, A.M. Bradshaw, J. Pritchard and K.W. Sykes, Surface Sci.,12,426(1968).
5. R. Gopalakrishnan,R. Vetrivel and B. Viswanathan, Indian J. Technol., 21,344(1983).
6. R. Balaji Gupta, Ph.D. thesis, IIT, Madras.
7. R.C. Reuel and C.H. Bartholomew, J. Catal.,85,63(1984).
8. C.H. Bartholomew and R.J. Farranto, J. Catal.,45,41(1976).
9. R.Gopalakrishnan and B. Viswanathan, React. Kinet. Catal. Lett., (Communicated).
10. R. Dus and W. Lisowski, Surface Sci.,61,635(1975).