

TEMPERATURE PROGRAMMED DESORPTION (TPD) OF CARBON MONOXIDE FROM COBALT SURFACES

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Three different binding states of CO on cobalt surfaces have been identified by TPD studies. The energetics of these adsorption states and their relevance in Fischer-Tropsch synthesis are considered.

Три различных состояний связи CO с поверхностью кобальта были идентифицированы методом температурно-программированной десорбции. Рассматривается энергетика этих адсорбционных состояний и их правомочность в синтезе Фишера-Тропша.

The activation and subsequent hydrogenation of CO on metal catalysts, known as the Fischer-Tropsch (FT) synthesis, have been the subject of investigation by various workers /1/. Two concepts prevail, namely, the activation of CO on metal surfaces takes place either dissociatively or associatively, so that subsequent hydrogenation yields surface intermediate species with and without oxygen /2/. Studies relating to the nature of activation of CO on cobalt surfaces, an active catalyst for the FT reaction, seem to be limited. From detailed calorimetric and geometric considerations applicable to various configurations of adsorbed CO, Brennan and Hayes /3/ have concluded that CO is mostly held in a bridged associative form on hexagonal and cubic close-packed metals.

Benndorf and Thieme /4/ accounted for the observed characteristic energy loss peaks in terms of an energy level diagram applicable to the associatively adsorbed form of CO. Bridge et al. /5/ identified two types of ordered adsorbed phases of CO on Co (0001) and reported a desorption enthalpy of $103 \pm 8 \text{ kJ mol}^{-1}$ at low coverages and a fairly sharp fall in the enthalpy values for coverages greater than 0.33. Dissociative chemisorption of CO and its role in subsequent hydrogenations have been well recognized on various metal surfaces. However, the picture with respect to cobalt surfaces appears to be not clear, which is the basis for the present investigation.

The variation of the heat of adsorption of CO on polycrystalline powdered cobalt metal surfaces (Fig. 1) revealed that the nature of CO adsorption on this surface is coverage dependent. At least three different forms are discernible, namely, (a) strongly adsorbed CO which extends up to $\Theta = 0.33$, whose heat of adsorption could not be evaluated from the isotherms; (b) another form of adsorbed CO (with $\Theta = 0.33$ to 0.6) whose heat of adsorption decreases steeply with increasing coverage; (c) weakly adsorbed CO, whose heat of adsorption remains almost constant (29 kJ mol^{-1}) and extends from $\Theta = 0.6$ to 1.0.

The TPD trace of adsorbed CO obtained after adsorption at 300 K (Fig. 2) shows two peaks, one at 370 K and another at 470 K. The species desorbing in this temperature range have been identified to be pure CO. However, it was observed that the total amount of CO desorbed up to 570 K amounted to only 65% of the total amount adsorbed. It was deduced that the remaining 35%, retained on the surface even after desorption at 570 K, could give rise to one or more adsorbed states. Bridge et al. /5/ have reported that there can be different binding states for CO, depending on the coverage which gave different LEED patterns. The energetics of the binding state corresponding to the second peak (470 K) were evaluated using first order desorption kinetics. The value of the activation energy for desorption was found to be $\sim 50 \text{ kJ mol}^{-1}$.

With the hope of elucidating the other binding states for the remaining 35% of undesorbed CO at 570 K, the desorption was continued up to 770 K. The TPD spectrum obtained is shown in Fig. 3. It is seen that there is another desorption peak around 640 K. However, when the experiment was repeated, the amount of

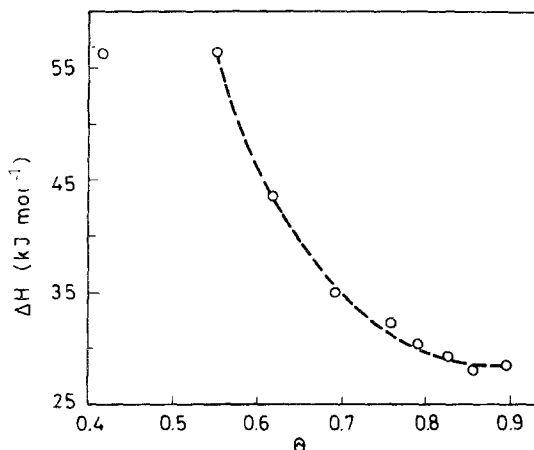


Fig. 1. Change in heat of adsorption vs. surface coverage

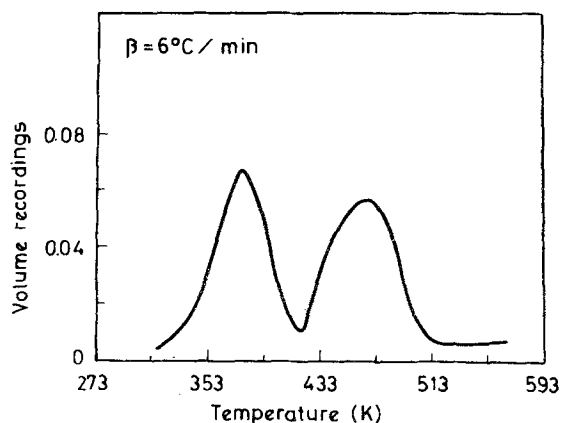


Fig. 2. Desorption of CO from cobalt powder (first sample)

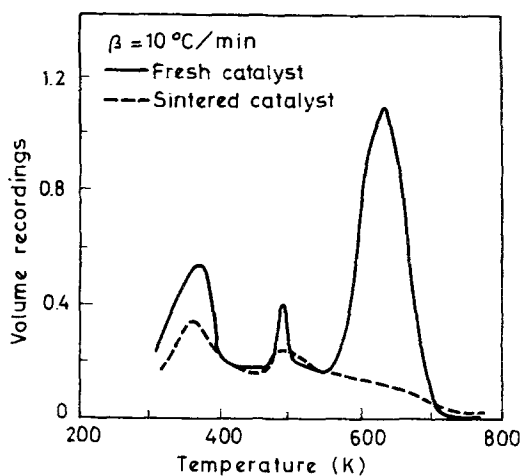


Fig. 3. Desorption of CO from cobalt powder (second sample)

CO adsorbed drastically decreased to 0.35 ml on the same amount of the catalyst and, moreover, 0.34 ml of CO desorbed even below 570 K. It is probable that the catalyst might have undergone sintering on heating to 770 K and the adsorption capacity of the catalyst might have been drastically changed due to this sintering.

Infrared spectroscopic studies by Braker et al. /6/ and Cho and Schulman /7/ have revealed the presence of two forms of adsorbed CO as shown by two bands

at 1990 and 1800 cm^{-1} , which could be attributed to associatively adsorbed forms. However, in addition to these two associative forms, it appears that CO is adsorbed in another form, which on energy considerations, can be presumed to be dissociative. The dissociative form of adsorption should have taken place on specific sites with the requisite symmetry. It has been reported /8/ that 3-fold symmetry sites are required for the dissociative adsorption of CO on nickel surface. Similar site geometries might have been responsible for the dissociative adsorption of CO on cobalt surfaces. It is relevant to point out here that Ponc and Van Barneveld /9/ indicated that the FT reaction can occur through the participation of an ensemble of sites. This implies that only those metals that can provide such symmetric sites which can promote the dissociative adsorption of CO are active for FT synthesis and it is probable that such type of sites are easily available on metal surfaces like Fe, Co, and Ni which are active for FT synthesis.

REFERENCES

1. M. A. Vannice: *Catalysis Rev. Sci. Eng.*, *14*, 153 (1976).
2. M. V. C. Sastri, T. S. Viswanathan: *J. Amer. Chem. Soc.*, *77*, 3969 (1955).
R. B. Gupta, B. Viswanathan, M. V. C. Sastri: *J. Catal.*, *26*, 212 (1972), *32*, 325 (1974).
D. W. Goodman, R. D. Kelley, T. E. Madey, J. T. Yates: *J. Catal.*, *63*, 226 (1980).
J. G. Ekerdt, A. T. Bell: *J. Catal.*, *62*, 19 (1980).
3. D. Brennan, F. Hayes: *Phil. Trans. Roy. Soc. (London)*, *A258*, 347 (1965).
4. C. Benndorf, F. Thieme: *Z. Phys. Chem.*, *102*, 231 (1976).
5. M. E. Bridge, C. M. Comrie, R. M. Lambert: *Surface Sci.*, *67*, 393 (1977).
6. F. S. Braker, A. M. Bradshaw, J. Pritchard, K. W. Sykes: *Surface Sci.*, *12*, 426 (1968).
7. J. S. Cho, J. H. Schulman: *Surface Sci.*, *2*, 245 (1964).
8. J. J. Burton, T. M. Pugel: *J. Catal.*, *47*, 280 (1980).
9. V. Ponc, W. A. Van Barneveld: *Ind. Eng. Chem. Prod. Des. Dev.*, *18*, 268 (1979).