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NOTES

Temperature Programmed Desorption of CO from Supported Cobalt

During recent years several authors have been using the temperature programmed desorption (TPD) method for studying the activity of catalytic surfaces and for obtaining kinetic parameters of desorption processes (*1*–*5*). This note is concerned with the application of this method to the study of carbon monoxide adsorbed at 40°C on a commercial cobalt catalyst supported on kieselguhr.

The catalyst, which was the same one as used by Adrian and Smith (*6*), was a commercial hydrogenation catalyst (G-61, Girdler Corp.) consisting of 60% cobalt (as oxide) on kieselguhr. The particles were obtained by grinding 3/16 × 1/8 in. tablets and sifting through a 28–35 mesh sieve. The catalyst was reduced *in situ* as described by Kokes (*7*): pure hydrogen, obtained directly from an electrolytic generator (Milton Roy Co.), was streamed over the catalyst at 30 cm^3/min for 12 hr at 300°C. The reducing temperature was reached in two stages: from room temperature to 100°C at a rate of 10°C every 10 min, and from 100 to 300°C at a rate of 5°C every 10 min. The heating was controlled manually and was performed in one of two ways, either in air at atmospheric pressure or in a stream of 99.99% helium (Matheson Ultrahigh Purity) flowing at 8 cm^3/min. We designate as solid *a* the catalyst which was heated in air at atmospheric pressure prior to its reduction, and as solid *b* the catalyst which was heated in helium. After the reduction the solid kept for 1 hr at 300°C and 10^{-5} Torr (1 Torr = 133 N m^{-2}), and then cooled to 40°C keeping the pressure constant. The adsorption and TPD experiments were performed 5 hr after the end of the reduction.

The TPD equipment was similar to that employed by Amenomiya and Cvetanović (*1*). A 0.73 g sample of the solid, having a total BET area of 77 m^2/g, was used, and it was replaced for each experiment. After reducing and cleaning the solid as described above, the adsorption of carbon monoxide (Matheson, CP grade) was allowed to proceed at 40°C. Equilibrium was reached rapidly, but in all cases a total time of 15 min was allowed for the adsorption. In the TPD experiment the adsorbate was then desorbed in a stream of carrier gas (99.99% He), using a thermal conductivity cell as the detector. After obtaining the signal corresponding to the gas phase sufficient time (approximately 15 min) was allowed for the recorder to return to the base line, and the temperature of the reactor was increased linearly at the desired rate by means of a Carlo Erba L. T. programmer. A TPD chromatogram was obtained in which the peaks are due to the gas desorbed at different temperatures. The quantity of desorbed CO was calculated from the areas under the peaks corresponding to known amounts of CO. Buffer volumes in the circuit helped reduce fluctuations in the flow rate of the gas. The desorbed gases corresponding to the peaks were collected on 5A zeolite in a liquid nitrogen trap, and examined in a Leitz Model III G infrared spectrophotometer; in all cases, only carbon monoxide could be detected.

To supplement the TPD results, the adsorption isotherm for carbon monoxide on

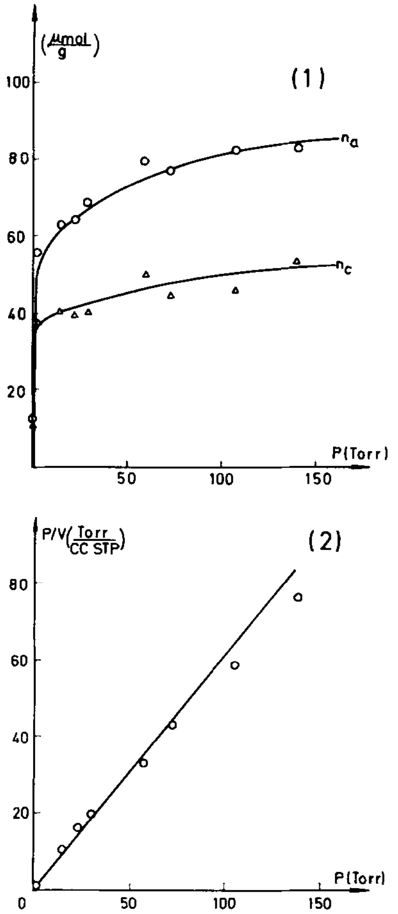

FIG. 1. (1) Adsorption isotherm of carbon monoxide on solid *b* at 40°C. n_a: Total adsorbed quantity; n_c: adsorbed quantity from the chromatogram. (2) Langmuir plot for the data shown in (1).

the reduced cobalt/kieselguhr catalyst was determined at 40°C in a volumetric apparatus. Figure 1a shows the isotherm for a sample of solid *b*, where the respective curves correspond to the total adsorbed quantity obtained volumetrically (n_a) and calculated from the area under the TPD chromatogram (n_c). The curves coincide for low values of the equilibrium pressure, *P*, but not for high values. The P/V_{ads} vs *P* plot for the n_a isotherm is shown in Fig. 1b, showing adherence to the Langmuir equation below 100 Torr. The monolayer value, V_m, obtained using a least squares treatment was 1.47 cm^3 (STP) for solid *a* and 1.69 cm^3 (STP) for solid *b*. This corresponds to 6.6% and 7.3%, respectively, of the total surface area, and provides an estimate of the cobalt surface.

In all the TPD experiments the adsorption stage was performed at 40°C, but the rate of heating, β, of the linear temperature program was varied, as was the initial fraction of the surface covered by the adsorbed carbon monoxide. The chromatograms of solids *a* and *b* were very similar. Examples of TPD chromatograms are shown in Fig. 2, but neither shows the peak belonging to the gas phase. Curve 1 was obtained with solid *b* at a low equilibrium pressure of CO (10^{-2} Torr), and in this case $n_c/n_a = 1$. Curve 2 refers to an experiment in which the adsorption was performed on solid *b* at an equilibrium pressure of 72.5 Torr; in this case $n_c/n_a = 0.5$, which means that only 50% of the adsorbed gas appears in the chromatogram. Curve 3 relates to solid *a* at an equilibrium pressure of 10^{-2} Torr, giving $n_c/n_a = 1$. The remaining 50% is retained by the solid, since it does not come out with the gas phase.

Two peaks were obtained on each chromatogram in every case: one at low temperatures, peak I, and the other at higher temperatures, peak II. These facts, together with the increase of peak II with the adsorbed quantity, would point to a mechanism that requires the previous existence of surface species I for the formation of surface species II.

In all the examples a large quantity of water gives rise to a signal that occurs at approximately 400°C for solid *a*, and 480°C for solid *b*, corresponding to the thermal decomposition of the solid.

If the chromatography is extended beyond these decomposition temperatures, desorbed CO cannot be distinguished from water of decomposition. Experiments performed on pure kieselguhr show a much lower degree of decomposition, suggesting

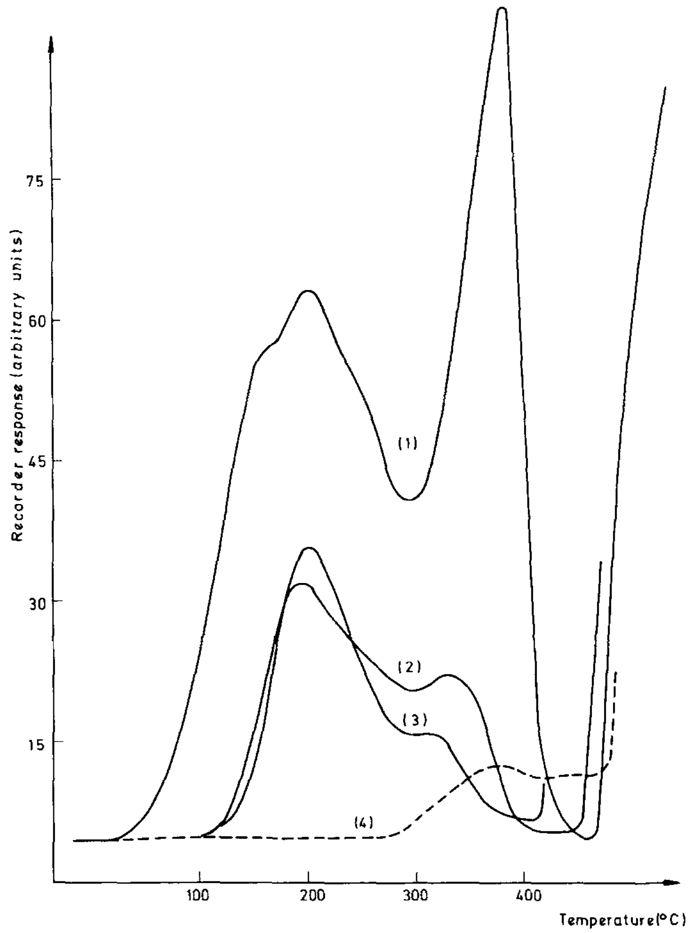

FIG. 2. TPD chromatograms. (1) Solid *b*, $n_a = 76.5$ (μmol/g) $\beta = 19.6$ (°C/min); (2) solid *b*, $n_a = 11.8$ (μmol/g) $\beta = 22.9$ (°C/min); (3) solid *a*, $n_a = 11.7$ (μmol/g) $\beta = 18.3$ (°C/min); (4) blank.

that kieselguhr undergoes some change during the catalyst preparation. Some blanks were run by heating the solids without having them previously adsorb CO, and the same peak was obtained, in addition to a very small one for water at about 350°C in the region of the high temperature peak in the TPD experiments. The latter is shown with a broken line in the chromatogram for solid *b* in Fig. 2.

In order to test the influence of the reduction temperature of the solid, some experiments were performed on this at 380°C. Within the accuracy of our experiments, no differences were observed in the chromatograms, except for the decomposition temperature, which was higher than that for the solid reduced at 300°C. Adsorption experiments performed on pure kieselguhr showed that CO is not adsorbed on the support.

It would seem reasonable to assume that species I are linear forms of CO adsorbed on cobalt, while species II are bridged forms, although infrared examination of the adsorbed phase should lead to a direct confirmation of this assumption. These structures have been suggested in the literature on the basis of the infrared spectra of CO adsorbed on metals (*10–12*).

A mathematical analysis of the desorption chromatogram allows one to obtain the following simple analytic expression for the case of linear heating, first order desorption, homogeneous surface, and a sufficiently high flow rate of the carrier gas to prevent readsorption (*3*):

$$(2 \log T_m - \log \beta) = \frac{E_d}{2.303\,RT_m} + \log \frac{E_d}{AR}, \quad (1)$$

where β is the heating rate, E_d the activation energy of desorption, R the gas constant, A the rate constant of desorption, and T_m the temperature of the peak maximum.

By measuring T_m in experiments performed at different heating rates β, it is possible to plot $(2 \log T_m - \log \beta)$ against $1/T_m$ to obtain straight lines from whose slopes either E_d or ΔH_a can be calculated depending on whether the process takes place without or with readsorption. Since in systems such as the ones under consideration equilibrium is reached rapidly, it can be assumed that adsorption is nonactivated ($E_a = 0$) (*6*), and the heat of adsorption can be obtained from the slope ($E_d = -\Delta H_a$).

One way of avoiding readsorption is to make sure that T_m is the same for different flow rates of the carried gas. In our case a flow rate of 19 cm^3/min of He was used, and it was observed that when this rate, F, was increased, the value of T_m varied slightly, showing that the value of A calculated from Eq. (1) must be taken as an approximation; fortunately this variation does not happen with the heat of adsorption.

We have already seen that two peaks appear in the chromatograms in all cases. It is not possible to obtain good straight lines when Eq. (1) was plotted for peak II, but

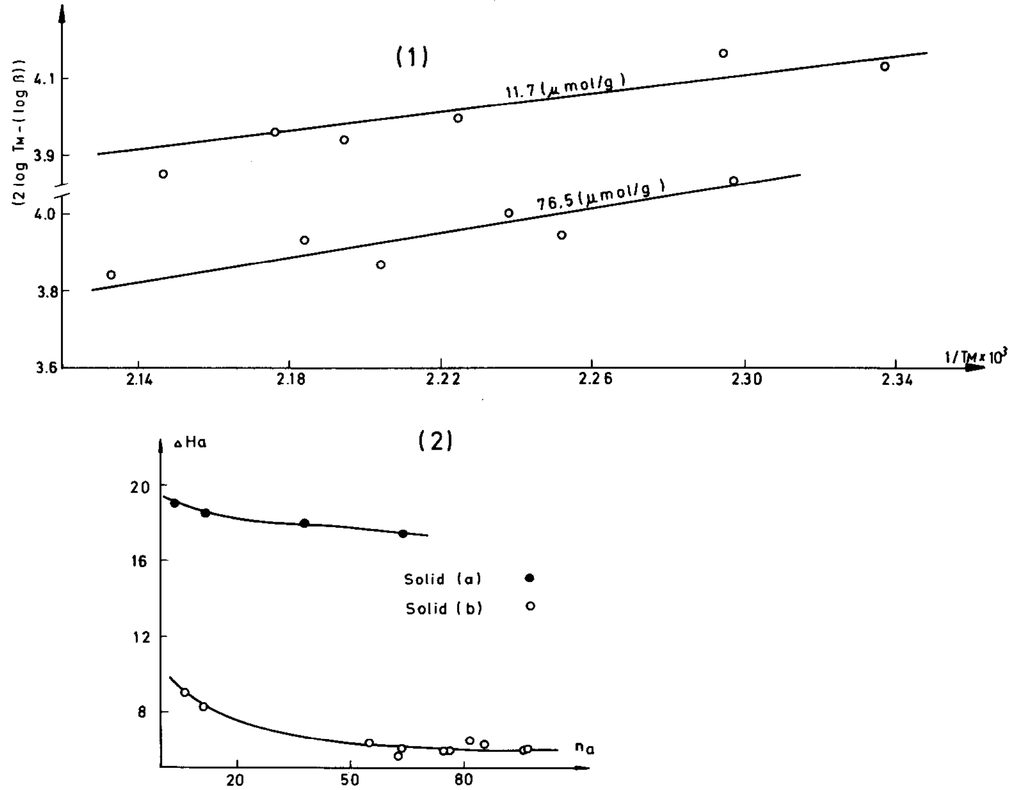

FIG. 3. (1) Plot of Eq. (1) for the first TPD peak of carbon monoxide on solid *b*. (2) Plots of heat of adsorption against amount adsorbed.

this was always possible with peak I. Figure 3a shows the straight line plots for peak I and for adsorbed amounts of 11.7 and 76.5 μmol/g, respectively, for solid *b*. The values of β were between 12 and 35°C/min, and from a least squares fit of the plots values of 8.3 and 5.9 kcal/mol, respectively, are obtained for ΔH_a. In Fig. 3b ΔH_a is plotted against n_a. The values just given provide two points of the curve for solid *b*; the other points were obtained from experiments performed with different adsorbed quantities. The sites seem to be quite homogeneous, except in the region of very low equilibrium pressures, ΔH_a, which had values up to six times larger than the heat of liquefaction of CO, was much smaller for solid *b* than for solid *a*, where at an equilibrium pressure of 10^{-2} Torr and 11.8 μmol/g adsorbed, a heat of adsorption of 18.6 kcal/mol is obtained. For solid *a* the sites that should correspond to peak I are also quite homogeneous because ΔH_a, which has a value of 19 kcal/mol for $n_a = 3.4$ μmol/g, decreases only to 17.5 kcal/mol for $n_a = 64.4$ μmol/g, retaining always values more than ten times larger than the heat of liquefaction of CO.

Hayward and Trapnell (*9*), who made experimental determinations of the BET constant *c*, have established 6 kcal/mol as the upper limit for the heat of physisorption of CO, so that a larger value should be an indication of chemisorption. If this criterion is valid, it indicates chemisorption in our experiments, though in the case of solid *b* the heat for the peak I adsorption at high coverage is close to the physisorption limit.

At this stage it has not been possible to suggest a reasonable explanation for the differences found between the results for solids *a* and *b*, although the study of this problem constitutes, in our opinion, the most interesting aspect in continuing this work.

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