JOURNAL OF CATALYSIS 58, 28–33 (1979)

Hydrogen Chemisorption and the Carbon Monoxide–Hydrogen Interaction on Cobalt (0001)

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Received October 5, 1977; revised October 16 1978

At 300 K hydrogen chemisorbs dissociatively on Co(0001) with an initial sticking probability of ~0.04, and the surface saturates at a coverage of $\Theta \sim 0.1$. Desorption occurs from a single adsorbed state with second-order kinetics and an activation energy of ~67 kJ mol^{-1}. Coadsorption of hydrogen and carbon monoxide leads to no detectable interaction between these species in the mixed adlayer, but at ~300 K CO dosing of a hydrogen-covered surface leads to displacement of the latter with an efficiency of ~0.7.

INTRODUCTION

We have recently undertaken studies of adsorption behavior of simple gas molecules on the surfaces of single crystals of the hexagonal metals ruthenium and cobalt, the interest in these systems arising from the importance of these two metals as catalysts for the Fischer–Tropsch synthesis. We have already published (*1*) the results of an investigation of the adsorption/desorption behavior of CO on the basal plane of cobalt, and the subject of this paper is the adsorption of hydrogen on Co(0001) and the coadsorption of hydrogen and carbon monoxide on this surface. There have been very few studies of hydrogen chemisorption on macroscopic cobalt specimens, and only one UHV study has been reported (*2*). In that work, Dus and Lisowski using thermal desorption and surface potential methods, observed four states for hydrogen on an evaporated cobalt film. These they labeled A, B, B$_1$, and C. The A state they believe to be molecular, and the A, B, and B$_1$ states will desorb below 300 K, while in order to populate these states, adsorption temperatures of 78 K and standing pressures of 10^{-2} Torr were required. The C state, attributed to an electronegatively polarized atomic state of hydrogen, desorbs in the temperature range 300 to 450 K, and the desorption enthalpy is estimated at 79 kJ mol^{-1}. Rudham and Stone (*3*), using reduced cobalt, also estimated the heat of adsorption of hydrogen as a function of surface coverage, obtaining values in excess of 105 kJ mol^{-1} on the bare surface, falling to 13 kJ mol^{-1} at coverages in excess of one-third a monolayer. The background vacuum in these experiments was ~10^{-6} Torr.

EXPERIMENTAL METHODS

Our experiments were carried out in a stainless-steel UHV chamber, fitted with a three-grid retarding field analyzer and quadrupole mass spectrometer; this system has already been described in detail (*4*). Base pressures of ~5×10^{-11} Torr were routinely available. Hydrogen adsorption experiments were performed on a (0001)

0021-9517/79/070028-06$02.00/0

single crystal specimen of cobalt oriented to within 0.5°, and some auxiliary experiments were also carried out on a well-annealed polycrystalline ribbon in order to check whether the presence of grain boundaries had any appreciable affect on the adsorption properties. LEED observations (*1*) showed that ~95% of the surface of this specimen consisted of crystallites with (0001) surface orientation. The preparation of both specimens has already been described (*1*). All H_2/CO coadsorption experiments were carried out on the single crystal. H_2 and CO used were X-grade (B.O.C.), and formaldehyde was generated from trioxan in tha gas handling line, giving an estimated purity of >97% (as estimated from comparison of the mass spectrum of the formaldehyde with published data) in the vacuum chamber, the chief contaminant being H_2O. All adsorptions were carried out at ~300 K.

RESULTS AND DISCUSSION

Hydrogen was found to adsorb on the polycrystalline specimen at ~300 K, and thermal desorption spectra after exposure and subsequent pumping show a single peak at ~370 K (Fig. 1). This is very similar in shape and position to the desorption peak for the C-state of hydrogen observed by Dus and Lisowski (*2*). The intensity of the peak was found to be sensitive to the pumping time under UHV conditions, and also to the adsorption temperature; Fig. 1 shows a typical set of curves exhibiting this dependence. Therefore, the following procedure was adopted in taking thermal desorption spectra of H_2 from cobalt: (i) The specimen was flashed to 680 K in UHV, which removes all CO (*1*) and H_2. (ii) The specimen was cooled to ~290 K in UHV. (iii) Hydrogen was admitted to the system at a chosen pressure to give the required exposure in a short time (<2 min). (iv) The flash desorption spectrum was taken with the standing pressure of H_2 still in the system.

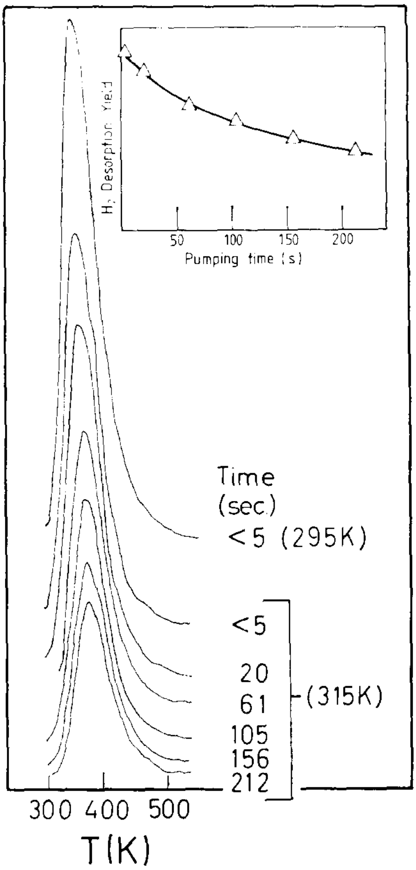

FIG. 1. H_2 desorption spectra from cobalt polycrystal following 2-L dose as a function of pumping time (1 L = 10^{-6} Torr sec). Heating rate, 11 K sec^{-1}. Inset: H_2 desorption yield vs pumping time for 2-L dose at 315 K.

The pressures used during hydrogen exposure were chosen so as to minimize the exposure time, thus improving the reliability of sticking probability data by reducing the pumping effects during the exposure. They varied between 5×10^{-9} and 5×10^{-7} Torr. The desorption spectra thus obtained for the single crystal are shown in Fig. 2. It can be seen that they resemble the spectra from the polycrystal and show typical second-order kinetics. A second-order Arrhenius plot taken from these curves {ln (rate/Θ^2) vs $1/T$} gives a good straight line, the slope of which gives

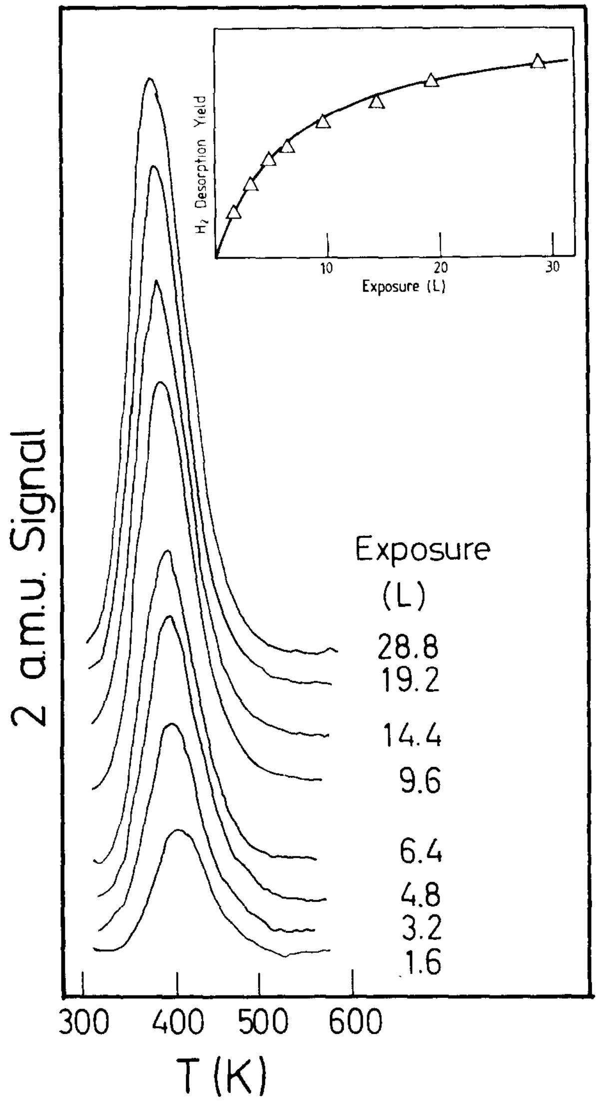

FIG. 2. H_2 desorption spectra from Co(0001) single crystal. Heating rate 10 K sec^{-1}. Adsorption temperature, <300 K. Inset: H_2 desorption yield as function of exposure.

a value of 67 ± 8 kJ mol^{-1} for the activation energy to desorption. Attempts to fit the data to other desorption models (e.g., a first-order desorption) did not produce satisfactory straight lines. This value for $E_d = 67 \pm 8$ kJ mol^{-1} is lower than, but in reasonable agreement with, the value of Dus and Losowski (*2*), and is also consistent with the reported desorption energies for H_2 on the basal planes of the other Group VIII metals for which data are available, i.e., Ni(111) (*15, 16*), Pt(111) (*5, 6*), Pd(111) (*7*), and Ru(0001) (*18*), although, as is the case of CO on this surface, the desorption energy of H_2 from Co(0001) is slightly lower than any of these other values. The pumping conditions in the chamber were such (*4*) that the data of Fig. 2 may be used to construct the relative sticking probability curve shown in Fig. 3. This curve is characteristic of random two-site adsorption via a mobile precursor state (*7, 8*), although it should be borne in mind that the results at high coverage contain significant errors due to hydrogen pump-off. Thus both the adsorption kinetics and the desorption kinetics indicate that hydrogen is dissociatively chemisorbed on Co(0001), and indeed the adsorption behavior suggests that this dissociation occurs upon chemisorption at room temperature. LEED observations showed that hydrogen adsorption did not lead to the formation of ordered overlayers, and do not therefore provide a calibration which would permit a calculation of the absolute initial sticking probability (S_0). However, given the known mass spectrometer and ionization gauge sensitivities to CO and H_2, an approximate calibration for S_0 and the maximum coverage (Θ_{max}) of hydrogen on Co(0001) at 300 K can be carried out by reference to the equivalent CO desorption data (*1*) for which LEED structural information *is* available. This procedure gives $\Theta_{max} = 0.13$ and $S_0 \sim 0.045$. It is of some interest to compare these quantities with the corresponding values for hydrogen chemisorption on Ni(111). The Co(0001) and Ni(111) surfaces have, of course, identical atomic arrangements in the surface plane, with nearest-neighbor separations differing by only 1%. Furthermore, the kinetic and structural characteristics of CO, NO, and O_2 chemisorption on Ni(111) (*19–21*) are almost identical with those observed on Co(0001) (*1, 22*); for Ni(111)/H_2 at 300 K Horgan and Dalins (*9*) obtain $S_0 \leqslant 0.01$ while Lapujoulade and Neil (*15*) find $S_0 = 0.1$ and $\Theta_{max} = 0.14$.

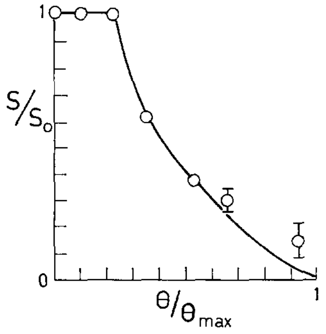

FIG. 3. Coverage dependence of relative sticking probability (S/S_0).

Confirmation of the above values of S_0 and Θ_{max} for H_2 on Co(0001) is obtained from the results of formaldehyde adsorption on this surface (*10*). It was found that chemisorbed formaldehyde decomposes with unit efficiency on Co(0001), and at low exposures (<0.5 L; 1 L = 10^{-6} Torr sec) the H_2 and CO yields are in the ratio 1:1. Comparison of the H_2 desorption yields following (a) H_2 and (b) CH_2O adsorption, and the CO yields following (a) CO and (b) CH_2O adsorption provides the basis for yet another kind of sensitivity calibration. When applied to the present data for H_2, this leads to $S_0 = 0.042 \pm 0.02$, $\Theta_{max} = 0.12 \pm 0.03$. With these values and data similar to those presented in Fig. 1, taken at temperatures of 296, 307, and 314 K, the second-order rate constant for hydrogen desorption from the single crystal may be determined, leading to a value for the desorption energy (E_d) of 73 ± 7 kJ mol^{-1} for H_2 on Co(0001). A similar procedure on the polycrystal gives $E_d = 72 \pm 9$ kJ mol^{-1}. These values are likely to be somewhat less reliable than that obtained above by analyzing the data over a complete desorption sweep, because the range of temperature variation is rather restricted. However, they serve to show that there appears to be no significant difference between the single crystal and polycrystalline surfaces.

Coadsorption of H_2 and CO on the single crystal specimen led to no detectable change in the binding energy of either species. No new ordered phases were formed, and the Co(0001)-($[3]^{\frac{1}{2}} \times [3]^{\frac{1}{2}}$) R30°/CO phase (*1*) was unperturbed by hydrogen dosing. Sequential adsorption experiments were carried out (dosing first with H_2 then with CO and vice versa) which showed that the desorption yields of

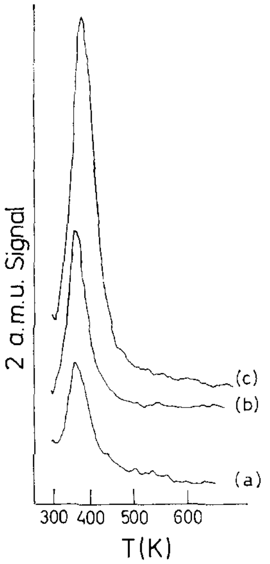

FIG. 4. Hydrogen desorption spectra for $H_2 + CO$ coadsorption (a) 32 L H_2 followed by 3 L CO. (b) 3 L CO followed by 32 L H_2. (c) 32 L H_2 only.

both gases were altered. Figure 4 shows the hydrogen yields from a surface exposed to H_2 alone (curve c), to CO and then H_2 (curve b), and to H_2 and then CO (curve a). The corresponding curves for CO desorption are shown in Fig. 5. These data are reproducible, and the experiments do not appear to be affected by pretreatment of the system with CO in the amounts used in these experiments (<10 L). The decrease in H_2 desorption yield after exposure of the hydrogen-covered surface to CO is much greater than can be accounted for merely by slow pump-off having occurred during the total time elapsed (v.s.). This indicates that CO displaces hydrogen from the surface at 300 K, while curve (b) shows that the hydrogen sticking probability is substantially reduced from the clean surface value by preadsorbed CO. It can also be seen that H_2 dosing of a surface bearing preadsorbed CO has little or no effect on the CO coverage, although preadsorbed hydrogen *does* have an appreciable effect in reducing the CO sticking probability below the clean surface value [$\sim$0.9 (*1*)].

Exposure of the clean Co(0001) surface to 1:1 H_2:CO mixture resulted in CO uptakes which were very close to those obtained by using pure CO, while the hydrogen uptakes were reduced by about two orders of magnitude. This behavior is consistent with the lower adsorption energy of hydrogen as compared with CO, the very different sticking probabilities of these two species, and the observed displacement of adsorbed hydrogen by CO. Energetic considerations suggest that the preferred gaseous product of this displacement reaction should be molecular H_2 rather than atomic H. If, as seems reasonable, the displacement reaction proceeds by a mechanism in which CO chemisorbs from a mobile precursor state onto a vacant site, followed by associative desorption of a pair of neighboring H atoms, then the H_2 displacement rate depends directly on the CO adsorption rate. Using the known kinetic parameters for CO adsorption on Co(0001) (*1*) and assuming that a CO molecule cannot adsorb directly onto an H-filled site, the above data yield a value of $\sim$0.7 for the probability that an adsorbing CO molecule displaces two adjacent H atoms from the surface. This high efficiency is entirely consistent with the

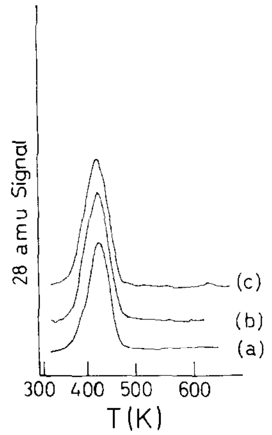

FIG. 5. CO desorption spectra for $H_2 + CO$ coadsorption. (a) 32 L H_2 followed by 3 L CO. (b) 3 L CO followed by 32 L H_2. (c) 3 L CO only.

results of the competitive adsorption experiments which were presented above.

The apparent lack of interaction between coadsorbed hydrogen and CO on Co(0001) as reflected by the unperturbed desorption spectra is somewhat surprising considering that cobalt is a good Fischer–Tropsch catalyst. Platinum and nickel are *not* good catalysts for this reaction, and yet H_2/CO coadsorption on these metals does lead to significant interaction between the two species. Thus Baldwin and Hudson (*11*) observed very substantial changes in the CO and H_2 desorption spectra from Pt when these two species were coadsorbed. The desorption energies of both molecules were increased, and electron impact data indicated the presence of a CO–hydrogen surface complex. It has also been reported that the heat of adsorption of H_2 on Ni is increased by the presence of CO (*13*), and that the maximum coverage of CO on Ni at temperatures above 300 K is increased by the presence of H_2 (*14*). On the other hand, the displacement of H_2 by CO from Ni films (*12, 13*) does resemble the behavior found for Co(0001).

ACKNOWLEDGMENT

M.E.B. thanks the Science Research Council for the award of a Research Fellowship.

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