THERMAL DESORPTION: CHEMISORPTION OF CARBON MONOXIDE ON POLYCRYSTALLINE TUNGSTEN

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The adsorption isotherm was constructed from thermal desorption spectra of carbon monoxide on tungsten. Comparison of the experimental results with model isotherms supports a concept of the dissociative adsorption of carbon monoxide on tungsten.

The adsorption of carbon monoxide on transition metals is among the most frequently studied systems[1,2]. Great interest in this reaction is connected with its numerous practical applications. The catalytic formation of hydrocarbons by methanation or by the Fischer–Tropsch synthesis could be of help in the future in the solution of the energy problems[3].

Despite the primary attention paid within the group of transition metals to the carbon monoxide–tungsten system, several problems remain yet unsolved. Of special importance is the structure of the adsorbate and its kinetic behaviour[4,5]. Both of them were originally studied by the thermal desorption method, by measuring pressure changes in the vacuum system resulting from heating of the sample.

Three groups of maxima were found in the CO-W thermal desorption spectra, differing according to the temperature of desorption. The desorption maximum at 500 K corresponds to the α-state; the multiple maxima in the temperature range between $900 - 1\,500$ K are denoted as the β-states[6]. For the case of adsorption at low temperatures the observed low-temperature maximum is designated as the virgin state of the adsorbed carbon monoxide[7].

The complexity of the above system is caused by changes in the individual states of the adsorbed particles and by the sensitivity of the system to structural changes in the adsorbent. For this reason polycrystalline materials were replaced by single crystals. In addition, new techniques, mainly spectroscopic, have been applied, adding complementary information to the thermal desorption data[4]. The present knowledge of the CO-W system is very much different from the situation 10 years ago, when a comprehensive review was published[1]. First, there is now considerable experimental evidence for the dissociative character of the CO β-states on tungsten[4,8]. It should be mentioned that some of the experiments with labeled CO were originally

used to support the molecular adsorption model. However, even those results were later shown to be in agreement with the concept of dissociative adsorption[9]. The vibrational spectra obtained by means of electron energy loss spectroscopy give unambiguous proof of the dissociative character of the β-states.

The dissociative adsorption of CO is assumed to be one of the decisive steps in the mechanism of methanation and the Fischer–Tropsch synthesis[2]. Tungsten, as a metal which easily dissociates CO, could find therefore practical application in catalysis, since in addition to the methanation activity which is comparable with nickel, it shows higher resistivity against sulphur poisoning. The technology of preparing a very pure tungsten surface on a substrate seems to be a rather difficult problem since the usual methods of preparation lead to contaminated catalyst surface[10]. In this paper we were concerned with the kinetics of adsorption and desorption of CO on tungsten and we have shown that the data obtained from thermal desorption spectra are in agreement with the concept of the dissociative character of adsorption.

THEORETICAL

The mass balance in a continuously pumped system can be expressed as follows[11]

$$dP/dt = (RT_s U/V) - (FP/V) + (ART_g/V) \cdot (r_a - r_d), \qquad (1)$$

where P denotes the pressure, V the volume of the system, F the pumping speed, T_s and T_g the temperatures of the surface and gas, U the leak rate, A the area of the sample surface and r_a and r_d the rates of adsorption and desorption, respectively. Under steady-state conditions and in the absence of adsorption or desorption, the leak rate U is given as $U = FP_{eq}/RT_g$, where P_{eq} signifies the background pressure of the apparatus. The difference between the rate of adsorption and desorption can be expressed as:

$$r_a - r_d = (V/ART_g) \cdot (((P - P_{eq})/\tau) + dP/dt), \qquad (2)$$

where τ is the characteristic pumping time of the apparatus, given by the ratio $\tau = V/F$. The desorption rate can be expressed by means of the Polanyi–Wigner equation

$$r_d = - dn/dt = v \cdot n^m \cdot \exp(-E_d/RT_s), \qquad (3)$$

where n denotes the number of moles of the desorbing product per unit area, v the preexponential factor, E_d the activation energy of desorption and m the kinetic order of desorption.

Equation (2) represents a basic relation, allowing the determination of the kinetic parameters of desorption E_d, m and v from the experimental data. Evaluation of the experimental data would be very difficult in the given form and the experimental con-

ditions are therefore selected so as to ensure that the measured pressure is directly proportional to the rate of desorption. For that, as the first condition, the rate of adsorption during the thermal desorption experiment must be negligible in comparison with the rate of desorption. From the analysis of equations (2) and (3) one can also obtain the maximum permissible rate of heating, defined as $\gamma = \mathrm{d}T_{\mathrm{s}}/\mathrm{d}t$. By detailed analysis Chan and Weinberg showed[12] that the product $\gamma \cdot \tau$ had to be less than 2, so that the measured pressures would really correspond to the rate of desorption.

From the obtained experimental data one can first of all determine the values of the kinetic parameters of desorption m, ν and E_{d} (ref.[13]). Additional parameters can be also obtained: the area below the desorption curve is proportional to the adsorbed amount and plotting its dependence on the exposure one can obtain the adsorption isotherm. A tangent drawn at the zero-coverage point of the adsorption isotherm gives the value of the sticking coefficient S_0 (ref.[14]).

Several approaches have been worked out for the determination of the kinetic parameters, both for the case where E_{d} and ν remain constant[15] or where their values depend on the coverage[16,17]. On polycrystalline surfaces the situation in the desorption spectra is frequently complicated by the appearance of a series of maxima. Their existence can result from a superposition of the simple desorption curves corresponding to the various types of adsorption sites or it may result from the dependence of the desorption parameters on the coverage[18]. To distinguish between these two cases only on the basis of the thermal desorption data, is very difficult.

EXPERIMENTAL

The temperature of the sample with the adsorbed gas is increased linearly in time and the recorded pressure dependence is referred to as the desorption spectrum. The experiment must be carried out under ultra-high-vacuum conditions, since both the sample and the adsorbed gases must be of highest purity.

Fig. 1 shows the experimental arrangement used. A glass reaction chamber R containing a tungsten filament spot-welded on the molybdenum feedthrough is pumped out by a sublimation and getter-ion pump. The total pressure is measured with a commercially calibrated Bayard–Alpert ionization gauge, located on the dead-end of the reaction vessel. The partial pressures of the individual gases are measured by a Finnigan 400 residual gas analyzer. The gases are introduced into the apparatus by means of a leak-valve or by a ground-glass-sliding valve from a gas reservoir, which is independently evacuated by the oil diffusion pump equipped with a cold trap. The usual background pressure was less than $2 \cdot 10^{-7}$ Pa, with H_2 and CO forming the major background components. The framed part of the apparatus on Fig. 1 is heatable to 600 K; during the bake-out the system is pumped by the oil diffusion pump with a cold trap.

The tungsten filament, 0·1 mm diameter and 200 mm long, was purified by standard procedures[19]: An alternating sequence of oxidation and reduction cycles (consisting of heating at 1 600 K in oxygen at $1 \cdot 10^{-4}$ Pa and at 2 000 K in hydrogen at $1 \cdot 10^{-5}$ Pa), with subsequent flashes at 2 300 K resulted in readily reproducible CO thermal desorption spectra. The reproducibility of the spectra indicates that the cleanliness of the filament was sufficient since the desorption spectra are very sensitive to surface impurities.

In order to simplify the interpretation of the thermal desorption spectra it is of advantage to increase the temperature of the filament linearly with time. The dependence of the filament temperature on the applied voltage was obtained by measuring the resistance of the filament and the value thus obtained was compared for higher temperatures with the pyrometer readings. The time dependence of the applied voltage was set to assure a constant rate of heating. A modified programmer GP-1 from the development facilities of the Czechoslovak Academy of Sciences (Vývojové dílny akademie) was used for this purpose.

From the pressure decrease in the apparatus, following the flash of the tungsten filament, the characteristic pumping times $\tau_{H_2} = 0.067$ s and $\tau_{CO} = 0.167$ s were determined. The maximum applicable heating rates are according to[12] $\gamma_{H_2} = 30$ K . s^{-1} and $\gamma_{CO} = 12$ K . s^{-1}.

The tungsten filament used was supplied by TESLA company (ČSR), oxygen and hydrogen were the products of Reinstgase Berlin (GDR) and carbon monoxide of BOC (Great Britain).

RESULTS

Thermal desorption spectra of CO, adsorbed on polycrystalline tungsten at room temperatures, were measured. For simplicity, only some of the spectra are shown in Fig. 2. The applied rate of heating $\gamma = 7$ K . s^{-1} was chosen with respect to the characteristic pumping time τ_{CO} of our apparatus.
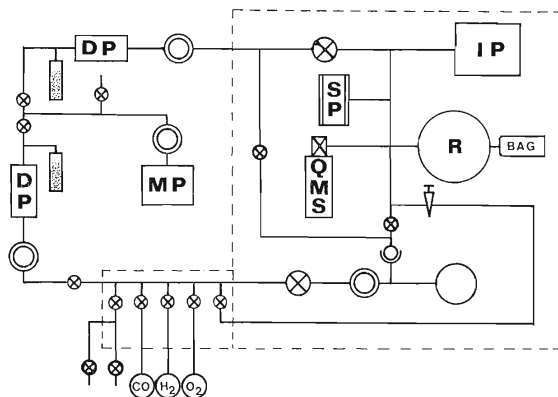

FIG. 1

Schematic diagram of the ultra-high vacuum apparatus for thermal desorption: R reaction vessel with a sample, BAG Bayard–Alpert ionization gauge, QMS quadrupole mass spectrometer, IP ionization pump, SP sublimation titan pump, DP difussion pump, MP rotary pump

The increased exposure ε leads at first to the filling of the β-states, that is of states desorbing at higher temperatures. The filling of the α-states occurs et $\varepsilon > 1$ L = $= 1·33 . 10^{-4}$ Pa . s, when the β-states are already covered to the extent of about 50%. For $\varepsilon > 17$ L, the desorbed amount remains constant. The temperatures of the maxima of the individual desorption states do not change with increasing coverage for a given experimental arrangement, at least within the experimental error of the measurement. The only exception can be observed with the β_3-maximum, which is with increasing exposure shifted to lower temperatures. Such a shift is usual in second order desorption for constant kinetic parameters, however, one can not exclude that the observed shift is caused by the large increase of the adjacent β_2-maximum, which is of much higher intensity. At saturation, the α-state represents 1/10 of the total amount of CO adsorbed on the tungsten. The desorption kinetic parameters were not determined because of the complicated desorption spectra, containing three β states and one α state.

The integration of the desorption curves led both to values for the total coverage and coverage in the β-states, the dependence of which on the exposure ε is given in Fig. 3. The coverage θ is presented in relative units normalized to the full coverage $\theta = 1$. From the adsorption isotherm thus obtained it is possible to determine the value of S_0, expressing the magnitude of the sticking coefficient at zero coverage. One needs, however, to know the values for the number of molecules per unit area in the saturated layer. Since the total pressure measurement was carried out with a non-calibrated ionization gauge and the mass spectrometer was not calibrated for sensitivity, we used published data[6] for the saturated layer.
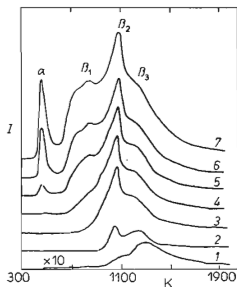

FIG. 2

Thermal desorption spectra of CO on poly-crystalline tungsten. Heating rate 7 K/s, adsorption temperature 300 K. Exposure of CO: 1 0·07 L, 2 0·36 L, 3 0·69 L, 4 1·0 L, 5 1·38 L, 6 2·63 L, 7 17·4 L. (1 L = 1·33 . . 10^{-4} Pa. s = 3·83 . 10^{14} collisions of CO molecules per cm^2)

It is known that the method used for purification of the polycrystalline tungsten filament leads to its recrystallization[20]. In such a case the surface is formed mainly by crystallites with the (100) planes oriented towards the vacuum side. King[6] gives for recrystallized tungsten a number of $5.2 . 10^{14}$ molecules/cm² for the amount adsorbed in the β-states and $1.8 . 10^{14}$ molecules/cm² for adsorption in the α-states.

It is evident from Fig. 3 that in the region of exposure $\varepsilon < 1$ L (where the α-state has not yet appeared), the dependence of the coverage θ on the exposure ε exhibits a first order character. For this reason a straight line was fitted through this region, using the least-squares analysis, giving a slope of $S_0 = 0.62$. The S_0 value was used for calculation of the adsorption isotherms of the β-states using two simple models: a) The Langmuir adsorption isotherm was derived for the case of dissociative adsorption from the relation

$$\mathrm{d}\theta/\mathrm{d}\varepsilon \sim (1 - \theta)^2 .$$

This model does not fit the observed experimental behaviour. While the β-states are saturated already at $\varepsilon = 17$ L, the Langmuir isotherm gives for such an exposure only a 85% coverage. b) The constancy of $S = S_0$ at the low coverage region can be explained by the existence of a mobile precursor[21]. In this case the adsorption isotherm was obtained by a procedure analogous to the model of Kisliuk[22,23]. It was assumed that the migration probability of the mobile precursor was independent
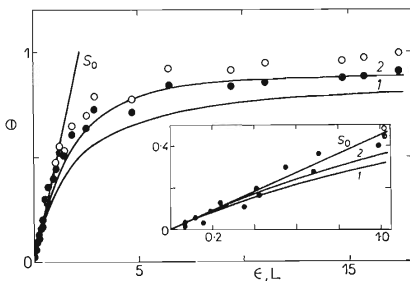

Fig. 3

Carbon monoxide adsorption isotherm on polycrystalline tungsten: 1 second-order Langmuir isotherm, 2 second order precursor model. Experimental points: ○ total coverage, ● coverage in the β-states

on the coverage. The adsorption isotherm can then be obtained from the expression:

$$d\theta/d\varepsilon \sim (1 - \theta)/(1 + K\theta/(1 - \theta))$$

with the constant $K = S_0 \cdot f_d/f_a$, where f_d is the probability of desorption of the precursor from a state above the filled adsorption site and f_a is the probability of the chemisorption of the precursor above the empty site at zero coverage.

The value $K = 0 \cdot 1$ was chosen to achieve the best fit to the experiment in the threshold region. The comparison of both models shows that the model with the mobile precursor fits the experimental data much better in the whole range of exposures. For the exposure 17 L the precursor model gives a 98% saturation for the β-states, in very good agreement with the results obtained.

The fit between the experimental results and the second order precursor model can be regarded as another evidence for the dissociative character of the carbon monoxide adsorption in the β-states.

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