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The detailed kinetics of the adsorption of hydrogen on polycrystalline copper studied by reactive frontal chromatography

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The coverage-dependent sticking probabilities of molecular hydrogen on polycrystalline copper supported on alumina have been determined in the temperature range 213–273 K by analysis of the hydrogen frontal adsorption line shape. In this temperature range the initial sticking probabilities increase from 8×10^{-13} (213 K) to 1.3×10^{-10} (273 K). The overall activation energy to adsorption has been found to be 42 kJ mol^{-1}. The application of reactive frontal chromatography for the measurement of hydrogen sticking probabilities on copper is a novel variant of the N_2O reactive frontal chromatographic method, developed for the measurement of copper surface areas. Its use here shows that reactive frontal chromatography may be applied generally to any adsorbate/adsorbent system involving activated adsorption and low sticking probabilities.

Keywords: hydrogen, copper, activation energy, adsorption, sticking probability

1. Introduction

It is well known that the adsorption of hydrogen on copper is activated [1–9]. We have determined a lower limit of the activation energy of the adsorption of hydrogen on Al_2O_3-supported polycrystalline copper of 27 kJ mol^{-1} [10]. This value is slightly higher than those obtained by Balooch and co-workers for the adsorption of hydrogen on Cu(110) and Cu(100) [3]. Using a pulsed supersonic hydrogen molecular beam they found energy barriers of 12 kJ mol^{-1} for the adsorption of hydrogen on Cu(110) and 20 kJ mol^{-1} for its adsorption on Cu(100). However, subsequent research [4–9] has suggested that these values obtained by Balooch and co-workers [3] are too low.

Anger, Winkler and Rendulic measured the adsorption and desorption kinetics of hydrogen on the (111), (110) and (100) faces of copper using a heated-nozzle molecular beam source and temperature-programmed desorption [4]. No value of the adsorption activation energy was obtained in this work. However, at beam energies lower than 20 kJ mol^{-1}, the sticking coefficient was found to be immeasurably small ($<10^{-5}$). At beam energies greater than 25 kJ mol^{-1}, there was no levelling off of the sticking coefficient. This should have been observed had the 20 kJ mol^{-1} activation energy to hydrogen adsorption reported by Balooch and co-workers been the correct value. Anger and co-worker also checked for the contribution that vibrational excitation might make to the sticking of hydrogen on copper by using deuterium beams which at any temperature have a higher population of vibrationally excited states, concluding that “the majority contribution to the adsorption mechanism is one of the kinetic energy” [4].

Campbell and Campbell [5] by measuring the rate of hydrogen reduction of surface oxidised Cu(110) claimed to have obtained a “true” activation energy of 57 kJ mol^{-1} for hydrogen adsorption on Cu(110). They also claimed that the chemisorption of hydrogen occurs by a direct mechanism in which translational energy is most effective in scaling the energy barrier, a conclusion which agrees with that of Anger and co-workers.

The contribution that vibrational excitation makes to scaling the adsorption energy barrier was measured directly by Hayden and co-workers [6–8] by “cold seeding” a superthermal hydrogen molecular beam with helium. This lowered the translational energy (the extent of which depended on the amount of helium doping) while leaving the vibrationally excited ($v = 1$ state) population of hydrogen virtually unaltered. They found that for a nozzle temperature of 1150 K and perpendicular kinetic energies of the impinging hydrogen molecular beam lowered from 26 to 13 kJ mol^{-1}, the sticking coefficient remained constant, confirming the paramountcy of vibrational excitation in overcoming the energy barrier.

Chorkendorff and co-workers [9] agree with Hayden and Lamont in respect of importance of vibrational excitation in overcoming the energy barrier to dissociative adsorption. They measured the sticking probabilities of H_2 and D_2 on Cu(100) at 218–258 K as a function of pressure and from the observation of the increase in sticking probability from 10^{-13} to 5×10^{-12} on lowering the pressure from 10^2 to 10^{-3} atm concluding that vibrational excitation is efficient in scaling the energy barrier to adsorption. They further determined that the energy barrier to adsorption was 48 kJ mol^{-1} for H_2 and 56 kJ mol^{-1} for D_2.

Measurement of the activation energy of adsorption of hydrogen on supported polycrystalline copper appears to afford the possibility of obtaining some indication of the morphology of the copper. Sandoval and Bell have carried out just such a measurement on a silica-supported copper [10]. The amount of hydrogen adsorbed in the temperature range 133–333 K was determined by temperature-programmed desorption from which an overall adsorption activation energy of 42 $kJ\,mol^{-1}$ was obtained. Using the same technique, we obtained an activation energy for the adsorption of hydrogen on $Cu/ZnO/Al_2O_3$ of 27 $kJ\,mol^{-1}$ [10], but argued that the value so obtained was an underestimate since measurements of hydrogen coverage taken at $\sim$300 K will be equilibrium values as opposed to kinetically determined ones. This is due to the fact that in temperature-programmed desorption the peak maximum for hydrogen desorption is $\sim$300 K and so there will be considerable desorption of the hydrogen during dosing at or near this temperature.

The purpose of this paper is to determine the activation energy for the adsorption of hydrogen on polycrystalline copper supported on alumina. As in the previous paper, this material is used in preference to the $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst to avoid complications due to adsorption on the zinc oxide. The technique employed is temperature-dependent hydrogen reactive frontal chromatography – a variant of the N_2O reactive frontal chromatography technique which is commonly used for copper metal area determination [12]. The value obtained will be compared with those determined for single-crystal surfaces, in an attempt to link those measurements to a real catalyst and to gain some indication of the surface morphology of the polycrystalline copper supported on Al_2O_3.

2. Experimental

2.1. The microreactor, the catalyst and the gases

The microreactor, the Cu/Al_2O_3 catalyst, the weight of catalyst used (0.5 g) and the gases employed have been described in detail [10].

2.2. Experimental method

In N_2O reactive frontal chromatography the amount of nitrogen evolved by the decomposition of N_2O on its adsorption and simultaneous reaction on the copper metal component of an oxide-supported copper is measured continuously on a mass spectrometer. The catalyst is contained in a reactor tube (20 cm long, 0.4 cm i.d., packed length 2 cm) and N_2O/He (5% N_2O in He) is flowed continuously over the catalyst. When the oxygen coverage of the copper reaches saturation (0.5 monolayer), the reaction ceases abruptly and the N_2 evolution is cut off. What is obtained is a square wave of N_2 with no diffusional broadening. Integration of this square wave is easily and accurately accomplished, thus rendering the method as particularly apt for copper metal area determination. It is the self-regulating and *in situ* aspects of the technique which render its utility and which distinguish it from the earlier static high-vacuum methods of Dell, Stone and Tiley [13] and of Scholten and Konvalinka [14].

In hydrogen reactive frontal chromatography, the Cu/Al_2O_3 catalyst is first reduced by temperature programming in a H_2/He stream (5% H_2, 1 bar, 25 $cm^3\,min^{-1}$), from ambient to 513 K at 1 $K\,min^{-1}$ and holding the temperature at that value under the flowing H_2/He stream for 16 h. The temperature is then lowered to ambient under the H_2/He stream, the flow is switched to He (25 $cm^3\,min^{-1}$) and the surface hydrogen is desorbed by temperature programming from ambient to 500 K. The temperature is then lowered to the derived adsorption temperature under the He stream and the flow is then switched to the H_2/He stream (5% H_2, 1 bar, 25 $cm^3\,min^{-1}$). The amount of hydrogen then adsorbing is determined by monitoring the hydrogen frontal line shape on the mass spectrometer. Since, by definition, the sticking probability is the amount adsorbed per collision, then the experimental conditions must preclude desorption and re-adsorption which would result in an equilibrium measurement of the heat of adsorption. The experiments must be carried out at temperatures below the desorption peak maximum and with a short plug of catalyst (ideally one theoretical plate) to minimise second collisions. The hydrogen reactive frontal chromatograms so obtained for the adsorption temperatures 213, 233, 253 and 273 K are shown in figure 1.

3. Results and discussion

If we consider the frontal line shape at 273 K in figure 1, the total amount of hydrogen adsorbed at any time t is the integrated difference between line shape obtained and the rectangular line shape corresponding to no adsorption. This area is shown hatched in figure 1. The ambient pressure producing this hydrogen atom coverage is the average of the inlet and exit pressures. This implicitly assumes a linear decrease in pressure along the 2 cm packed length of the reactor, an assumption which is justified on the basis that single-crystal copper studies have shown hydrogen adsorption to be activated, resulting in extremely low values for the sticking probability ($\sim 10^{-11}$) [1–9]. There will therefore not be a step change in the hydrogen pressure at the front of the reactor bed.

The fractional hydrogen atom coverage of the copper component of the Cu/Al_2O_3 catalyst at 253 and 273 K as a function of the ambient pressure, obtained by this technique, is shown in figure 2 (the fractional coverage is obtained by taking the surface copper atom density to be 1.4×10^{15} $atom\,cm^{-2}$ which is an average value of the low-index faces of copper [12]). The uptake/pressure curve shown in figure 2 is quite different from the normal concave shape of uptake as a function of pressure observed in the Langmuir type or heteroenergetic Langmuir adsorption isotherms. The difference is that the measurement made

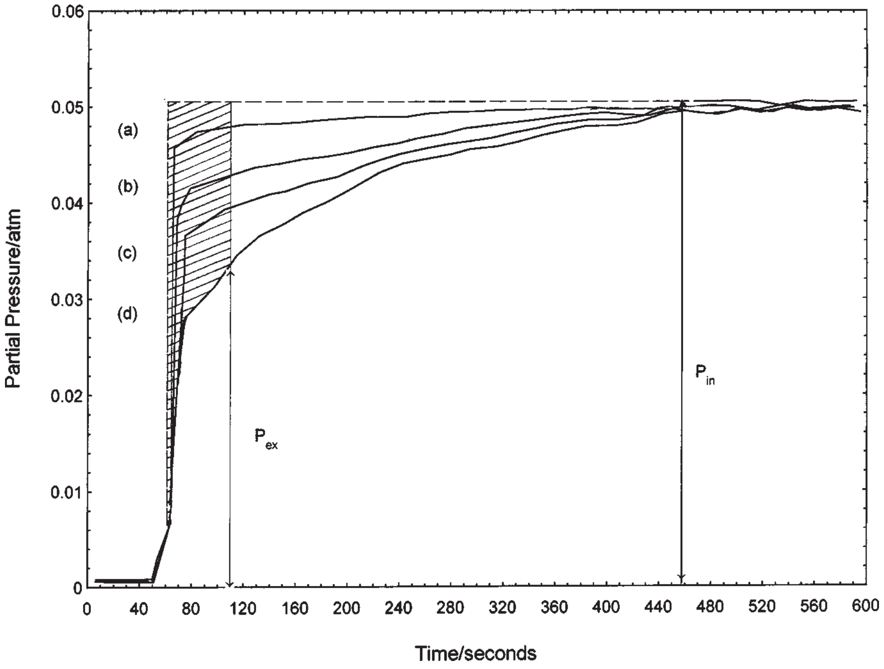

Figure 1. The time-dependent hydrogen pressure change during the adsorption on Cu/Al_2O_3 at 213 (a), 233 (b), 253 (c), and 273 K (d) by reactive frontal chromatography.

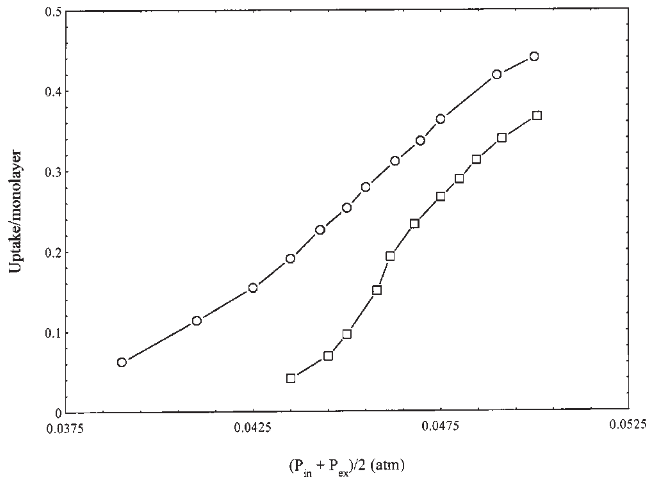

Figure 2. Hydrogen uptake as a function of pressure on Cu/Al_2O_3 at 253 (□) and 273 K (○).

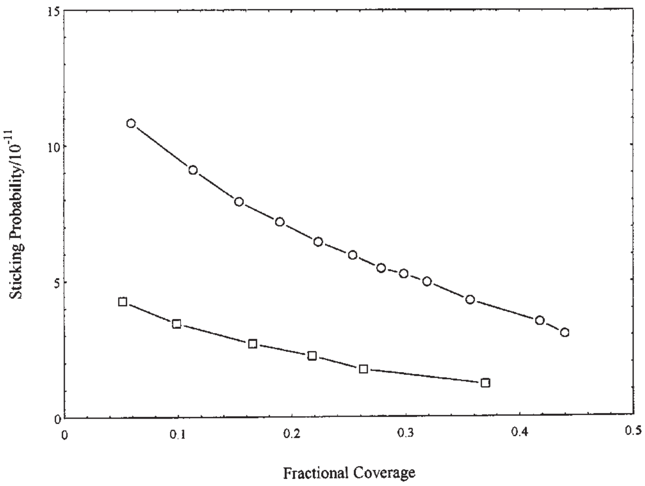

Figure 3. Sticking probability of hydrogen on Cu/Al_2O_3 at 253 (□) and 273 K (○) as a function of hydrogen coverage.

here is a kinetic one and not the equilibrium one associated with adsorption isotherms. It would be impossible to measure the sticking probability in an equilibrium experiment.

The sticking probability at any pressure is obtained from figure 1. The rate of hydrogen adsorption is obtained by dividing the hydrogen coverage by the time taken to produce that coverage. The sticking probability is then obtained by dividing this rate of adsorption by the rate of collision, z, at the given pressure ($z = P/(2\pi mkT)^{1/2}$, where P is the pressure in pascal). The coverage-dependent sticking probabilities at 253 and 273 K so obtained are shown in figure 3. Extrapolation of the coverage-dependent sticking probability to zero coverage gives an initial sticking probability $S(0)$ of 1.3×10^{-10}. The values of the initial sticking probabilities obtained, at all of the temperatures studied, are listed in table 1 and shown in figure 4.

An activation energy to adsorption of 42 kJ mol^{-1} is obtained by plotting the logarithm of the initial sticking probabilities versus reciprocal temperature (figure 5). This value of the activation energy to adsorption is the same as that of Sandoval and Bell for the adsorption of hydrogen on silica-supported polycrystalline copper [11].

We have determined an overall desorption activation energy of hydrogen from Cu/Al_2O_3 of 68 kJ mol^{-1}, a value which is only 4 kJ mol^{-1} lower than that obtained by Anger

Table 1
Temperature dependence of the initial sticking probabilities, $S(0)$.

Temperature (K)	$S(0)$	Fraction of molecules in $v = 1$ state
213	8×10^{-13}	1.4×10^{-13}
233	5×10^{-12}	1.8×10^{-12}
253	5×10^{-11}	1.5×10^{-11}
273	1.3×10^{-10}	9.4×10^{-10}

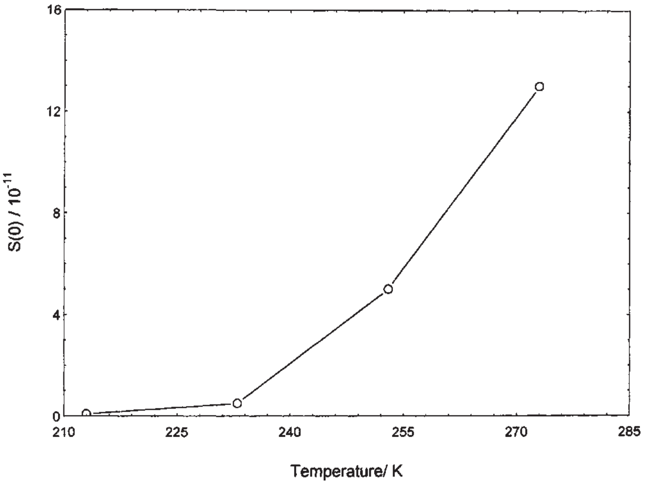

Figure 4. Initial sticking probability, $S(0)$, versus dosing temperature.

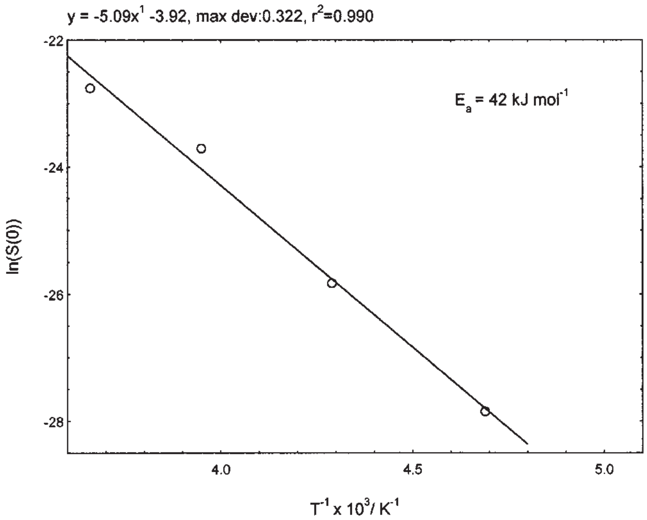

Figure 5. Plot of $\ln S(0)$ versus reciprocal temperature.

and co-workers for Cu(111) [15]. When this desorption activation energy of 68 kJ mol^{-1} is combined with adsorption activation energy of 42 kJ mol^{-1}, the heat of adsorption obtained is 26 kJ mol^{-1}. This apparently low value of the heat of adsorption is not a consequence of any inaccuracy in the method employed here for the measurement of the adsorption activation energy. Were this to have been the case and were we to have underestimated the adsorption activation energy, remembering that Campbell and Campbell have reported an adsorption activation energy of 57 kJ mol^{-1} [5], then the estimated value of the heat of adsorption would be even lower.

Additional evidence that this value is not an underestimate is to be found in a recent microkinetic analysis of the temperature dependence of the reverse water–gas shift reaction [16]. In this analysis, the overall reaction was deconvoluted into its component elementary reactions, each of which (forward and reverse) was assigned its activation energy and pre-exponential term derived from the literature. The model predicted the experimentally determined $H_{(a)}$ coverages and rates of the reverse shift reaction using a value of 38 kJ mol^{-1} for the adsorption of hydrogen and a value of 60 kJ mol^{-1} for the desorption of hydrogen (i.e., a heat of adsorption of 22 kJ mol^{-1}). Higher heats of adsorption predicted a surface which was saturated with $H_{(a)}$.

Beebe and co-workers reported a value of 48 kJ mol^{-1} for the heat of adsorption of hydrogen on polycrystalline copper [17]. The determination was made calorimetrically. However, the amount of gas adsorbed was measured volumetrically in a high-vacuum apparatus, on a large sample of copper (58 g), with no measurement of gas composition. Their report of an "autocatalytic" adsorption, i.e., the amount adsorbed increased with coverage, coupled with the large size of the copper produced in a static system by reduction of copper oxide suggests that the copper oxide was not fully reduced.

Hayden and co-workers [6–8] have shown that the origin of the activation energy for the dissociative adsorption of hydrogen on copper resides in achieving a significant population of the first vibrationally excited state. The fraction of the total number of the molecules, P_v, in a vibrationally excited state v, whose energy is ε above the ground state, is given by

$$P_v = \left(1 - \mathrm{e}^{-\varepsilon/kT}\right)\mathrm{e}^{-v\varepsilon/kT}.$$

The energy difference ε between the first vibrationally excited state ($v = 1$) of hydrogen and the ground state ($v = 0$) is $\varepsilon = 8.7 \times 10^{-20}$ J molecule^{-1}. The fractions of the total number of hydrogen molecules in the first vibrationally excited state calculated from this at 213, 233, 253 and 273 K are listed in table 1 alongside the fractions of the total number of colliding molecules which chemsorb (the sticking probabilities). Table 1 shows that at all temperatures the v sticking probability is higher than the fraction of hydrogen molecules in the $v = 1$ state, indicating that there are certain sites possibly high-index faces on the polycrystalline copper which facilitate dissociative adsorption. For Cu(110) and Cu(100), the measured adsorption activation energies are 57 and 48 kJ mol^{-1} both of which are roughly the same as the energy difference (52 kJ mol^{-1}) between the $v = 0$ and the $v = 1$ states. For the polycrystalline copper, the sticking probabilities are higher than the fractional population of the $v = 1$ state and the activation energy to adsorption (42 kJ mol^{-1}) is significantly lower than the energy gap between the $v = 0$ and $v = 1$ states.

4. Conclusions

1. The activation energy for the adsorption of hydrogen on polycrystalline copper supported on alumina has been found to be 42 kJ mol^{-1}. This value is identical to that found by Sandoval and Bell for the adsorption of hydrogen on silica-supported copper [10]. It is less than the values found in single-crystal studies for low-index faces of copper, suggesting that some more active sites for hydrogen adsorption exist on the alumina- and silica-supported copper.

2. Taken in conjunction with the previous paper which found the low-coverage desorption activation energy to be 68 kJ mol^{-1}, the heat of adsorption of hydrogen specifically on the surface of the polycrystalline copper is 26 kJ mol^{-1}.

3. Analysis of the temperature-dependent frontal uptakes is a ready method for the determination of the initial sticking probabilities and activation energies for the adsorption of hydrogen on copper and for any other similarly activated adsorption on a catalyst.

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