On the Use of Magnetic Methods for studying the Adsorption of H_2, O_2, CO, and Hydrocarbons on Supported Palladium

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Chemisorption of H_2, O_2, CO, C_2H_2, C_2H_4, and C_2H_6 on Pd–SiO_2 results in discontinuous variations in the paramagnetic susceptibility of Pd; these results indicate that magnetic methods already used with ferromagnetic catalysts may be extended in use to paramagnetic catalysts to estimate the number of metal atoms involved in chemisorption.

So far, magnetic studies related to chemisorption on supported metals have been devoted mainly to ferromagnetic catalysts.[1,2] Discontinuous variations of the susceptibility of the metal occur when H_2, CO, or hydrocarbons are chemisorbed at various temperatures and coverages; these variations may be interpreted in terms of different modes of co-ordination of the adsorbed molecule on the surface. For paramagnetic metal catalysts there is only one report by Eley and co-workers[3] which showed that the paramagnetic susceptibility of Pd powder was reduced by 6—8% on chemisorption of Me_2S.

We report that magnetic methods may be used with the paramagnetic catalyst Pd–SiO_2 to show that its behaviour is similar to that observed with Ni during chemisorption. This approach was made possible through the use of a Pd–SiO_2 sample which contains less than 8 p.p.m. of metallic Fe as determined by magnetic measurements. The catalyst (5.95% by weight of Pd) was obtained by ion-exchange on very pure silica[4] (850 m^2 g^{-1}, less than 1 p.p.m. Fe) with $Pd(NH_3)_4(OH)_2$ in a way similar to that described for the Pt catalyst.[5] After calcination under O_2 at 300 °C (5 h) and reduction with H_2 (1 atm) at 300 °C for 5 h, the size of the palladium particles varied mainly between 7 and 12 Å (a few were also observed in the range 100—200 Å). These results were confirmed by volumetric measurements (assuming $H_{ads}/Pd_S = 1$, H_{ads}/Pd_S is the ratio of adsorbed H to surface Pd).[6] The technique used for magnetic measurements on the Faraday balance has already been described.[7] Due to the small ferromagnetic contribution

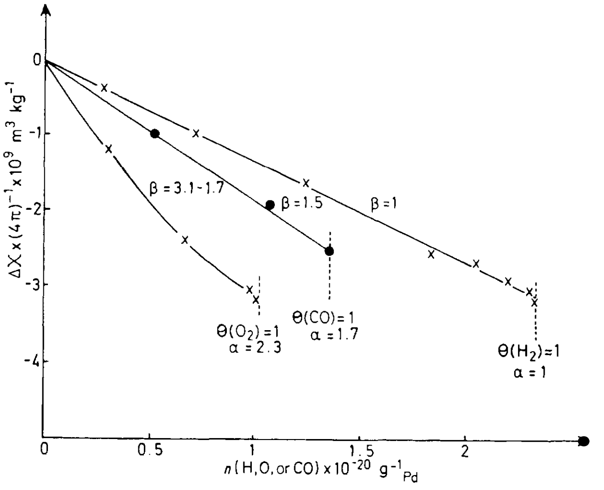


Figure 1. Decrease in the Pd susceptibility *vs.* the number (n) of H, O, and CO chemisorbed. α: Relative stoicheiometries of chemisorption assuming that one H atom is equivalent to one Pd_S atom. β: Number of Pd atoms involved in chemisorption assuming that one chemisorbed H atom cancels out the magnetism of 1 Pd atom.

of the catalyst, it was possible to measure accurately the dia- or para-magnetic susceptibility χ as a function of the amount of adsorbed gas.

The χ value of the fresh catalyst was -1.0×10^{-9} m^3 kg^{-1}. The respective contributions of the support and the palladium to this value were obtained according to Laddas *et al.*[8] who assumed that saturation with hydrogen cancels out the overall magnetism of the palladium. The values deduced from this method were -4.5×10^{-9} and $+16.7 \times 10^{-8}$ m^3 kg^{-1} respectively.

Volumetric measurements of H_2, O_2, or CO chemisorbed on $Pd–SiO_2$ indicate the following relative stoicheiometries of chemisorption [assuming $H_{ads}/Pd_S = 1$ for $P(H_2) = 5$ Torr, ref. 6] (Figure 1), $Pd_S/O = 2.3$, $Pd_S/CO = 1.7$, and $Pd_S/H = 1$. The relative decreases in magnetic susceptibility follow the same order (assuming that each H atom cancels out the magnetism of one Pd atom, ref. 8) (Figure 1), *i.e.* $Pd/O = 2.6$, $Pd/CO = 1.5$, $Pd/H = 1$. The results indicate a parallel between the number of Pd atoms involved in the chemisorption and the decrease in magnetism of the Pd.

When applied to hydrocarbons such as C_2H_6, C_2H_4, and C_2H_2, magnetic methods give the results in Figure 2. It is of note that C_2H_6 was not chemisorbed below 50 °C. From the variation in magnetic susceptibility (assuming that each H atom cancels out the magnetism of one Pd atom) in Figure 2 the following values were obtained: $\beta(Pd–C_2H_6) = 16$ at 50 °C; $\beta(Pd–C_2H_4) = 6.5$ at low coverage, and 3.3 at high coverage; $\beta(Pd–C_2H_2) = 2$ at any coverage (C_2H_4 and C_2H_2 chemisorbed at 22 °C).

For C_2H_6 it is possible that there would be a complete cracking of the molecule with formation of surface or bulk carbide and hydride (14 Pd could be involved in the chemisorption) as shown in reaction (1).

$$14\,Pd + C_2H_6 \rightarrow 2\,Pd_4C + 6\,Pd\text{–}H \qquad (1)$$

For ethylene at low coverage, the existence of at least a partially dehydrogenated species may be possible with perhaps small amounts of complete cracking. At higher coverage only 3.3 Pd atoms are involved in the chemisorption and the possible dipalladium species (**1**) is similar to that postulated at low temperatures by Gates and Kesmodel.[9]

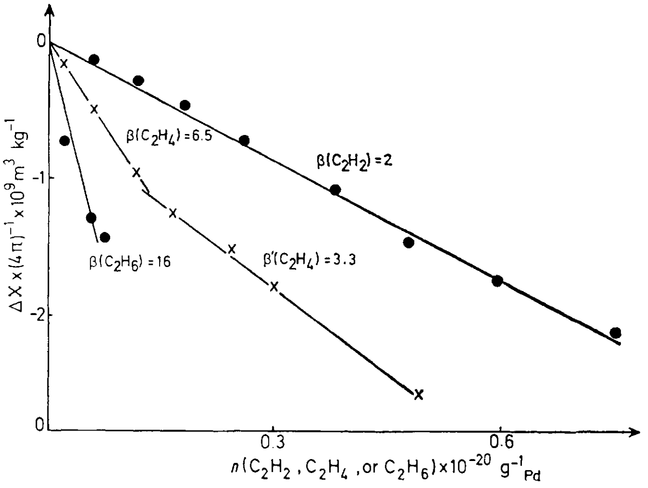
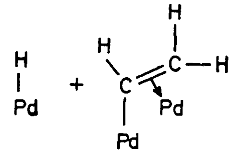
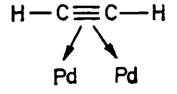


Figure 2. Decrease in the Pd susceptibility *vs.* the number (n) of C_2H_2, C_2H_4, and C_2H_6 molecules chemisorbed. β: Number of Pd atoms involved in chemisorption assuming that one H atom cancels out the magnetism of 1 Pd atom.



(1)



(2)

With acetylene a bis-π-co-ordination of the molecule could occur which would involve two Pd atoms as in (**2**).

In conclusion, our results indicate that magnetic studies on paramagnetic metal catalysts may be used to estimate the number of metal atoms involved in chemisorption on that metal's surface.

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