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Magnetic Study of CO and C_2 Hydrocarbons Adsorption on Pd/SiO_2 Catalyst

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The adsorption of H_2, CO, C_2H_2, C_2H_4, and C_2H_6 on a Pd/SiO_2 catalyst has been studied by measuring the variation of the paramagnetic susceptibility of the metal in relation to the adsorbate and its coverage. For H_2, it is assumed that each adsorbed atom cancels out the magnetization of one surface palladium atom (Pd_s). For CO, only one state of chemisorption is detected which involves 1.5 Pd_s/CO. For C_2H_6, complete breaking may occur since 16 Pd_s are concerned by the chemisorption of one molecule of C_2H_6. With C_2H_4, two species are observed. The first, at low coverage is probably dehydrogenated, the other, at high coverage, is linked with 3 or 4 Pd_s. With C_2H_2, only one species is detected, over the full range of coverage, which involves 2 Pd_s. A bi-π coordinated model, in good agreement with recent work done by electronic spectroscopies, has been proposed.

INTRODUCTION

The knowledge of the interaction between a chemisorbed molecule and a surface is essential for a better understanding of catalysis. In particular, it is necessary to determine the number of bonds between the adsorbate and the surface during chemisorption in order to get some insight on the reaction intermediates. For such a purpose, Selwood (*1*, *2*) was the first to use magnetic measurements with ferromagnetic metals. Later on, Martin and co-workers (*3–5*) have applied this method to the case of H_2 or hydrocarbons adsorption on nickel catalysts. In such a method, it is assumed that each nickel atom, which is involved in the bonding between the adsorbed molecule and the surface does not participate any more in the overall ferromagnetism of the particle. As a consequence, the number of bonds (σ or π) can be derived from the ratio of the decrease of magnetization per molecule adsorbed to the magnetic moment of one nickel atom.

The application of this method to noble metal catalysts is even more difficult. Palladium or platinum are not ferromagnetic. They exhibit a paramagnetic susceptibility which is nearly the d electrons Pauli susceptibility and can be considered proportional to the density of states at the Fermi level. In order to have a high surface/volume ratio, it is necessary to prepare very small particles of metal fixed on a support. Since the magnetism of noble metals is several orders of magnitude lower than that of ferromagnetic compounds, the magnetic contribution of the support and its ferromagnetic impurities can be much higher than that of the metal. It is therefore imperative to prepare a support which is highly pure from a magnetic point of view. Moreover, it is also possible that a support which is apparently free from ferromagnetic impurities becomes ferromagnetic after activation under H_2 in the presence of metal, e.g., we cannot exclude that traces of FeO/SiO_2 are reduced in the presence of noble metal to metallic iron. Blank experiments on the support itself may be therefore misleading. It is probably such a phenomenon which explains the very different values of magnetic susceptibility of Pd from one sample to another in the works of Reyerson and Solbakken (*6*).

In order to overcome these difficulties, it is possible to estimate the real magnetism

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of the support in the presence of Pd by the method used by Laddas *et al.* (*7*). By a simple absorption of hydrogen by palladium with formation of a palladium hydride, it is possible to cancel the magnetic susceptibility of this metal (*8*) and to obtain thus that of the support. Moreover, palladium is a metal well suitable for magnetic measurements since it exhibits the strongest paramagnetic susceptibility of the noble metals ($\chi = 5.29 \times 10^{-6}$ cgs g^{-1}).

As a consequence, we have tried in this work to extrapolate to Pd, the magnetic method already used with nickel for studying the interaction between metal catalyst and hydrogen or hydrocarbons. Such a work was made possible by the use of highly pure Pd supported on highly pure silica.

EXPERIMENTAL

Catalyst. The support is a silica aerogel obtained by hydrolysis of tetramethylsilane according to a procedure already described (*9*) which avoids pollution. It exhibits a very high surface area close to 850 m^2 g^{-1}. Pd is fixed on the support by exchange with $Pd(NH_3)_4(OH)_2$ in a similar way to that described for Pt (*10*). After drying at 393 K in an oven, the precursor complex is decomposed under flowing O_2 with a heating rate of 0.5 K min^{-1} up to 573 K. It is then reduced at 573 K under flowing H_2–He (1/5 mixture) during 5 hr. The Pd content was found equal to 6.0 ± 0.1% (w/w) with 20 ppm of Fe and less than 5 ppm of Ni and Co. Electron microscopy measurements showed small metal particles ranging between 7 and 12 Å. A few larger particles were found in the range 100–200 Å.

Gravimetric and magnetic measurements. They were carried out with a high vacuum microbalance built in the laboratory (*11*) with a sensitivity of 3 μg. The smallest pressure obtained (10^{-8} Torr, 1 Torr = 133.3 N m^{-2}) was achieved by means of an ionic pumping device. Magnetic susceptibility, χ, was measured according to the Faraday method. The force F, applied to a mass of catalyst m was determined by

$$F = m\chi\left(H\frac{\partial H}{\partial z}\right) \quad (1)$$

where H is the magnetic field (the highest value is 6060 Oe in our experimental conditions). The calibration of the field gradient along the z axis $H\partial H/\partial z$ was determined with $HgCo(SCN)_4$ ($\chi = 16.38 \times 10^{-6}$ cgs g^{-1} at 294 K).

The force contribution of the bucket itself, made of highly pure silica, was determined in a blank experiment and its value was always substracted from the total measured forces.

The sample being composed of various dia-, para-, and ferromagnetic substances (with respective susceptibilities χ_{di}, χ_{pi}, and specific magnetization σ_{fi}), the following equation could be used:

$$m\chi = \sum_i \left[m_i(\chi_{di} + \chi_{pi}) + m_i\frac{\sigma_{fi}}{H}\right] \quad (2)$$

By plotting $m\chi$ versus $1/H$, it was possible to obtain, by extrapolation to infinite field, the overall dia- and paramagnetic susceptibility. The ferromagnetic magnetization was obtained by the slope of the linear relationship.

Experimental procedure. The same sample was used for all experiments. Before each chemisorption measurement, the sample (m = 0.393 g of catalyst was reduced under H_2 (100 Torr) at 673 K for one night. It was then evacuated ($P = 10^{-8}$ Torr) at the same temperature for 5 hr. After cooling and stabilization at 294 K (or 323 K) the adsorbate was introduced by successive doses. For each increment, the equilibrium pressure, the amount of adsorbed gas and the magnetic susceptibility were measured for various values of the field. In the case of hydrogen adsorption, the pressure was limited to 1 Torr in order to prevent the palladium hydride formation which could occur at a few Torr pressure for well dispersed catalysts. Total H_2 absorption was measured at 100 Torr pressure.

RESULTS

Preliminary Experiments

Since the same sample was used, it was necessary to know if it was magnetically stable during all our experiments. We have represented on Fig. 1 the variation of magnetic susceptibility versus $1/H$ at 294 K for differently treated catalyst. The curves a_i and b_i correspond respectively to an evacuated sample and to a saturated sample with hydrogen (100 Torr), after i regeneration processes. The experimental points follow a linear relationship in agreement with Eq. (2). The slopes of this linear relationship indicate the value of the ferromagnetic contribution of the sample σ (Table 1). According to Eq. (2) and to Laddas (*7*) hypothesis, the extrapolation of b_i to infinite field leads to the diamagnetic contribution of the support (Table 1). In the same way, the extrapolation of a_i to infinite field leads to the overall magnetic contribution of the sample (Table 1). Consequently, the difference between the two extrapolated values represents the paramagnetism contribution of pure Pd. It is interesting that the extrapolated values are found identical within experimental error. The calculated susceptibility is 3.56×10^{-6} cgs g^{-1}. This value is less than that of bulk Pd, consistent with the fact that surface atoms of dispersed palladium exhibit a lower susceptibility than the bulk (*7*). The σ values increase slightly (10%) with the number of regeneration (H_2 treatment at 673 K overnight) probably due to progressive reduction of small amount of FeO. From these values, we can estimate that the amount of ferromagnetic impurity considered as Fe was nearly 7 ppm. These preliminary experiments indicate a fairly good magnetic stability of the catalyst.

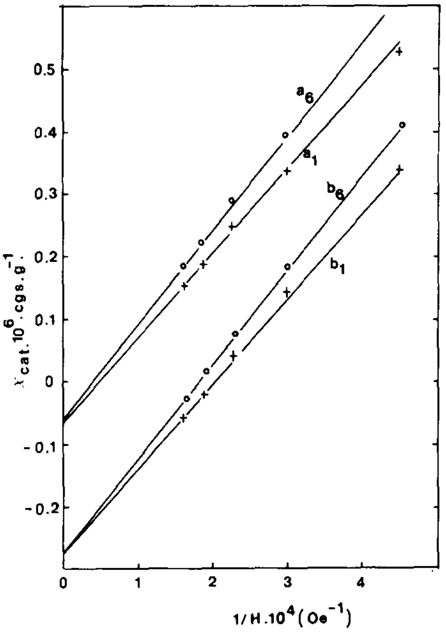


FIG. 1. Magnetic susceptibility, χ, versus reciprocal field 1/H, for a_1 and a_6, evacuated sample after respectively 1 and 6 regeneration processes. b_1 and b_6, hydrogen saturated sample, after respectively 1 and 6 regeneration processes. To obtain the susceptibilities in S.I. units (m^3 kg^{-1}) multiply the cgs values by 12.56 $\times 10^{-3}$.

Magnetic Isotherm of H_2 Adsorption

The decrease of the Pd susceptibility

TABLE 1

Ferromagnetic Impurities Magnetization and Extrapolated Magnetic Susceptibility of a Clean or H_2 Saturated Pd/SiO_2 Catalyst[a]

Catalyst state	a_1	b_1	a_3	b_3	a_6	b_6
$\sigma \times 10^3$ cgs g^{-1} cat	1.38	1.34	1.42	1.42	1.50	1.50
$\chi_\infty \times 10^6$ cgs g^{-1} cat	−0.06	−0.28	−0.06	−0.28	−0.06	−0.28

[a] a_i is referred to catalyst evacuated 5 hr at 673 K. b_i is referred to catalyst saturated with H_2 (100 Torr). i is the number of regeneration process.

($\Delta\chi$), given in Fig. 2 as a function of the amount of hydrogen adsorbed on surface palladium atoms ($P_{H_2} \leq 1$ Torr) ($T = 294$ K) is linear. The results obtained on a fresh sample as well as on regenerated samples are identical within experimental error. For $P_{H_2} > 5$–10 Torr, a change in the slope is observed, connected with the hydride formation. However the results are not reported here, since this study concerns only the surface. The linear relationship obtained between the decrease of susceptibility and the amount of adsorbed H_2 indicates that each hydrogen atom modifies the magnetic susceptibility of the Pd regardless of the coverage. It is thus possible to deduce from the slope, the variation of susceptibility of Pd per mole of chemisorbed hydrogen ($\alpha_{H_2} = 690 \times 10^{-6}$ cgs mole^{-1} or $\alpha_H = 345 \times 10^{-6}$). Assuming that each surface palladium atom Pd_s chemisorbs one hydrogen atom (*12, 13*), it is possible to calculate the number of Pd_s($n_H = n_{Pd_s} = 7 \times 10^{-3}$ atom-gram g^{-1}).

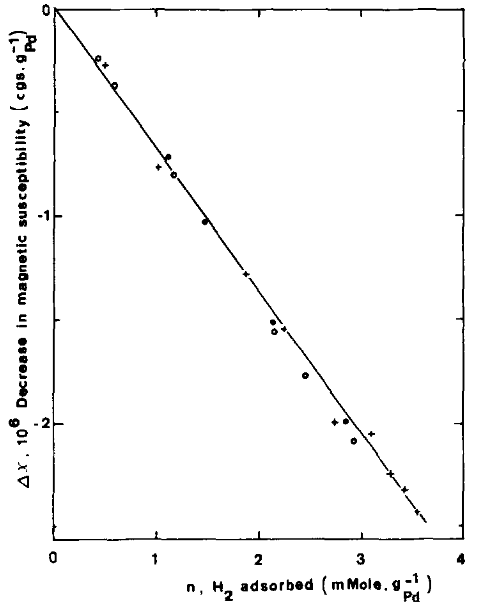


FIG. 2. Magnetic isotherm of H_2 chemisorption at 294 K after respectively 1, 3, and 6 regeneration (+, ○, ●). To obtain the susceptibilities in S.I. units (m^3 kg^{-1}) multiply the cgs values by 12.56×10^{-3}.

Magnetic Isotherms for CO, C_2H_2, C_2H_4, and C_2H_6

These isotherms (Figs. 3 and 4) have been obtained with a maximum equilibrium pressure of adsorption of 5 Torr. All the experiments were carried out at 298 K except for C_2H_6 chemisorption which could be observed only at 323 K. In all cases the decrease of the magnetic susceptibility versus the amount of gas x adsorbed exhibits one or many linear portions (slope α_x). The α_x values vary with the nature of the gas adsorbed and with coverage. For example, with C_2H_4, three slopes are obtained: $\alpha_{C_2H_4} = 2260 \times 10^{-6}$ cgs mole^{-1} at low coverage, $\alpha_{C_2H_4} = 1160 \times 10^{-6}$ cgs mole^{-1} at medium coverage, and $\alpha_{C_2H_4} = 0$ at high coverage. It is likely that a zero value for α_x corresponds to a physisorption process. By comparison of α_x with α_H, we can define a "magnetic bond number" $\mu_x = \alpha_x/\alpha_H$. Assuming that each hydrogen atom cancels out the magnetization of one palladium atom, the μ_x value represents in fact the number of palladium atoms magnetically perturbed per one molecule of gas x (Table 2). The maximum amount of chemisorbed molecules "n_x" can be deduced from the intercept between

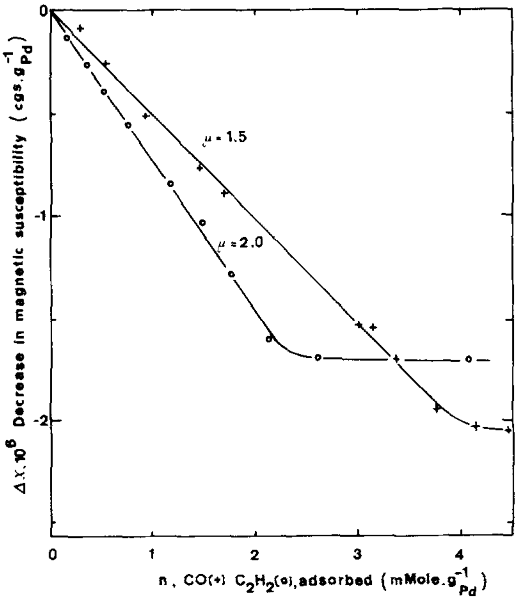


FIG. 3. Magnetic isotherms for CO and C_2H_2 adsorption at 294 K. To obtain the susceptibilities in S.I. units (m^3 kg^{-1}) multiply the cgs values by 12.56×10^{-3}.

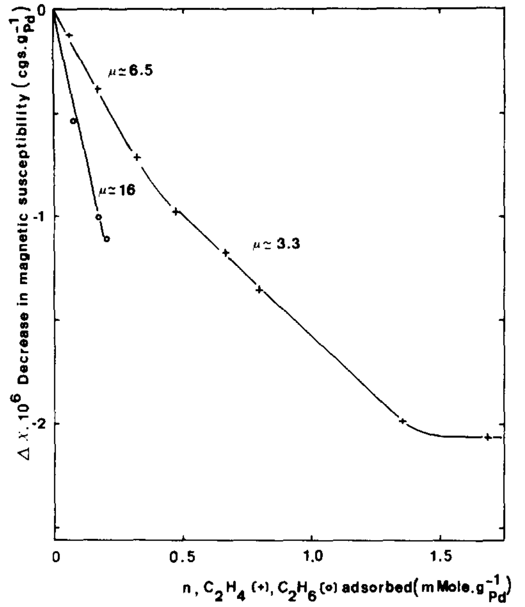


FIG. 4. Magnetic isotherms for C_2H_4 at 294 K and C_2H_6 at 323 K. To obtain the susceptibilities in S.I. units ($m^3\ kg^{-1}$) multiply the cgs values by 12.56×10^{-3}.

the $\alpha_x = 0$ and $\alpha_x \neq 0$ lines. From n_x and n_H, it is possible to calculate the average number of surface palladium atoms or "geometric bond number" γ_x involved in the chemisorption of one molecule of x: $\gamma_x = n_H/n_x$ (Table 2). We also give in Table 2 the maximum variation of magnetic susceptibility observed during the chemisorption of x: $\Delta\chi_x$.

DISCUSSION

It is necessary to recall here our starting hypothesis:

At $P_{H_2} \simeq 1$ Torr, the monolayer of adsorbed hydrogen is achieved with the stoechiometry $Pd_s/H = 1$ (12)

Each hydrogen chemisorbed on surface palladium ($P < 1$ Torr) cancels out the magnetization of one palladium atom.

During the chemisorption of any molecule x, the cancellation of the magnetization of one palladium atom corresponds to the formation of at least one σ or π bond between a fragment of the molecule and the palladium atom.

For CO, quantitative chemisorption measurements indicate a ratio Pd_s/CO: $\gamma_{CO} = 1.7$ (Table 2). There is a fairly close agreement between such result deduced from quantitative measurements and magnetic measurements: $\mu_{CO} = 1.5$. This last parameter indicates that on the average each CO

TABLE 2

Summary of Magnetic Results Obtained during the Adsorption of Various Adsorbates at 294 K

	Adsorbate x					
	H	CO	C_2H_2	C_2H_4		C_2H_6[a]
Magnetic susceptibility variation $\alpha_x \times 10^6$ cgs $mole^{-1}$	345	510	720	2260	1160	5500
Mean "magnetic bond number" μ_x	1.0	1.5	2	6.5	3.3	16
Mean "geometric bond number" γ_x	1.0	1.7	3.1	4.7		—
Maximum magnetic susceptibility variation $\Delta\chi_x \times 10^6$ cgs g^{-1} cat	0.14	0.12	0.10	0.12		—

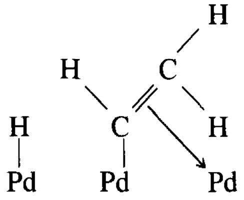
[a] Adsorption temperature = 323 K.

molecule is adsorbed on 1.5 Pd_s which is not far from the previous value (1.7). It is known from infrared data that with Pd, both linear and bridged CO are observed (*14*). This is in agreement with those values. The fact that we observe a linear decrease of magnetization versus the coverage suggests that the linear and bridged CO are in equilibrium regardless of the coverage on our catalyst.

For hydrocarbons, there is a general trend: the higher H/C ratio, the higher the μ_x value. For $x = C_2H_6$, $\mu = 16$ which seems to indicate a complete breakdown of the molecule with formation of surface carbide and chemisorbed hydrogen (14 Pd would be involved in the chemisorption process):

$$14Pd + C_2H_6 \rightarrow 2Pd_4C + 6Pd\text{-}H$$

With C_2H_4, two states of chemisorption (A and B) must be involved, corresponding to $\mu_{C_2H_4} = 6.5$. at low coverage and $\mu_{C_2H_4} = 3.3$ at higher coverage. At low coverage there would be a rather strong dehydrogenation. At higher coverage, the linear decrease suggests the presence of only one species. Since the $\Delta\chi_{C_2H_4}$ value is close to that of $\Delta\chi_H$, one must conclude that most of the surface palladium atoms are involved in the overall chemisorption process. This result seems to indicate the presence of some hydrogen atoms which can occupy the holes between chemisorbed molecules. These hydrogen atoms may arise from the first fraction of ethylene molecules chemisorbed at low coverage (species A). At higher coverage, the number of bonds is 3.3 which can be explained by models **1** and **2**.



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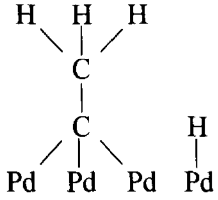

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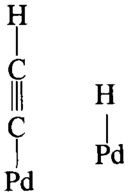
These models are in agreement with recent proposals by Kesmodel and Gates based on electron energy loss spectroscopy measurements (*15*, *16*).

With acetylene, a single and unique stoechiometry of chemisorption occurs ($\mu_{C_2H_2} = 2$). From this value, four models may be considered (**3** to **6**):



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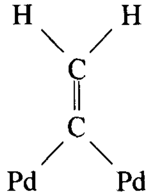

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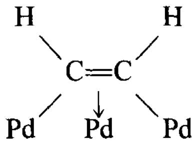

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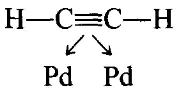

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Although we have no definite proof to make a choice between the four possibilities, recent work by Fischer and Kelemen (*17*) showed that the electron diffraction spectrum of C_2H_2 adsorbed on Pd[100] at room temperature is essentially the same as that of gaseous C_2H_2 with a slight increase of the C–C distance and with stabilization of the π orbitals. Such results are in favor of the di-π state represented in model **6**.

In conclusion, our results indicate that provided a careful approach is used, magnetic methods may be generalized to paramagnetic metal as Pd to estimate the number of metal atoms involved in a chemisorption process. Although the technique does not describe precisely the type of bonding between the surface and the chemisorbed molecule, it may be a very useful tool to estimate the number of bonds of the molecule with the surface. Obviously, this method must be used in parallel with other spectroscopic techniques to fully describe the chemisorbed state at a molecular level.

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