Fourier-Transform Infrared Study of Weak Adsorption of Hydrogen on Pt/SiO$_2$

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Infrared spectra of weakly bound hydrogen were studied between 300 and 400 K and 1 to 10^5 Pa. A Temkin-type isotherm was found, indicative of surface heterogeneity. Asymmetric infrared band shapes show that several kinds of weakly bonded hydrogen coexist on the surface, having essentially the same kind of bonding but differing slightly in bond strength. The type of interaction between adsorbed hydrogen and carbon monoxide in the surface layer is also discussed. © 1990 Academic Press, Inc.

1. INTRODUCTION

Adsorbed hydrogen plays a key role in the metal-catalyzed reactions of hydrocarbons, and therefore its characterization is of great practical and theoretical importance. However, the investigation of its structural properties is not an easy matter, as most of the surface probing experimental methods are relatively insensitive to adsorbed hydrogen (1).

On Pt surfaces, hydrogen is known to adsorb dissociatively in several different forms (2). First, a strongly bound monolayer is formed and saturation is reached at very low pressures (below ca. 10^{-4} Pa) when the coverage (expressed as H/Pt$_{surface}$ atomic ratio) equals unity. As shown by electron energy loss spectroscopy and inelastic neutron scattering experiments (3–5), this surface layer consists of H atoms coordinated to bridge sites and to trigonal or tetragonal holes; thus it is generally referred to as "multibonded" hydrogen. At higher pressures (above 10^{-2} Pa) another weakly bound form of adsorbed hydrogen appears, as detected, for example, by temperature-programmed desorption (6). In this case the adsorption is reversible, i.e., hydrogen desorbs if the gas phase is removed. This latter adsorbed form cannot be studied by electron spectroscopy since the pressure is far beyond the range where those experimental methods are applicable. However, since these pressure conditions do not exclude investigation by infrared (IR) spectroscopy, such studies of weakly bound hydrogen adsorbed on supported Pt catalysts have been reported several times (7–13). In the IR spectra two bands are generally observed. One of them appears at 2120 cm^{-1} (or at 1520 to 1530 cm^{-1} if D$_2$ is adsorbed), which, by analogy with the IR spectra of the transition metal–hydride complexes, can be unambiguously assigned to the Pt–H stretching of H atoms coordinated to one Pt atom only (commonly referred to as "on-top" hydrogen). However, opinions vary concerning the origin of another band usually present at 2080–2040 cm^{-1} as a shoulder or partly resolved from the high-frequency (2120 cm^{-1}) component. Different explanations have been reported, some regarding it as due to carbon monoxide impurity (9, 10), and others considering it as a different kind of adsorbed hydrogen (7, 8, 13). Some other aspects, e.g., the nature of H–CO interaction in the adsorbed phase, seem to deserve further consideration as well. Moreover, the Pt–H system represents the infrequent case where the properties of a metal–adsorbate bond can be directly investigated, and thus the importance of any new structural information can hardly be exaggerated.

In the present work an IR investigation of

hydrogen adsorbed on a Pt/SiO$_2$ catalyst is reported with special regard to the questions outlined above.

2. EXPERIMENTAL

A Pt/SiO$_2$ catalyst of high metal loading (Table 1) was prepared by impregnating Cab-O-Sil-HS5 silica (BET surface area 300 m^2/g) with a solution of H$_2$PtCl$_6$. The dried catalyst was pressed into a thin pellet (10 mg/cm^2), calcined in air at 720 K, and reduced in a flow (8 liters/h) of pure H$_2$ for 2 h at 620 K in the adsorption cell. The cell and vacuum system have been described elsewhere (14). Dispersion (as a ratio of surface metal atoms to total Pt atoms, Pt$_s$/Pt$_t$) was calculated from CO chemisorption data measured gravimetrically in a sartorius microbalance on catalyst samples pretreated under the same conditions. An average particle diameter (Table 1) was calculated supposing spherical particle shape and using a value of surface atomic density of 1.5 × 10^{15} atom/cm^2, which takes into account the known reconstruction of certain Pt crystal faces (20). (If the value of 1.24 × 10^{15} atom/cm^2, i.e., the average of the atomic densities of the unreconstructed low-index faces (111), (110), and (100), is used, a somewhat smaller particle size results (5.4 nm), but for the present study the difference is not significant.)

The infrared spectra were recorded by a Digilab FTS-20C spectrophotometer at a nominal resolution of 4 cm^{-1}. First, the spectrum of "pure" sample was taken, stored on the disk, and used as background later.

After completing the reduction, either samples were allowed to cool in the hydrogen atmosphere and evacuated at room temperature or the H$_2$ flow was stopped and the cell was evacuated at the reduction temperature and cooled under vacuum. In the former case, samples are believed to be covered with a monolayer of strongly bonded hydrogen (i.e., nonevacuable at 300 K), so they are "hydrogen-covered" (15). Samples treated in a manner similar to the latter are often referred to as "hydrogen-free." Nevertheless, in the present work samples cooled under vacuum were found to contain a significant amount of strongly bound hydrogen. Although the cell was not constructed for accurate volumetric measurements, a rough estimation of the adsorbed amount was possible in certain cases (i.e., when introduction of a known amount of gas to the sample resulted in a relatively large pressure drop in the cell as a result of strong adsorption). Thus it was found that samples evacuated at 620 K were still covered by ca. 0.3 monolayer of strongly bound H. In addition, experiments performed under comparable conditions resulted in identical spectra in both pretreatment cases.

Carbon monoxide is always present as a contamination in such measurements and the band of chemisorbed CO appears very close to that of adsorbed H in the spectra. From the band area the CO coverage was calculated by making use of integrated absorption intensity data published in the literature (9, 16) and was found to be less than 3% on all samples at room temperature.

3. RESULTS AND DISCUSSION

3.1. Band Structure of On-Top Hydrogen

Typical IR spectra of weakly bound H (D) are shown in Fig. 1. Upon H$_2$ adsorption a characteristic band system is seen above 2000 cm^{-1}. It consists of positive peaks at 2120 and 2065 cm^{-1} and a negative peak at 2040 cm^{-1} (Fig. 1A). Adsorption of D$_2$ (Fig. 1B) resulted in the appearance of

TABLE 1

Parameters of the Pt/SiO$_2$ Catalyst

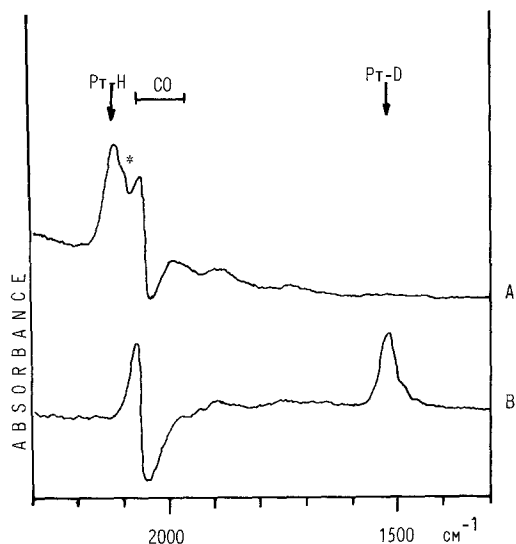|	
Metal loading	16.3% (w/w)
CO chemisorbed at 300 K	152 μg/g catalyst
Dispersion	0.21
Average particle size[a]	6.5 nm
specific surface area	7.0 m^2/g catalyst

[a] See text.

FIG. 1. IR spectra of weakly bound (A) hydrogen, (B) deuterium. Pressure: 150 Pa.

an asymmetric band at 1530 cm^{-1} and the 2120 cm^{-1} peak on the high-frequency band was missing. However, the other two components were still present and show a derivative shape which is characteristic of a band shifted to higher frequencies. Its intensity was independent of the H_2 (D_2) pressure and it did not disappear (as the 2120 or 1530 cm^{-1} band did) if the gas phase was pumped out. Hence it cannot originate from a hydrogen vibration; instead, it is clearly caused by CO, as was similarly interpreted in earlier reports (9, 10).

Both bands at 2120 and 1530 cm^{-1} are asymmetric (in the former case it is difficult to observe, but a shoulder denoted by an asterisk in Fig. 1A is clearly discernible), and thus they are composites of several overlapping components. Besides the constant intensity negative–positive pair constituting the shifted CO band of derivative shape, H_2 pressure-dependent components were found around 2100 cm^{-1} and above. These can be assigned to groups of adsorbed H atoms coordinated to Pt atoms by essentially the same type of bonding but having slightly different bond strength. The frequency and band shape remained the

same in all cases throughout the investigated pressure range, i.e., the bond strength of on-top hydrogen is independent of coverage.

It might be supposed that the more coordinatively unsaturated the Pt atom involved, the stronger is the Pt–H bond (and the higher the frequency). However, in the case of a disperse catalyst, a significant proportion of the surface is composed of edge and corner atoms, defect sites, high index faces, etc. Moreover, for Pt a possible rearrangement of the (110) and (100) faces should also be taken into account (17). Thus, after all, the nature of the adsorption site (i.e., the properties and position of those Pt atoms to which the H atoms are linked) cannot be deduced unequivocally from these measurements. Reflection measurements performed on well-defined single crystal surfaces would be very helpful in solving this problem.

3.2. Pressure Dependence of the Adsorbed Amount

The IR band of on-top hydrogen is discernible at adsorbate pressures higher than ca. 1 Pa. However, because of the presence of the relatively strong CO band, a higher pressure was necessary for accurate band area calculations. Therefore the adsorption isotherm was measured between 10 and 10⁵ Pa.

The pressure-dependent part of the band area (which is proportional to the adsorbed amount, see below) is linearly related to the logarithm of the H_2 pressure (Fig. 2); i.e., a Temkin isotherm (18) is found, indicating surface heterogeneity. No saturation occurred until 10⁵ Pa. This is in accordance with the results of adsorption studies performed on Pt-black (15). On the other hand, a dissociative Langmuir isotherm was observed on Pt/Al₂O₃ (11). A possible reason for this discrepancy may be a more homogeneous surface or a stronger metal–support interaction in the latter case. Obviously, the absolute value of the adsorbed amount cannot be calculated from the band
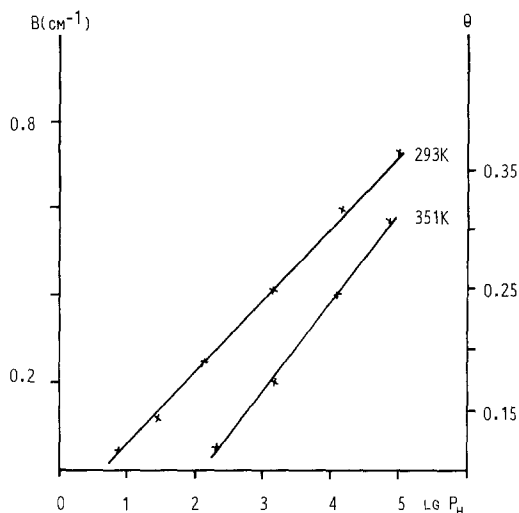
FIG. 2. Pressure dependence of the hydrogen band intensity at different temperatures. Pressure unit: Pa.

area alone. However, if the same absorption coefficient is presumed for all the three H bands and if it is also supposed that the chemisorption process on Pt/SiO$_2$ (this case) is similar to that observed on Pt-black in Ref. (15) (i.e., the coverage is the same in both cases at the same pressure), then further semiquantitative comparisons can be made with earlier reports. The total hydrogen coverage (θ') is related with on-top hydrogen coverage (θ) as

$$\theta' = 1 + \theta \quad (1)$$

Furthermore, the band area (B) is related to on-top hydrogen coverage by

$$\theta = \frac{n_H}{n_S} = \frac{2.303\,B}{An_S}, \quad (2)$$

where n_H is the number of adsorbed H atoms, n_S is the number of surface Pt atoms, and A is the integrated absorption intensity of on-top hydrogen. Taking θ values from Ref. (15) (approximately 0.1–0.4 at pressures 1–10^5 Pa) and substituting B, A can be calculated and gives 1.6 × 10^6 mol^{-1} cm, in good accordance with the value reported in Ref. 9 (0.9 − 3 × 10^6 mol^{-1} cm).

Band intensities drastically decreased with increasing temperature and practically no weakly bound H is observed in the spectra above ca. 400 K. It is seen in Fig. 2 that the slope is increasing with the temperature as is expected for Temkin isotherms. Making use of the Clausius–Clapeyron equation the isosteric heats (q_{st}) of adsorption can be approximately calculated from the two isotherms depicted. At coverage 0.15 and 0.3, q_{st} values of 40 and 25 kJ mol^{-1} were found, respectively, in fair accordance with those values published in Ref. (15) (54 and 23 kJ mol^{-1}, respectively).

3.3. Interaction between Adsorbed H and CO

As shown in (Fig. 1) the vibrational frequency of adsorbed CO is increased as a result of hydrogen chemisorption. However, the shift is already observed as the first dose of H$_2$ is introduced to a "hydrogen-free" sample, i.e., when the surface is saturated by strongly bound H prior to the appearance of the weakly bonded hydrogen and the CO frequency is not altered by further increase in H$_2$ pressure. Consequently the shift is not induced by on-top hydrogen; instead, the interaction occurs between multicoordinated H and CO bonded to the same Pt atom (Fig. 3A). H atoms of strong electron–acceptor character (i.e., hydride) would produce a larger shift to higher frequencies as a result of the strongly decreased back-donation to the CO antibonding orbital. On the other hand, electron-donor H atoms would cause a decrease in the CO frequency by promoting back-donation. Therefore, the observed relatively small upward shift (24 cm^{-1}) implies a weakly polar Pt → H bond for the interacting multibonded hydrogen in accordance with other results (e.g., work function measurements (19)).

In contrast to the present case (where the CO coverage is low) the weakly bound H was reported to effect a shift of the CO band to lower wavenumbers at high CO coverages (7), indicating that other types of interaction became dominating. The decrease in CO frequency in such cases can
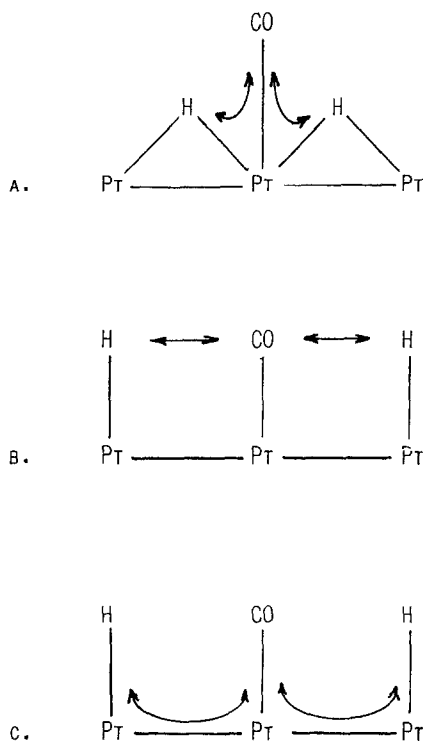
FIG. 3. Possible interactions between adsorbed hydrogen and CO.

be explained (*19*) by nonbonding interactions (dipole coupling or overlap of molecular orbitals between adjacent molecules) or by long-range forces through the metal (supposing a delocalized bond for chemisorbed molecules); see interactions B and C in Fig. 3, respectively.

4. CONCLUSIONS

Analysis of the IR band of weakly bound hydrogen reveals that H atoms are situated at several different surface sites when adsorbed on Pt/SiO₂. All types of Pt–H bonds are similar, differing only slightly in bond strength. The observed Temkin isotherm implies surface heterogeneity. If hydrogen is coadsorbed with a small amount of carbon monoxide, interaction occurs between CO molecules and strongly bound H atoms but the CO bond strength (and the CO vibrational frequency) is not affected by weak hydrogen adsorption. Thermodynamic and

spectroscopic parameters calculated from band intensities agree well with the results of other measurements.

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