

NOTES

Metal-Support Interactions on Palladium Catalysts as Probed by Raman Spectroscopy

Palladium has been observed to exhibit Surface-Enhanced Raman Spectroscopy (SERS). This effect is seen to be critically dependent upon the availability of chemisorbed hydrogen. The dependence of the SERS effect on hydrogen manifests itself in the appearance of a pronounced support effect on the intensity of the Raman spectrum of adsorbed molecules. © 1986 Academic Press, Inc.

INTRODUCTION

The solubility of hydrogen in palladium is well documented (1). Less well known to chemists is the "pseudo-silver" hypothesis proposed by metallurgists (2) to rationalize some of the physical properties of the β -phase of Pd/H alloy. An elegant piece of work by Fleischmann *et al.* (3) illustrated that hydrogen-saturated palladium electrodes, but not simple Pd electrodes, served admirably as substrates for enhanced Raman spectroscopy. They showed that Raman enhancement was present for the historically important, but relatively chemically inert adsorbate pyridine. A topic of more general interest is the study of adsorbates and surfaces which undergo real surface chemistry.

The nature of the enhanced Raman effect is poorly enough understood that the existence of an enhancement on a biased, immersed electrode is not sufficient to indicate that Raman enhancement will occur on a bare metal surface, such as those which display gas-surface chemistry. If an enhancement occurs, then one has an incisive probe of surface structure under conditions which are useful chemically. Yields and selectivities of catalytic processes are sufficiently sensitive to small changes in reaction conditions that such a probe would be quite desirable.

Palladium is widely used as a heterogeneous catalyst, and particularly for heterogeneous hydrogenation. For this reason,

we have chosen to study simple unsaturated hydrocarbon adsorbates. Actual catalytic hydrogenations are almost always performed on dispersed metal catalysts and under a partial pressure of hydrogen. It is therefore of extreme practical interest to know if the enhancement of the surface Raman signal seen on PdH electrode surfaces also exists on supported palladium.

We have measured the surface Raman spectrum of acetylene chemisorbed onto palladium which has been supported on both α -alumina and SiO_2 , two oxides which are believed to vary appreciably in their Lewis acidity (4) and in their participation in the hydrogen spillover phenomenon (5, 6). This availability of hydrogen to the metal surface will be shown to play a role in the SERS effect on the supported metal, and suggests new methods for probing surface chemistry on supported metals.

EXPERIMENTAL

Supported palladium samples were prepared according to the prescription of Yang and Garland (7). The palladium content was 10% by weight of metal. Both aluminum oxide, Linde high-purity abrasive ($r < 1 \mu\text{m}$), and silicon dioxide, Baker reagent grade (60-200 mesh), were boiled in 30% H_2O_2 for 2 h and then oven-dried before introduction of the metal. The impregnation was effected by dissolution of the appropriate amount of palladium chloride (59.98% Pd, Aesar) in water and creation of a slurry by the addition of the support material. This

was followed by removal of the water on a rotary evaporator. The slurry was then reconstituted with acetone (Fisher spectroscopic grade) and sprayed onto a warm CaF_2 window. The sample was quickly removed from the heat source and introduced into the spectroscopic cell. The B.E.T. surface area of the α -alumina was $76 \text{ m}^2/\text{g}$, and at 10% loading, this corresponds to a metal coverage of 0.5–1.0 monolayer. Reduction of the PdCl_2 to Pd metal occurred under 100 Torr of H_2 gas, Matheson research grade 99.9995%, at $150\text{--}170^\circ\text{C}$. After reduction the cell was pumped to its base pressure (5×10^{-7} Torr) and left to bake at the reduction temperature for a minimum of 8 h, then cooled before introduction of hydrocarbon to the cell. The adsorbate in these experiments was deuterioacetylene, Merck, Sharpe & Dohme 99% D, and it was used without further purification. The reductions and spectroscopic measurements were performed in a combination reactor and high-vacuum cell. The C_2D_2 was added to the cell without added hydrogen. Evacuation was accomplished with sorption and ion pumping in order to exclude stray hydrocarbon contamination. The Raman spectra were collected on a spectrometer of conventional type and are reported relative to the 488.0-nm line of an Ar^+ laser.

RESULTS

There has been considerable discussion of the role that surface roughness plays in the mechanism of the enhanced Raman effect (8). The experimental observation is that it seems to be a requisite for production of an intense Raman signal (9). The need for roughness is evidenced in the necessity of carefully preparing the electrode surface (3). This detail is unnecessary in the study of supported metal crystallites as they are by their nature rough on the microscopic scale (10). This innate roughness has been exploited in the study of supported rhodium catalysts (11–13), so there is reason to believe that a signal may be observed on supported palladium as well.

Figure 1A shows the Raman spectrum of $\text{C}_2\text{D}_2/\text{Pd}/\text{Al}_2\text{O}_3$. It is essentially like that observed for this hydrocarbon on $\text{Rh}/\text{Al}_2\text{O}_3$ (12) and shows strong bands at 1410 and 851 cm^{-1} assigned to C—C stretching and C—D bending vibrations, respectively, in $\sigma_2\pi\text{-C}_2\text{D}_2(\text{ads})$. It demonstrates as well a dramatic increase in adsorbate scattering intensity relative to the same catalyst system on silica (Fig. 1B). This result strongly implies the operation of a strong metal–support interaction on alumina. Figure 1C shows the Raman spectrum of C_2D_2 chemisorbed onto a more hydrogen-rich Pd/SiO_2 crystallite prepared by allowing freshly reduced Pd/SiO_2 to cool under 100 Torr hydrogen pressure and then evacuating to the base pressure at 120°C for only 2 h. Equiva-

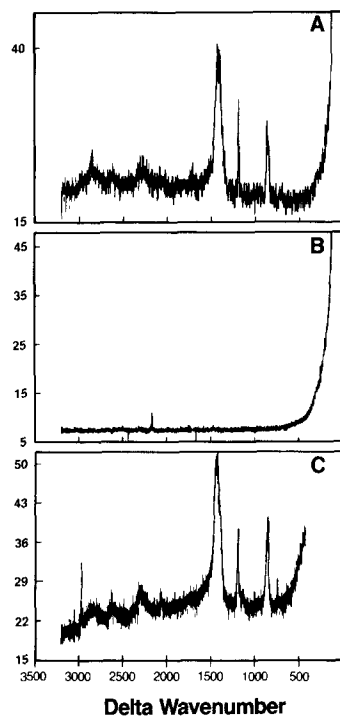


FIG. 1. Raman spectra of C_2D_2 on supported palladium, pressure approximately 50 Torr, laser line 4880 \AA , laser power 200 mW. (A) is 10% $\text{Pd}/\text{Al}_2\text{O}_3$, (B) is 10% Pd/SiO_2 , and (C) is the spectrum over a hydrogen-rich 10% Pd/SiO_2 sample. Starred bands are combination bands. The band marked with a plus is believed due to a C_2HD impurity (14).

lent results were obtained in an experiment where evacuation to base pressure was performed at room temperature. The spectrum of the adsorbate on this hydrogen-rich crystallite is much more intense than on the normal Pd/SiO₂ crystallite, and is of roughly comparable intensity with that seen on the Pd/Al₂O₃ catalyst (Fig. 1A). Under partial pressures of hydrogen the intensity of the adsorbate Raman spectrum increases by approximately a factor of 100 regardless of the support material and spectroscopic evidence of chemical reaction is observed (14).

DISCUSSION

Both the pseudo-silver hypothesis and Fig. 1C implicate hydrogen as an important determinant of SERS intensity on supported palladium. The pseudo-silver hypothesis (15, 16) links palladium hydrogen sites with the change in magnetic susceptibility of Pd metal. It is believed (2) that atomic hydrogen migrates to defect sites in the Pd lattice and donates its electron to the partially filled *d* band of the metal. Palladium metal has been calculated to have 0.4 holes/Pd atom in its *d* band (2), and the β -phase of the Pd/H alloy has the stoichiometry PdH_{0.4}. These extra electrons fill the *d* band and thus impart "free electron-like" character to the electronic properties of this alloy phase. The very large enhancement observed for Pd/SiO₂ may be rationalized by noting that under the experimental conditions, alumina, but not silica, is expected to participate effectively in the hydrogen spillover phenomenon (5, 6). This spilled over atomic hydrogen is then much more difficult to remove from the vacuum chamber. It has been guessed that this spilled over hydrogen may back-migrate to the metal crystallite and be available for chemical reactions catalyzed by metal particles. In this instance the back-migrated hydrogen is unavailable for chemistry, but is capable of affecting the electronic properties of the particle. The enhancement of the Raman signal is clearly evidence of a strong metal-support interaction and these experi-

ments imply that the effect is due to back-migration of hydrogen from the support.

We consider that these results are important to the study of supported metal catalysts. Raman spectroscopy offers a potentially powerful probe of the surface chemistry which occurs on palladium supported on alumina (and potentially other acidic oxides). It is particularly useful in systems in which hydrogen is one of the reactants because of the unusually intense, surface specific Raman signals obtainable in the presence of interstitial hydrogen.

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