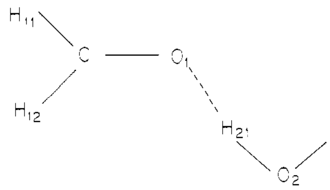

Figure 1. Labeling of atoms in H_2CO-H_2O.

Table I. H_2CO-H_2O and Component Geometries[a]

	X(^{1}A')	A(^{1}A'')
$r(CO_1)$	1.188 (1.184)	1.358 (1.351)
$r(CH_{11})$	1.104 (1.104)	1.079 (1.081)
$r(CH_{12})$	1.104 (1.104)	1.079 (1.081)
$\angle(H_{11}CO_1)$	121.6 (122.1)	116.6 (118.8)
$\angle(H_{11}CH_{12})$	116.6 (115.8)	126.8 (122.4)
$r(O_2H_{21})$	0.958 (0.950)	0.951 (0.950)
$r(O_2H_{22})$	0.951 (0.950)	0.949 (0.950)
$\angle(H_{21}OH_{22})$	102.5 (105.4)	105.9 (105.4)
$r(O_1H_{21})$	1.898	2.143
$\angle(CO_1H_{21})$	116.4	166.6
$\angle(CO_1O_2)$	116.7	165.6
E_H, kcal/mol	2.9	1.9

[a] Component geometries in parentheses. Distances in Å, angles in degrees.

Table II. $n-\pi^*$ Excitation Energies (eV)

	$\Delta E_{vertical}$	$\Delta E_{adiabatic}$ (T_e)
H_2CO	3.42 (3.50)[a]	2.52
H_2CO-H_2O	3.57	2.57

[a] Experiment (ref 13).

angles by Iwata and Morokuma.[5] Unlike the conclusion of Del Bene[4] that there is no excited-state hydrogen bond near the *ground*-state geometry, the variation of energy with $r(O_1H_{21})$ at $CO_1H_{21} = 120°$ is not purely repulsive[4] but gives a weak (~0.5 kcal/mol) bond at larger (~2 Å) r values, as could be inferred from the work of Iwata and Morokuma.[5]

Changes induced in the internal geometry of solute and solvent are generally small (Table I). Exceptions are the closing of the water HOH angle in the $\tilde{X}(^1A')$ state and the very large increase in $H_{11}CH_{12}$ in the $\tilde{A}(^1A'')$ state. Clearly, such changes in the r_e geometries will, as a result of the Franck–Condon principle,[2,12] alter the vibrational band structure of the $n-\pi^*$ transition relative to the non-hydrogen-bonded case. It may be noted that the prediction of Beecham et al. that $r(CO_1)$ in the excited state is considerably increased on hydrogen bonding is not substantiated in this study.

Vertical and adiabatic (T_e) $n-\pi^*$ transition energies are given in Table II. While a vertical blue shift is indeed observed, it is evident that little of it arises from a change in T_e. The major component of the blue shift arises from the changes induced in the component molecule geometries by hydrogen bonding. Naturally, studies such as those of ref 4 and 5, in which component geometries are held frozen, may predict a blue shift but cannot provide information on its origins. On the other hand, given that the solute excited state can sustain a strong hydrogen bond and given the "Franck–Condon" origins of the blue shift, it is not justifiable to identify experimentally determined blue shifts with hydrogen-bond energies.[2]

A study of nonplanar geometries, together with a more extensive discussion of the planar results (including basis set comparisons) will be given in a forthcoming publication.

Acknowledgment. I am grateful to A. C. Hurley and the late A. F. Beecham for helpful discussions.

Registry No. H_2CO, 50-00-0; H_2O, 7732-18-5.

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Effect of Particle Size on the Activity of Supported Palladium Catalysts

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We have performed experiments on the kinetics of the H_2-D_2 exchange reaction in the presence of a Pd/C model catalyst. Our results reveal that the phenomenological activation energy for this reaction increases with a decrease in the average palladium particle size.

Many experiments have been carried out in order to study the effect of particle size in supported metal catalysts prepared by impregnation or precipitation.[1] However, such preparation methods make it difficult to observe fine metal particles, to prepare clean metal surfaces, and to characterize the surface of the catalyst particles by electron spectroscopy. These difficulties may be substantially overcome by using a model catalyst, consisting of metal particles evaporated onto a carbon film within an ultra-high-vacuum system.[2-8] For example, Doering and co-workers[7,8] were able to examine the effect of particle size on the chemisorption and desorption kinetics of carbon monoxide by Pd/mica and Ni/mica model catalysts. These workers found a dramatic decrease in the rate of carbon formation, as the average particle size decreased.

In the present study we investigated the effect of particle size in a Pd/C model catalyst on the kinetics of the H_2-D_2 exchange reaction. This study is the first to be carried out with a model catalyst prepared in situ in an ultra-high-vacuum system (UHV) and to use X-ray photoelectron spectroscopy to characterize the electronic energy levels within the palladium particles. Experiments were carried out by vacuum-depositing palladium particles on a carbon film of ~10 nm thickness, supported by a mica sheet. A two-chamber UHV apparatus permitted us to prepare the catalyst in one chamber and transfer it to a second reaction chamber without exposure to air. Both chambers of the vacuum system were bakeable at 200 °C and achieved background pressures of 10^{-9} torr. The sample preparation chamber was equipped with a metal evaporator and a quartz thickness monitor (Anelva, EVM-32 B). The reaction chamber, separated from the separation chamber by a greaseless stopcock, was equipped with a quadrupole mass spectrometer and a variable leak valve for introducing gas. The average size of the palladium particles was determined for each sample subsequent to the kinetics experiments, by removing the catalyst sample from the vacuum system and examining it with a transmission electron microscope (JEOL JEM-200 CX). Figure 1 shows a typical electron micrograph of this catalyst, in which one can see palladium particles ranging in size from the observation limit of 0.6 nm to approximately 2 nm. The surface area of the model catalyst system was always 10 × 10 mm or smaller.

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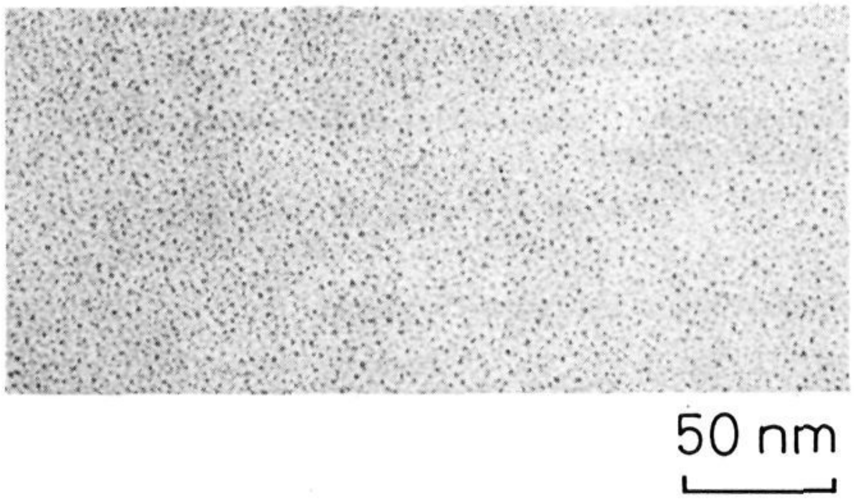

Figure 1. Electron micrograph of a Pd/C model catalyst. The amount of the incident palladium atoms measured by the quartz thickness monitor was 1.6×10^{15} atoms cm^{-2}. The mean diameter of palladium particles, $\bar{d}$, is 1.2 nm; bright field.

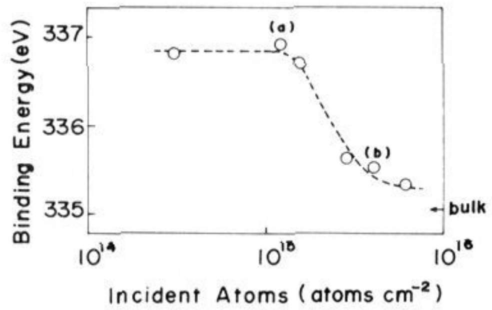

Figure 2. Binding energy of the peak energy of Pd $3d_{5/2}$ level of the Pd/C model catalyst system measured by XPS. The mean diameter of palladium particles, $\bar{d}$, is (a) 1.0 nm and (b) 1.8 nm.

The mean diameter of the palladium particles, $\bar{d}$, was controlled by varying the total amount of palladium deposited. The average particle size determined by electron microscopy was found to correlate with electronic energy levels of the particles as determined by X-ray photoelectron spectroscopy (VG, EXCA-3 Spectrometer, Mg Kα). In Figure 2 we show the binding energy of the $3d_{5/2}$ electrons as a function of the number of palladium atoms per unit area deposited. In the range 10^{15}–10^{16} atoms cm^{-2}, the binding energy decreases rapidly and approaches that of bulk palladium. The energy of the valence band in the palladium particles is thought to shift with that of the $3d_{5/2}$ band.[4] It is not known whether this energy shift originates in the interaction between the metal particles in the support or is a property of the metal particles themselves. Tauster et. al.[9] have recently described alterations in the electronic structure of small metal particles that are attributable to strong metal–support interactions.

Rates of the H_2–D_2 exchange reaction were measured over a temperature range of 0–30 °C, in the presence of H_2 and D_2 pressures of 2.8×10^{-2} torr. The reaction chamber volume was 166 cm^3. Attempts to determine the specific activity of the catalyst are hampered by difficulty in estimating the surface area. If a hemisphere model is used to estimate the surface area, the specific activity appears to exhibit a maximum at a particle size of $\bar{d}$ = 1.3 nm at a rate of $k_m = 3 \times 10^{17}$ molecules cm^{-2} s^{-1}. At higher and lower average particle size, specific activities estimated from the hemisphere model decline by a factor of about 3 from the maximum value. Further studies of the meaning of this activity maximum are in progress. The principal result of our studies so far concerns the variation of the activation energy for the catalyzed reaction, which is not affected by problems in determining the surface area of the catalyst. In Figure 3, we show the phenomenological activation energy, as a function of mean particle diameter in the range from 1–2 nm. This is the same range of average particle size in which the $3d_{5/2}$ energy level of palladium was observed to shift by about 1.5 eV. As the average particle diameter increases in this range, the activation energy for the catalyzed exchange reaction declines from about 50 kJ mol^{-1} at $\bar{d}$ = 1.1 nm to 20 kJ mol^{-1} at $\bar{d}$ = 1.8 nm. We postulate that as the particle size decreases and the binding energy of the core and valence electrons within the palladium particles increases, the adsorption energy of hydrogen on the palladium particles decreases. If this is the case, then the increase in the apparent activation energy for the H_2–D_2 exchange reaction with decreasing particle size is likely to be caused by a decrease in the rate of dissociation of the adsorbed hydrogen.

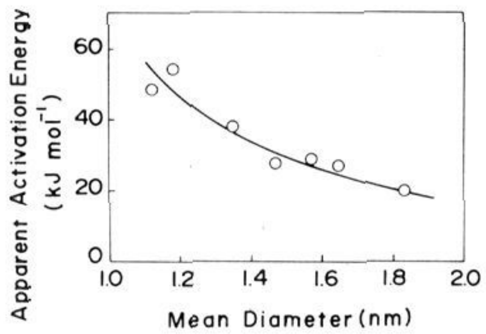

Figure 3. Apparent activation energy for the H_2–D_2 exchange reaction, catalyzed by the Pd/C model catalyst, as a function of mean palladium particle diameter $\bar{d}$. The temperature range was 0–30 °C.

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Registry No. Palladium, 7440-05-3; carbon, 7440-44-0; hydrogen, 1333-74-0; deuterium, 7782-39-0.

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Asymmetric Induction in Reactions Employing Enolates Generated from Cyclic Organo Transition-Metal Acyl Complexes

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Organo transition-metal acyls comprise a ubiquitous class of complexes made easily by acylation at nucleophilic metal centers, migratory insertion in alkylcarbonylmetal complexes, or attack by nucleophilic carbon reagents at metal-bound CO.[1] Because of the electron-donating properties of the low-valent metal centers in acylmetal complexes, they can be viewed as close relatives of ketones or esters. This analogy has been utilized in developing much of their chemistry (especially reduction and alkylation[2]). However, one esterlike property that should be characteristic of acyls—the ability to activate α hydrogens toward reaction with basic reagents, leading to alkali metal salts of enolate anions (eq

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