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Deuterium Nuclear Magnetic Resonance Characterization of Particle Size Effect in Supported Rhodium Catalysts

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Deuterium adsorbed onto Rh particles of various sizes (1.1–9 nm) supported on Al_2O_3 was studied by ^2H NMR spectroscopy. Near zero overpressure of D_2, δD shifts downfield with increasing size of particles, approaching a limiting value ca. −120 ppm when particle size exceeds 2 nm. The dependence of δD on particle size of the odd-electron metal Rh($4d^7$) is opposite to the dependence observed for the even-electron metal Pt($5d^8$) which we have also investigated. δD also shifts downfield upon increased overpressure of D_2. All these variations of chemical shifts can be satisfactorily accounted for by considering the spin density on the metal particle. The linewidth depends on the particle size but not on the overpressure of D_2. Hence the major relaxation mechanism is not paramagnetic interaction which is responsible for the variations of δD. © 1992 Academic Press, Inc.

INTRODUCTION

The size of particles of a supported catalyst has a profound effect on the rate of a catalytic reaction. This effect shows up clearly in the most common testing reactions, namely hydrogenation (*1–4*) and hydrogenolysis (*4–8*). For some catalysts, the turnover frequencies increase up to 50-fold as the particle size decreases from a few nm to ca. 1 nm. For other catalysts, maximum turnover frequencies are found in the range of 1–6 nm depending on catalyst, substrate, and reaction conditions. The electronic structure of the catalyst is conceivably the most important factor in the particle size effect; the structural properties of the support and self-poisoning are the other important factors. The electronic properties have been studied by various spectral methods (*9–16*) and theoretical calculations (*17–30*). For example, according to IR results that when particles are small, it is relatively electron-deficient, back-donation to to adsorbed NO on Pt/Al_2O_3 is reduced. From ESCA investigation of Pt/zeolite, the binding energy increases when the particle size is reduced. This result also indicates that small particles are electron-deficient.

We sought to study the effect of particle size by comparing ^2H NMR spectra of D_2 adsorbed on metals (Rh and Pt) supported on Al_2O_3 to find the difference between even- and odd-electron metal systems. Although the metal-dependent size effect has been investigated theoretically (*29, 30*), it has been overlooked experimentally, this work can fill in this gap.

METHODS

Catalysts used in this study were prepared by the method of incipient wetness impregnation. $RhCl_3$ or $PtCl_4$ (Merck) solution was impregnated into Al_2O_3 (Merck, 160 m^2/g) or SiO_2 (M-20 Cabosil, 200 m^2/g). The metal dispersions of the samples were characterized with deuterium chemisorption according to the conventional volumetric method. Deuterium adsorption isotherms on Rh/Al_2O_3 are shown in Fig. 1. The results corrected according to the model proposed by Kip *et al.* (*31*) are collected in Table 1.

The detailed procedures of sample preparation for NMR measurement have previously been described (*32*). Deuterium NMR spectra were recorded on a Bruker MSL-200 spectrometer by free induction decay and solid echo (for low temperature

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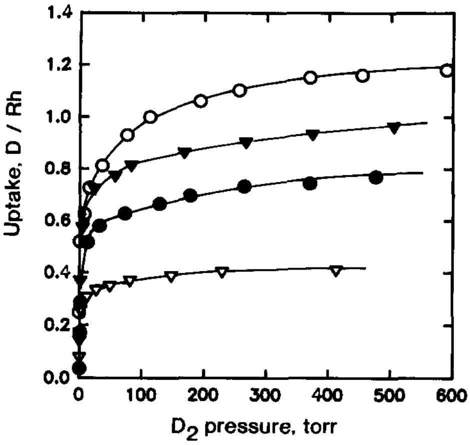

FIG. 1. Deuterium chemisorption isotherms of deuterium adsorbed on Rh/Al_2O_3 with various metal loadings; ○ is for 1.5%, ▼ is for 3%, ● for 5, and ▽ for 10% loading.

measurement) techniques with a 6 μs 90° pulse, and a 0.2 s repetition interval. The chemical shift was determined with respect to CH_3OD.

RESULTS AND DISCUSSION

When D_2 is adsorbed on a supported rhodium catalyst, three types of adsorbed species, Dr, Dm, and Dw, are identified by ^2H NMR (32). Dr is rigidly adsorbed on the Rh surface; its NMR peak is too broad to be observed, presumably because of quadrupolar relaxation. Dm is mobilely adsorbed on the Rh surface; it is detected at −120 ppm. This species is converted to Dr on decrease of temperature. Dw is weakly adsorbed on the Rh surface; it is characterized by a sharp signal ($\Delta\nu_{1/2}$ is in the range 300–700 Hz at 180 K depending on the nature of the support) at 0.0 ppm. All the dependence on overpressure of D_2 of the NMR chemical shifts and linewidths can be accounted for by this simple model. The effect of support (SiO_2, Al_2O_3, TiO_2 in non-SMSI state, NaY zeolite, and MgO) has also been found in the numbers of adsorption sites and mobilities of Dm and Dw, but not in the electronic structure of the adsorption sites (33). Al_2O_3 is an exceptional support in that both the chemical shift and the linewidth of D_2 adsorbed on Rh/Al_2O_3 are nearly independent of overpressure. Hence Dw is almost nonexistent on Rh/Al_2O_3. Besides the Dw abnormality, Rh/Al_2O_3 also exhibits a profound effect of metal loading (Fig. 2). At D_2 overpressure close to 0 Torr (1 Torr = 33.3 N m^{-2}), the chemical shifts (δD) are −200 and −180 ppm for 1.5 and 3.0% Rh loading, respectively. When the loading increases to 5 and 10%, δD remains near −120 ppm. When the D_2 overpressure increases, δD of the little loaded samples shifts downfield whereas the heavily loaded sample the chemical shift remains essentially the same. When other common supports (SiO_2, Al_2O_3, TiO_2 in non-SMSI state, NaY zeolite, and MgO) are used to prepare Rh catalysts, the ^2H NMR spectra of deuterium adsorbed on the low Rh loading (1.5 and 3.0%) catalysts are observed with difficulty, presumably because only a small amount of sample can fit into the detecting coil since these supports are fluffy. Moreover, these catalysts have a particle size greater than 2.0 nm. To prepare small Rh crystallites on these supports, it is necessary to use a low metal loading in the preparation. Consequently, deuterium adsorbed on these small particle

TABLE 1

Dispersions D of Catalysts Used in This Work

Catalysts	$D(\%)^a$	$D(\%)^b$	$d(\text{nm})^c$
5% Rh/SiO_2	46	37	2.4
10% Rh/SiO_2	10	10	9.0
1.5% Rh/Al_2O_3	112	78	1.2
3% Rh/Al_2O_3	90	68	1.3
5% Rh/Al_2O_3	60	46	2.0
10% Rh/Al_2O_3	35	29	3.1
1.5% Pt/Al_2O_3	95	86	1.1
3% Pt/Al_2O_3	80	78	1.4
5% Pt/Al_2O_3	58	58	1.6
10% Pt/Al_2O_3	20	20	4.5

[a] Obtained from deuterium chemisorption.

[b] Corrected by Kip *et al.* model (31).

[c] Mean diameter of metal particles which were calculated by $d(\text{nm}) = 0.9/D$, Where D is from ^{b}.

catalysts cannot be observed by ^2H NMR because of sensitivity limitation. The only other support which we found to exhibit a size effect similar to that of Al_2O_3 is $MgAl_2O_4$, which is dense like Al_2O_3.

The linewidths as a function of D_2 overpressure (Fig. 3) are essentially constant for all samples. But the linewidths depend on loading; the smaller the loading, the greater the linewidth. One reasonable explanation of the variations of chemical shifts of low loading catalysts as a function of D_2 overpressure is exchange of deuterium at zero overpressure and another kind of deuterium with smaller chemical shift which may exist at high D_2 overpressure. If the exchange mechanism is operative, one expects to see a bell-shaped dependence of linewidth on overpressure (*32*, *33*), unless the exchange rate is extremely fast. From the results of surface exchange between Dm and the loosely bonded Dw (*32*), the exchange rate cannot be fast enough to depart from the bell shape dependence. The deuterium adsorbed on small Rh particles is expected to be tightly held and the exchange rate not to be as fast as that between Dm and Dw. The absence of the bell-shaped linewidth dependence on overpressure (Fig. 3) leads to the conclusion that dependence of δD on overpressure is not due to exchange process.

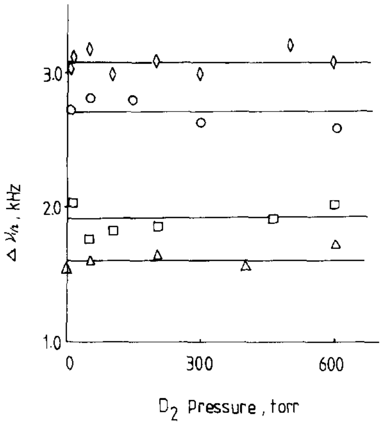

FIG. 3. ^2H NMR linewidths $\Delta\nu_{1/2}$ of deuterium adsorbed on Rh/Al_2O_3 as a function of D_2 overpressure with various Rh loadings; ◇ is for 1.5% loading, ○ for 3.0%, □ for 5.0%, △ for 10%.

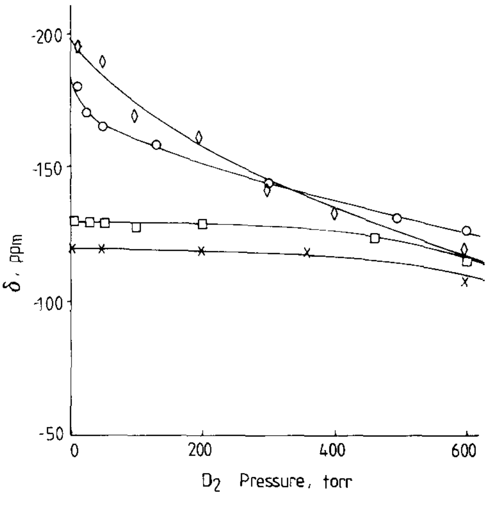

FIG. 2. Deuterium chemical shifts of deuterium adsorbed on Rh/Al_2O_3 as a function of D_2 overpressure with different Rh loadings; ◇ is for 1.5% loading (d = 1.2 nm), ○ for 3.0% (d = 1.3 nm), □ for 5.0% (d = 2.0 nm), × for 10% (d = 3.1 nm).

The temperature dependence of the ^2H NMR spectra (Fig. 4) also furnishes information on the origin of δD dependence on overpressure (Fig. 2). If there is exchange between different adsorbed species on low loading Rh/Al_2O_3, on decrease of temperature, one expects to observe line-broadening initially. On further decrease of temperature, one expects to detect line splitting into a limiting spectrum of which the individual NMR peaks of the exchanging partners are well separated. The adsorption at − 120 ppm (Fig. 4) remains at its position despite continuous broadening as with decreasing temperature. Based on comparison with the exchange between Dm and Dw, exchange in low loading Rh/Al_2O_3 is expected to be suppressed completely at 200 K. Therefore, the results in Fig. 4 strongly indicate that there is no exchange process occurring at 600 Torr D_2 overpressure, consistent with the conclusion drawn from linewidth analysis.

In Fig. 5, δD at zero pressure is plotted against particle size of Rh/Al_2O_3. δD

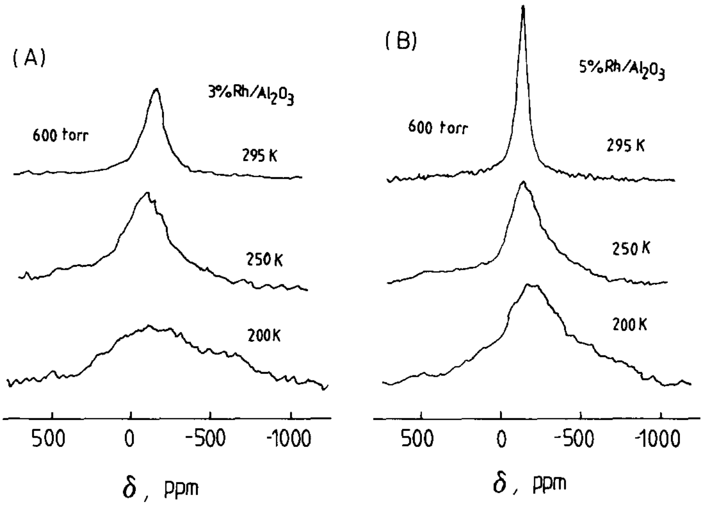

FIG. 4. ^2H NMR spectra of deuterium adsorbed on Rh/Al_2O_3 as a function of temperature at different Rh loadings, (A) 3.0% and (B) 5.0%.

changes dramatically at a particle size near 2 nm. For comparison, the chemical shift of deuterium adsorbed on Pt/Al_2O_3, which is known to exhibit a size effect (*34*), has also been investigated. δD of Pt/Al_2O_3 system also exhibits rapid change at a particle size near 2 nm (Fig. 5). However, the directions of changes are opposite for the two systems. For Rh/Al_2O_3, δD increases rapidly from -200 ppm to a steady value -120 ppm when particle size increases from 1.1 nm to over 2 nm. For Pt/Al_2O_3, δD decreases from -15 ppm and reaches a steady value around -50 ppm when the particle size increases from 1.0 nm to over 2 nm. The range of chemical shift change is much larger, 80 ppm, for Rh/Al_2O_3 than for Pt/Al_2O_3, 35 ppm. In contrast with this trend of δD vs particle size, the dependencies of δD on overpressure are in the same directions; i.e., δD shifts downfield for both systems on overpressure increase.

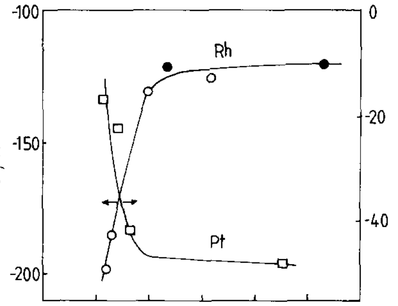

FIG. 5. Deuterium chemical shifts of deuterium adsorbed on Rh/Al_2O_3 (○), Rh/SiO_2 (●) (data from Ref. (*32*)), and Pt/Al_2O_3 (□), as a function of particle size.

An effect of particle size on chemical shift of an odd-number electron catalyst, Rh/Al_2O_3 ($4d^7$), is here observed for the first time. Two phenomena need to be explained; that δD shifts downfield but the linewidth remains unchanged with increasing overpressure, and that δD shifts downfield with increasing particle size.

To explain the dependence of δD on particle size (Fig. 2), the electronic structure of the metal particle must be considered. When the size of the metal particle exceeds 2 nm, its electronic structure is described according to the band theory (*35*); the spin density is relatively constant. Therefore, when particle size exceeds 2 nm, δD is constant, independent of particle size. When the particle size is less than 2 nm, the electronic structure approaches that of the atomic state. The binding of deuterium with the small metallic particle is expected to differ from that with the large metallic particle. Therefore, a strong dependence of δD on particle size (less than 2 nm) is expected. For Rh($4d^7$), there is unpaired electron spin in the atomic state. Therefore δD lies much upfield for a small particle. As the particle size increases, the unpair spins begin to pair to approach the band structure. This effect leads to diminished paramagnetism, and δD shifts downfield to a limiting value -120 ppm which corresponds to a large particle described completely according to the band theory. In Pt/Al_2O_3, the even electron configuration $5d^8$ should dominate the electronic structure of the small particle with almost zero paramagnetism. This effect is consistent with $\delta D = -15$ ppm for a Pt particle about 1 nm. When the Pt particle becomes larger, the band structure with paramagnetism becomes more important and δD shifts upfield as predicted. Therefore, the effect of particle size is opposite for Rh and Pt. In fact, the relationships of particle size and electronic structure have been predicted theoretically by Kubo (*29*) and Denton *et al.* (*30*).

Regarding the D_2 overpressure dependence of δD in small particle, δD is controlled by the electronic state of the Rh particle (vide supra). As the overpressure of D_2 increases, the amount of adsorbed deuterium increases (Fig. 1). In turn, the electronic structure of Rh particle is modified. When deuterium adsorbs onto the metal surface, a covalent bond with one electron from deuterium and one electron from metal is likely to form. Therefore the number of unpaired electrons in the small metallic particle decreases as more deuterium becomes adsorbed on the Rh particle. Consequently the spin density on the metallic particle is reduced as D_2 overpressure increases. This effect leads to a downfield shift of adsorbed deuterium atoms. This model of consumption of spin density (*36*) is equally applicable whether the small particle has atoms with even or odd numbers of electrons. Therefore the trend of δD vs overpressure in the small Pt system is the same as in the Rh system. This interpretation is consistent with the fact that the paramagnetic susceptibility is reduced when H_2 overpressure is increased in the small particle Pt/Al_2O_3 system (*37*).

The linewidth independence of D_2 overpressure (Fig. 4) in no way contradicts the spin density argument for the chemical shift variation. The spin density change on deuterium for a chemical shift range 80 ppm is near the absolute value of the spin density on the adsorbed deuterium. Therefore the results on linewidth independent of overpressure indicate that the paramagnetic relaxation mechanism makes no important contribution to the deuterium linewidth. The negligible contribution of paramagnetic interaction to the relaxation of adsorbed deuterium can also be deduced from the dependence on metal loading. Near zero overpressure, the chemical shift represents the strength of paramagnetic interaction characterized by a hyperfine coupling constant A. If the paramagnetic interaction is the dominant relaxation pathway, then the relaxation theory predicts that $\Delta\nu_{1/2}$ is proportional to the square A. Hence, one expects that a plot of $\Delta\nu_{1/2}$ vs chemical shifts at different Rh loadings follows a quadratic equation, whereas the experimental data give a good straight line. Therefore paramagnetic relaxation has negligible contribution to the linewidth. This conclusion is in complete accord with our results (*32*) that quadrupolar relaxation is the dominant mechanism of adsorbed deuterium. Both the quadrupolar interaction parameters (coupling constant and asymmetry parameter) and the motion of the adsorbed deuterium affect the linewidth. It is not possible at present to identify exactly which is the controlling factor.

In the small particle region of Pt/Al_2O_3, only about 20% of adsorbed deuterium is detected by ^2H NMR; the amount of detected deuterium is inversely proportional to the particle size. The same dependence of detectability on particle size of adsorbed deuterium is expected to hold for Rh/Al_2O_3. Excessive quadrupolar broadening prevents these adsorbed deuteriums from being detected. The broadening is likely due to the slow motion caused by tight binding. In these conditions, the NMR-detectable deuterium is the most chemically active deuterium. All catalytic reactions with hydrogen transfer as the rate determining step can be correlated with the ^2H NMR results. Because most catalytic reactions have a rate determining step other than hydrogen transfer, our results from ^2H NMR spectra in relation to particle size may not have a direct bearing on the chemistry related to the effect of particle size. The dependence of δD on particle size for Rh/Al_2O_3 and Pt/Al_2O_3 is similar to the dependence of particle size on enthalpies of hydrogen adsorption and absorption on supported palladium catalysts. The enthalpies change rapidly for particle size less than 2.5 nm and reach a limiting value for particle size greater than 2.5 nm (*38*).

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