JOURNAL OF CATALYSIS 77, 53–56 (1982)

Proton Resonance of Hydrogen Adsorbed on Supported Platinum Metals

TAI-CHENG SHENG[1] AND IAN D. GAY

Department of Chemistry, Simon Fraser University, Burnaby, B. C. V5A 1S6, Canada

Received November 10, 1981; revised March 11, 1982

Proton resonance data exist to date for hydrogen adsorbed on Pt with various supports (*1–4*) and for Rh supported on TiO_2 (*5*). We report here data for all of the platinum metals, Ru, Rh, Pd, Os, Ir, and Pt, supported on SiO_2.

Experimental techniques for adsorption and NMR measurements were the same as previously described (*4*). All catalyst samples were prepared by impregnation of Davison 923 silica gel with sufficient metal chloride or chloro acid to give 5% by weight of the metal after reduction. After drying, the catalysts were reduced in flowing hydrogen, and stored. Before use, catalysts were further reduced in static hydrogen, evacuated at the reduction temperature, and used for adsorption or NMR experiments. Table 1 gives the final reduction/pumping temperatures for the catalysts, together with the metal dispersion as estimated from hydrogen adsorption, assuming one H atom per surface metal atom. Isotherms were extrapolated to $P = 0$ as in (*4*). In the case of Pd, only the part of the isotherm below 1 Torr was used, to avoid bulk incorporation of hydrogen (*6*). The large disperson value found for Ir by this calculation is in accord with previous observations (*7*) that highly dispersed Ir can adsorb up to two H atoms per surface Ir atom.

Proton NMR measurements show for all samples a resonance arising from support SiOH groups, together with a high field resonance due to adsorbed H. The position of the latter resonance is in general coverage dependent. The positions of the resonances are plotted in Fig. 1, against fractional surface coverage. In no case do we observe more than one resonance line arising from adsorbed hydrogen. In the case of Pd, equilibration in H_2 at pressures above 1 Torr results in the appearance of a new resonance at 28 ppm to low field of tetramethyl silane (TMS). We attribute this to dissolved H which would be expected with Pd at higher pressures (*6*). As pressure is further increased, the intensity of the low field peak grows, but little change occurs in the shift, which reaches 30 ppm at 100 Torr. There is no condition under which we see both a high field and a low field peak from H on Pd. This suggests rapid exchange on the NMR timescale (milliseconds) with a shift that is a weighted average of those for adsorbed and dissolved hydrogen populations.

As we pointed out previously (*4*), it is difficult to make intensity measurements for the metal–H peak in the presence of the large SiOH peak. Such measurements can only be attempted when the M–H resonance at high coverage is relatively well separated from the SiOH resonance. For the present data, this is only possible for Ru, Rh, and Pt. Our previous intensity measurements (*4*) showed that essentially all of the H adsorbed on Pt resonates in the high field peak. The present measurements for Ru and Rh show 70 and 30%, respectively, of the expected intensity in the high field peak. Since the uncertainty of our measure-

---

[1] Permanent address: Shan Dong University, Ji Nan, Shan Dong, China.

0021-9517/82/090053-04$02.00/0

TABLE 1

Metal	Reduction temperature (°C)	Dispersion
Ru	450	0.2
Rh	450	0.5
Pd	400	0.6
Os	350	0.2
Ir	350	1.7
Pt	400	0.3

ments is probably ±20%, the Ru result is perhaps ambiguous, but it is clear in the case of Rh that there is substantial missing intensity. We have searched for this, using a frequency synthesizer to cover the shift range $\pm 2 \times 10^4$ ppm. We have also looked for a peak under the SiOH peak, using a 180°-T-90° pulse sequence, with T adjusted to null the resonance from the SiOH peak. Neither of these expedients reveals any further intensity. This indicates that some of the adsorbed H or Rh resonates in a line which is either too wide (>20 kHz) to observe on our instrument, or which lies under the SiOH peak and has either the same T_1 or T_2 as the latter, in which case our two pulse experiment will not detect it.

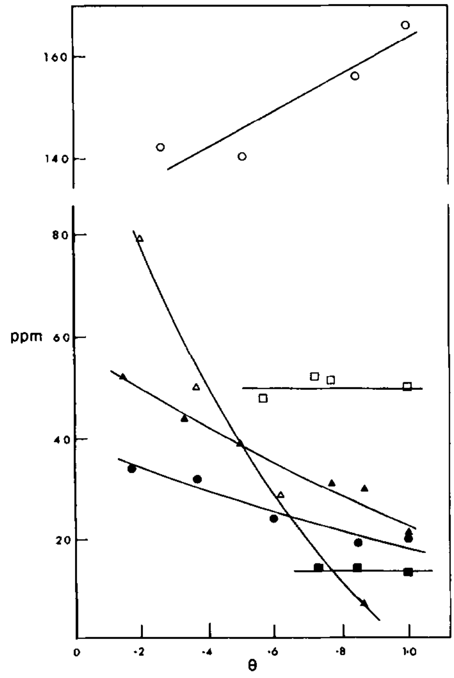

FIG. 1. Shift of hydrogen adsorbed on various metals as a function of fractional surface coverage. Shifts are in parts per million upfield of TMS. □, Ru; ○, Rh; △, Pd; ■, Os; ●, Ir; ▲, Pt.

As with platinum (*4*), it is found that adsorbed D_2 exchanges with support SiOH groups, to give a high field M–H peak that grows in time. It is also found that adsorption of H reduces the spin-lattice relaxation time of the support OH protons. Although all of the metals studied are similar in these respects, there are quantitative differences. We report representative data in Table 2, which gives the half time for deuterium exchange, and the SiOH T_1 value at a fractional coverage of 0.5.

As can be seen in Fig. 1, all metals show a substantial upfield shift for adsorbed hydrogen. There are, however, quite distinct differences among the metals. For Ru and Os, the shift is independent of coverage, within experimental error (±2 to 5 ppm). Pt, Pd, and Ir show a decrease in shift with increasing coverage, whereas Rh shows an anomalously large shift (note the interrupted scale in Fig. 1) and an increase of shift with coverage. Our lowest coverage points for Rh have a larger experimental error, 10 to 15 ppm, but the results of repeated measurements on the same, and on different samples show a definite increase,

TABLE 2

Metal	Exchange time[a]	T_1[b]
Ru	5 days	7.6
Rh	10 min	7.0
Pd	6 days	2.8
Os	[c]	6.7
Ir	5 hr	1.9
Pt	2 hr	2.5

[a] Time for 50% exchange of adsorbed D_2 at $\theta = 1$ with support SiOH groups.

[b] Spin-lattice relaxation time of support SiOH groups in seconds, for $\theta_H = 0.5$.

[c] Not measured.

which could, however, be somewhat smaller than suggested by the average results plotted in the figure.

An explanation of these shifts could be given in the same terms as previously suggested for Pt (*2*, *4*). A covalent contribution to the M–H bond could cause an interaction between the proton and unpaired metal *d* electrons. The decrease in shift with increasing coverage on Pt was previously explained as due to a pairing of electron spins in the metal, due to bonding of H. To retain this explanation, one would have to suggest that in the case of Ru and Os, where the shift is independent of coverage, the larger number of *d* vacancies in the metal leads to a smaller perturbation of the metal electronic structure by adsorption. In this case, one would expect the behavior of Rh and Ir to be intermediate. This is indeed the case for Ir—the shift is coverage dependent, and the slope smaller than for Pd and Pt. Rh, however, is anomalous.

There are several anomalies in the case of Rh. These are, notably, the much larger shift, the increase of shift with coverage, and the substantial missing intensity, mentioned above. All of these suggest that Rh is in some way a special case, and worthy of further study. Apple *et al.* (*5*) observed a line for H on Rh/TiO_2 at very high field, similar to that found by us. These authors explained the large shift as due to interaction with paramagnetic Ti^{3+} created by hydrogen spillover.

It might be asked whether the present shifts could be accounted for by interaction with paramagnetic species, which might be present due to incomplete reduction of the catalyst precursor compounds. The proton NMR properties of molecules interacting with paramagnetic ions deposited on silica have been well studied, notably by Borovkov and collaborators (*8–10*). It is found that hydrogen, olefins, and benzene undergo large shifts, typically tens of ppm due to interaction with such ions. The more weakly interacting paraffins undergo somewhat smaller shifts, typically about half as large. For all of the present catalysts, we have measured the spectrum of physically adsorbed TMS as a chemical shift reference. In the cases of Pt and Rh we have also measured the spectrum of adsorbed methane and ethylene. In none of these cases do we observe a shift which deviates from the free molecule shift by more than 1 ppm. The small observed shifts agree within 0.2 ppm with what would be expected for a susceptibility correction based on the gross composition of the catalyst. We do not therefore think that paramagnetic contaminants are the cause of the present shifts with hydrogen. This conclusion is reinforced in the case of Pt by the fact that H_2 adsorbed on unsupported metal particles gives similar shifts (*1*).

An alternate interpretation of the results of Apple *et al.* would be that the high field line arises from H on Rh, and that this is the H which can spill over to create Ti^{3+}. Thus the latter ion could be an effect, rather than a cause. The absence of the high field line which these authors find after high temperature reduction could simply be due to the inhibition of H_2 adsorption by metal–support interaction, as found by Tauster *et al.* (*11*) for the Rh/TiO_2 system. The present results do not, of course, definitely establish this, but it would appear that the alternate explanation is consistent with existing data.

Since Rh is an odd-electron element, it is possible to have small particles with an odd number of metal electrons, and hence, necessarily, an unpaired spin. It might be postulated that some of the above anomalies are caused by this. In this case, it is difficult to understand why Ir should not behave similarly to Rh.

As noted in Table 2, there are substantial variations in the rate of metal–support hydrogen exchange, and in the effect of adsorbed H on the SiOH spin-lattice relaxation time. If the latter effect is attributed to spillover (*4*), the lack of correlation between the two sets of data in Table 2 suggests that the exchange proceeds by a mechanism which has little to do with the spillover process.

ACKNOWLEDGMENTS

We thank the Science Council of British Columbia, and the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

REFERENCES

1. Ito, T., Kadowaki, T., and Toya, T., *Japan J. Appl. Phys. Suppl.* **2,** 257 (1974).
2. Bonardet, J. L., Menorval, L. C., and Fraissard, J., *in* "Magnetic Resonance in Colloid and Interface Science," Vol. 34, p. 248. A. C. S. Symposium Series, 1976.
3. De Menorval, L. C., and Fraissard, J. P., *Chem. Phys. Lett.* **77,** 309 (1981).
4. Sheng, T.-C., and Gay, I. D., *J. Catal.* **71,** 119 (1981).
5. Apple, T. M., Gajardo, P., and Dybowski, C., *J. Catal.* **68,** 103 (1981).
6. Aben, P. C., *J. Catal.* **10,** 224 (1968).
7. McVicker, G. B., Baker, R. T. K., Garten, R. L., and Kugler, E. L., *J. Catal.* **65,** 207 (1980).
8. Borovkov, V. Yu., and Kazanskii, V. B., *Kinet. Katal.* **13,** 1439 (1972).
9. Borovkov, V. Yu., Shuklov, A. D., Surin, S. A., and Kazanskii, V. B., *Kinet. Katal.* **14,** 1081 (1973).
10. Kazansky, V. B., Borovkov, V. Yu., and Zhidomirov, G. M., *J. Catal.* **39,** 205 (1975).
11. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).