NMR OF SMALL PLATINUM PARTICLES

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ABSTRACT

We present ^{195}Pt NMR lineshapes as well as relaxation data in three different samples of platinum metal particles (46%, 26%, and 15% dispersion) supported on alumina. We show that the electronic properties of these particles are very much different from that of bulk Pt metal. A prominent peak in the lineshape has been identified as a "surface resonance" which arises from Pt nuclei on the surface of the Pt particles. We find that these surface Pt atoms are "non-metallic" when coated with adsorbed molecules.

MASTER

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INTRODUCTION

Heterogeneous catalysis is a field of great interest because of its important technological applications. However, the fundamental understanding of catalytic phenomena is not well developed [1]. In an effort to learn more about the microscopic details of heterogeneous catalysis, we have been applying nuclear magnetic resonance (NMR) to the study of a typical catalyst, platinum metal. In this paper, we present NMR data [2-4] on ^{195}Pt in small platinum metal particles supported on alumina. We show that the electronic properties of these particles are very much different from that of bulk platinum metal. Furthermore, the Pt atoms on the surface are "non-metallic" when coated with adsorbed molecules.

SAMPLES

We have used three different samples (prepared by one of the authors, JHS) which we label 1, 2, and 3. These samples consist of small Pt particles supported on alumina. (All samples are 10% Pt by weight.) The dispersion (fraction of Pt atoms which are on the surface of the particles) of samples 1, 2, and 3 was measured by hydrogen chemisorption and was found to be 46%, 26%, and 15%, respectively. After the samples were prepared, they were opened to air. The nature of the resultant adsorbed molecules on the surface of the Pt particles in these samples is unknown.

KNIGHT SHIFT

When a material is placed in an applied magnetic field H_0 , interactions between the nuclei and nearby electrons give rise to a displacement of the NMR frequency ν_0 . Polarization of the electron orbital moments gives rise to a displacement called the chemical shift. In metals, polarization of the conduction-electrons spins gives rise to an additional displacement called the Knight shift. For a given nucleus, Knight shifts are usually an order of magnitude larger than chemical shifts [5].

In non-metallic Pt compounds, the ^{195}Pt nuclear resonance is usually observed between $H_0/\nu_0 = 1.093$ and 1.100 kG/MHz, a spread of about 0.6% [6]. This spread of resonances is due to chemical shifts alone, since the Knight shift is zero in an insulator. By convention, the zero chemical shift (and zero Knight shift) of ^{195}Pt is chosen to be at $H_0/\nu_0 = 1.0996$ kG/MHz which is the position of the ^{195}Pt resonance in H_2PtI_6 , one of the least paramagnetic compounds [6]. In bulk Pt metal, a large Knight shift is observed. The ^{195}Pt resonance is at $H_0/\nu_0 = 1.1422$ kG/MHz, a Knight shift of -3.37% with respect to H_2PtI_6 [6].

The Knight shift is a local effect, arising from interactions with electrons which are very near the nucleus [5]. Thus the Knight shift is very sensitive to local variations in the state of the conduction electrons. In small metallic particles which contain only a few atoms, the state of the conduction electrons is expected to vary greatly as a function of position in the particle, resulting in a large variation of Knight shifts. This results in a rather broad NMR absorption lineshape.

LINESHAPES

The NMR absorption lineshapes were measured using a pulsed-NMR spin-echo technique, varying H_0 while holding ν_0 constant. The results are shown in Fig. 1. We observe in our samples absorption lineshapes which extend from the full-Knight-shift position of bulk Pt metal to approximately the position of non-metallic Pt compounds, a distance of 4.5 kG at 74 MHz.

In sample 3 (see Fig. 1), a prominent peak in the lineshape can be seen at the position of the ^{195}Pt resonance in bulk Pt metal ($H_0/\nu_0 = 1.1422$ kG/MHz). This peak arises from ^{195}Pt nuclei in larger particles where the conduction electrons are in an environment similar to bulk Pt metal. The absence of this peak in samples 1 and 2 indicates that very few of the Pt particles in those samples are large enough to exhibit the electronic properties of bulk Pt metal.

In all three samples (see Fig. 1), another peak in the lineshape can be seen at $H_0/\nu_0 = 1.0897$ kG/MHz. We have identified this peak as a "surface resonance" [2,3] which arises from Pt nuclei on the surface of the particles. From the position of this peak on the line, we see that these nuclei are in a non-metallic environment. The conduction electrons at the surface of the Pt particles are most likely tied up in chemical bonds with various adsorbed molecules. This conclusion is further supported by relaxation measurements discussed below.

From Fig. 1, we see that the intensity of the surface resonance decreases with decreasing dispersion, as expected. Since the area under an NMR absorption line is proportional to the number of nuclei contributing to the absorption, the ratio of the area under the surface resonance peak to the area under the complete lineshape ought to be equal to the dispersion. Measuring the dispersion in this manner by integrating the lineshapes shown in Fig. 1, we obtain 46%, 20%, and 12% for samples 1, 2, and 3, respectively, in good agreement with the values measured by hydrogen chemisorption (46%, 26%, and 15%, respectively).

SAMPLE TREATMENTS

We "cleaned" sample 1 by exposing it alternately to hydrogen gas and then oxygen gas at 300 C. The final exposure was to hydrogen gas which was then pumped off. The sample was then cooled to room temperature and sealed in a glass ampoule under vacuum. The lineshape for this sample is shown in Fig. 2. We see that the surface resonance peak is gone and that much of the intensity of the lineshape is shifted towards the position of bulk Pt metal. It appears that in our "cleaned" sample, the electrons previously tied up in chemical bonds to adsorbed molecules are now free, and the surface of the Pt particles is more metallic in nature.

We next broke open the ampoule and exposed this sample to air, allowing various molecules to be adsorbed on the Pt particles. A surface resonance peak reappeared (see Fig. 2), however, somewhat broader and at a different position ($H_0/\nu_0 = 1.0944$ kG/MHz). This displacement of the surface resonance is caused by a chemical shift and thus depends on the nature of the adsorbed molecules.

We repeated the "cleaning" process on sample 1 and then exposed it to hydrogen gas at room temperature. The gas was then pumped off and the sample sealed in a glass ampoule under vacuum. Now, only hydrogen is adsorbed on the surface of the Pt particles and we again see a surface resonance peak (see Fig. 2), this time at $H_0/\nu_0 = 1.0952$ kG/MHz.

RELAXATION

We measured the spin-lattice relaxation time T_1 as a function of position on the absorption line in samples 1, 2, and 3 (see Fig. 3). As can be seen, the data from each of the three samples fall on the same curve. This result suggests that at each position of the resonance line, the electronic environment is the same, without regard to particle size. At $H_0/\nu_0 = 1.1422$ kG/MHz, we find $T_1 = 390$ μ s which is the value of T_1 measured in bulk Pt metal [6]. The relaxation here is caused by interaction with the conduction electrons [5]. This is a very effective relaxation mechanism and produces a very short T_1 as we can see.

Near the position of the surface resonance, T_1 is considerably longer and also field dependent. This is characteristic of relaxation in a non-metal. (Relaxation via conduction electrons is field independent [5]). Thus we conclude that the Knight shift is zero at the surface resonance, and the observed displacement of this resonance from H_2PtI_6 is purely a chemical shift.

We also measured the spin-spin relaxation time T_2 as a function of position on the line (see Fig. 4). In this case, T_2 is mostly limited by T_1 and thus has some of the same general characteristics of the T_1 data in Fig. 3. As with T_1 , we see that T_2 is field independent over most of the line except near the surface resonance.

Some T_1 and T_2 data was also taken on the treated samples. Of special interest is the T_2 data on the sample which was exposed to hydrogen (the crosses on Fig. 4). As can be seen, the T_2 in this sample is much shorter than the other samples. Here we see how a particular surface treatment can have a rather dramatic effect on the NMR properties of the ^{195}Pt nuclei. If we place a ^{195}Pt nucleus in the vicinity of other nuclei with strong magnetic moments, its T_2 can be greatly reduced via the dipolar interaction [5]. Hydrogen nuclei have a very strong magnetic moment. Sitting on the surface of the Pt particles, they are close enough to the ^{195}Pt nuclei to produce this effect, as we indeed observe.

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FIGURE CAPTIONS

1. NMR absorption lineshapes of ^{195}Pt in samples 1, 2, and 3.
2. NMR absorption lineshapes of ^{195}Pt in sample 1 under various surface treatments.
3. Spin-lattice relaxation time T_1 as a function of position on the line in samples 1, 2, and 3.
4. Spin-spin relaxation time T_2 as a function of position on the line in samples 1, 2, and 3. The symbols have the same meaning as in Fig. 3. The crosses (+) are T_2 data taken in sample 1 after exposure to hydrogen.

NMR Absorption (arbitrary units)