

Surface Study of Supported Metal Particles by ^{129}Xe NMR

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The surfaces of platinum clusters in the supercages of NaY zeolite have been studied by ^{129}Xe NMR over the temperature range 80–293 K. The sensitivity of this weakly perturbing technique makes it possible to reveal the heterogeneity of the electronic structure of the particle surface. The temperature dependence of the ^{129}Xe spin-lattice relaxation indicates that the surface sites with the highest adsorption energy possess metallic character.

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The microscopic details of the electronic and geometric structures of the surface of supported metal particles are crucial to understanding fundamental interfacial processes involved in adsorption and heterogeneous catalysis [1]. Several ultrahigh vacuum surface-selective techniques have been applied to the study of supported metallic microaggregates. However, these approaches usually require model systems, and the experimental results often must be extrapolated to more physically relevant conditions. Scanning tunneling microscopy, for example, can provide a real space image of the surface density of both filled and empty electronic states [2,3]; however, it requires an electrically conductive support with an atomically flat surface. Although such systems may possess important features of a model catalyst, they differ substantially from the highly dispersed metals that are used in practical catalysts.

Following the pioneering work of Rhodes *et al.* [4], NMR has also been widely applied to surface studies of supported metal clusters [4–9], with techniques in existence for probing the spins of the metal nuclei or molecules adsorbed at metal surface sites. Direct investigation of the metal species is limited to the study of a few transition metals (e.g., platinum) that possess NMR-active isotopes with sufficient sensitivity. ^{195}Pt NMR spectra of supported platinum particles are broadened by a large Knight-shift distribution caused by the electron density oscillations in the cluster [4] and by metal particle interactions with the support [6]. While double resonance techniques make it possible to distinguish between surface and bulk contributions to the spectra [9], it would be useful to obtain information about the structure of the surface, which is likely to present a variety of sites with different electronic densities and chemical reactivities [10]. Furthermore, NMR of chemically adsorbed molecules, which form covalent bonds with the surface, involve a strong perturbation of the system. Because of the high surface-to-volume ratios of small clusters, the presence of such strongly interacting species at the surface can dramatically affect the electronic structure of the entire particle [11,12]. Carbon-13 NMR spectra reported by Rudaz *et al.*

[7] of ^{13}CO adsorbed on Pt/alumina show a broad featureless line, which provides crucial information about surface-adsorbate interactions, although it is of limited use in characterizing unperturbed cluster surfaces.

In this Letter, we report a variable-temperature ^{129}Xe NMR study of xenon physically adsorbed on platinum particles in NaY zeolite, a technique introduced by de Menorval, Fraissard, and Ito [13]. The large polarizability of the Xe electron cloud, and thus the large ^{129}Xe chemical shift range, make ^{129}Xe NMR spectroscopy a sensitive technique to probe surfaces and microporous materials [13,14]. Because of the closed-shell configuration of the electronic ground state ($5s^2p^6$) of xenon, interactions of Xe atoms with the adsorbing medium are relatively weak and therefore unlikely to perturb significantly the atomic arrangement of the surface [15]. Rapid exchange among adsorption sites can induce coalescence of the ^{129}Xe lines, with consequent averaging of information about local environments. For sufficiently low temperatures [16] or in molecule-size host cavities [17], however, the xenon diffusion can be reduced, so that ^{129}Xe NMR spectroscopy can be used to probe local features of heterogeneous surfaces. Using this approach, we show that Pt clusters in NaY zeolite supercages are characterized by surface inhomogeneity, with strongly attractive surface sites that are expected to play a dominant role in the chemical activity of this and other dispersed metal systems. From the temperature dependence of the ^{129}Xe spin-lattice relaxation, we conclude that the attractive sites are correlated with a large conduction electron density.

A dispersion of 15 wt % platinum in NaY zeolite was prepared by ion exchange with $\text{Pt}(\text{NH}_3)_4^{2+}$, followed by calcination in flowing O_2 at 673 K and subsequent reduction in flowing H_2 at 673 K, both for several hours. After evacuation to 10^{-5} Torr, the system was cooled to room temperature. The preparation procedure was optimized to ensure that the platinum clusters occupied locations accessible to Xe atoms in the zeolite supercages [18]. 76% of the platinum atoms in the sample occupied cluster surface sites, as measured by hydrogen chemisorption. This cor-

responds to metal particles with an average diameter of 1 nm (55 atoms, assuming a cuboctahedral or an icosahedral structure of the cluster), which is comparable to that of the supercage void space. Transmission electron microscopy reveals no large metal aggregates on the periphery of the zeolite crystallites. Xenon and N₂ adsorption isotherms were acquired at various temperatures.

Prior to the ¹²⁹Xe NMR experiments, xenon gas was admitted to the sample and allowed to adsorb and equilibrate for at least 1 h. The data were acquired at a magnetic field of 8.52 T with a home-built pulsed NMR spectrometer operating at 100.29 MHz. The duration of the $\pi/2$ pulse was between 6 and 18 μ s, depending on the coil configuration (saddle or solenoid). Interaction of xenon atoms with the reduced platinum particles dramatically shortens the ¹²⁹Xe spin-lattice relaxation time T_1 . For pure NaY zeolite, the ¹²⁹Xe T_1 is ~ 1 s [19], whereas the presence of Pt clusters in the NaY supercages shortens the ¹²⁹Xe T_1 to the order of milliseconds (strongly dependent on the temperature and on the concentration of adsorbed xenon). This allowed the use of short recycle times (50–500 ms) and the acquisition of up to 10⁵ signal averaged NMR transients.

For temperatures in the range 163–293 K, the ¹²⁹Xe NMR spectrum of xenon adsorbed on Pt-NaY zeolite consists of a single motionally averaged line, the shift of which depends on the concentration of adsorbed xenon and on the temperature. Below 163 K, the line broadens considerably, consistent with diminished xenon mobility. Because of the high adsorption energy of xenon on the metal particle surfaces (45 kJ/mol [20]), the sticking time of Xe atoms adsorbed on Pt clusters at such low temperatures becomes long enough to prevent motional narrowing caused by exchange between metal and support.

Similarly, ¹²⁹Xe line narrowing due to diffusion of adsorbed xenon atoms on the surface of a Pt particle is not expected to be significant for the conditions employed in this study. Though xenon diffusivity on a Pt(111) surface is still high enough to affect the spectral width even at 80 K for very low coverages, it decreases dramatically at saturation coverages, such as used here [21]. Adsorbate diffusion on the surface of the Pt particles is further limited by restrictions imposed by confinement within the zeolite cage structure.

¹²⁹Xe NMR spectra were acquired below 163 K using a frequency-swept spin-echo technique ($\pi/2 - \tau - \pi - \tau - \text{echo}$) [4,5] with $\tau = 100 \mu$ s. Figure 1 shows the ¹²⁹Xe NMR spectrum obtained at 80 K, referenced to xenon gas at room temperature. The ¹²⁹Xe spin-spin relaxation time T_2 was measured for each frequency and the points were weighted to compensate for the different rates of magnetization decay during the evolution period τ . The sample was sealed in the NMR tube after adsorption of ≈ 5 Xe atoms per Pt particle, as determined from the xenon adsorption isotherm and from the average size of the metal particles. As shown by Ryoo *et al.* [20], particles of this size almost fill up the host cage, and only four Xe atoms can

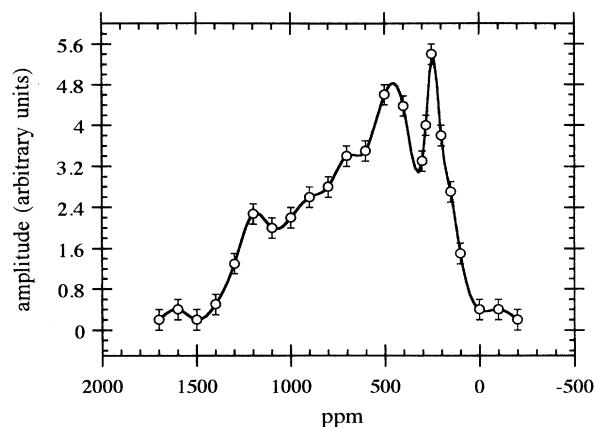


FIG. 1. NMR spectrum of ¹²⁹Xe adsorbed on NaY-zeolite-supported platinum at 80 K obtained by using a frequency-swept spin echo. The individual data points have been weighted by their T_2 values. The narrow component at ca. 250 ppm is assigned to xenon adsorbed on the NaY support material; the broad component in the range 300–1300 ppm represents xenon adsorbed on the surface of the Pt clusters, revealing significant surface heterogeneity.

interact with each Pt cluster through the 0.74 nm apertures of the NaY zeolite supercages. The narrow component of the spectrum at ≈ 250 ppm corresponds to xenon adsorbed on the zeolite support and can be attributed to xenon in excess of that needed for monolayer coverage of the exposed metal atoms. The broad component ranging from 300 to 1300 ppm originates from ¹²⁹Xe atoms adsorbed on the surface of the platinum particles. The broadening can be caused by differences of the Pt susceptibility at different sites and by ¹²⁹Xe chemical-shift anisotropy. In addition, the particle size distribution affects the ¹²⁹Xe spectral width.

To demonstrate that the inhomogeneous broadening is due to the platinum particle surfaces, we repeated the experiments following chemical adsorption of hydrogen or carbon monoxide on the metal clusters [7]. Complete coverage of platinum sites was obtained by exposing the sample to 700 Torr of H₂ or CO for several hours and then removing the H₂ or CO adsorbed on the NaY zeolite support by evacuation at 10⁻⁵ for several more hours. For a xenon pressure of 600 Torr and a complete monolayer coverage of CO at room temperature, the ¹²⁹Xe shift is ≈ 120 ppm. At 80 K, after prior adsorption of hydrogen or carbon monoxide, only the narrow component of the ¹²⁹Xe NMR spectrum in Fig. 1 remains. Partial coverages of H₂, followed by equilibration at 673 K and by slow cooling to room temperature, produce a narrower ¹²⁹Xe spectrum, as the adsorbed xenon species with large resonance shifts disappear. At higher temperatures, the dependence of the ¹²⁹Xe shift on the concentration of xenon after CO or H₂ chemisorption is similar to that of xenon adsorbed on the pure NaY zeolite support alone.

The Xe adsorption sites with the largest shifts are characterized by the highest adsorption energies. This is

inferred from the dependence of the ^{129}Xe NMR resonance signal on xenon uptake over the temperature range 163–293 K (i.e., in the regime of motional narrowing). Figure 2 shows the ^{129}Xe shift as a function of the number of Xe atoms adsorbed per NaY supercage on bare Pt clusters at different temperatures and in the presence of coadsorbed CO. For xenon in contact with the bare Pt clusters, the ^{129}Xe shift increases dramatically as the amount of adsorbed Xe decreases, consistent with a fraction of strongly attractive sites that are populated preferentially and which produce greater perturbation of the distribution of electrons about the xenon nuclei [13,20]. The width of the line, which ranges from 15 to 100 kHz, also depends on the concentration of adsorbed Xe and on the temperature. The shift of the ^{129}Xe atoms adsorbed on the most attractive Pt metal surface sites, measured according to the procedure of Ryoo *et al.* [20], is $\delta_{\text{Pt}} = 1300 \pm 100$ ppm, in agreement with the value reported in [20] for a similar sample. This also corroborates the idea that the ^{129}Xe line broadening is dominated by a distribution of isotropic shifts from different adsorption sites, rather than by ^{129}Xe chemical shift anisotropy. If the spectrum in Fig. 1 was entirely determined by shift anisotropy, the isotropic shift would be ≈ 700 ppm. The observed isotropic shifts, however, at temperatures above 163 K are much larger, and approach the limiting value of 1300 ppm at very low Xe pressures. This is consistent with the results of Zilm *et al.* [22], who showed that the ^{13}C NMR spectra from CO adsorbed on Pt particles are not narrowed by magic angle spinning.

Assuming random orientations of the Pt particles in the zeolite supercages, i.e., assuming that all the sites are statistically equally exposed to the apertures of the supercages

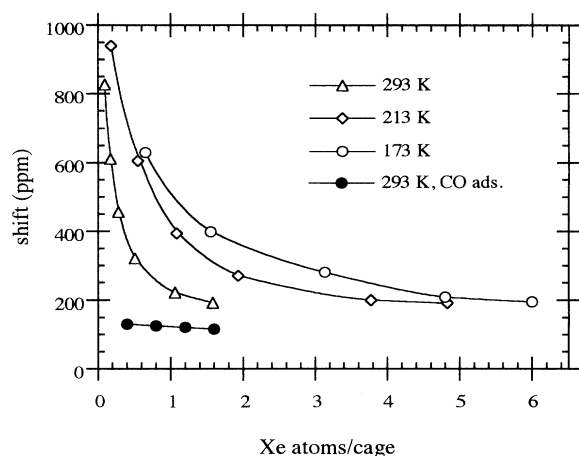


FIG. 2. Dependence of the ^{129}Xe shift on the number of xenon atoms per supercage in the presence of bare Pt clusters at different temperatures (\circ , \triangle , \diamond) and after chemical adsorption of CO at 293 K (\bullet). For xenon adsorbed on bare Pt clusters at low pressure, the ^{129}Xe shift approaches the limiting value of 1300 ppm. After CO adsorption, the ^{129}Xe shift exhibits a much weaker dependence on xenon pressure, indicating that the large shifts observed for the bare clusters are due to interaction with the Pt particles [13].

and accessible to adsorbing Xe atoms, the ^{129}Xe NMR spectrum provides a map of the surface site distribution of the metal clusters. We cannot exclude that specific metal sites preferentially associate with the zeolite support. However, these sites will not be accessible to adsorbed species, and are not expected to play a significant role in the chemical activity of the exposed metal surface.

The nature of the Xe-metal interaction and the issue of whether the shift can be regarded as a chemical or rather a Knight shift will be addressed in a future paper. Here, it suffices to report the temperature-dependent ^{129}Xe spin-lattice relaxation time T_1 (see Fig. 3). For temperatures between 163 and 293 K, i.e., when the spectrum consists of a single narrow line, the magnetization decay is monoexponential. At low Xe coverages, the ^{129}Xe T_1 corresponds predominantly to fluctuations experienced by the Xe atoms in the proximity of the metal particle surfaces [19]. In Fig. 3, ^{129}Xe T_1 values extrapolated to low Xe loadings display a minimum at 213 K, which indicates that the dominant relaxation mechanism is the diffusion of xenon atoms [7]. The large ratio T_1/T_2 observed at the minimum of T_1 (≈ 7) can be related to the large distribution of xenon adsorption energies at different adsorption sites [23].

However, chemical-shift relaxation due to Xe site exchange cannot alone account for the very short T_1 values experimentally observed, so that contributions from one or more other relaxation mechanisms must be considered. In fact, below 163 K, i.e., when Xe motion is hindered, the linear dependence of the ^{129}Xe spin-lattice relaxation time on reciprocal temperature is characteristic of metal-like Korringa behavior (Ref. [24]) for the high-energy adsorption sites associated with the large ^{129}Xe shifts. This im-

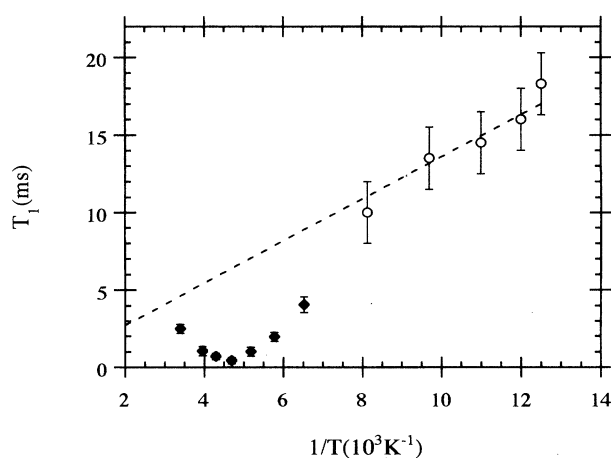


FIG. 3. The ^{129}Xe spin-lattice relaxation time T_1 plotted as a function of reciprocal absolute temperature. For temperatures between 163 and 293 K, T_1 depends strongly on the equilibrium Xe pressure. The filled circles represent ^{129}Xe T_1 values extrapolated to low Xe pressures. A T_1 minimum due to Xe atomic motion is observed at 213 K. The open circles correspond to the T_1 values of the ^{129}Xe spectral component at 1300 ppm for temperatures below 163 K. The linear behavior is consistent with a Korringa-like relaxation mechanism.

plies that the xenon nuclei experience scalar coupling with the conduction electron density spilling out of the metal surface [15]. The ^{129}Xe shift is mainly determined by the interaction of the adsorbed xenon with the s electrons of the Pt metal clusters, as the d electrons of the metal are much more localized. This is in agreement with theoretical calculations of Eigler *et al.* [15], in which the Xe-metal interaction is modeled by describing the metallic surface as a *jellium*. For the sites characterized by smaller shifts, the spin-lattice relaxation is not monoexponential and an accurate analysis is not possible. Fitting the decay of the ^{129}Xe magnetization with two exponential functions characterized, respectively, by a short and a long T_1 , we notice, as a general trend, that the contribution of the slow decaying term is more important for the spectral components corresponding to smaller shifts.

If the ^{129}Xe shifts are correlated with the densities of conduction electrons at different Pt adsorption sites, the sites producing the large shifts correspond to the metal atoms with a larger coordination number [25], i.e., atoms on the faces of the cluster. Lower coordination sites (i.e., metal atoms at corners or edges of a cluster) correspond to smaller shifts. The relative intensities of the different parts of the spectrum yield information on the adsorption properties of the different sites and their distribution.

In related studies, the broadening of ^{195}Pt NMR spectra of supported clusters is usually interpreted in terms of Bardeen-Friedel oscillations of the electron density [4,5]. Within this picture, each shell of metal atoms in the cluster presents a different Knight shift [11], which ranges between 0% at the surface and -3.4% in the bulklike core of the cluster. Our results suggest that the surface heterogeneity contributes to the spectral broadening and may, in fact, dominate in very small clusters with high surface-to-volume ratio. Homogeneous metallic features cannot be attributed to the surface of the metal particles, as sites with different conduction electron densities are present.

In conclusion, we have studied the surface of platinum particles supported on NaY zeolite by variable-temperature ^{129}Xe NMR spectroscopy. This technique has revealed a distribution of metal surface sites, which is usually inaccessible by other surface-selective techniques. The surfaces of the supported Pt particles display significant heterogeneity and the presence of strongly attractive sites. The ^{129}Xe spin-lattice relaxation behavior reveals a scalar interaction of the ^{129}Xe atoms with the conduction electrons of the metal and provides evidence of the metallic character of the strongly attractive sites. The general applicability of this technique for probing metal cluster surfaces is expected to lead to extensions of this work to particles consisting of NMR-insensitive metal nuclei, for example, palladium.

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