

Correlation between the Stretching Frequency of Carbon Monoxide Adsorbed and the Fermi Level Local Density of States at Surfaces of Platinum Catalysts

Y. Y. Tong,^{*,†,‡} J. Billy,[†] A. J. Renouprez,[†] and J. J. van der Klink[‡]

Contribution from the Institut de Recherches sur la Catalyse, CNRS, 2. Av. A. Einstein, F-69626 Villeurbanne Cedex, France, and Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, CH-1015 Lausanne, Switzerland

Received June 25, 1996[⊗]

Abstract: We have studied the stretching frequency (extrapolated to zero coverage) of adsorbed CO and the ¹⁹⁵Pt NMR (before adsorption of CO) of Pt catalysts on zeolite-NaY (three dispersions), on zeolite-NaHY (two dispersions), and on zeolite-NaX (one dispersion); we have also measured the hydrogen and oxygen chemisorption capacity of these samples. For comparison, we studied three samples on an oxidic carrier (unpromoted and promoted by Li or K salts, all from the same initial batch) by infrared and by NMR. In the zeolite case, we find a direct correlation between the CO stretching frequency and the density of states at the Fermi energy on surface sites (surface E_F -LDOS) derived from the clean-surface NMR data, but the chemisorption results seem to be determined by steric as well as electronic effects, and show no simple relation to the two other quantities. The values for the oxidic samples appear to form a distinct set, with probably some promotor-specific effects. The zeolite data support an interpretation of the concept of “electron deficiency” not in terms of missing electronic charge, but in terms of a low density of states at the Fermi energy on surface sites. This is consistent with ideas derived from the frontier-orbital picture for metal–adsorbate interaction. It remains unclear why the surface E_F -LDOS show a systematic variation with the acidity of the faujasite framework.

I. Introduction

The acidity of the aluminosilicate frameworks of zeolites is determined by the type of counterions: when the usual alkali metals in X- or Y-type zeolite are replaced by protons or by di- or trivalent cations, the acidity increases. At constant kind of cation, the acidity increases as the Si/Al ratio increases, and certain types of zeolite, e.g., zeolite-L, have basic frameworks.¹ When small transition-metal particles are incorporated into such zeolites, most of their chemisorption and catalytic properties are found to vary with the framework acidity.^{2,3} It is usual to ascribe these variations to a framework-induced “electron deficiency” of the metal particles.^{4,5} This electron deficiency is usually neglected in the description of bifunctional applications, where both an acidic and a hydrogenation function are required. An important example of such an application is the hydrogenation of benzene, to reduce the levels of this potential carcinogen, in gasoline-manufacturing processes.

In this paper, we focus on electron deficiency in the restricted context of the well-documented correlation between the stretching frequency of CO molecules adsorbed on the metal particles and the acidity of the embedding zeolite matrix.¹ Generally speaking, a lower stretching frequency indicates a weakening of the C–O bond; a related increase in the C–O distance upon chemisorption has been quantitatively determined by Susan Shore et al. in an elegant application of double-resonance NMR.⁶ In a forward–backward donation picture of metal–adsorbate bonding, a stronger C–O bond means that the metal has put fewer electrons into the antibonding $2\pi^*$ orbital of the CO molecule, and this is said to occur because the metal is electron-deficient (with respect to another metal, which causes a weaker C–O bond). This picture has been corroborated by calculations for different adsorption geometries.⁷ It has been found that the back-donation to CO $2\pi^*$ is much more sensitive to geometry than are the forward donations from 4σ and 5σ . This strongly suggests that the observed *variation* of the stretching frequency with geometry is mainly due to differences in back-donation.

Experimentally it is found that the more acidic the matrix, the higher the stretching frequency,⁸ and in basic zeolites the frequency is lower than in acidic ones.⁹ The traditional explanation is a tendency of acidic matrices to extract some electronic charge from the metal. In early work using X-ray absorption near-edge structure (XANES) measurements,¹⁰ it has

* To whom correspondence should be addressed. Present address: Chemistry Department, University of Illinois at Urbana-Champaign, 600 S. Mathews Avenue, Urbana, IL 61801.

† CNRS.

‡ Ecole Polytechnique Fédérale de Lausanne.

⊗ Abstract published in *Advance ACS Abstracts*, April 1, 1997.

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Table 1. Data of Oxygen and Hydrogen Chemisorption, FT-IR-Measured CO Stretching Frequencies ν_{CO} , Which is an Extrapolation to $\theta = 0$ of the ν_{CO} vs Coverage Curve (Figure 2a), and the NMR Measurement-Deduced Surface E_{F} -LDOS for Pt/Zeolite Samples^a

sample	particle size (nm)		chemisorption			FTIR ν_{CO} (cm^{-1})	E_{F} -LDOS (1/(Ry·atom))
	d_s	d_v	H/Pt _{total}	O/Pt _{total}	O/Pt _{surf}		
PtNaX-65	1.52	1.55	1.2	0.48	0.74	2030	20.0
PtNaY-77	1.09	1.19	1.6	0.61	0.79	2055	18.3
PtNaY-64	1.51	1.63	1.1	0.54	0.84	2057	18.3
PtNaY-56	1.85	1.95	0.8	0.48	0.86	2056	18.3
PtNaHY-72	1.29	1.36	1.5	0.40	0.56	2063	17.3
PtNaHY-79	1.06	1.10	1.7	0.54	0.68	2062	17.3

^a The E_{F} -LDOS values are the typical ones (at 1.100 G/kHz) obtained by the typical-value procedure (see section III for details). d_s and d_v are the usual surface- and volume-average diameters obtained from the TEM measurements.^{18,19}

been concluded that the data indicated a charge transfer from the metal clusters to the matrix, but later work⁵ using the same technique, but a different method of data analysis and better controlled sample preparations, did not support this idea: the authors concluded that the platinum particles are in a zerovalent state, independent of the acidity of the matrix. Although the spectrum-difference method used in that work⁵ is perhaps not the best one,¹¹ because of the uncertainty in the choice of the energy limits that define the white line of the Pt L_{II} and L_{III} spectra, it probably still leads to qualitatively correct conclusions concerning the Pt 5d vacant states.

Samant and Boudard⁵ have suggested that electron deficiency might be due to an increase in the workfunction of electrically neutral particles (but without providing a model of the supposed relation between particle workfunction and framework acidity). An experimental determination of the workfunction in these systems would be difficult to perform, so that this suggestion cannot be verified directly. However, there are some closely related ideas in recent theoretical approaches to metal–surface chemistry. In the frontier-orbital picture of metal–adsorbate interaction,^{12,13} the states near the Fermi energy play the role of the HOMO and the LUMO in molecular bonding; thus, an increase in the surface LDOS (of the initial surface, free of CO) will upon chemisorption lead to an increased back-donation into the $2\pi^*$, and thus to a lowering of the CO stretching frequency. This connects to the idea of Samant and Boudard through a qualitative relation between the workfunction φ and the surface LDOS at the Fermi level that has been found in calculations:¹⁴ when the φ decreases, the E_{F} -LDOS increases. While the workfunction approach focuses on the minimum energy required to free a single electron from the metal, the frontier-orbital picture stresses the number of electrons that can be moved between occupied and unoccupied orbitals at the lowest price in energy.

The use of the surface E_{F} -LDOS, rather than the workfunction, to quantify the concept of electron deficiency has the important advantage that changes in surface E_{F} -LDOS can be measured independently as changes in the NMR behavior (Knight shift of the resonance frequency K and Korringa product of the spin–lattice relaxation time and the temperature, T_1T) of the metal nuclei. The Knight shift is a change of the NMR frequency, with respect to some standard, caused by (but not necessarily simply proportional to) the Pauli paramagnetism of the conduction electrons; T_1 is the nuclear spin–lattice relaxation time that characterizes the return to equilibrium of the nuclear magnetization after a perturbation. This relaxation process is governed by local fluctuations in the magnetization of the conduction electrons. In particular ¹⁹⁵Pt NMR is advantageous to study local effects at the surface,^{15,16} since the nuclei on a clean surface resonate at a frequency very different from that of bulk nuclei.

Changes in the E_{F} -LDOS must be distinguished from changes in the total electron density. These are two different concepts:

the latter is proportional to the integral over the whole LDOS spectrum up to the Fermi energy, while the former is only the electron density at the Fermi energy. One can in principle change the form of the LDOS spectrum, and more specifically the E_{F} -LDOS, through some kind of chemical interaction, while keeping the total electron density (integral of the spectrum) constant. This is probably the main difference between the approach of the frontier-orbital-interaction picture and that of the total electron density, as already pointed out by Fukui for the molecular reaction cases in his Nobel lecture.¹⁷

II. Experimental Section

Five samples of Pt in zeolite-Y (Si/Al = 2.4), described under a), b), c), e), and f) in Table 2 of ref 18, are designated here as PtNaY-77, PtNaHY-79, PtNaHY-72, PtNaY-64, and PtNaY-56, where H stands for protons exchanged with Na. The exchange degree was about 73%. Details of sample preparations are given in ref 18. A sample of Pt in zeolite-X (Si/Al = 1.1) is labeled PtNaX-65.¹⁹ Its Pt concentration determined by atomic absorption after calcination at 1200 K is 13.2% (wt), which is smaller than the nominal concentration 15.6% estimated from the degree of ion exchange. A sample of Pt/TiO₂ and two alkali-metal-doped samples from the same batch are labeled Pt-60, Pt-60-Li, and Pt-60-K.²⁰ The number in the sample denominations, for example “65” in PtNaX-65, indicates the sample dispersion obtained from transmission electron microscopy (TEM). The average particle diameters given in Table 1 are based on particle size histograms published earlier.^{18,19}

The *in situ* FT-IR measurements of CO were carried out on a Bruker IFS-84 spectrometer with nominal resolution of 2 cm^{-1} . The pressed wafers were first treated following the procedure described in ref 18. About 15 Torr of CO was then admitted to the sample cell at 25 °C. An IR spectrum was first taken before all subsequent evacuations at different temperatures. The evacuation times were 30 min at 25 °C and 60 min at all other temperatures.

The NMR techniques were the same as used before,^{19,20} and some of the E_{F} -LDOS values shown in Tables 1 and 2 have been deduced from data published earlier.^{19,20} The theory and methods used to extract E_{F} -LDOS values from the measured NMR data will be given briefly in the next section.

The chemisorption isotherms of hydrogen and oxygen were measured at room temperature by a conventional volumetric method on a high vacuum system with small dead volume ($23.35 \pm 0.18 \text{ cm}^3$) to improve

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Table 2. FT-IR-Measured CO Stretching Frequencies ν_{CO} Extrapolated to $\theta = 0$ and the NMR Measurement-Deduced Surface E_F -LDOS Obtained by the Surface-Average Procedure (See Section III for Details) for the Three Pt/Titania Catalysts

sample	FT-IR ν_{CO} (cm ⁻¹)	E_F -LDOS (1/(Ry·atom))
Pt-60	2049	15.4
Pt-60-Li	2039	19.4
Pt-60-K	2019	19.4

the sensitivity and precision. Before taking the isotherms, all samples were cleaned by the standardized procedure described in ref 18. The isotherms were measured up to about 800 Torr. Two experiments were carried out on all samples to check the reproducibility and agreed generally within 5%. The results, given in Table 1 as the ratios of H/Pt_{total}, O/Pt_{total}, and O/Pt_{surf}, are based on the values of oxygen and hydrogen uptakes at 100 Torr, following the same convention as adopted in ref 18.

III. Deduction of the Surface E_F -LDOS: Theory and NMR Data Analysis

In this section, we briefly describe the theory on which the analysis is based for deduction of the surface E_F -LDOS. The readers are referred to the relevant references for the details.

For simple metals like alkali metals, the relation between NMR observables and the E_F -LDOS can be obtained in a relatively direct way in the context of an independent electron picture due to the dominant contact hyperfine interaction between s-electrons and nuclear spins:²¹ the Knight shift is proportional to the E_F -LDOS of s-electrons, and the Korringa product (T_1T) is instead proportional to the square of its reciprocal. This simplicity still remains even when the electron–electron interactions are taken into account.^{22–24}

For transition metals, however, the d valence electrons polarize the s-like wave function of the core electrons through exchange interactions and produce the so-called core polarization that contributes also to the contact hyperfine interaction. The (effective) hyperfine field $H_{hf,d}$ of d-electrons²⁵ has a sign opposite that of $H_{hf,s}$, the hyperfine field of s-electrons. Furthermore, there is orbital contribution to the susceptibility, the Knight shift, and the spin–lattice relaxation rate.²⁶ Consequently the relatively transparent picture of simple metals usually collapses here. To regain (at least partially) such transparency, some modeling and simplifying assumptions are necessary.

The scheme that we shall follow is a two-band model that was first proposed by Yafet and Jaccarino and their co-workers²⁵ and then further developed by Bucher and van der Klink¹⁵ to take into account the Stoner-like enhancement of the Knight shift and the desenhancement of the relaxation rates. The model can be mathematically expressed as follows for the susceptibility χ , the Knight shift K , and the spin–lattice relaxation rate T_1^{-1} :

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$$\chi = \frac{1}{1 - \alpha_s} \mu_B D_s(E_f) + \frac{1}{1 - \alpha_d} \mu_B D_d(E_f) + \chi_{orb} \quad (1)$$

$$K = \frac{1}{1 - \alpha_s} \mu_B^2 D_s(E_f) H_{hf,s} + \frac{1}{1 - \alpha_d} \mu_B^2 D_d(E_f) H_{hf,d} + \chi_{orb} H_{hf,orb} / \mu_B \quad (2)$$

$$S(T_1T)^{-1} = k(\alpha_s) K_s^2 + k(\alpha_d) K_d^2 R_d + [\mu_B D_d(E_f) H_{hf,orb}]^2 R_{orb} \quad (3)$$

where T is the absolute temperature, S is the Korringa constant $[(\gamma_s/\gamma_n)^2(\hbar/4\pi k_B)]$, and μ_B is the Bohr magneton. $D_s(E_f)$ and $D_d(E_f)$ are the separate s-like and d-like densities of the states at the Fermi level. The indexes s, d, and orb stand for s-band, d-band, and orbital contributions. R_d and R_{orb} are the reduction factors due to the orbital degeneracy at the Fermi level:^{25c}

$$R_d = \left[\frac{1}{3} f^2 + \frac{1}{2} (1 - f)^2 \right] \quad \text{and} \quad R_{orb} = \frac{2}{3} \left(2 - \frac{5}{3} f \right) \quad (4)$$

where f is the relative weight of the Γ_5 and Γ_3 d orbitals at the Fermi energy. No interband interactions are taken into account, and the separate s-like and d-like Stoner factors are introduced as

$$\alpha_s = I_s D_s(E_f) \quad \text{and} \quad \alpha_d = I_d D_d(E_f) \quad (5)$$

where I_s and I_d are exchange integrals. The relation between the Stoner factor and Korringa desenhancement factor $k(\alpha)$ is assumed to be given by the Shaw–Warren relationship,²⁴ for both s-like and d-like electrons.

When these equations were applied for bulk platinum metal, I_s , I_d , and $H_{hf,s}$ were considered as fittable parameters, the others were taken either from theoretical calculations or from experimental determinations. An excellent consistency of experimental and theoretical data has been achieved. It is interesting to note that the d-like Stoner enhancement factor obtained by the fitting procedure ($a_d = 0.77$) is in good agreement with the theoretical estimate by Fradin et al. ($a_d = 0.72$).²⁴ Recently, on the basis of the local-density approximation of density-functional theory, van der Klink²⁸ has given a more rigorous validation of this scheme for the case of bulk metals.

Equations 1–3 were originally derived for bulk metals. Moving to small Pt particles introduces some important concerns. The first is whether one can still express separately the Korringa relationship for s-like and d-like electrons. Second, the above equations should be replaced by anisotropic variants, and third, all parameters become site dependent. In their data analysis of Pt catalysts,¹⁵ Bucher and van der Klink dropped eq 1 from consideration because no information was available, but kept eqs 2 and 3. Only the s- and d-like densities of states were supposed to be locally adjusted, as a reflection of the site dependence of the problem; the other parameters were set to be constant and equal to those found for bulk Pt.¹⁵ Thus, by resolving the combined eqs 2 and 3, a pair of experimentally determined K and T_1T gives a pair of s- and d-like E_F -LDOS values. Actually, no *a priori* justification of such an extension can be found; one possible relation might be the local characteristic of the muffin-tin orbitals used in ref 28. Also the good agreement found between the results obtained by applying this parametrized scheme to Pt catalysts after different surface treatments and the existing theoretical calculations^{15,20,29}

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validates so far the soundness of such an extension. While due to the approximation nature of the scheme the actual E_F -LDOS values obtained must be treated with some caution, it is believed that the physical (increasing or decreasing) trends among these values, on which our conclusion is based, are correct.

The nuclear spin–lattice relaxation curve measured at some fixed position (fixed value of the Knight shift K) in the NMR spectrum of a small platinum particle should, in general, not be a simple exponential,^{15,30} and a time–temperature scaling of experimental data obtained at several different temperatures^{19,29} must be used to demonstrate that the Korringa relaxation mechanism is active. This is due to the fact that the E_F -LDOS is not identical at all surface sites, and that one must consider the *distribution* of surface E_F -LDOS values instead. Different procedures have been used to extract relevant values (width and average) for this distribution from the NMR data, depending on the experimental details. For the zeolite-encaged Pt catalyst, all measured spin–lattice relaxation curves were nonexponential; more experimental data points are therefore needed (which is consequently very time-consuming) to ensure the simplest two-exponential fit reliable. We adopted therefore in this case a typical-value procedure. A single “representative” value of K was chosen in the surface region of the NMR spectrum (usually its maximum), and time–temperature scaling was used to collapse all data points onto one curve, which was represented by the simplest possible nonexponential decay: a sum of two exponentials. This gave two values of T_1T at the same value of K , and therefore two pairs of the E_F -LDOS values. These two values found at the representative point were considered to characterize the whole distribution of E_F -LDOS values over all surface sites; e.g., the relative weights of the higher and the lower values of the E_F -LDOS were set proportional to the amplitudes of the fast and of the slow parts of the relaxation curves, and their average and rms deviation from the average (of two points only, which of course is quite an approximation) are calculated. For the oxide-supported Pt catalysts (Pt/TiO₂), it appeared experimentally that a simple exponential decay could be a good approximation for the relaxation curves.²⁰ In this case, a surface-average procedure was adopted. The relaxation curves were measured for several values of K in the surface region (field/frequency ratios lower than 1.105 G/kHz) of the spectrum, and each curve is fitted to a simple exponential. Each pair of K and T_1T values was then converted into values for the E_F -LDOS, and the distribution was obtained by weighing the different values with the amplitude of the corresponding point in the NMR spectrum. In this paper we will discuss only average values (not the width of the distribution) of the surface E_F -LDOS found either by the surface-average (for samples on oxide carriers) or by the typical-value (for the zeolite-encaged samples) procedure.

IV. Results and Discussion

Correlation between the Stretching Frequency of Chemisorbed CO and the Clean-Surface E_F -LDOS. As pointed out in section I, the main purpose of this paper is to show that the electron deficiency in zeolite-encaged platinum catalysts, a very important concept that is extensively used in heterogeneous catalysis, can be explained (or predicted) by the variation of the clean surface E_F -LDOS of the corresponding Pt catalysts. For this purpose, two types of experiments have been done on each of the samples studied here: the IR measurement of chemisorbed CO on one hand which indicates the electron

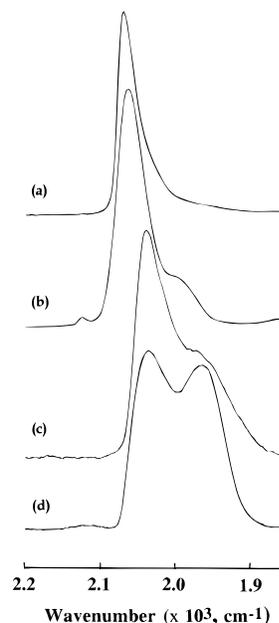


Figure 1. Some typical FT-IR spectra to show the characteristics after evacuations at higher temperatures: (a) Pt-60, 150 °C; (b) PtNaY-77, 200 °C; (c) Pt-60-K, 150 °C; (d) PtNaX-65, 300 °C. See the text for the detailed description.

deficiency and the ¹⁹⁵Pt NMR measurement on the other hand which measures the surface E_F -LDOS of Pt catalysts.

In order to eliminate the possible influence caused by some direct and/or indirect adsorbate–adsorbate interactions, the IR experiments were designed to obtain the C–O stretching frequency toward the zero coverage. A series of FT-IR spectra (2500–1000 cm⁻¹) were recorded after each evacuation at several temperatures until the vibration bands of adsorbed CO disappeared. All FT-IR spectra show a characteristic peak of linearly bonded (on-top) CO (see Figure 1). For samples Pt-60, Pt-60-Li, and Pt-60-K, two bands (not shown here) at 1500–1750 and 1150–1350 cm⁻¹ appear at 25 °C but disappear after evacuation at 100 °C. We therefore attribute them to species adsorbed on the support. The band of the bridged–bonded CO (ca. 1850 cm⁻¹) is very weak in all cases and is therefore neglected in the following considerations. We repeated the experiments at 25 °C for several samples (PtNaY-77, PtHNaY-72, and Pt-60-K and -Li) to check the influence of sample preparations. The reproducibility of the peak was within 2 cm⁻¹, as shown by the error bars in Figure 2.

At a room temperature of 25 °C, all FT-IR spectra show only one linearly bonded CO band with a slower descent on the low-wavenumber side. For Pt/zeolite systems, almost all samples show a small shoulder (at about 2000 cm⁻¹) emerging from this slow descent side after evacuation at 150 °C. The exception is PtNaX-65, which, at 25 °C, shows already the indication of a low-frequency band. This low-frequency band becomes more important and emerges as a separated band after evacuations at high temperatures and stabilizes at about 1965 cm⁻¹. For Pt-60 and Pt-60-Li, no such low-frequency band has been observed, while for Pt-60-K, it behaves much similar to that for PtNaX-65: a low-frequency band appears at about 1965 cm⁻¹. Some typical FT-IR spectra are presented in Figure 1. The appearance of the low-frequency band probably indicates some different on-top sites and/or reflects some specific local effect which might be more important at low coverages, for example, on the atoms of the corner and edge that have a lower coordination number³¹ or on the atoms close to the region where the whole metal particle has been anchored to the support.

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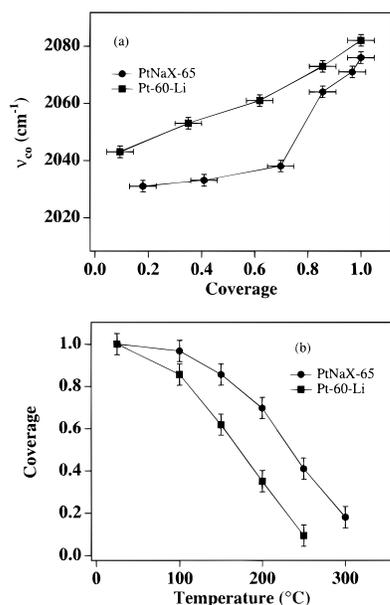


Figure 2. Typical results of the FT-IR measurements: (a) ν_{CO} vs coverage data of Pt-60-Li and PtNaX-65. The coverage was estimated with the normalization of the peak integral by that recorded at 25 °C (saturated). (b) Desorption data of the same samples in (a). The estimated uncertainty was $\pm 2 \text{ cm}^{-1}$ for ν_{CO} and ± 0.05 for coverage, as represented by the error bars. The solid lines are only for guide of the eye.

The coverage dependence of ν_{CO} (of the high-wavenumber band) shows a qualitative difference between samples encaged in zeolite and those supported on TiO_2 : the former shows a larger red shift before $\theta = 0.75$ and then reaches an almost constant regime, while the latter shows an approximately linear red shift. The coverage was determined by scaling the peak integral by that recorded at 25 °C (saturated). Typical curves are shown in Figure 2a, Pt-60-Li for TiO_2 -supported samples and PtNaX-65 for zeolite-encaged samples, respectively. The error bars show the estimated uncertainty about the coverage. By extrapolating these curves to $\theta = 0$, the values of ν_{CO} collected in Tables 1 and 2 were obtained. Note that the ν_{CO} values in Table 1 are carrier (acidity) rather than particle size dependent, which can be explained by the NMR observations (see below). In Figure 2b, we present the desorption curves of Pt-60-Li and PtNaX-65 which show that CO desorbs more easily from Pt particles on TiO_2 than from those encaged in zeolite.

In parallel with the IR measurements, the E_F -LDOS values were determined by ^{195}Pt NMR carried out on the *same* samples with clean surfaces. The E_F -LDOS values for the oxidic samples were taken from ref 20. Those for the NaX and NaY samples were calculated from relaxation curves given in ref 19, at 1.100 G/kHz, and for temperatures at and above 80 K (at lower temperatures, indications for nonmetallic behavior have been found). Additional relaxation curves have been measured at the same spectral position (1.100 G/kHz), at 80 K, for the two NaHY samples. Within experimental errors, the temperature-scaled spin–lattice relaxation curves for the three NaY samples coincide well and can be fitted by a two-exponential function alone, though their dispersion varies from 56% to 77%. The same is true for the two NaHY samples. Such experimental observations imply that for a given zeolitic support (constant acidity) there is no measurable dependence of the average surface E_F -LDOS on the dispersion of the metal particles. This gives a reasonable explanation of the fact that the ν_{CO} values in Table 1 do not show significant size dependence within a given zeolitic carrier: the extrapolated value of ν_{CO} is still a

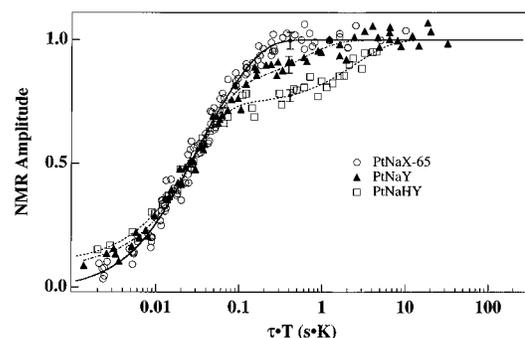


Figure 3. Normalized time–temperature-scaled experimental relaxation curves and their corresponding fits of a two-exponential function for PtNaX-65 (80–250 K), PtNaY (–77, –64, and –56 at 80 K), and PtNaHY (–72 and –79 at 80 K). The error bars show the rms deviations obtained from the fit for each case. See Table 3 for details about the fit parameters.

clean surface property, namely, determined mainly by the electronic properties of the clean surfaces.

In Figure 3 we show the three normalized relaxation curves (for NaY, NaHY, and NaX) in semilogarithmic plots. The error bars show the rms deviations obtained from the fit for each case. Qualitatively, it is immediately seen that the density of states is the highest in NaX (the fastest relaxation curve), intermediate in NaY, and lowest in NaHY (the slowest relaxation curve). The parameters of the three double-exponential fits are given in Table 3 and the calculated surface E_F -LDOS values in the last column of Table 1.

It has been shown before³² that for clean-surface Pt/oxide catalysts (without being promoted or poisoned) the spin–lattice relaxation is independent of the choice of support material (silica, alumina, titania) and of the method of preparation (ion exchange, colloidal process, impregnation). The change of particle size only changes the surface to bulk signal ratio but not the spin–lattice relaxation rate at a given spectral position. In contrast, Figure 3 and Table 1 show a systematic variation of the spin–lattice relaxation in the surface region of the spectrum with the framework acidity of the encaging zeolite. An increase of acidity in clean-surface Pt/zeolite samples decreases the metal surface E_F -LDOS. Which mechanism is responsible for this particle–zeolite interaction is not clear at the moment, but it is easy to understand the correlation between the increase in CO stretching frequency and the decrease in surface E_F -LDOS on the basis of the frontier orbital picture.^{12–14} The increase of electron deficiency indicated by an increase of the stretching frequency of chemisorbed CO may arise from the decrease of the metal surface E_F -LDOS which measures the number of (occupied and/or unoccupied) frontier orbitals available for chemisorption bonding on metal surfaces.

For the three Pt/titania catalysts, though their absolute values should perhaps not be compared directly to those in the zeolite catalysts due to different data-processing procedures (see section III for details), the important effect is that promotion with Li or K salts leads to an increase of the surface E_F -LDOS, as predicted by the theoretical calculations.¹⁴ There is the expected accompanying *red shift* in the CO stretching frequency, in agreement with the idea that increasing the surface E_F -LDOS will reduce the electron deficiency and therefore weaken further the C–O bond, but we do not know why the shift for the sample treated with K is more important than that for the case of Li.

Using unconventional NMR methods,³³ D. Fick and co-workers have obtained the E_F -LDOS on the site of ^6Li adsorbed

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Table 3. Fit Parameters of the Spin–Lattice Relaxation Curves Shown in Figure 3^a

sample	spectral position G/kHz	temperature range (K)	fast fraction	fast T_1T (ms·K)	slow T_1T (ms·K)	rms deviation
PtNaX-65	1.100	80–250	0.49 ± 0.02	18 ± 3	84 ± 15	0.034
PtNaY	1.100	80	0.80 ± 0.05	32 ± 2	710 ± 180	0.034
PtNaHY	1.100	80	0.73 ± 0.04	26 ± 2	2488 ± 250	0.024

^aThe “rms deviation” is the root-mean-squared difference between fitted and measured amplitudes, setting the fully relaxed amplitude to 1.

at extremely low coverage on the surfaces of different single crystals (Mo, Ru, W, Ir, and Pt). They found a marked trend of the E_F -LDOS on the Li site to decrease with increasing workfunction of the substrate. If we assume that the E_F -LDOS on the Li site is related to that on the surface of the substrate, then these results can be considered as an experimental connection between our interpretation of electron deficiency and that of Samant and Boudart.⁵

Oxygen and Hydrogen Chemisorption. Both the CO stretching frequency (extrapolated to zero coverage, and therefore in a sense a clean-surface property) and the NMR spin–lattice relaxation are found to be essentially independent of particle size for a given type of zeolite. This is not true for our chemisorption data: as do many others, we find that the ratio (total atoms of hydrogen)/(surface atoms of Pt) increases with sample dispersion and has values between one and two. The ratio (total atoms of O)/(surface atoms of Pt) for our three NaY samples has an average value of 0.83, and for the two NaHY samples an average of 0.62. This is similar to the results of ref 5 for a sample on HY and for another on NaY. Extrapolating these result toward the least acidic of the three frameworks, NaX, we expect therefore a value larger than 0.83, but experimentally we find 0.74 (in ref 5 only Y-type zeolites have been studied). The number of surface atoms used in these ratios has been found from the particle size distribution; to avoid their use, one might consider the ratio (atoms of O)/(atoms of H) instead, but again no correlation with acidity is found for NaX. Perhaps this can be explained by steric effects: the preparation method used for this sample is believed to minimize damage to the faujasite structure (see the corresponding values of d_s and d_v in Table 1), which might result in such a tight fit of the platinum particles inside the matrix that not all electronically favorable surface sites are accessible to oxygen. Another evidence of the possible steric effect is that, within a given zeolitic matrix (NaY), the ratio (total atoms of O)/(surface atoms of Pt) increases with a decrease of the dispersion (see Table 1). A lower dispersion means larger engaged particles which may cause more damage to the faujasite structure and therefore make more surface sites accessible to oxygen. Therefore, caution must be taken in reaching a conclusion from the change of oxygen chemisorption in the case of zeolite-encaged small metal particles since it is difficult in practice to separate the electronic from the steric effect on oxygen chemisorption.

V. Conclusion

Originally, the expression “electron deficiency” referred to the experimental fact that catalysts of platinum or palladium on zeolites, when compared to the same metals on oxidic carriers, often seem to behave as their left-hand neighbors in the periodic system, iridium and rhodium.^{3,4} In relation to our results, it should be pointed out that not only the number of electrons but also the (calculated) densities of states at the Fermi energy in the bulk metals³⁴ decrease when a step is made to the left: the value in Rh (18.68 states per Ry and per atom) is clearly less than that in Pd (32.16 per Ry and per atom); the

same holds for Ir (12.71 per Ry and per atom) and Pt (29.90 per Ry and per atom). The ¹⁰³Rh NMR spectrum of small Rh particles³⁵ has been qualitatively interpreted assuming that for Rh, contrary to Pd and Pt, the surface E_F -LDOS is higher than that of the bulk, i.e., that the surface E_F -LDOS is larger than 18.68 per Ry and per atom, and the Pd surface E_F -LDOS smaller than 32.16 per Ry and per atom. More precise experimental values are not available at present, but it seems quite possible that there is a direct correlation between the phenomenon of “behavior like the left-hand neighbor” and a lower value of the density of states at the Fermi energy on surface sites.

The frontier-orbital picture asserts that the clean-surface E_F -LDOS should in certain respects have a predictive value for the chemical activity of a metal surface.¹² We have demonstrated the expected relation between variations in the zero-coverage CO stretching frequency, usually described in terms of electron deficiency, and the clean-surface E_F -LDOS, but it is not clear which interaction exactly is responsible for the relation between surface E_F -LDOS and zeolite acidity. For Pt/TiO₂ catalysts, we have shown that there also exists an accompanying red shift of the stretching frequency of chemisorbed CO after the surface E_F -LDOS has been enhanced by promoters. Although more experimental as well as theoretical studies are needed to determine how far the surface E_F -LDOS can be used as a simple physical quantity to characterize the reactivity of a clean metal surface for chemisorption, our results show already a new and promising scientific approach to refresh one of the most important concepts in heterogeneous catalysis—the electron deficiency. It bridges a well-defined physical quantity, which is both theoretically calculable and experimentally measurable, to an idea based somewhat on alchemy.

In earlier work,³⁶ a decrease of total oxygen chemisorption capacity with increasing zeolite acidity has been ascribed to increasing electron deficiency as well. We do not find a good correlation between oxygen chemisorption capacity and surface E_F -LDOS. It seems that the total chemisorption capacity cannot be discussed solely in terms of average electronic properties of the clean surface. The averaging procedure erases much information of the kind used, e.g., in ensemble models,³⁷ where groups of specific surface sites define a catalytic entity. Another viewpoint sees the difficulty as due to the progressive change of E_F -LDOS on the metal surface atoms while the coverage is going up: on Pt/oxide catalysts these changes are different for hydrogen²⁹ and for oxygen³⁰ chemisorption, and can be related to the rate (rather than the capacity) of chemisorption.

Acknowledgment. We thank Professor G. Schultz-Ekloff (University of Bremen) for preparation of sample PtNaX-65 and Dr. P. Mériaudeau (IRC, Villeurbanne) for his critical suggestion on IR measurements. This research was partially supported by the Département des Sciences Chimiques du CNRS (France) and by the Swiss National Science Foundation (Grant 21-31127.91).

JA962156Y

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