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LETTER TO THE EDITOR

¹⁹⁵Pt NMR observation of local density of states enhancement on alkali-promoted Pt catalyst surfaces

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Abstract. Theoretical results in the literature for an Rh film indicate that the Fermi level local density of states (E_F LDOS) at a fixed (small) distance from the atomic planes increases upon coverage with $\frac{1}{4}$ monolayer of atomic Li. This should change the response of the surface to incoming reactants, and might be an important factor in the ‘promotion’ effect of alkalis in catalysis on transition metals. Experimental data on ¹⁹⁵Pt NMR parameters measured on Pt catalysts can, under certain assumptions, be analysed to obtain the average E_F LDOS at a given type of Pt site (surface, subsurface, bulk). Such an analysis is applied here to Pt catalysts promoted with alkali salts. It is shown that the average E_F LDOS at surface sites increases by 10–15%. At other sites no detectable changes occur.

The catalytic properties of metal catalysts are significantly affected by the addition of alkali promoters [1]. Partly for this reason, the study of the perturbation of transition metals by foreign adatoms is an important subject of surface science [2]. As a rule, electronegative elements [3] (such as P, S and Cl) reduce the catalytic activity of metal surfaces, while electropositive additions [4–6] (such as the alkalis) enhance it. While these effects are generally discussed in a forward–backward electron donation picture based on a molecular orbital scheme [7], an interesting alternative has been put forward by Feibelman and Hamann [8]. They argue that charge density perturbations due to a ‘poison’ or a ‘promoter’ will be screened over a short distance by the metallic electron gas, and that therefore the effect of such low-coverage agents cannot occur via these perturbations. Their calculations for a two-layer Rh(001) film with $\frac{1}{4}$ monolayer coverages of atomic P, S Cl or Li identify however a non-screened quantity that does change with coverage: the Fermi level local density of states (E_F LDOS). The electronegative S, P and Cl reduce, and the electropositive Li increases the E_F LDOS just outside the sample surface. Feibelman and Hamann suggest that the first interaction of an incoming reactant molecule with the metal surface is through Fermi level electrons, since these can be rearranged at low energetic cost. Other authors [9] have developed similar ideas, but at the moment most of the reasoning remains qualitative.

We [10] and others [11] have previously shown that ¹⁹⁵Pt NMR data reflect adsorbate induced modifications of the surface density of states. While it is true that some modelling is needed to go from the data to the local raw densities of states, this modelling is rather straightforward and NMR is unique in its capability to study these quantities in real catalysts, virtually without perturbation of the electronic structure (the probing quanta having typical energies of about 0.01 K). We therefore decided to see what can be learnt by NMR about this specific question.

The starting material to prepare our samples is from the same batch as sample 3 in [12]. It is 4.4 wt% Pt on TiO₂ anatase. The average dispersion determined from electron

microscopy is 60%, and we will refer to the material as Pt-60. We also repeated some measurements on a sample used previously, sample 1 (spectrum 2a) from [12]. This has 36% dispersion and a nominally clean surface: it will be referred to as Pt-36-clean. Two samples of Pt-60 with nominally clean surfaces (Pt-60-clean1 and Pt-60-clean2) were prepared by the same treatment as Pt-36-clean (see [10] for details). There was a 17-month interval between the two preparations. Two samples were impregnated, one with LiNO_3 and one with KNO_3 and re-reduced: these are designated Pt-60-Li and Pt-60-K. The impregnation was done with a nominal alkali/Pt atom ratio of two. The samples were dried at 100 °C for 1 h. The re-reduction consisted of degassing at 300 °C, reduction under 1 bar of static H_2 at the same temperature, and degassing again at 430 °C. A final reference sample, Pt-60-red, was prepared by performing the re-reduction step only, without initial impregnation. All samples were sealed in a glass ampoule under He pressure of about 400 Torr immediately after preparation without exposure to air.

The quantity, the dispersion and the valence state (atomic or ionic) of the alkalis on the Pt surface after such impregnation treatment are not known at present. Model catalysts of Pd and Ni on SiO_2 , promoted by alkali nitrates in the precursor state, have been studied by various techniques. After reduction, the alkali has been found in ionic form, associated with a counter-ion (oxygen, hydroxyl, silicate), both on the support and on the metal [13–16]. The situation on our Pt surfaces might therefore be different from that in the theoretical model [8]. On the other hand, the x-ray photoelectron binding energies of the metallic Pd are substantially lowered after alkali addition [13]. This might be related to the lowering of the work function after atomic Li coverage in the theoretical model.

The feasibility of ^{195}Pt NMR in studying the physical and chemical properties of small supported Pt particles has been well demonstrated by the work of Slichter's group [17] and in our laboratory [18]. The main feature is that the small Pt particles give a very broad NMR lineshape because of the significant fraction of surface and subsurface Pt atoms with respect to the bulk like ones [18]. Due to differences in local electronic structure, the nuclei in bulk like Pt atoms resonate at 1.138 G kHz^{-1} , giving the largest Knight shift (about -3.34%), and those in clean surface like atoms resonate in the region of 1.100 G kHz^{-1} (the conventional position of zero Knight shift for metal Pt). This feature permits us to distinguish easily the surface like spectral region from the bulk like one and therefore facilitates the investigation of surface phenomenon. However, the technical disadvantage of this situation is the poor signal/noise ratio at a given spectral position (for a fixed number of atoms in the NMR samples) and one has to resort to long measuring to reach an acceptable signal/noise ratio.

In figure 1, we show the ^{195}Pt NMR spectra of Pt-60-clean1, Pt-60-Li and Pt-60-K. They were recorded point by point by scanning the frequency with a spin echo sequence at 80 K. The experimental details have been described in a previous paper [10]. The three spectra here are normalized to the same area under the line. The spectra of Pt-60-clean2 and Pt-60-red coincide with that of Pt-60-clean1, and all three are in very good agreement with our earlier result (spectrum 3a of [10]). The change in spectrum upon alkali doping is only slight, when compared with the marked effects of H_2 chemisorption, or those of high-temperature reduction (see spectrum 3b and 3c of [10]). We present in figure 2 the spin lattice relaxation times measured across the spectra at 80 K using a saturation recovery technique. All relaxation curves could very well be represented by single exponentials over time intervals of at least five t_1 periods. At the high-field side of the spectrum (field/frequency ratios above 1.11 G kHz^{-1}) the values are independent of treatment: it seems that the influence of alkali impregnation is restricted to surface Pt atoms. The impregnation treatment shortens the t_1 of the surface atoms, in contrast to CO or H_2 chemisorption, which lengthens the relaxation times. The details of the surface treatment seem to have some influence on the

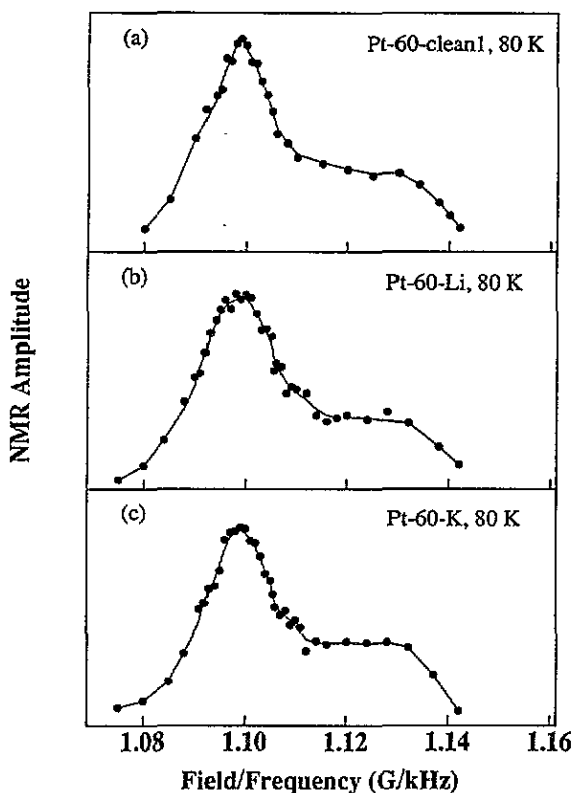


Figure 1. ^{195}Pt NMR spectra obtained by the point by point spin echo method. All spectra were recorded at 80 K and normalized to the same area. The spin-spin relaxation (t_2) effect has not been corrected; the time interval between the two pulses that generate the spin echo is 20 μs . No considerable change of NMR spectra was observed upon adsorption of Li and K.

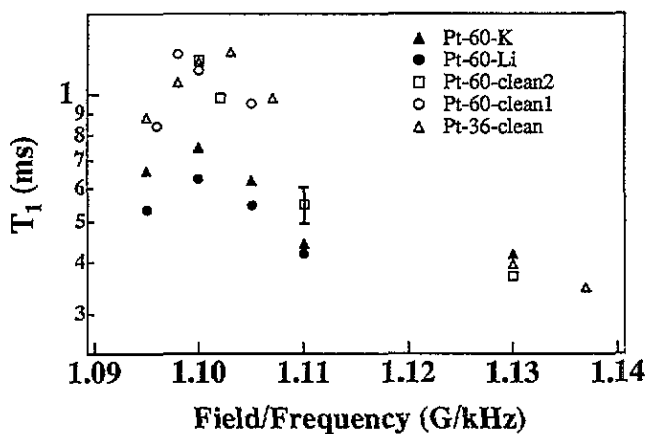


Figure 2. The spin lattice relaxation times across the spectra for clean surface and alkali impregnated Pt catalysts. The temperature is 80 K (the data for Pt-36-clean are from [9] and have been scaled). A typical error bar of $\pm 10\%$ is shown. Below a field/frequency ratio of 1.11 G kHz^{-1} (in the spectral region of the surface atoms) there is a significant shortening of t_1 in the alkali impregnated catalysts.

t_1 measured at 1.10 G kHz^{-1} : the values for Pt-60-clean1, Pt-60-clean2 and Pt-36-clean, all three prepared according to the same protocol, coincide very well, at $1.21 \pm 0.07 \text{ ms}$. The Pt-60-red value seems to be slightly lower at 1.0 ms , while Pt-60-Li and Pt-60-K have t_1 values of 0.61 and 0.71 ms .

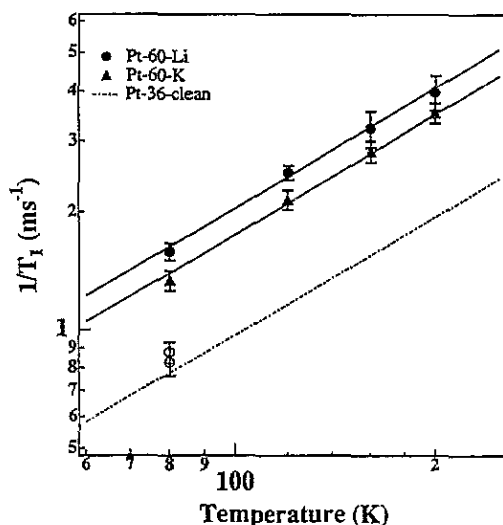


Figure 3. The spin lattice relaxation rates of Pt-60-Li and Pt-60-K as function of temperature. The straight lines show that the Korringa relation—the NMR fingerprint of metallic state—holds for both samples ($t_1 T = 49.1 \pm 1.5 \text{ ms K}$ for Pt-60-Li and $57.3 \pm 1.7 \text{ ms K}$ for Pt-60-K). Shown also here is the Korringa relation ($t_1 T = 103 \pm 7 \text{ ms K}$) of Pt-36-clean found in [10] and the points at 80 K from figure 2 for Pt-60-clean (open circles) and the re-measured value for Pt-36-clean (open triangle).

The spin lattice relaxation rates as a function of temperature measured at 1.10 G kHz^{-1} for both Li-Pt and K-Pt are shown in figure 3. The straight lines indicate the Korringa relation $t_1 T = \text{constant}$, the NMR fingerprint of metallic state. Shown also in figure 3 is the Korringa relation found for Pt-36-clean in [10] (at 1.10 G kHz) and the points at 80 K from figure 2. The equilibrium amplitudes of the NMR signal follow Curie's law indicating that the same number of nuclei contribute to the signal at all temperatures. To within the experimental precision, all surface Pt nuclei are in a metallic environment.

Both the Knight shift and the spin lattice relaxation rate t_1^{-1} contain contributions from spin and from orbital susceptibility. A correct description of the spin dependent parts is complicated by enhancement effects, which result in a Stoner type enhancement of the uniform susceptibility, and in core polarization contributions to the hyperfine fields. (There is no enhancement of the orbital parts and we will follow the treatment given by Jaccarino [19] for bulk Pt). To describe the spin effects, one needs to consider the enhancement of the complex non-local susceptibility $\chi(r, r')$. To keep the problem tractable, and also to maintain contact with earlier treatments, we suppose distinguishable s like and d like susceptibilities and hyperfine fields. Each static susceptibility is enhanced by a factor characterized by an exchange integral. The relation between static (in K) and dynamic (in t_1^{-1}) enhancements is considered to be known [20], and to be the same for s and d like susceptibilities. The site dependence of K and of t_1^{-1} is then taken as the site dependence of the (bare) densities of states appearing in the equations, all other parameters (specifically the hyperfine fields and the exchange integrals; but also the so called reduction factors that describe the relative

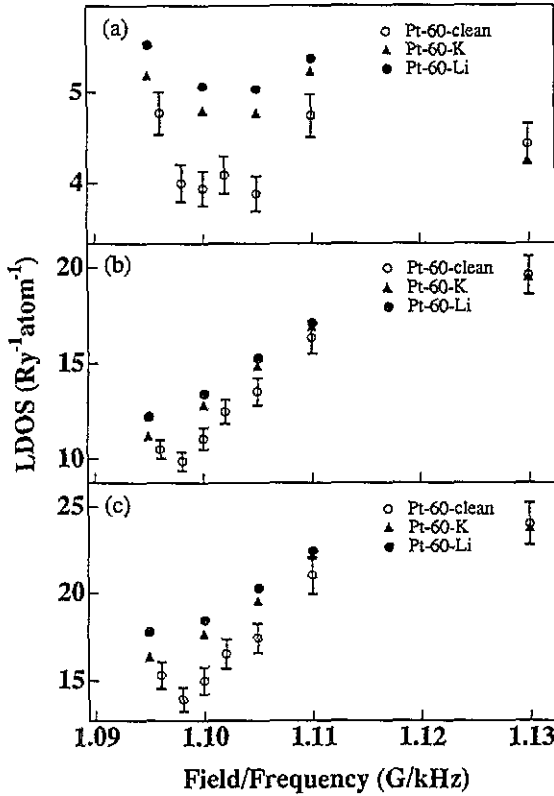


Figure 4. E_F LDOS obtained from data in figure 2 and (1) and (2). We present in panel (a) the s like, (b) the d like and (c) the total E_F LDOS. The shortening of times t_1 in figure 2 gives an enhancement of both s like and d like E_F LDOS and hence the total E_F LDOS for Pt-60-Li and Pt-60-K in almost the whole surface like region compared with those of Pt-60-clean. The error margin is about $\pm 5\%$ of the corresponding values and reflects the about $\pm 10\%$ error of measured t_1 values. For clarity, we only show the error bars for Pt-60-clean.

importance of e_g and t_{2g} symmetries in the d like densities of states) are taken as site independent. The equations so adopted are

$$K = [1/(1 - \alpha_s)]\mu_B^2 D_s(E_F)H_{hf,s} + [1/(1 - \alpha_d)]\mu_B^2 D_d(E_F)H_{hf,d} + K_{orb} \quad (1)$$

$$S(t_1 T)^{-1} = k(\alpha_s)K_s^2 + k(\alpha_d)K_d^2 R_d + [\mu_B D(E_F)H_{hf,orb}]^2 R_{orb} \quad (2)$$

where the different notations are $D(E_F)$ for the (bare) density of states at the Fermi level, α for the Stoner enhancement factor for the static susceptibility, and $k(\alpha)$ for the Korringa enhancement factor [20]; H_{hf} represents hyperfine fields, indexes s, d and orb stand for s band, d band and orbital contributions and R_d and R_{orb} are reduction factors due to the orbital degeneracy [19]. The relation between α and $D(E_F)$ is taken as

$$\alpha_\lambda = I_\lambda D_\lambda(E_F) \quad \lambda = s, d \quad (3)$$

where I is an appropriate exchange integral. The constant S is given by

$$S = (\gamma_e/\gamma_N)^2 \hbar/4\pi k_B \quad (4)$$

where γ_e and γ_N are the electronic and nuclear gyromagnetic ratios and k_B is the Boltzmann constant.

While this scheme clearly cannot be totally justified, it has shown its utility as a model, to which experimental data can be fitted: the pair of values K , t_1^{-1} is transformed in the

pair $D_s(E_F)$, $D_d(E_F)$ (the s and d like densities of states at the Fermi energy). Notably, the E_F LDOSs so obtained for Pt catalysts with a nominal clean surface or an H_2 chemisorbed surface [10] are in qualitative agreement with theoretical calculations: the E_F LDOS at the surface decreases with respect to the bulk value for the clean surface case [21] and diminishes further upon H_2 chemisorption [22]. The LDOSs in our parametrization, (1) and (2), should represent some average over the Wigner-Seitz cell; the quantities discussed by Feibelman and Hamann [8] are the (non-averaged) densities of states when going outwards from the surface atomic plane. One may expect though that if one increases or decreases, so does the other.

The data from figure 2 are analysed according to (1) and (2) in figure 4. It is clearly seen that alkali impregnation increases the LDOS at E_F on the surface (in sharp contrast to H_2 chemisorption, which diminishes the LDOS at the surface). It is known that ^{195}Pt NMR parameters are essentially independent of support material, but rather sensitive to the surface condition. It seems therefore reasonable to assume that at least some of the added alkali ends up on the surface (but not in the interior) of the Pt particles. Since we detect only a single-exponential relaxation, it seems that all surface Pt atoms are in a very similar environment. We do not find an important fraction (of more than say 5 or 10%) of non-metallic surface Pt atoms: it seems likely that alkalis do not form a significant quantity of ionic bonds on the surface of the Pt particles. All the characteristics are a strong indication that the increase in LDOSs at E_F on the surface, predicted to occur as a result of atomic alkali coverage [8], is indeed present in our alkali salt impregnated Pt catalysts. A more quantitative study of the relation between alkali coverage and LDOS change is clearly desirable, and in principle feasible; but we hope that already this qualitative result will lead to renewed interest in the (possible) relation between Fermi level properties of a metal surface and its surface chemistry.

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