

Tailoring the Frontier Orbitals at the Surfaces of Platinum Catalysts

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Received: August 13, 1997; In Final Form: October 15, 1997[⊗]

Within the frontier orbital picture for metal chemistry, the local density of states at the Fermi energy (E_F -LDOS) plays the equivalencies of the *highest-occupied molecular orbitals* (HOMO) and the *lowest-unoccupied molecular orbitals* (LUMO) in the molecular cases. We show here that one can effectively engineer the clean surface E_F -LDOS, i.e., the frontier orbitals, of a platinum catalyst *already* formed within a zeolite–NaY matrix, by simply exchanging the counterion in the matrix. The potassium (K) increases while the proton (H) decreases the clean surface E_F -LDOS. The degree of enhancement or reduction depends on the degree of ion-exchange. When the intramolecular stretching frequencies of chemisorbed carbon monoxide (CO) on these E_F -LDOS enhanced and decreased samples were measured, the values extrapolated to zero coverage show an almost linear relationship with their corresponding clean surface E_F -LDOS before chemisorption.

I. Introduction

The frontier orbital picture for metal surface chemistry^{1–3} attempts to correlate quantitatively the catalytic activity of a metal for chemisorption with attributes of its clean surface. In the simplest case, just a single number, the Fermi level local density of states (E_F -LDOS) at the clean surface sites, is considered.⁴ Molecular chemisorbed carbon monoxide (CO) on transition metal (Ni, Pd, and Pt) surfaces is a frequently used model system for developing these ideas.¹ The weakening of the intramolecular CO-bond after chemisorption is described as a result from interactions between the frontier orbitals of the metal (the orbitals at the Fermi energy) and those of the CO molecule (the 5σ and $2\pi^*$ orbitals). In a recent paper,⁵ by combining the ¹⁹⁵Pt NMR of Pt catalysts^{6–12} and the in situ FT infrared spectroscopy, the authors have given strong experimental support to this picture. How to engineer these frontier orbitals, therefore, is of great interest, since it may have potential important impact on future design and/or finding of new efficient metal catalysts. As a further step from ref 5, we shall show in the present paper that, for a platinum catalyst *already* formed within a zeolite–NaY matrix, one can effectively *tailor* the clean surface E_F -LDOS, i.e., the frontier orbitals, by simply exchanging the counterion in the matrix, as monitored by the conventional ¹⁹⁵Pt NMR of Pt catalysts.^{5–12} When the intramolecular stretching frequencies of carbon monoxide (CO) chemisorbed on these E_F -LDOS enhanced and decreased samples were measured in situ, the values extrapolated to zero coverage show an almost linear relationship with their corresponding clean surface E_F -LDOS before chemisorption: the higher the clean surface E_F -LDOS of platinum catalyst, the lower the stretching frequency of CO chemisorbed on it. The interception of this linear relationship at zero E_F -LDOS is ca. 2120 cm^{−1}, close to but lower than 2143 cm^{−1}, the value of free CO,¹³ suggesting the soundness of the frontier orbital interaction picture.

TABLE 1: The Exchange Degrees of Counterion, the Surface E_F -LDOS Values, and the Extrapolated Zero-Coverage FT-IR Results

sample	exchange degree (%)	E_F -LDOS (1/Ry·atom)	FT-IR ν_0 (cm ^{−1})
PtKY	93	23.5 ^a	2030
PtNaKY	70	20.4	2049
PtNaY ^b	0	18.3	2057
PtNaHY ^b	73	17.3	2063
PtHY	94	12.9	2069

^a This is a very rough estimate. See text for details. ^b Data taken from ref 5.

II. Experimental Section

Our starting material is a batch of a well characterized PtNaY catalyst^{10,14} with 11% platinum loading. The metal particles, already formed in the matrix, have a dispersion of 64%, as determined by transmission electron microscopy (TEM). From this batch, three additional samples were prepared by exchanging the counterion Na⁺: two exchanged by K⁺ with exchange degrees of 93% and 70% respectively; the other exchanged by H⁺ with an exchange degree of 94%. The exchange degrees were determined by atomic absorption after calcination at 1200 K and are shown in Table 1. The samples are designated respectively as PtKY, PtNaKY, and PtHY. The exchange procedure was done at 60 °C in aqueous solutions of KCl and of NH₄Cl under stirring, followed by washing with deionized water, and was repeated several times to obtain the desired degree of exchange. The materials so obtained were dried under vacuum at room temperature and the H⁺-exchanged sample was carefully calcinated in order to decompose the NH₄⁺. All samples were finally rereduced¹⁴ by hydrogen.

The conventional ¹⁹⁵Pt NMR techniques of Pt catalysts^{5–12,14} were used to obtain the clean surface E_F -LDOS. The NMR samples were sealed into glass ampules under He atmosphere without contact with air after the standard cleaning procedure.¹⁴ The measurements were carried out on a home-assembled spectrometer equipped with a 8 T superconducting magnetic field.¹⁰

For each of the samples studied by ¹⁹⁵Pt NMR, a small amount of sample from the same batch was used for in situ CO IR measurements after chemisorption. The techniques used

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[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1997.

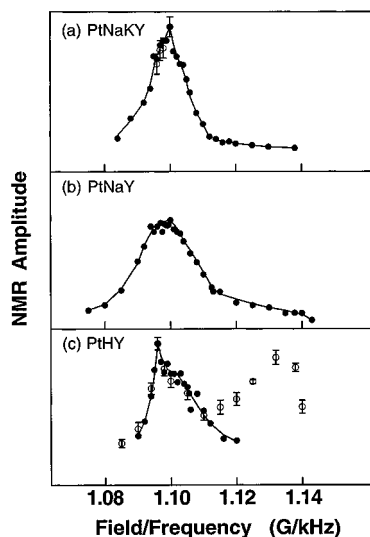


Figure 1. ^{195}Pt NMR spectra obtained at 80 K by the point-by-point spin-echo method. All spectra of solid symbols were normalized to the same area: (a) PtNaKY, (b) PtNaY, and (c) PtHY. The open symbols in panel a are the spectral points of another K^+ -exchanged sample PtKY. The signals were normalized by equaling the signal at 1.100 G/kHz (maximum) to that of PtNaKY (solid symbols). The open symbols in panel c are the spectral signals from the second rereduced PtHY sample after opening the glass ampule of the first treated one (see text for details). They were normalized by equaling the signal at 1.096 G/kHz (maximum) to that of the first treated sample (solid symbols). The spectrum of open symbols shows that the second rereduction made bigger particles appear. The dispersion estimated from the spectrum (ratio of surface peak to total) is ca. 42%. The original sample (panel b) has 11% platinum loading and a TEM-determined dispersion of 64%. The TEM measurements on samples just after ion-exchange show no detectable variation of particle size distribution. This is confirmed by the spectra of PtNaKY and of the first treated PtHY since no significant signals have appeared in the high-field region.

were the same as before.⁵ The pressed wafers were rereduced in the sample cell before the introduction of 15 Torr of CO at room temperature. The subsequent measurements were carried out on a Bruker IFS-84 spectrometer with nominal resolution of 2 cm^{-1} . A series of CO IR spectra were recorded at room temperature after the sample was evacuated at successively higher temperatures starting from room temperature for a constant period of time. The relative integral of the IR band at each temperature gives an estimate of the corresponding relative coverage. By extrapolating the stretching frequency-vs-coverage plots to zero coverage, we obtained the results collected in Table 1. Readers are referred to ref 5 for more detailed information.

III. Results and Discussions

In Figure 1, we show the ^{195}Pt NMR spectra of the clean surface samples, where all spectra of solid symbols were normalized to the same area. In Figure 2 are the corresponding nuclear spin-lattice relaxation curves, measured at their spectral maxima and at a temperature of 80 K. The poor signal/noise ratio due to an insufficient sample quantity of PtKY, caused by the loss of material during the ion-exchange procedure, prevented us from obtaining the experimental data as completely as for the other samples within reasonable time. The open symbols in Figure 1a are the measured spectral points of PtKY that were normalized by the signal amplitude of PtNaKY at 1.100 G/kHz. The good coincidence of the rest points with the spectrum of PtNaKY suggests that PtKY may have a similar Pt surface spectrum. The solid symbols in Figure 1c are the spectral points for PtHY after first cleaning and sealing

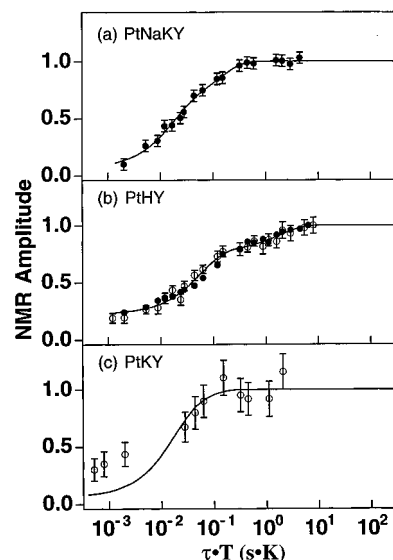


Figure 2. Normalized time-temperature scaled relaxation curves: (a) for PtNaKY, (b) for PtHY, and (c) for PtKY. The relaxation curves were measured at 80 K and at the spectral maxima: 1.100 G/kHz for PtKY and PtNaKY, 1.096 G/kHz for PtHY. The error bars represent the relative noise amplitudes. In panel b the solid symbols are the data of the first treated sample, and the open ones are those of the second treated sample. The good coincidence of these two data sets suggests that both samples have the same surface electronic properties. The solid lines were from a two-exponential function fit. Note that the fit for PtKY was obtained from a very rough estimate (see text for details).

procedures for NMR sample. To check whether the observed variations are due to an unintended residual hydrogen adsorption,¹² we opened the NMR ampule and treated the sample again. Unfortunately, the second treatment increased the particle size, as indicated by an increase of signals in high-field bulk-like spectral region (open symbols). However, the normalized spectra (by equaling the signals at 1.096 G/kHz) show an excellent overlap of the surface peaks. Note that, as far as the electronic properties as seen by ^{195}Pt NMR are concerned, change of particle size will *not* affect our conclusion here. It has been shown^{5,10} that, for a given zeolite matrix, i.e., constant acidity, the E_F -LDOS at the surface is independent of dispersion. The excellent coincidence of the relaxation data after both treatments (Figure 2b) is consistent with this statement.

The spin-lattice relaxation data in Figure 2 were fitted to a two-exponential function of five adjustable parameters: two T_1 's, the residual amplitude $M(0)$, the fully relaxed amplitude $M(\infty)$, and the fraction ratio of one component. The details about the data analysis and the deduction of the clean surface E_F -LDOS values can be found in ref 5. We used here a typical-value procedure for data analysis.⁵ The E_F -LDOS values so obtained are shown in Table 1. Note that the value of PtKY was obtained from a very rough estimate. Clearly seen from Figure 2, this is the fastest relaxed sample, but the data available do not permit a meaningful five-parameter double-exponential fit as we normally performed: the result is essentially the same as a single-exponential fit that gives a big unsaturated fraction (ca. 0.34 with fully relaxed amplitude equal to 1). Such a big unsaturated fraction may arise from a very rapidly relaxed component. By assuming that this component is not slower than the fast component of PtNaKY, i.e., by fixing the fast relaxation rate and the residual amplitude at $t = 0$ to those of PtNaKY, we obtained the solid line in Figure 2c and the value shown in Table 1. The E_F -LDOS data for PtNaY and PtNaHY in Table 1 were taken from ref 5. Though PtNaHY was not prepared from the same starting material, it has an interesting intermediate exchange degree (73%) of H^+ . For this sample,

the H^+ -exchange was done before the loading of platinum. The data in Table 1 show clearly that the frontier orbitals of platinum catalysts encaged in zeolites can be effectively engineered by simply modifying the counterion through standard procedures.

In his seminal works on the reactivity of aromatic molecules,^{15–17} Fukui abolished the traditional total-electron-density approach and stressed the paramount importance of the frontier electrons among all electrons in the molecule. He established an almost one-to-one relation between the sites possessing the highest calculated frontier electron densities in an aromatic molecule *before* the reaction and the substitution sites found experimentally *after* the reaction. One can therefore consider the distribution of the frontier orbitals—both the *highest occupied molecular orbital* (HOMO) and the *lowest unoccupied molecular orbital* (LUMO)—as an attribute of a “clean” aromatic molecule that *predicts* the substitution sites for the following reaction. After reaction, such an attribute will certainly be changed and different from that of the “clean” aromatic molecule.

Theoretical work by Hoffmann, Feibelman, van Santen, and their co-workers^{1–4} has extended this frontier orbital concept to the chemisorption reactivity of transition metal surfaces. In a metal, the HOMOs and the LUMOs are not so well defined energetically as in the molecular case. In the quasi-continuum of the valence band no energy gap appears between occupied and unoccupied levels, i.e., those below and those above the Fermi level. Formally, the inverse of the density of states at the Fermi level (E_F -LDOS) can be used as a measure of an effective HOMO–LUMO splitting for metal atoms in the bulk. On surfaces, the surface E_F -LDOS should be used.

Adopting the frontier orbital picture for chemisorption on a metal surface, Fukui's findings suggest that there should exist some correlation between the clean-surface E_F -LDOS and its reactivity. For CO chemisorbed at a very low coverage, it interacts with an essentially unmodified clean surface. The surface E_F -LDOS measures at the Fermi level the number of the metal's LUMOs that are available to pull electrons out of CO's bonding HOMO and that of the metal's HOMOs that are ready to put their electrons into CO's antibonding LUMO. The result is a weakening of the CO-bond, through a CO 5σ forward- and $2\pi^*$ backward-donation mechanism, first proposed by Blyholder¹⁸ and then confirmed by many others.¹⁹ It will be indicated by a lowering of the stretching frequency measured by IR spectroscopy, with respect to its value in the free molecule. As a consequence, one would anticipate that the higher the clean surface E_F -LDOS is *before* the chemisorption, the lower the stretching frequency of CO will be *after* the chemisorption. In Figure 3, we show the plot of the stretching frequency of chemisorbed CO vs the corresponding *clean* surface E_F -LDOS before chemisorption. Indeed, the anticipated correlation is nicely confirmed here and is almost linear. The solid line in Figure 3 is a linear fit of the data with an intercept of ca. 2120 cm^{-1} at zero E_F -LDOS. Though some caution should be taken, it may be suggestive to compare this value with the stretching frequency of free CO, which is 2143 cm^{-1} .¹³

The result of present work may be of both *practical* and *fundamental* importance for future efforts toward a better understanding of heterogeneous catalysis. First, it shows that for a platinum catalyst already formed in a zeolite matrix, the frontier orbitals of the catalyst can be easily tailored by simply exchanging the counterions of the matrix. This may be of practical interest in the future design and/or engineering of metal catalysts. Second, by supplying more detailed data which confirm the findings of ref 5, it demonstrates again the soundness of the simple frontier orbital approach that singles out just one physical quantity, i.e., the average surface E_F -LDOS, to char-

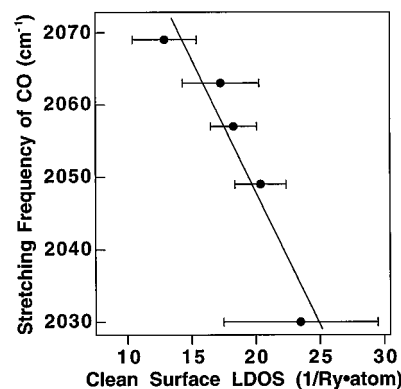


Figure 3. Graphical representation of the results in Table 1. Note that its intercept is 2120 cm^{-1} , a value quite close to stretching frequency of free CO, which is 2143 cm^{-1} .¹³ The error bars show the estimated uncertainty of the E_F -LDOSs propagated from the uncertainty of the relaxation rates and the corresponding amplitude fractions. The nominal uncertainty of IR measurement was $\pm 2 \text{ cm}^{-1}$.

acterize the frontier orbitals on metal surfaces in a way that may be used to *predict* and/or characterize the reactivity for the (CO) chemisorption. Note that a similar statement has been reached by Ruckman and Strongin on the basis of some spectroscopic and theoretical studies of the thin late transition metal overlayers on early transition metal surfaces.²⁰ They also concluded that the number of occupied and unoccupied states at the Fermi level controls the bonding of adsorbates in the cases examined and therefore play a crucial role in CO–metal surface bonding and the dissociation of molecular hydrogen on the surface.²⁰

The correlation found here is the correlation between the bonding strength (measured by the zero-coverage stretching frequency of chemisorbed CO) *after* the chemisorption bond has been formed and the clean surface E_F -LDOS *before* chemisorption, no matter what kind of chemisorption kinetics was involved. Strictly speaking, it is not exactly the correlation between the chemisorption reactivity and the E_F -LDOS. The chemisorption reactivity of a surface site is more related to the idea of the capability of its electrons to reach out and grab the incoming molecule.²¹ However, the correlation does show that a metal having higher clean surface E_F -LDOS is more capable of *weakening* the intramolecular bond of chemisorbed CO and of *strengthening* the metal–CO bond. Extrapolating this observation would suggest that for a given adsorbate, lowering the clean surface E_F -LDOS produces weaker adsorbed molecule that will have higher intramolecular stretching frequency, as usually observed in the cases of noble metals with a full d-band like Cu, Ag, and Au.

Besides being frequently used as a model system, the dissociative or/and molecular chemisorption of CO is also an important reaction step for large scale hydrocarbon synthesis in industry.²² More specifically, it was observed that for CO hydrogenation over transition metal surfaces, the presence of potassium usually enhances the rate as well as selectivities for C_{2+} hydrocarbon production. It is believed²² that weakening the intramolecular bond of chemisorbed CO and strengthening the metal–carbon bond due to the presence of potassium, as indicated by the red-shift of CO stretching frequency, would facilitate the dissociation of CO and therefore enhance the rate as well as selectivities for C_{2+} hydrocarbon production. Relevant to the correlation observed in the present paper and in ref 5, it may be informative to note that there *was* indeed an enhancement of clean surface E_F -LDOS on potassium-promoted Pt/TiO₂ catalyst, accompanied by the usually observed red-shift of the stretching frequency of chemisorbed CO.⁵

IV. Conclusions

The present work shows a promising approach to engineer the frontier orbitals at the surfaces of platinum catalyst. Exchanging existing counterion Na with potassium (K) increases while with the proton (H) decreases the clean surface E_F -LDOS. The degree of enhancement or reduction depends on the degree of ion-exchange, which in turn determines the acidity of the matrix. The exact mechanism that makes the surface E_F -LDOS of platinum catalysts show a systematic variation with the acidity of the faujasite framework is still unknown. One possible explanation might be in term of the average electronegativity of zeolite matrix. One of the important properties of zeolites is that the surrounding of an atom by positive (negative) charges effectively increases (decreases) the electronegativity of the atom.²³ Extrapolating this to a neutral metal particle encaged inside the matrix, it means that the less negatively charged matrix (with higher acidity) could make the particle have higher electronegativity, i.e., higher work function and therefore lower surface E_F -LDOS.² An alternative to this explanation would be to consider the framework-generated electric field around the metal particles, which is indeed very sensitive to the type of counterions.²³ Exchanging the counterions modifies significantly the electric field around the encaged metal particles and may therefore change the distribution of their surface charges,²⁴ then consequently the work function of catalysts, which is consistent with the recently published electrochemical NMR results with electropotential control.²⁵ To explain the acidity dependence of electron deficiency of an encaged neutral metal particle, Samant and Boudart²⁶ have proposed similar work function-related approach, but without providing a model of the supposed relation between particle work function and acidity.

In a recent XPS and IR study of the Pd/K-LTL system,²⁷ Koningsberger and co-workers found that, addition to the well documented C–O bond weakening and turnover frequency (TOF) dropping for neopentane and propane hydrogenolysis from acidic to neutral support, the trend persists *further* into the basic zeolite matrix. Although they disagreed with the classic charge-transfer explanation of the electron deficiency and richness, both of which were used to rationalize their results, they did not give a concrete mechanism accounting for the deficiency and richness. In line with the idea developed here and in ref 5, their experimental data would suggest that the clean surface E_F -LDOS of catalyst may further be enhanced as the basicity of the matrix increases and therefore produce the electron richness observed. Although it is clear that more studies are highly desirable to gain insight into the exact mechanisms responsible for the systematic variation of the clean surface E_F -LDOS with the acidity and basicity of zeolite matrix, it may, however, be still reasonable to state, as a rule of thumb in practice, that increasing the acidity (basicity) of zeolite matrix by properly varying the type of substitution counterion will decrease (increase) the clean surface E_F -LDOS of the encaged Pt (or Pd) catalysts.

Though our results show that the changes in CO chemisorption in our specifically prepared samples can be explained in a simplest way within the frontier orbital picture by variation of the (absolute) value of surface E_F -LDOS, we feel that the importance of orbital symmetries should be emphasized properly. In fact, Fukui's frontier orbital theory in molecular case was not really self-consistent until the works of Hoffmann and co-workers,²⁸ which demonstrated the nodal (symmetrical) properties of the frontier orbitals is as important as its absolute density value. Therefore, rather than just singling out a single number, i.e., the total clean surface E_F -LDOS, a better approximation within the frontier-orbital-interaction picture would

be to consider three numbers: the σ -, the π -, and the δ -like E_F -LDOSs. Their repartition might play an important role in the so-called structure sensitive reactions in which the "matching" of symmetrical characteristics of bonding orbitals between active sites on metal surfaces and the reactants should be crucial.

Acknowledgment. We thank Mrs. G. Wicker and J. Billy for the TEM measurements and the excellent IR measurements and Mrs. M. Dufaux and G. Sapaly for the preparation of ion-exchanged NMR samples. Y.Y.T. thanks the Département des Sciences Chimiques du CNRS (France) for making a position of staff scientist available and the Institut de Physique Expérimentale (EPFL, Switzerland) for accessing NMR facilities. The final version of the manuscript was completed at Chemistry Department, University of Illinois at Urbana-Champaign, and Y.Y.T. benefited from the discussions with Professors E. Oldfield and A. Wieckowski about their electrochemical NMR results.

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