

Research Note

Electronic conditions for carbon–carbon bond rearrangements on metallic surfaces

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Abstract

The relation between the electronic structure of platinum metallic aggregates and their selectivity is discussed. A correlation is underlined between the energy of the d -band center, ε_d , and the catalytic reactions such as hydrocarbon isomerization. Similar behavior appears when CO chemisorption on a platinum surface is compared with activity in alkane isomerization. This relationship can be used to interpret the changes in the mechanisms observed in acid catalysis, with bimetallic systems, and with catalysts treated by microwaves. © 2003 Elsevier Science (USA). All rights reserved.

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1. Introduction

In this research note, our aim is to show that the global knowledge acquired in heterogeneous catalysis and surface science can lead to unified view of catalytic processes such as hydrocarbon isomerization on Pt-based catalysts.

In order to be concise, we will limit our attention to the isomerization of hexane hydrocarbons, the mechanisms of which have been studied in detail in a great number of papers [1–6]. It is worth noting first that hydrocarbon isomerization takes place on Pt, Pd, and Ir only. Following the literature, two basic mechanisms have been evidenced, namely the cyclic and the bond shift mechanisms, hereafter referred as CM and BS, respectively. They are illustrated in Fig. 1.

The former mechanism is characterized by the C5 cyclic intermediate formed on the surface via a dehydrocyclization reaction, before the breaking of one of the five C–C bonds of the cycle. The latter mechanism involves, in the adsorbed phase, a C–C bond breaking before the formation of

a new one. The two mechanisms, BS and CM, can be distinguished by performing experiments with ^{13}C -labeled molecules [7–9]. Fundamental information on the conditions required by each of these mechanisms was given by the study of alumina-supported Pt catalysts as a function of the metal dispersion [10–13]. This is illustrated in Fig. 2, which gives

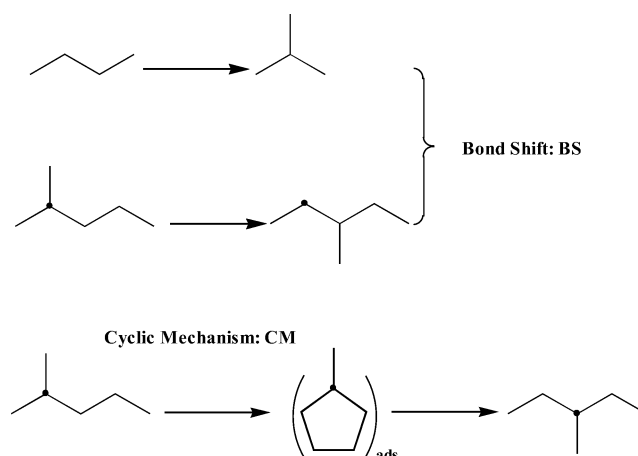


Fig. 1. Bond shift mechanism “BS” and cyclic mechanism “CM.” Cyclic type isomerization involves first carbon–carbon bond formation and then carbon–carbon bond rupture; it is also responsible for the isomerization of large molecules [1]. In contrast, bond shift isomerization involves first carbon–carbon bond rupture and then carbon–carbon bond recombination, and it also accounts for the isomerization of short-chain paraffins.

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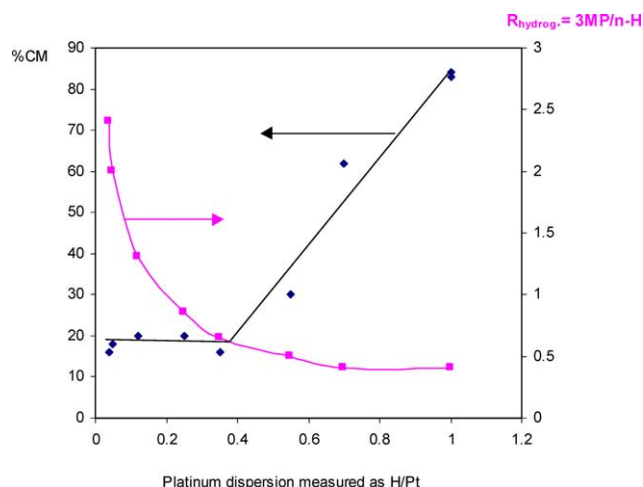


Fig. 2. Influence of the platinum particle sizes in 2-methylpentane isomerization reactions (black diamonds) and methylcyclopentane hydrogenolysis (black squares). (1) The percentage of the cyclic mechanism (black diamonds) is determined in the 2-methylpentane [2- ^{13}C] (2-MP-2 ^{13}C) to 3-methylpentane [3- ^{13}C] (3-MP-3 ^{13}C) reaction and the bond shift is determined in the 2-methylpentane [2- ^{13}C] to 3-methylpentane [2- ^{13}C] (3-MP-2 ^{13}C) reaction as represented in Fig. 1. $\% \text{CM} = (3\text{-MP-3 } ^{13}\text{C}) / [(3\text{-MP-3 } ^{13}\text{C}) + (3\text{-MP-2 } ^{13}\text{C})] \times 100$. (2) The ratio R_{hydrog} (black squares) is equal to 3-methylpentane/ n -hexane and is obtained from the methylcyclopentane (MCP) hydrogenolysis reaction. (3) There are no crystallites smaller than 1 nm in the catalysts of low dispersion: for hydrogen chemisorption on platinum particles $(\text{H}/\text{Pt}) \leq 0.5$. In that case the MCP hydrogenolysis is selective, and the value of the ratio R_{hydrog} is higher than 0.5. Above $(\text{H}/\text{Pt}) \geq 0.5$, the MCP hydrogenolysis is nonselective, R_{hydrog} is equal to 0.5, and crystallites smaller than 1 nm are present, as determined by electron spectroscopy and SAXS analysis.

the evolutions of (i) CM as a percentage of the total isomerization reactions in the isomerization of 2-methylpentane to 3-methylpentane and (ii) methylcyclopentane hydrogenolysis, measured as the ratio of 3-methylpentane to n -hexane versus the Pt dispersion.

We can see in Fig. 2, that CM is largely in the minority (about 20%) for low dispersions up to 50% ($\text{H}/\text{Pt} = 0.5$). However, it starts to increase from this value so that it is essentially the only mechanism evidenced at complete Pt dispersion. Furthermore, at the break of the slope, a change in the mean metallic particle sizes was observed by small angle X-ray scattering (SAXS). It was carefully checked that no crystallite smaller than 1 nm was present on the low-dispersal catalysts. Clearly, CM requires that the Pt particles be smaller than 2 nm, whereas BS dominates on bigger particles.

All the experimental results mentioned above, as well as in this research note, were obtained under a large excess in hydrogen; this explains why we do not raise the role of surface hydrocarbon residues in alkane reactions even if we have already worked on this subject [14].

Now, we can switch to results obtained for the same isomerization mechanisms on various Pt single crystal surfaces: (557), (119), (311). These are stepped surfaces labeled respectively in Somorjai's notation Pt(S) [6(111) \times (100)], Pt(S) [5(100) \times (111)], and Pt(S) [2(100) \times (111)]. We can examine in Table 1 the percentage of CM in the isomerization of 2-methylpentane-[2- ^{13}C] to 3-methylpentane-[3- ^{13}C] on these surfaces, together with those obtained on a polycrystalline Pt ribbon and two alumina-supported Pt catalysts [15–17].

We note first that the results obtained on a Pt(111) surface are not reported simply because the activity of this surface for this reaction was very low. The presence of a high step density on the surface makes the activity noticeable even for (111) terraces, where a low CM percentage could be recorded. However, the CM percentage is far better when terraces are (100) oriented, although the CM percentage is in no case as high as on the best-dispersed catalysts. An important observation is that during the reaction, the so-called (5 \times 1) reconstruction on the (100) terraces of the clean (119) surface is elevated whereas this reconstruction does not take place on the narrow terraces of the (113). This means that the coordination number of the Pt atoms on the (100) terraces is only 8, that is, one unit less than on the (111) terraces. More importantly, during the reaction, the (557) was demonstrated to reconstruct as a Pt(S) [11(111) \times (113)] surface [18–20], so that this surface (as well as the (113) face) presents a high density of the so-called B5 sites already described by Van Hardeveld et al. for the fcc cubooctahedron with an incomplete atomic overlayer [21,22].

At this level of discussion, we can sum up our observations as follows: (i) noticeable isomerization requires a high density of low-coordination sites; (ii) the CM percentage increases at the expense of the BS mechanism when the surface atom coordination decreases, so that CM becomes dominant only on highly dispersed Pt particles, which cannot be mimicked by stepped surfaces. Now that the importance of low-coordination sites for CM appearance has been stressed, we can discuss this point in terms of the local electronic changes which take place correlatively at these sites. It has long been known that the valence band width increases with

Table 1
Isomerization reactions of 2-methylpentane [2- ^{13}C]: relative contributions of the cyclic mechanism [15]

Catalysts used	Pt(557)	Pt(119)	Pt(113)	Pt (polycryst.)	5% Pt/ Al_2O_3	0.2% Pt/ Al_2O_3
Terrace index	(111)	(100)	(100)			
Step site density	0.204	0.153	0.385		0.2 ^a	1.0 ^a
CM%	14	39	42	49	34	76
$\Sigma \text{CM} / \Sigma \text{BS}^b$	2.6	8.3	6.0	5.7	2.9	45.5

^a Accessibility measured as H/Pt by hydrogen chemisorption.

^b $\Sigma \text{CM} / \Sigma \text{BS} = \text{total number of molecules formed via the cyclic mechanism} / \text{total amount of molecules formed via the bond mechanism}$.

roughly the square root of the coordination number [23], so that the local density of states distribution (LDOS) should be reduced for the sites responsible for the CM. Moreover, for more than half-filled *d*-band metals such as Pt, the *d*-band center moves up to lower binding energies as the coordination decreases. This is, for example, the origin of the low binding energy shift of the Pt surface core levels, as demonstrated by photoemission experiments [24]. This suggests that, whatever the surface atom coordination could be, a narrow and low binding energy Pt local density of states would favor the CM for hydrocarbon isomerization. Now, we will see how the suggestion can stand when confronted to various situations encountered with Pt-based catalysts.

2. Support acidity

The term acidity is taken in its global meaning. The consequences of the support acidity for the electronic system of a supported metal have been examined in theoretical [25, 26] and experimental works [27]. It has been stressed that the important parameter to determine the acidity of the support is not its ionicity but the site-dependent Madelung potential. This induces metal polarization and charge transfer at the interface [25,26]. This is equivalent to a positive charge pushing down the metal electronic states. The overall effect will be that the *d*-band center of the metal shifts to high binding energies with increasing support acidity. This has been confirmed experimentally by near-edge X-ray absorption [27]. So we expect that an increasing acidity of the support will reduce the Pt ability for hydrocarbon isomerization by CM. Indeed, on 0.2 wt% Pt/sulfated zirconia, the isomerization pathway via a cyclic mechanism does not take place, although the platinum aggregates are so small that they cannot be observed by transmission electron microscopy [28,29]. Due to its strong acidity [30], we can suppose that the support polarization would induce a shift of the LDOS center of the neighboring metallic sites, increasing its binding energy. Although polarization has short-range influence, this turns out to be especially important for a highly dispersed metal.

3. Bimetallic catalysts

The consequences of alloying for the catalytic activity of a metal are far from a simple affair, as pointed out by the pioneer work of Sachtler and co-workers [31–33]. The effect on the local electronic system can be discussed only on a case-by-case basis. So we will limit ourselves to one example. We examined the case of a Pt atom diluted in the surface of Au. The surface behavior of Pt–Au alloys has been the object of very limited experimental work. This is certainly due to the quite complicated phase diagram of these alloys [34]. However, some work devoted to surface segregation in transition metal alloys gives indications of the

general trends expected on these surfaces [35,36]. In Pt-rich alloys, Au segregation energy is strongly negative, so that Au would largely enrich the surface. In Au-rich alloys, Pt segregation energy is predicted to be clearly positive. Thus Pt would be strongly overwhelmed by Au atoms on the surface in most cases. In order to illustrate what the local electronic structure could be in such a case we constructed a model with a three (111)-layer slab of Au. In one of the external layers, one Au atom was replaced by a Pt atom to obtain a (2×2) surface unit mesh with a $\frac{1}{4}$ Pt coverage. The local DOS of Pt was then obtained by ab initio calculations using a spherical-wave basis [37] with 33 *k*-points in the irreducible Brillouin zone. A similar calculation was then conducted on the Pt surface atom of a three-layers Pt(111) slab. Figure 3 illustrates the calculated Pt *d*-DOS for the two models.

We see easily that the Pt *d*-band is largely narrower after dilution in Au. Its center shifts from 2.66 eV in pure Pt to 2.10 eV in the surface alloy with respect to the Fermi level. From this, we can expect for diluted Pt a high propensity to catalyze hydrocarbon isomerization through CM. Actually dramatic changes in reaction mechanisms were observed when platinum was alloyed with gold [38]: while the mechanism of hexane isomerization on 10 wt%

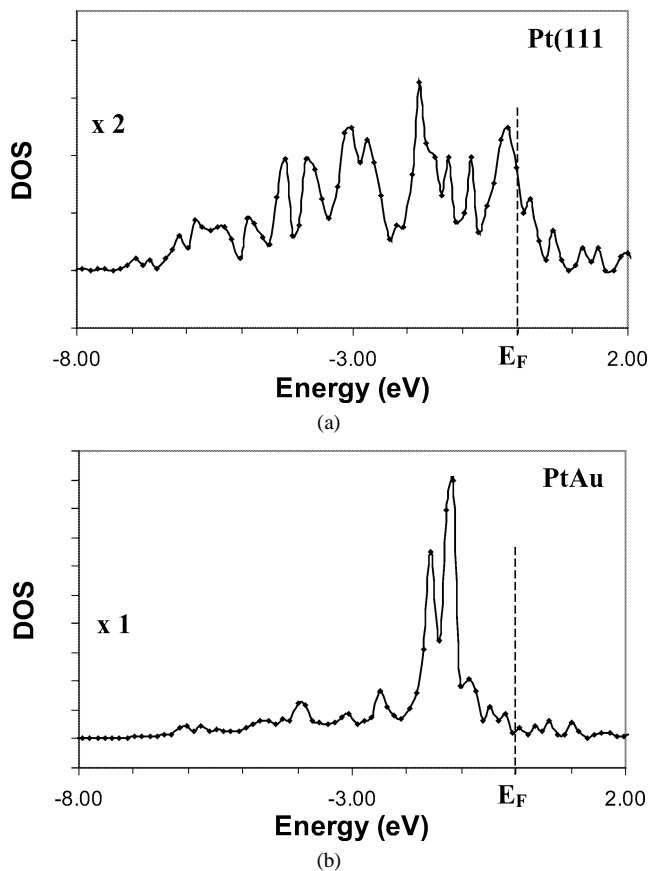


Fig. 3. (a) Local density of states on a surface Pt atom of a three-layer Pt(111) slab. (b) Local density of states projected on a Pt atom diluted in the surface plane of a three-layer Au(111) slab.

Pt/Al₂O₃ was mostly bond shift, on platinum–gold alloy (10% by weight of metal, 15 atom % Pt), only the cyclic mechanism took place; moreover, no noticeable change in selectivity was observed when gold was alloyed to palladium. These results could also be interpreted using the concept of “ensemble size” as introduced by Sachtler [39] and Ponec and Sachtler [40]. The change of selectivity by active site dilution in an alloy surface was attributed to the change of the number of active metal atoms forming this site. We simply note that our argument based on the change of the local electronic structure in relation to the surface atom coordination does not contradict the notion of “ensemble size.”

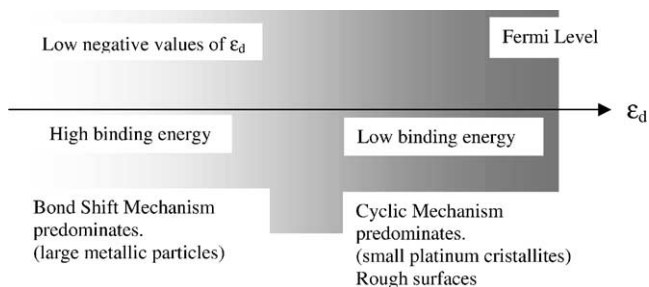
It is time now to recognize that the position of the *d*-band center was already identified as a key parameter in the molecule–surface interaction. A first step can be found in the theoretical work of Nørskov’s group concerning the CO adsorption on flat and vicinal Pt surfaces [41]. The calculations showed strong structure sensitivity of the chemisorption bond between the terraces, steps, and kinks of these surfaces. The lower the coordination of the metal atom was, the stronger the metal–CO bond. This finding was not a surprise by itself as this was in accordance with many previous experimental observations [42]. The most interesting was that this study established a linear relationship between the CO chemisorption energy and the adsorption site electronic structure: the lower the binding energy of the Pt *d*-band center, the higher the chemisorption energy. The explanation is simply that the CO chemisorption bond implies a charge transfer from the metal *d*-band to the unoccupied $2\pi^*$ molecular orbital of CO. By an upward shift of the *d*-band center to the Fermi level (ε_d being the mean energy of the valence band referred to the Fermi level), the occupied metal states get closer to the molecular unoccupied orbital, increasing the coupling between the two levels and the strength of the chemisorption bond. The correlation of the chemisorption bond strength and the adsorption site structure via its local electronic structure was reinforced by the dependence on the metal–metal bond length [43]. This was illustrated by calculation of the CO chemisorption energy on the Ru(0001) surface. The lattice constant of the metal was varied by $\pm 2.5\%$ around its equilibrium value. The longer the Ru–Ru distance was, the higher the chemisorption energy (defined by a positive value). The authors stressed that this was essentially dependent on the in-plane Ru–Ru distance and more or less insensitive to the interplanar distance. Again, the fundamental reason for this behavior was the dependence of the *d*-band center on the surface bond length. Obviously, the roles played by the coordination around an atom on one hand, and the distance between this atom and its first nearest neighbors on the other hand, are qualitatively similar: a lower coordination number (longer 1st neighbors distance) decreases the bandwidth and the *d*-band center binding energy. This can be stated as follows: increasing the metal–metal surface bond length is equivalent to decreasing the metal coordination.

Experimental evidence in agreement with the above theoretical predictions can be found in the reactivity of the bimetallic systems, especially those obtained by depositing a thin transition metal overlayer on a metallic substrate. Many systems were recently examined and a clear correlation appeared between the adsorption energy of CO on the overlayer and the XPS binding energy shift of the surface atom core-levels [44]: the lower the CO chemisorption energy, the higher the binding energy shift. As the latter more or less tracks the position change of the surface *d*-band, we come again to the same point. This change could be related both to the structure of the overlayer and to the chemical interaction with the substrate. Recent experimental results on Pt/Co(0001) [45] put in evidence a case where the former argument is likely to be determining. Indeed, there are strong indications that the surface Pt islands are under compressive stress while keeping a symmetry similar to the Pt(111) surface [46]. As could be expected, the Pt 4*f* core-levels are shifted to higher binding energy in comparison with the Pt(111) surface core-levels. This results in a CO chemisorption energy decrease by some 38%, in agreement with recent density functional calculations [43].

We can now sum up our conclusions as follows:

- (i) The *d*-band center position is a determining parameter for the behavior of static surface reactions (i.e., chemisorption) as well as dynamic processes such as catalytic reactions (e.g., hydrocarbon isomerization). It is one of the parameters monitoring the molecule–surface overlap.
- (ii) Similar behavior appears when CO chemisorption on a surface is compared with its activity in hydrocarbon isomerization. This suggests that the knowledge of CO behavior on a surface could be used to anticipate its catalytic activity, especially for hydrocarbon isomerization.

To illustrate the latter point we can examine some surprising results obtained on microwave-treated 0.2 wt% Pt/neutral γ -alumina. In that case, the relative contribution of the cyclic mechanism was increased compared to that obtained with classical 0.2 wt% platinum γ -alumina catalysts taken as a reference, although the mean metallic particle size also increased [47,48]. At first this seems in contradiction to our above arguments. However, we noted that infrared experiments performed with CO adsorption on these catalysts revealed a 20 cm⁻¹ shift to lower frequency of the C–O stretching mode. This indicates a stronger *d* → $2\pi^*$ electron back-donation, weakening the C–O bond, and hence a better molecule–surface overlap. This should be the signature of a *d*-band shift to lower binding energy or a higher electron density of state near the Fermi level for such catalysts. Hence, to explain these results, we suggest that on the microwave-treated catalysts, the metallic aggregates present very rough surfaces like those present on highly dispersed metallic catalysts, which consequently enhances the cyclic mechanism contribution.



Scheme 1. Schematic representation of the variation of the d -band center, ε_d . A correlation is made between this ε_d variation and the alkane isomerization reactions.

Scheme 1 summarizes the catalytic behavior of platinum catalysts in reforming reactions of hydrocarbons. In this scheme ε_d variation in the valence band is presented, and a parallel is made between this variation and the two main isomerization mechanisms of alkanes on metallic catalysts. No scale is used in Scheme 1, but we may keep in mind that a small variation of ε_d , of a few tenths of an eV, can change the mechanism selectivity between bond shift and cyclic mechanism.

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