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New catalytic concepts from new materials: understanding catalysis from a fundamental perspective, past, present, and future

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Abstract

The thesis of this review is that new catalytic concepts may be derived or discovered from new materials or newly recognized material properties. This thesis is demonstrated by a brief discussion of four materials, and the associated concepts, which enjoyed a certain fashion in the *Journal of Catalysis* and became themes of the author's research. The four materials (or material properties) described are restricted to platinum (exemplary in most cases) supported on TiO_2, yttrium-stabilized zirconia, L–zeolite, and the mesoporous molecular sieve, MCM-41. While it was not recognized at the time, nor was it the driving force for the author's interest, all four materials can be shown to alter catalysis by a kind of metal–support interaction that, in part or entirely, underlies the concept that is being illustrated. Thus, the common metal Pt and the emphasized catalytic property, interaction between a metal particle and an oxide support, are used as the glue to hold together a discussion of otherwise disparate catalytic systems whose selection was dictated by the interests of the author.

1. Introduction

As we survey progress of advancing our understanding of heterogeneous catalysis, our interest will be on new concepts (from the Latin conceptum to conceive in the mind; an abstract or generic idea generalized from particular instances) [1]. While the synonym here is idea, the idea or concept that advances heterogeneous catalysis might be a new material, e.g., the zeolite ZSM-5 [2], a new method for characterizing a material, e.g., X-ray absorption [3], a new catalytic reaction, e.g., olefin metathesis [4], a new technique for studying a catalytic reaction, e.g., in situ transient response infrared absorption spectroscopy [5], or a new and testable mechanism, e.g., restricted transition-state selectivity [6]. Any one of these conceptional areas is a worthy topic for a book. For the purpose of this brief review, I will focus on the catalytic material per se and will choose examples that have involved my personal research. That I thought then (and still believe) that these materials present new and challenging behavior that might lead to new concepts is testified to by the time and interest I have given to them. In no case did the catalytic material or its investigation originate in my laboratory, but in each case one or two publications got my attention, and that of many others in heterogeneous catalysis research, and we all competed to understand the new phenomena, to ascertain the new concept the particular new catalytic material was trying to teach us.

The four materials that I wish to use as examples are (i) noble metals supported on reducible oxides, titanium dioxide in particular, that undergo strong metal-support interaction (SMSI) [7], (ii) noble metal electrodes on yttria-stabilized zirconia (YSZ) that undergo non-Faradaic electrochemical modification of catalytic activity (NEMCA) [8], (iii) aromatization reactions on Pt supported on KL–zeolite [9], and (iv) first-row transition-metal-substituted MCM-41 (mesoporous molecular sieves) [10]. The focus will be on oxide supports, with particular attention to interaction between a metal cluster and the oxide support. While the discussion topic will be the catalyst (support material), the analysis of what was discovered to be conceptionally new will to some extent involve new (in the 40-year history of the *Journal of Catalysis*) methods and techniques of characterization and in one case (Pt/KL–zeolite), a new mechanism, so that to a degree we will be able to touch on advances in concepts in all five areas I have listed above.

My goal is not to demonstrate how these materials have found their way into new industrial processes (although that is the case for Pt/KL–zeolite), but to attempt to isolate the kernel idea that came out of the investigation of these

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materials that has led (in my opinion) to a discontinuity in the way we think about heterogeneous catalysis, i.e., a new catalytic concept. While it is not true that we can identify or date the origin of an interesting and surprising observation from which further investigation leads to complete and accepted explanation, there is a certain pattern of the development of interest in such materials that is generally followed.

In each case, there is a seminal paper(s) which stimulates widespread interest and research in many laboratories around the world, there is a certain season of increasing publications on the catalytic material, and then there is a waning of interest (number of publications). This does not so much signal complete understanding as it does a change of (scientific) fashion or decreased funding because there is a new bandwagon or simply a perceived diminishing returns from investment in additional research in this area. This wave of interest might typically last about a decade; e.g., in the case of SMSI, we might date the "high interest" period from the initial Tauster et al. [7] paper in 1978 to the Haller and Resasco review in 1989 [11].

Before reviewing the four catalytic material areas in some detail, let me summarize the nature of the new catalytic materials that I will attempt to illustrate in each case and outline the order of presentation. For some concepts (perhaps for all) it may not necessarily be the case that no version of the concept had been previously articulated; it may be that the physical nature of the phenomena has been clarified in such a way that it is essentially a different concept, e.g., the case of interaction between a metal particle and an oxide support before and after SMSI.

The idea that metals might behave differently when placed on different supports had been largely viewed as an electronic effect (band theory of delocalized electrons as opposed to shared electrons in a molecular orbital) [12] not involving chemical bond formation between the zero-valent metal and the support [13–15]. The perception, the new concept that is illustrated post-SMSI, is that one or more elements that comprise the support can chemically react with metal particles, that this reaction provides a thermodynamic driving force for moving these elements onto the surface of the metal particles (the so-called decoration model, where a suboxide of the support covers or "decorates" the metal surface) and alters its catalytic activity. It would be fair to say that now we are required to assume that there is no such thing as an inert support, that instead each support, that a varying interaction, depending on the reducing/oxidizing treatment and the temperature of this treatment.

Non-Faradaic electrochemical modification of catalytic activity would not at first appear to have anything to do with SMSI, the NEMCA originating from an electrical current or potential between the catalyst and a second electrode, both deposited on the same solid electrolyte (support). However, we have come to understand that the result of this applied potential is to move oxide species (in the case of oxygen-conducting electrolytes such as YSZ) onto the catalytic metal electrode decorating the metal surface in a way parallel to SMSI. This species is different than that formed from TiO_2 support in that it may not be accompanied by a cation (Ti^{n+}, $n \leqslant 4$, for TiO_2 support) and is an anion that cannot be formed directly from adsorption of gas-phase oxygen. Moreover, we now know that for those reactions involving charge transfer (all reactions to some degree), NEMCA, and metal–support interactions in general, can be interpreted in terms of a work function change that accompanies the decoration of the metal by cations, anions, and/or ion pairs. Thus we find that the concept of SMSI illuminates NEMCA, that NEMCA in turn teaches us more about the phenomena of SMSI, and that both concepts are more fully realized when viewed as a whole. For a more complete discussion of the double-layer approach (NEMCA) to metal–support interaction, see Vayenas et al. in this issue [21].

The aromatization of alkanes, n-hexane in particular, on Pt/KL–zeolite may again be viewed as a dramatic metal–support effect. That is, the investigation of reforming of alkanes on Pt has a history stretching across most of the last century, but supporting Pt in the pores of KL–zeolite results in selectivity of n-hexane to benzene approaching 100% and does not involve bifunctional catalysis (both metal and acid sites, as in conventional catalytic reforming). That the KL support stabilizes very small Pt clusters (perhaps as small as six or seven atoms) against both sintering and deactivation by coke is well established, but the mechanism of the interaction is still in need of further determination. The mere fact that a support not only alters activity and selectivity but also effectively blocks the many thermodynamically possible reactions in favor of one is conceptionally a revelation if not a revolution.

Whether we speak of diatomaceous silica or some more industrially evolved form of silica, it is no exaggeration to say that the use of amorphous, high-area silicas as supports has been around more or less since Berzelius defined catalysis. Thus, to discover that amorphous silica could be synthesized in a new form with highly ordered, uniform mesopores was a clear discontinuity in technology and catalytic science. While a number of new inorganic structures comprised of many different oxides have been spawned by the original Mobil discovery, I will focus only on the structure which has hexagonal arrayed, one-dimensional pores (MCM-41), is comprised primarily of silica, and is used as both a catalyst (incorporating first-row transition metals substitutionally) and a support for metal particles.

The first three materials introduced present different aspects of metal–oxide support interaction and when Al–MCM-41 is used as a support for Pt, so is MCM-41 (see Sections 2.4 and 3). After I have finished with metal–support interactions, I will turn to the substituted MCM-41 as a catalyst per se, but I mostly discuss it in the present, i.e., regarding research in which I am still actively engaged. In this case, the interest, fashion, fascination, etc., of MCM-41 and related structures probably has not yet peaked, so we are close enough to this that a perspective on what the nature of the new concepts may be is less settled. I will emphasize my own work and prejudice and, in this instance, attempt to provide a perspective on fundamental catalytic science of the present and future. Finally, I will pause to assess the state of our understanding of metal–support interaction and contrast and compare four very different systems having in common a metal interacting with an oxide support. I think of this as a personal perspective of what we have learned in the recent past and how we use this information in the present, and I will summarize what we would still like to know (future).

2. Interaction at the metal–oxide interface

2.1. Strong metal–support interaction (SMSI)

In retrospect, perhaps the place to begin thinking about the metal–oxide support interface, even in anticipation of chemical reaction between the metal and oxide, is classical thermodynamics and this is the approach taken by Knözinger and Taglauer [16]. Of course, the thermodynamics of spreading and wetting only provide a framework for thinking about the energetics of the metal–oxide interface because very small clusters of metal on an oxide surface are not in thermodynamic equilibrium (they are *meta*-stable with respect to sintering) and a suboxide of molecular dimensions (as has been observed for SMSI [17]) does not exhibit the bulk phase that is presumed by classical thermodynamics. While the tendency to undergo SMSI can be correlated with oxide reducibility [18], it can also be correlated with surface free energies; i.e., TiO_2, V_2O_5, Nb_2O_5, and Ta_2O_5 have smaller surface free energies than do SiO_2, Al_2O_3, ZrO_2, and MgO [16] and the former are known to more easily undergo SMSI. As noted by Knözinger and Taglauer [16], the surface free energies of reducible oxides increase if they become oxygen deficient. Thus, we can deduce that it is probably the concentration gradient and the molecular bonding between the noble metal and the suboxide that are the driving forces for spreading, that migration probably precedes reduction to the final *meta*-stable state, and that reduction decreases the mobility of the suboxide, limiting the decoration to a thickness on the order of a monolayer. These predictions pretty much concur with surface science findings from model systems, but there exists an inherent contradiction that reduction may be necessary for migration and immobilization of the migrated species. Perhaps there is some intermediate reduced state that migrates.

Consider the case of Pt clusters on $TiO_2(110)$ studied by Pesty et al. [17] using low-energy ion scattering (LEIS), which is mainly sensitive to the topmost layer, while angular-dependent (electron detection 10–70° off crystal normal) X-ray photoelectron spectroscopy (XPS) averages over several layers. When the LEIS of Pt is very significantly attenuated (see Fig. 1), the $4f_{3/2}$ and $4f_{5/2}$ Pt XPS peaks are hardly changed, even at the 70° takeoff angle (see Fig. 2), suggesting a covering of Pt by a layer of TiO_x on the order of a monolayer. Pesty et al. also deduce that x is less than or equal to one and depends on time and temperature, but they find no evidence for metallic Ti (in the limited temperature range they used).

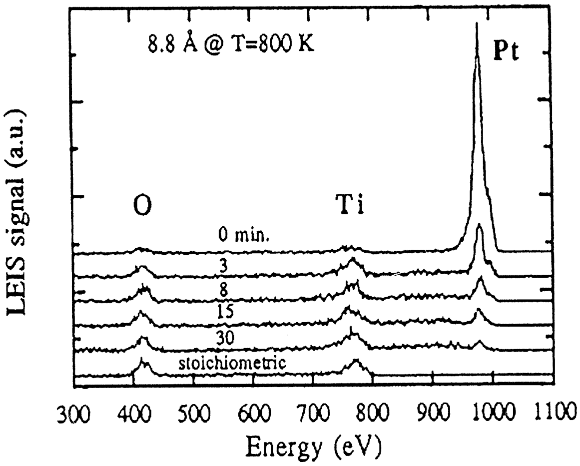

Fig. 1. Evolution of LEIS spectra as a function of cumulative annealing time, for 1-keV-incident He^+ ions on an 8.8-Å layer annealed at 800 K for 0, 3, 8, 15, and 30 min, and stoichiometric.

In a more recent scanning tunneling microscope (STM) study of Pt on $TiO_2(110)$, Dulub et al. [19] propose an ordered atomic model that resembles a slightly oxygen-rich, oxygen-terminated $TiO_{1.1}$ double layer. The film exhibits a dipole moment, caused by the uneven distribution of negative and positive charges between the O-rich first and Ti-rich second layer. Assuming that a similar (dipolar) structure prevails locally when the Pt is not completely covered, these local dipoles would result in a work function change that would effect adsorption and reaction and be consistent with the hypothesis that “the difference between electrochemical and classical promotion is thus operational

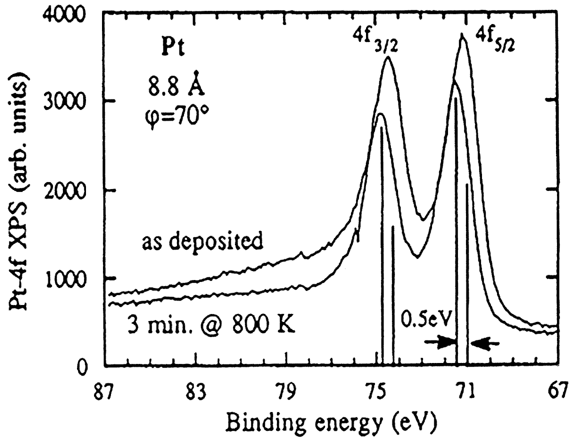

Fig. 2. XPS of the Pt 4f doublet, plotted as a function of binding energy, for an 8.8-Å Pt layer. (Top spectrum) As deposited (Pt evaporation with sample at room temperature); (bottom spectrum) layer heated at 800 K for 3 min (grazing emission).

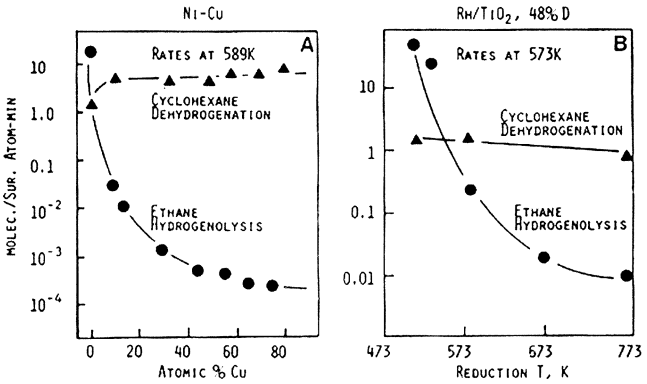

Fig. 3. Ethane hydrogenolysis and cyclohexane dehydrogenation rates on (A) Ni–Cu catalysts as a function of Cu content (after Sinfelt et al. [53]) and (B) Rh/TiO$_2$ catalyst as a function of reduction temperature (after Resasco and Haller [54]). Both Cu and TiO$_x$ on Rh are thought to block the structure-sensitive hydrogenolysis reaction but hardly effect the structure-insensitive dehydrogenation reaction.

and not functional” (see, Ref. [20, p. 283]). We will return to this assertion in the next section.

Pesty et al. [17] summarize their comparison of metals (interaction with TiO$_2$) as follows: “the less reactive the deposited metal towards the oxide, the less effective the wetting, and the more reduced the suboxide migrating on the top of the islands.” Their primary comparison was between Pt and Fe. We had performed a somewhat different comparison between Pt and Rh and concluded that Pt enters into the SMSI state more easily (at a lower temperature or in a shorter time) than does Rh, that the SMSI state for Pt/TiO$_2$ is more difficult to reverse than Rh/TiO$_2$ is, and that the (nonstoichiometric) M$_{sur}$TiO$_x$ surface complex is more oxygen-rich on Rh than on Pt [11]. These two generalization appear to be mutually consistent but may just be different ways of saying that the overall metal–support interaction is driven by the competition between M–Ti and M–O bond formation, which would then order the three metals Fe $<$ Rh $<$ Pt in terms of their tendency to enter the SMSI state.

The consequences of SMSI depend on the metal, the oxide, and the reaction and so generalizations are not simple. To the extent that decoration occurs, it is likely to slow down all reactions and be particularly detrimental to the more structure sensitive ones, such as ethane hydrogenolysis (see Fig. 3) but this may be outweighed by a positive effect of new sites created for reactions involving the C–O bond, e.g., methanation of carbon monoxide, so that the overall rate change is positive [11]. Of course, steady-state reaction in the SMSI state more or less rules out oxidation reaction, because both the oxygen and the water produced tend to reverse SMSI, if we mean this term to imply decoration of the metal surface by a reduced TiO$_x$ species.

2.2. *Non-Faradaic electrochemical modification of catalytic activity (NEMCA)*

The 20-year history of the discovery and elucidation of NEMCA has been reviewed in book form recently [20]

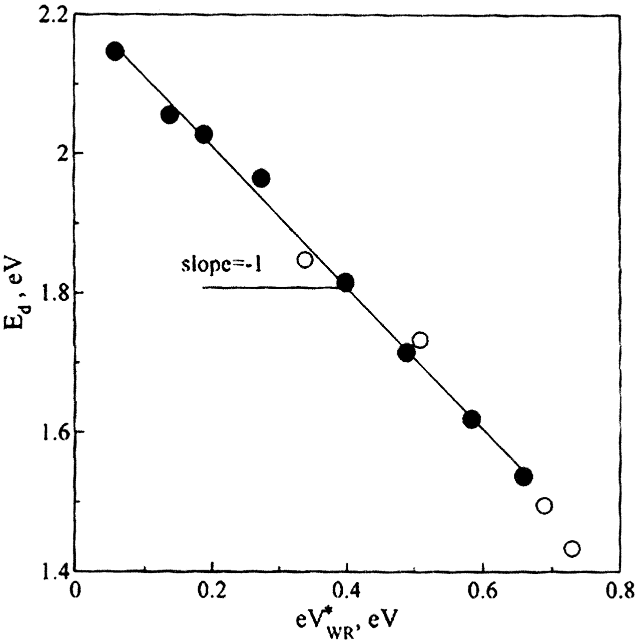

Fig. 4. Effect of catalyst potential on the desorption activation energy calculated from the modified Redhead analysis (●) and from the initial slope of the TPD spectra (○), after Neophytides et al. [23].

(see also Vayenas et al. in this issue [21]). I will restrict discussion to metals on YSZ, particularly Pt, so that the ion-carrying current in the solid electrolyte will be O^{2-} and it is the chemistry of this species at the three-phase boundary (tpb; between the gas phase, solid electrolyte, and metal) and the species that it evolved to as it migrates over the metal surface that is of interest. The essential facts that have been established experimentally are that an oxygen anion, perhaps O^{2-}, migrates across the tpb and is more or less uniformly distributed over the metal surface. This species can be distinguished from the oxygen species adsorbed from the gas phase (in a given temperature range) by temperature-programmed desorption (TPD) and XPS.

The electrochemically pumped oxygen species is more strongly bonded to Pt than oxygen adsorbed from the gas phase (as determined by TPD; it desorbs at higher temperature), but the latter is promoted (becomes more weakly bonded) by the former. The electrochemically formed oxygen has an O 1s binding energy of about 528.8 eV (compared to 530.2 eV for normally chemisorbed atomic oxygen) and is therefore more negatively charged and, perhaps for this reason, is much less reactive with gas-phase H$_2$ and CO in the UHV background [22] or with organic reductants. The strongly bonded ionic state (formed electrochemically) acts as a sacrificial promoter of the weakly bonded state (formed from gas-phase adsorption). The desorption activation energy of the weakly bonded state is linearly correlated with the catalyst potential, as shown in Fig. 4 [23]. The E_d decreases from 2.14 to 1.42 eV as V_{WR} is increased by 0.7 V or, equivalently, as the work function, Φ, is varied by 0.7 V, since the change in voltage of the working electrode (relative to the reference electrode) is equal to the change in work function [20]. (Note, though, that Metcalfe [24,25] has argued themordynamically that the catalyst surface potential can be equal to the applied overpotential only if (i) equilibrium exits between oxygen ions in the electrolyte support and the catalyst surface, (ii) oxygen-ion coverages are intermediate, and (iii) there are no lateral interactions between surface ions.) This confirms that the catalyst potential and work function have a pronounced effect on the binding energy of atomic oxygen and therefore can be expected to affect the rate of oxidation reactions involving adsorbed atomic oxygen.

While the promotion effect of this electrochemical spillover oxygen on atomic oxygen formed from the gas phase has been quantified, the promotion effect on other reactants, e.g., hydrocarbons, has not been studied, and the overall effect on catalytic rate will depend on the combined effect on both (all) reactants. As anticipated, an appropriate Langmuir–Hinshelwood kinetic expression shows that the true activation energy for propylene oxidation is modified by the heats of adsorption of both O_2 and C_3H_6, which in turn are modified by the applied potential. The dominant effect is the strong adsorption of O_2 for negative potentials (and high relative partial pressures) and can rationalize the logarithmic correlation on the relative rate (rate under applied potential normalized by the open circuit rate) on the apparent activation energy [26].

A common observation, with addition of classical promoters, is a compensation effect where the rate changes in a log-linear fashion when the logarithm of the rate is plotted against $1/T$ (K) in a Arrhenius plot, resulting in different straight lines at different promoter loadings which intersect at an isokinetic temperature. The equivalent "loading" parameter for NEMCA is the applied voltage and, as shown in Fig. 5, an electrochemical-induced compensation effect is also observed for propylene oxidation on Pt supported on YSZ with an isokinetic temperature of 380 °C.

Vayenas et al. have developed heuristic rules for a variety of situations of electrochemical promotion [27]. For the case of propylene oxidation on Pt discussed above, propylene acts as an electron donor (D) and oxygen as an electron acceptor (A), and propylene is much more strongly adsorbed than oxygen. Rule G2′ states: *A reaction exhibits purely electrophilic behavior* (*the change of rate with change in potential, or work function, at constant partial pressure of* (*A*) *and* (*D*) *is less than zero,* $(\partial r/\partial \Phi)_{p_A p_D} < 0$), *when the electron donor reactant* (*D*) *is strongly adsorbed and much more strongly adsorbed on the catalyst surface than the electron acceptor reactant* (*A*). This kind of behavior can be seen in Fig. 5 when the rate is compared at constant T (and pressure of reactants) and different applied potential. Vayenas et al. have also developed mathematical models that rationalize these rules and apply to both classical and electrochemical promotion [27].

Nicole et al. have investigated several comparisons of electrochemical and conventional thermal-driven metal–support interaction effects on the oxidation of ethylene [28]. We will briefly consider the case of Rh, where the work function is varied by varying the support (TiO_2, SiO_2, Al_2O_3, ZrO_2 (8% Y_2O_3), and TiO_2 (4% WO_3)) and reducing the catalyst (Rh dispersed on support) at 400 °C in flowing H_2 for 1 h and by electrochemically pumping O^{2-} to/from Rh supported on ZrO_2 (8% Y_2O_3). The turnover frequency (TOF) is plotted against partial pressure of oxygen (at constant temperature and partial pressure of ethylene) in Fig. 6; the inset shows the same plot for the potentiostatically varied work function. The similarity between the kinetic behaviors is quite striking. Taken in the context of several other systems, this is good evidence for the equivalence of electrochemical and thermal-driven metal–support interaction. However, there are some caveats we need to keep in mind. Even though the C_2H_4/O_2 ratio is not net oxidizing, the SMSI discussed above that involved TiO_x decoration of the metal particles is not expected to survive under these reaction conditions; i.e., it is likely that there is only a steady-state decoration of a ionic oxygen species and the work function of the metal will only be equal to the support if this ionic oxygen species is in equilibrium with the oxide comprising the support. Note also that the highly dispersed Rh on ZrO_2 (8% Y_2O_3) does not have the same TOF (but nearly the same critical oxygen partial pressure where the Rh is converted to the oxide) as the Rh on ZrO_2 (8% Y_2O_3) under open-circuit conditions. Why might this be? First we must note that the electrochemical Rh has a counter Pt electrode so that "open circuit" does not mean zero potential and this potential will also be affected by the gas phase in contact with the Pt counter electrode (the reaction mixture for the single pellet CSTR reactors used). There are likely other

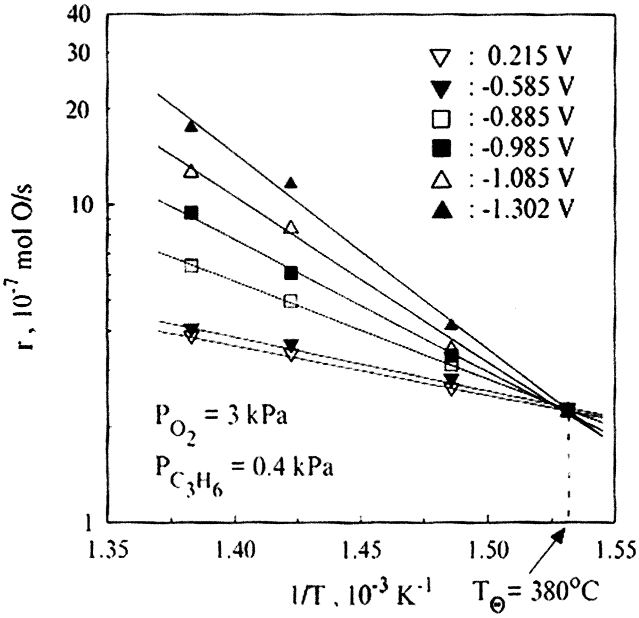

Fig. 5. Promotionally induced compensation effect: Arrhenius plots at various fixed negative catalyst potentials compared with the open circuit Arrhenius plot, 0.215 V, after Kaloyannis and Vayenas [26].

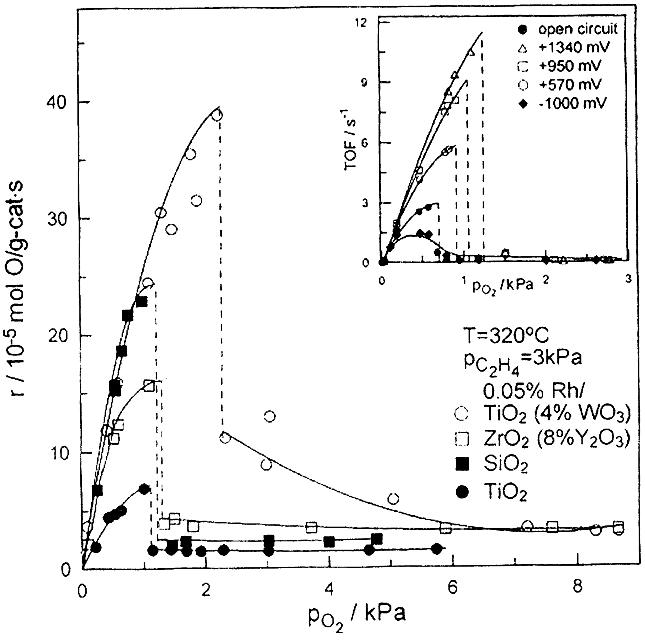

Fig. 6. Effect of p_{O_2} on the rate of C_2H_4 oxidation on Rh supported on four supports of increasing Φ. Catalyst loading, 0.05 wt%. (Inset) Effect of potentiostatically imposed catalyst potential U_{WR} on the rate and TOF dependence on p_{O_2} at fixed $p_{C_2H_4}$, after Nicole et al. [28].

differences, e.g., the effect of measuring the percentage of exposed Rh by different methods for the conventional and electrolyte-supported Rh, so our comparison of electrochemical and thermal driven promotion, as observed in Fig. 6, can only be qualitative.

2.3. *Pt/KL–zeolite aromatization catalysts*

When Pt/KL–zeolite first came to our attention, it was because of its unique selectivity for aromatization and, in particular, for the conversion of *n*-hexane to benzene [9]. However, as we have come to understand the nature of this reaction on Pt/KL–zeolite in more detail, it is now generally agreed that this selectivity is not unique per se because clean, small clusters of Pt on other supports can also have a high initial aromatization selectivity [29,30]. It is generally agreed that what is truly unique about Pt/KL–zeolite is that it both stabilizes very small clusters of Pt against sintering (and migration out of the KL–zeolite pores) [31] and stabilizes them against self-poisoning by coke formation under the rather severe reaction conditions required for aromatization [29,30]. A correlated property of Pt supported in KL–zeolite is that it is very sensitive to sulfur poisoning [32]. It would seem very improbable that all three of these alterations of the properties of Pt—stable small clusters, inert to hydrocarbon self-poisoning, but extraordinary susceptibility to sulfur poisoning—would not be related to the same chemistry. If one accepts this hypothesis, then one is led to favor an electronic interpretation of the KL–zeolite altered properties rather than a physical or geometric effect on reaction because only the electronic interpretation can explain all three properties in a consistent way.

There have, of course, been multiple proposed explanations of the unique Pt/KL–zeolite catalytic properties. The earliest hypothesis was that the KL–zeolite was basic and that the basicity of the support altered the selectivity in favor of benzene formation from *n*-hexane [33]. While added basicity can improve the benzene selectivity, it has been argued convincingly that basicity alone, e.g., as found in Pt/M(Al)O, cannot account for the benzene selectivity of Pt/KL–zeolite [34]. A subsequent proposal was that parallel, narrow (0.71-nm minimum diameter; 1.3-nm maximum diameter) pores might channel the linear reactant in such a way that would make terminal carbon adsorption (as opposed to adsorption at an internal carbon) more likely and that this would be more likely to lead to 1–6 ring closure [35]. Subsequently, it has been reasoned that there is room in the pore channels for a variety of conformations of linear C_6, C_7, etc., alkanes, and that 1–6 ring closure is an inherent property of small, clean Pt particles [29,30]. Thus, an initial encounter at the end of the molecule would not be more probable, and in any case, benzene is not a primary product but a secondary product of hexenes [34].

There is, however, another geometric or constraint argument having to do with the constraint on bimolecular encounters (to form coke precursors) that is more difficult to discount. Iglesia et al. have demonstrated that the initial activity for alkane aromatization is an inherent property of well-dispersed Pt on nonacidic supports, but what distinguishes the KL–zeolite support is the ability to retain the small Pt clusters free of coke formed by self-poisoning with reactant [29,30]. They have proposed that this is a result of small L–zeolite channels that constrain the formation of the bimolecular activated complexes that form coke rather than a electronic modification of the Pt making it more inert to coking reactions. However, such bimolecular coking reactions are not arrested in Y–zeolite, which has similar dimensions, but the intersection of pores might provide somewhat more space. A portion of the K in KL–zeolite can be exchanged for protons and then it is observed that Pt/HL–zeolite does decay from coke formation (neopentane reactant) but Pt/KL–zeolite does not under the same conditions [36]. Replacement of K^+ by H^+ does open the channels a bit and the acid sites also provide a second mechanistic pathway to coke (an argument for the difference between Y– and L–zeolites as well) but presumably bimolecular reaction is still required to form coke. While none of these arguments rules out inhibition of coke formation by bimolecular activation constraint, such geometric hypotheses do not provide a rationalization of associated unique properties of Pt/KL–zeolite, e.g., the extremely low sulfur tolerance, but these can be associated with the basicity of the KL–zeolite support [36].

It is recognized that sulfur tolerance correlates with support acidity, higher acidity resulting in greater sulfur tolerance so that low sulfur tolerance could be anticipated for a basic support such as KL–zeolite (see Ref. [36] and references therein). Sulfur tolerance is generally discussed in terms of electron transfer between the support and noble metals, but a true coulombic transfer of charge seems unlikely because most supports are insulators. Mojet et al. have recently recast this electronic argument in terms of a coulombic interaction between metal particle and support oxygen ions which affects the metal interatomic potential but does not require an actual electronic charge transfer [37]. Acidity/basicity, charge transfer, and perturbation of metal interatomic potential are all attempts to describe a particular kind of metal–support interaction, but while I believe this interaction is real, how it should best be described remains an open question.

2.4. *Pt/KL–zeolite and Pt/KAl–MCM-41: a comparison and the case for reaction probes*

The late Herman Pines was fond of reminding students of catalysis that "the most sensitive probe of a catalyst is a catalytic reaction." This cannot be denied, but he did often fail to warn them that it was not always easy to find a catalytic reaction probe where the rate could be interpreted unambiguously in terms of some chemical property, e.g., basicity. An obvious advantage (in addition to sensitivity) is that the catalytic reaction is probing a surface property, whatever it might be. Tri et al. [38] introduced a probe reaction that is both sensitive and can be directly related to a chemical property of the catalyst surface. It relies not on the rate per se but on a relative rate of toluene and benzene hydrogenation which is used to extract a ratio of equilibrium adsorption constants for toluene and benzene adsorption. By extracting the ratio of equilibrium constants from kinetic data, we avoid the complication that the reactants might also adsorb on nonreactive surface sites and therefore complicate the interpretation because we are primarily interested in those sites that catalyze reaction. The adsorption equilibrium constant is a thermodynamic property, which is only temperature dependent, so as long as the measurements are compared at the same temperature, other variables are not relevant. Because hydrogenations are generally believed to be structure independent, we can further assume that the ratio of the toluene to benzene adsorption constant, $K_{\mathrm{t/b}}$, does not depend on particle size or other effects on local geometric surface structure, although particle size might be expected to affect electron acceptor ability and thereby change $K_{\mathrm{t/b}}$.

The chemical interpretation of the ratio of $K_{\mathrm{t/b}}$ is rather straightforward [39]. Both toluene and benzene are π-electron donors, and by definition, an acid is an electron acceptor. The better the electron acceptor (interpreted as being more acidic or less basic), the more successful toluene (the better electron donor) will be in competition with benzene and the larger $K_{\mathrm{t/b}}$ will be [38]. As the site becomes less able to accept electrons, $K_{\mathrm{t/b}}$ becomes smaller, and in the limit, one might expect $K_{\mathrm{t/b}}$, to approach one when only the normal dispersion forces are involved in toluene and benzene adsorption. A strong base would repel π-electron donation and the dispersion forces alone would be roughly in the ratio of the electrons in molecular orbitals, e.g., 1–1.2. Based on this interpretation, Pt/KL–zeolite or Pt supported on KL–zeolite with partial exchange with alkaline earth metals (Mg^{2+}, Ca^{2+}, or Ba^{2+}) have the smallest $K_{\mathrm{t/b}}$ reported [38–41].

The disclosure of MCM-41 materials (discussed in more detail in the following section) provided a material that has a pore structure very similar to L–zeolite; i.e., both have one-dimensional pores in a hexagonal array. Both the pore size and the composition can be varied in MCM-41 (which is not possible for L–zeolite) and this stimulated a comparative study of Pt/KL–zeolite and Pt/KAl–MCM-41 catalysts [40]. Using knowledge of Al–MCM-41 gained from the investigation of Al–MCM-41 pore size on acidity [42], we prepared Al–MCM-41 with Si/Al ratios of 24, 6, and 3, the latter having the same Si/Al ratio as in L–zeolite. These materials were exhaustively exchanged with K^+ to prepare KAl–MCM-41; actual K/Al ratios were in the range of 1.12 to 1.2 for all examples; i.e., none of these materials has any Brønsted acidity. Some properties can be found in Table 1 and more details can be found in Ref. [40].

Here we only consider the last four columns, all data derived from a catalytic reaction. Column 4 is the parameter $K_{\mathrm{t/b}}$ described above and indicates that Pt in KL–zeolite is the least good electron acceptor, i.e., that Pt supported on KL–zeolite is the strongest base. The primary products of n-hexane reaction on these nonacidic catalysts are benzene and hexenes, which account for greater than 80% of the products. The benzene/hexene ratio (column 6) correlates with $K_{\mathrm{t/b}}$ (and thus with Pt electron acceptor ability). Likewise, benzene (1–6 ring closure) ratioed to methylcyclopentane plus methylpentanes (1–5 ring closure and products from 1–5 ring closure) also tracks with Pt electron acceptor ability (but see the qualifier below).

Although the trend is the same for all four of the last columns of Table 1, we acknowledge that in terms of 1–6/1–5 ring closure, this ratio varies by less than a factor of three across the range of Pt/KAl–MCM-41 catalysts, and that there is a factor of more than three between the most basic Pt/KAl–MCM(10)-41, Si/Al = 24, and Pt/KL; i.e., the latter is unique. A closer inspection of the kinetic data for benzene hydrogenation rate would make this same point. That is, Pt/KAl–MCM(10)-41, Si/Al = 24, and Pt/KL have TOFs of 0.3 and 0.27, respectively, which suggests a continuity between the MCM-41 and KL–zeolite-supported Pt catalysts, but the E_{a} for benzene hydrogenation is 13 ± 0.8 kcal/mol on all of the MCM-41 supports and 20 kcal/mol on KL–zeolite. This suggests that perhaps there is a continuity across all these catalysts with regard to basicity, as reflected in the $K_{\mathrm{t/b}}$, a thermodynamic property, but other kinetic factors, not included in the measure of basicity, make Pt/KL a unique catalyst for reactions of n-hexane.

Table 1

Samples[a]	H/Pt[b]	a_0[c] (nm)	$K_{t/b}$[d]	TOF, benzene hydrogenation[e]	Benzene/hexene ratio[f]	Ring closure (1–6/1–5)[g]
Pt/KL	1.15	–	2.18	0.27	1.23	9.40
Pt/KAl–MCM(C10), Si/Al = 24	1.42	3.37	2.70	0.30	0.94	2.97
Pt/KAl–MCM(C12), Si/Al = 24	1.42	3.51	2.80	0.53	0.89	2.93
Pt/KAl–MCM(C14), Si/Al = 24	1.28	3.91	2.82	0.61	0.71	2.10
Pt/KAl–MCM(C12), Si/Al = 6	1.11	3.64	3.00	8.63	0.67	1.97
Pt/KAl–MCM(C14), Si/Al = 6	1.20	4.06	3.55	8.48	0.52	1.86
Pt/KAl–MCM(C12), Si/Al = 3	0.99	3.73	3.97	20.54	0.50	1.66
Pt/KAl–MCM(C14), Si/Al = 3	1.24	4.10	4.80	23.15	0.24	1.18

[a] The values in parentheses indicate the alkyl chain length of the surfactant; shorter chains result in smaller pores, as reflected in the XRD a_0.

[b] Measured volumetrically at room temperature, extrapolated to zero pressure.

[c] a_0 is a hexagonal unit cell length measured by XRD.

[d] Ratio of toluene to benzene adsorption constants at 353 K.

[e] Turnover frequency, TOF, measured at 353 K.

[f] For hexane reaction at 733 K, atmospheric pressure, H_2/n-hexane = 20 and conversion = 9–11%.

[g] Ratio of benzene to methylcyclopentane plus all methylpentanes (formed from methylcyclopentane).

One final point needs to be made on the benzene hydrogenation TOF of the MCM-41-supported catalysts of Table 1. If we focus only on the Si/Al ratio the hydrogenation rate varies by more than a factor of 40 and linearly correlates with $K_{t/b}$. The basicity, as measured by $K_{t/b}$, varies by less than a factor of two, and the portion of this that might be attributed to radius-of-curvature effects (which can only be isolated at constant Si/Al ratio) never exceeds a factor of 1.2. What is the nature of the huge effect of Si/Al ratio? It is not simply addition of acidity. Recall that the K/Al ratio is constant and exceeds one, so decreases in Si/Al ratio add K and basicity overall. This is reflected in the overall increase of $K_{t/b}$. No simple explanation can be provided, but given that E_a is nearly constant for benzene hydrogenation on all the MCM-41-supported catalysts, it is proposed that these KAl sites increase the overall adsorption of benzene (on the support, the Pt is always at full coverage, resulting in zero order in benzene). Perhaps the result is similar to that described by Lin and Vannice [43] for benzene hydrogenation on very different supports that show a similar effect, which is also attributed to a kinetic contribution to benzene adsorption on the support (see also Poondi and Vannice [44] regarding caution needed in the interpretation of $K_{t/b}$ values when hydrogen-deficient species are formed).

While Chueh [40] and others [36,37] have tried to demonstrate an electronic interaction between small Pt clusters and different supports, the kinetically measured effect on $K_{t/b}$ and its correlation with rates of several other reactions of n-hexane (and with neopentane and coking deactivation [41]) are the most persuasive evidence that electronic interaction exists at the metal–oxide interface, or at least an associative chemical bonding, and affects catalysis. Of course, the NEMCA (see Section 2.2) also confirms that work function can be varied by applied potential and this, too, is an electronic perturbation of the metal that affects catalysis.

3. Mesoporous molecular sieves

I choose to close this brief discussion of catalytic advances, discontinuities in our thinking about heterogeneous catalysts provoked by new materials, with a short discussion of MCM-41 as a catalyst per se. It is chronologically the last to appear, interest may be about to crest, and more important, the catalytic science I want to end with does not have a metal–support component, as the previous topics did.

Work on a family of mesostructured materials composed of amorphous silica, the M41S family, must have been underway at Mobil for several years but was made public in a 1991 patent [45] and two 1992 publications [10,46] (with several patents and papers to follow). I will focus on MCM-41, and particularly on Al–MCM-41 and V–MCM-41, where a small fraction of the Si has been substituted by Al or V. As mentioned above, the MCM-41 pore structure is that of one-dimensional channels in a hexagonal array with amorphous silica walls of about 1 nm. They are rather easily synthesized using long-chain alkyl surfactants that aggregate into cylindrical micelles on which the silica polymerizes and then cross-links to make bundles of order of one micron. While most researchers have emphasized the properties of very narrow pore size distribution (typically 0.15-nm half-width at half-height in pore size distributions determined from a liquid nitrogen temperature nitrogen adsorption isotherm), our interest has been in the ability to synthesize materials of constant composition and structure but with varying pore size. The pore size is primarily a function of the alkyl chain length of the templating surfactant, but it can be further manipulated by other synthesis parameters.

Our original goal was to test the hypothesis that the activity and/or selectivity of a catalytic site might be systematically varied by changing the radius of curvature of the pore wall on which the site was situated. This idea was not new; it had been discussed some time ago by Derouane et al. for zeolites [47] and more recently the radius-of-curvature effect on cracking reactions has been demonstrated [48–50]. However, the basis of the catalytic rate effect in these micropores was not the direct influence of the radius of curvature on the catalytic activity but the indirect effect of radius of curvature on the heat of adsorption of the reactant (altering the apparent activation energy). In fact, the direct chemical effect on the catalytic activity could not be determined because there are no known zeolites where pore size can be varied without varying both the composition and the structure as well.

The radius-of-curvature changes in the mesoporous MCM-41 is going to be small compared to the microporous zeolites, so we are unlikely to see the same kind of reactant coverage effects observed for cracking reactions in zeolites. However, very minor changes in local geometry, e.g., bond angles of Si–O–V, might have significant effects on atomic properties of the V, e.g., binding energy of valence electrons, which might affect catalytic activity.

Our first attempt to observe a radius-of-curvature effect on catalytic activity used an acid-catalyzed isomerization (2-methyl-2-pentene) on Al–MCM-41 [42]. This molecule can undergo both a methyl shift (requiring a strong acid site) and a double-bond shift (requiring a weak acid site) and the ratio of the two rates is a reaction measure of acid strength. We found an apparent variation in acid strength of about a factor of five (using 3-methyl-2-pentene/2-methyl-3-pentene selectivity as a measure of acidity) [51] as the pore size was decreased about a factor of two (in the range of 2- to 4-nm diameter), but the results were rather scattered and ambiguous. These results are equivocal for two reasons: using very short surfactants (C_6 and C_8 in the case of 2-methyl-2-pentene reaction) might result in a small amount of molecular templating (creating a crystalline zeolite impurity, which would increase acidity), and in any case incorporation of Al^{3+} into the MCM-41 matrix always results in a degradation of structure, particularly for very low Si/Al ratios. What was unequivocal was that the stability of Al in the Si tetrahedral sites increased as the pore size decreased [42].

In fact, we can see a more prominent effect of pore size in Table 1, where the radius-of-curvature effect on reaction is mediated by a Pt particle (a metal–support effect, as discussed above). If we compare any two catalysts where the Si/Al ratio is constant, we find that $K_{t/b}$ decreases with pore size (when the Al–MCM-41 is synthesized using a shorter alkyl surfactant, e.g., compare C14 to C12 for Si/Al = 3). That is, the support appears to become more basic (smaller $K_{t/b}$), and the metal cluster senses this change, as the pore size becomes smaller.

A more convincing example of radius-of-curvature effect on catalytic activity has been observed for methanol oxidation on V–MCM-41 for a series of catalysts where the V loading was approximately 0.04 wt% (see Fig. 7). Here the rate changes about one order of magnitude and shows a maximum at midrange (which excludes transport as the dominant effect). The activity for methanol oxidation also correlates with a shift in the energy of the V pre-edge X-ray absorption feature, which we have interpreted as a change in the oxidation potential of V with change in pore size (see Fig. 8). However, there was no change in selectivity (between formaldehyde and total oxidation), which might have been expected if the radius of curvature in fact perturbed the oxidation potential and the catalysis was a result of a V^{+4}/V^{+5} cycle (where it is generally thought that the reoxidation of the site is the slow step).

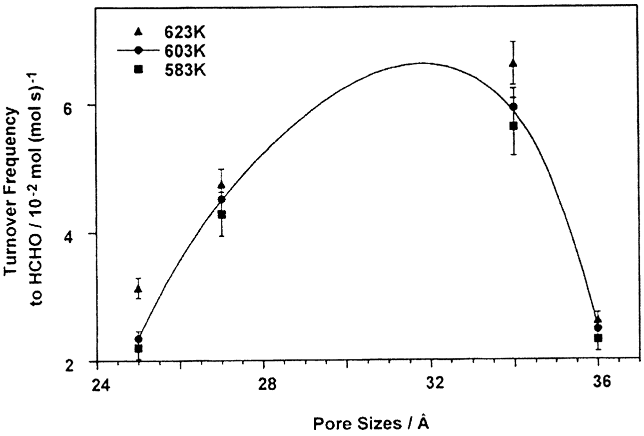

Fig. 7. The effect of pore size on the TOF of methanol oxidation to formaldehyde normalized by oxygen uptake at various temperatures. The pore size is estimated from the liquid nitrogen adsorption isotherm (see Wei [55] for details).

In a further investigation of methanol oxidation on V–MCM-41 we did not find a pore size effect at higher V loading; instead the rate increased linearly with V loading (based on total V loading) and this was not entirely compensated for when the rate was normalized to oxygen uptake on sites reduced with the reactant (methanol) at the reaction temperature [52]. What is now clear is that there may be a radius-of-curvature effect, but it is not going to be huge and to unambiguously prove it exists, we need to gain more control over the constancy of composition and structure. That is, if the synthesis conditions are held constant and the pore radius is varied by simply varying the

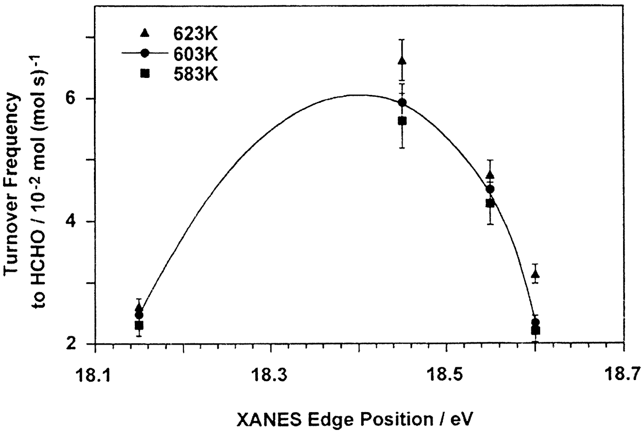

Fig. 8. The TOF of methanol oxidation to formaldehyde normalized by oxygen uptake at various temperatures varied with the edge energy measured on dehydrated V–MCM-41 (which correlated with pore size).

chain length of the templating surfactant, the composition and structure are only approximately constant. As the templating surfactant (pore size) is decreased, the efficiency of V incorporation increases and the structural order deteriorates, either of which may have a greater effect on catalytic activity and selectivity than the pore radius of curvature per se. The way around both these problems is obvious but requires a large number of experiments. That is, we need to develop a multivariable quantitative synthesis model which will allow us to adjust the synthesis parameters in such a way that the composition (fraction of source V in synthesis solution which is incorporated into the final product) and structure (pore volume, pore size distribution, normalized high index X-ray intensity, etc.) are constant. The number of synthesis parameters that may be varied is large and would include V source concentration, Si/H_2O, Si/surfactant, pH, time, and temperature. These experiments are now underway.

4. Summary and conclusions

Chemistry can be said to be the study of the making and breaking of bonds which are the result of a sharing of electrons, but there is merit in describing this sharing as equal (covalent), e.g., in molecular H_2, or unequal (partially ionic), as in HCl. Likewise, there may be some advantage in describing metal–support interaction as a combination of geometric, coulombic, and electronic contributions. By geometric, I imply a simple blocking of space so that all or part of a site is inaccessible to a reactant. Coulombic effects can be ascribed to any through-space interaction of charges, e.g., the repulsion of dipoles of parallel orientation, and electronic is everything else.

If we restrict our attention to reactions of bonds between carbon and hydrogen, e.g., alkane hydrogenolysis, we can view SMSI as mostly geometric, NEMCA as mostly coulombic, and Pt interaction with L–zeolite as mostly electronic. Even if we accept the rather detailed picture determined for Pt interaction with Ti(110) [19], we do not have a mechanistic description of migration of TiO_x across the tpb and the metal surface nor do we know the chemical composition of the migrating species. I would pose this as the central question for NEMCA also. There is some evidence that this species (from YSZ) is O^{2-}, but if so, how is this species stable on a metal surface when it is not in the gas phase and does not have the Madelung screening that makes it so in an oxide, and why is it so unreactive to exchange with other kinds of surface oxygen and reducing species? In the case of Pt in L–zeolite, catalytic reaction probes suggest a rather simple electron transfer or acid–base interaction, but this picture appears in conflict with some spectroscopic probes of the interaction. Fundamentally, we do not know how to describe the bonding between a small metal particle and an oxide surface in a way that would explain why, for example, a Pt cluster is more stable on an aluminum oxide than a silicon oxide when the Pt is essentially in contact with oxide ions in both cases.

There are many take-home lessons from the three different kinds of metal–support interactions I have discussed, but I would posit three that are exemplary. Now that we are aware that a reduced species of oxide support can block the surface of the metal (SMSI), we must always ask if the conditions of the reaction are extreme enough to make this a problem. Even on a support such as SiO_2, usually considered quite inert, those who design auto exhaust catalysts realize that it is important not to have Pt in contact with SiO_2 because there will be sufficiently high temperature to cause a silicon species (SiO_x or Si) to migrate and block the surface of Pt during the lifetime of the catalyst. From NEMCA we learn that a potential can be used to form a controllable double layer (the spillover ions that carries current in the solid electrolyte, e.g., O^{2-} from YSZ) that can affect catalysis. Perhaps it is just this double layer of TiO_x on noble metals that provides the sites that accelerate the reactions of C–O bonds that have been documented as another effect of SMSI, a hypothesis consistent with the double layer described by Dulub et al. [19]. Finally, I have both argued that basicity of L–zeolite offers an explanation of the unique properties of Pt in L–zeolite and quoted Jacobs et al. [34] to the effect that bascity alone cannot account for the unique Pt/KL–zeolite properties. This may not be a contradiction if we take into account the fact that a chemical, induced bascity may be augmented by a radius of curvature effect in the micropores of L–zeolite. That is the implication of the discussion in Section 2.4 comparing Pt supported on KL–zeolite and KAl–MCM-41 with various pore sizes, which brings us back to the current investigation of radius-of-curvature effects in various substituted MCM-41. While these materials may yet find a variety of practical catalytic uses and will surely advance our conceptional understanding of heterogeneous catalysis, they offer us our best hope for a comprehensive investigation of radius-of-curvature modification of a catalytic site.

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