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METAL-SUPPORT EFFECTS IN Pt/L-ZEOLITE CATALYSTS

Gustavo LARSEN and Gary L. HALLER

Department of Chemical Engineering, Yale University, New Haven, CT 06520, U.S.A.

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A series of Pt/L-zeolites with different cations (varying acidity) were prepared and characterized by H_2 and CO chemisorption and competitive toluene/benzene hydrogenation. The ratio of adsorption equilibrium constants for toluene/benzene was extracted from rates of hydrogenation. The variation of this ratio across a series of alkaline-earth exchanged Pt/L-zeolites indicates that there is a varying support interaction with Pt clusters in the zeolite and suggests that the clusters interact electronically with the support.

1. Introduction

The occurrence of electronic effects in supported metal catalysts and their influence on catalytic properties has been a matter of controversy for several years. These topics have been discussed wherever metal-support, metal-additive or metal-metal interactions have been considered. A particular example is the case of very small metal particles encaged in the internal pores of zeolites. Gallezot [1] has pointed out that, in addition to the intrinsic electronic effects due to the small size exhibited by the metal particles, a modification of the electronic structure of the metal by the different environment provided by the zeolite should be considered. This is a kind of metal-support interaction which may be more pronounced than on non-zeolite supports because the particle may interact with the zeolite cage over a substantial fraction of its surface.

Most of the early work where metal-zeolite support interactions were investigated involved Pt particles in Y-zeolite and the hypothesis was that interaction of the Pt particle with acid sites resulted in electron deficient Pt compared to Pt/SiO_2 [1,2]. However, a little later there was also reported a non-acidic system, Pt/KL-zeolite, which had very interesting activity for reforming reactions [3]. The Pt particles in this alkaline zeolite are suggested to be electron rich compared to Pt/Y-zeolite [4]. The latter catalyst is of considerable current interest because it provides a unique activity for converting hexane to benzene, a rather difficult reaction on conventional reforming catalysts [5]. In fact there is empirical evidence from chemisorption and reaction chemistry that the different direction of electron transfer between the Pt particle and the zeolite support may be a reality and have catalytic consequences. For example, Pt in the acidic zeolite is rather insensitive to sulfur poisoning [6], a fact that was originally associated with atomic dispersion of the metal, but was later shown not to be the case and the sulfur tolerance was attributed to the electron deficiency resulting from the metal-zeolite interaction [7]. The same arguments which rationalize the sulfur insensitivity to the electron deficiency of Pt particles in Y-zeolite would predict extreme sensitivity to poisoning by sulfur in the alkaline L-zeolite supported Pt if these particles were, in fact, electron rich. Indeed, this is one of the practical problems to be surmounted in the industrial use of these catalysts [5].

The original evidence that Pt particles in acidic Y-zeolites were electron deficient was obtained using synchrotron X-ray absorption near edge structure (XANES) analysis by Gallezot et al. [2]. However, a re-investigation of this question in the same laboratory has concluded that electron transfer from Pt clusters to the Y-zeolite either does not occur or at least cannot be detected by XANES analysis [8]. The earlier study was in error because the particle size, which also has a very large effect on the electronic state of the particle, was not well controlled. However, the correlation of the infrared frequency shift of CO with acidity of the zeolite support was reproduced in this re-investigation [8]. This kind of shift is usually attributed to electron availability in the metal particle to participate in backbonding in the anti-bonding orbitals of chemisorbed CO but such shifts can be complicated by coverage effects.

Besoukhamova et al. [4] have prepared 5 wt% (and 0.6 wt%) Pt catalysts impregnated on L-zeolites, previously exchanged with alkaline metals (Li, Na, Rb or Cs). Studying the n-hexane reaction over these catalysts they observed that increases in the basicity of the zeolite when going from the Li-exchanged zeolite to the Cs-exchanged zeolite caused corresponding increases in the selectivity towards aromatization. On the other hand, it was shown that the acidic sites of the support not only did not take part in the reforming reaction but their presence caused a decrease in catalytic activity and selectivity because they promote cracking/coking side reactions. The unique features of these catalysts have been ascribed to an interaction between the metal particles and the zeolitic support. Based on infrared spectroscopic data of adsorbed CO [4] it has been suggested that the Pt particles in these catalysts may be electron-rich (relative to Pt/Y-zeolite) as a consequence of a charge transfer from the L-zeolite to the small metal particles and that this may explain their unique selectivity for hexane to benzene conversion. However, Tauster and Steger [9] have proposed that the high aromatization selectivity of Pt supported in L-zeolite is caused by the ability of the channels to collimate the flux of hexane molecules, leading to end-on adsorption at the Pt surface. A somewhat similar view is held by Derouane and Vanderveken [10] who attribute the selectivity to a non-binding interaction of n-hexane with the active site environment which leads to the preorganization of n-hexane as a pseudo-cycle.

From the above discussion, it would appear useful to find a catalytic reaction that has some sensitivity to the electronic nature of the Pt particle. In a literature search for such a reaction we have again turned to the work of Gallezot and his coworkers [11]. Hydrogenations are generally considered structure insensitive [12], but this may be advantageous if it is the electronic nature of the metal particle that we are trying to probe. The competitive hydrogenation of aromatics is governed by their relative adsorption coefficients and these in turn reflect the local electronic charge on the metal particle. In the competitive hydrogenation of toluene and benzene, toluene is the better electron donor and therefore is expected to form stronger pi-bonds with Pt. As pointed out by Tri et al. [11], it is the ratio of adsorption equilibrium constants $K_{t/b} = (K_{\text{toluene}})/(K_{\text{benzene}})$ which we wish to measure because the rate is a product of the adsorption constants and rate constants. Because both toluene and benzene are pi-electron donors and their ionization potentials are known, it is possible to predict how $K_{t/b}$ should vary with charge on the Pt cluster. The effect on the rate constant is not so obvious.

The competitive hydrogenation of toluene and benzene has at least three advantages as a reaction to probe the electronic nature of Pt particles in L-zeolites: 1) Because the reaction is zero order in both toluene and/or benzene, there are no coverage effects of the kind encountered when CO infrared frequency shifts are measured. 2) The reaction can be carried out at low temperature which allows the catalyst calcination and reduction also to be performed at low temperature, a preparation which avoids the migration of the Pt out of the zeolite pores [1]. 3) One of the competitive reactions, benzene hydrogenation, must involve the reverse of some of the steps in the aromatization of hexane to benzene, i.e., if the mechanism of this reaction does not change with temperature, the electronic nature probed by the competitive hydrogenation should be directly relevant to the selective conversion of hexane to benzene over Pt/L-zeolite.

2. Experimental

We have prepared three different Pt/L-zeolite catalysts exchanged with different alkaline-earth cations. Two 4.00 g samples of 100–150 mesh hydrated form of the KL-zeolite from Tosoh Corp., Japan, were slurried at room temperature for 24 h with 30.0 mg (0.78Pt/KL-zeolite) of cis-$Pt(NH_3)_2Cl_2$ from Fluka in 250 ml of deionized water. The exchanged catalyst was washed until no Cl^- could be detected by $AgNO_3$ and dried for 6 h at 383 K. After drying, the catalyst was calcined by heating from 300 to 623 K over a period of 5 h in a 30 ml/min flow of O_2, flushed with He for 15 min at 623 K and reduced at the same temperature for 2 h in 30 ml/min flow H_2. At this point the Pt loading, measured by atomic absorption of the extracted metal, was 0.78 wt% Pt and the dispersion measured by hydrogen chemisorption was 1.10.

These catalysts should, in fact, be referred to as Pt/KHL since the reduction of Pt^{+2} by H_2 must result in a stoichiometric addition of H^+ to maintain charge balance. We followed a procedure similar to that described by Barrer et al. [13] to exchange the K cation. Three equal portions of 0.78Pt/KHL-zeolite were slurried for 60 h at room temperature with 250 ml of 0.5 M $BaCl_2$, $CaCl_2$ or $MgCl_2$ solutions, respectively, to prepare catalysts designated Pt/BaL, Pt/CaL and Pt/MgL. The cation exchange was intended to vary the acidity of the zeolite support and was performed after the exchange and reduction of the Pt in order to assure a constant particle size. This approach was pioneered by Foger and Anderson [14] and they demonstrated that the metallic Pt did not lead to loss of the remaining exchange capacity or the loss of Pt during subsequent exchange of cations.

The CO and H_2 uptakes of the different catalysts as well as of its precursor were measured by conventional static adsorption in a Pyrex system. The samples were re-reduced in-situ at the same temperature used for the initial reduction.

The competitive hydrogenation of toluene and benzene was carried out at 353 K in an atmospheric flow reactor with a hydrocarbon : H_2 ratio of 12 : 1. It is possible to derive from the Langmuir rate law the following equations:

$$R_b^* = (k_b K_b P_b)/(1 + K_b P_b) \cong k_b$$

$$R_b = (k_b K_b P_b)/(1 + K_b P_b + K_t P_t) \cong (k_b K_b P_b)/(K_b P_b + K_t P_t)$$

where k, K and P are the rate constant, adsorption coefficient and partial pressure, respectively, of benzene (b) and toluene (t). R_b^* is the rate of benzene hydrogenation in the absence of toluene and R_b is the rate of hydrogenation of benzene in competition with toluene. (As previously reported in ref. [11], we found the rates to be zero order in the aromatics.) The ratio of these two rates is:

$$R_b^*/R_b = 1 + (K_t P_t)/(K_b P_b) = 1 + K_{t/b} P_{t/b}.$$

If $K_{t/b}$ and $P_{t/b}$ are defined as the ratio of adsorption constants and partial pressures for toluene and benzene, respectively, then a plot of R_b^*/R_b against $P_{t/b}$ is linear with $K_{t/b}$ as the slope.

As a reference, we used a 1.92% Pt/SiO_2 (100–200 mesh Davison silica). This was prepared by impregnation at incipient wetness using 1.0 ml solution per g of silica. After 48 h air drying, this catalyst was oven-dried at 383 K for 8 h. The dried catalyst was purged with a flow of He (32 ml/min) at 373 K. The reduction temperature was 723 K and was reached at 2 K/min from 373 K (reduction time was 8 h).

3. Results

The H/Pt and CO/Pt measured volumetrically at ambient temperature is shown in table 1. The ratio of toluene/benzene adsorption coefficients extracted

Table 1
Hydrogen and carbon monoxide chemisorption

Catalyst	H/Pt	CO/Pt
Pt/KL	1.10	0.47
Pt/MgL	1.12	0.45
Pt/CaL	1.17	0.34
Pt/BaL	1.15	0.29

Table 2
Ratio of toluene/benzene adsorption constants [a]

Catalyst	Acidity of Support	R_b^* [b]	$K_{t/b}$ (353 K) [a]	$K_{t/b}$ (298 K)
Pt/CeY	very high			17.8 [c]
Pt/NaHY	high			14.1 [c]
Pt/KHL	moderate	4.7	6.5	10.1 [c]
Pt/SiO_2	neutral			8.6 [c]
Pt/SiO_2	neutral	4.0	5.8	8.2 [d]
Pt/MgL	low	1.8	3.5	2.3 [e]
Pt/CaL	low	0.4	3.0	1.9 [e]
Pt/BaL	very low	0.1	2.8	1.8 [e]

[a] Extracted from competitive hydrogenation rate measurements as a function of partial pressures of toluene and benzene as described in the text; the uncertainty is ±0.1.

[b] Because all of the H/Pt exceed one, we assume that every Pt is a potential site to calculate the turnover numbers, molecules/sec-Pt) at 353 K.

[c] From ref. [11].

[d] We have measured $K_{t/b}$ at 303 K as 8.6 from which we calculate the difference in the adsorption enthalpies of toluene and benzene to be 1.67 kcal/mol.

[e] We have used the measured difference in adsorption enthalpies of toluene and benzene to extrapolate our measurements to 298 K in order to compare them to those of ref. [11].

from the steady-state competitive hydrogenation of these aromatic molecules is shown in table 2 along with the turnover frequency of benzene.

In order to compare our results for Pt/SiO_2 with those of ref. [11], we also measured $K_{t/b}$ at two temperatures (353 K and 303 K) to estimate the difference in the adsorption enthalpies of toluene and benzene. The estimate of this difference was 1.67 kcal/mol and this value was used to extrapolate our measurements of $K_{t/b}$ at 353 K to 298 K for comparison to values from ref. [11] on more acidic supports, see table 2.

4. Discussion

Hydrogen chemisorption following the alkaline earth cation exchange suggests that the Pt particle dispersion is not much affected by exchange of cation and the particles are still accessible. However, the CO adsorption is more interesting here since the capacity is changed. The initially prepared 0.78Pt/KL (from which all of the alkanine earth exchanged catalysts were prepared) had a CO/Pt = 0.47, but after alkaline earth cation exchange, CO/Pt decreases systematically as radius-to-charge is increased. There appears to be a significant decrease in the CO chemisorption capacity and the hydrogen chemisorption suggests that it is unlikely to be a result of accessibility of the Pt particles. If the replacement of Mg by Ca or Ba exchange resulted in increasing electron charge transfer to Pt, it might be expected to increasingly inhibit CO chemisorption in the order Ba > Ca > Mg, as observed, since the primary bond to Pt is by electron donation from the 5 sigma orbital to Pt. However, it is not so obvious that this would not also affect hydrogen chemisorption.

The change in the rate of benzene hydrogenation parallels the change in the CO chemisorption capacity. This would imply that the rate constants decrease with acidity, and as discussed below, also parallel $K_{t/b}$. However, unlike the $K_{t/b}$ where one has a good physical basis to predict the effect of charge on its variation, how the rate constant should vary with charge on the Pt cluster is not so obvious.

The ratio of adsorption equilibrium constants extracted from the competitive toluene/benzene hydrogenation are also consistent with a charge transfer from the alkaline earth exchanged zeolite support to the Pt particle, i.e., to the extent that this occurs, toluene is expected to compete less effectively and $K_{t/b}$ would be expected to be smaller. As seen in the table 2, all of the alkaline earth exchanged L-zeolites result in smaller $K_{t/b}$ than Pt/SiO_2 (and very much smaller than on acidic Pt/Y-zeolites), where little metal-support interaction would be expected, and the Mg, Ca and Ba exchanged zeolites are ordered as might be predicted if increased ionic radius-to-charge (softer Lewis acid) implied less charge withdrawal.

There is a complication here concerning the effect of the alkaline earth cations on acidity, i.e., there is expected to be hydrolysis of the double charged cation to produce Brønsted acidity:

$$Ca(H_2O)^{+2} \rightarrow Ca(OH)^{+} + H^{+}$$

and this is expected to increase in the order Mg > Ca > Ba [15]. This is the kind of acidity which is supposed to be involved in Pt/CeY which has the highest measured $K_{t/b}$, see table 2, but it clearly is not the dominant effect for the alkanine exchanged Pt/L-zeolite catalysts. One implication of this observation is that the effect of the exchanged cation is unlikely to be direct, but more likely an indirect interaction through the zeolite lattice.

Finally we must ask, do the alkaline earth cations really affect the charge on the Pt particles? As noted in the introduction, in the re-investigation of Pt in the Y-zeolites, charge transfer could not be detected by XANES but was apparent in the infrared frequency shift of chemisorbed CO [8]. The suggested explanation was that the acidity of the zeolite framework affected the ionization potential of the Pt clusters. A similar rationalization of the results in table 2 is possible. Certainly there is a correlation between ionization potential, basicity and charge transfer. What is most obvious from physical measurements of our probe molecules is that they differ in their ionization potentials, benzene having an ionization potential of 9.6 eV which is 1.1 eV greater than toluene. From this one can deduce that partial charge transfer should also be energetically more favorable for toluene than benzene and this relative capacity for electronic charge transfer can be called greater basicity of toluene relative to benzene.

If we turn our attention to a Pt cluster, we can argue that its ionization potential will be affected by cluster size, molecular adsorption, support, etc. As in XPS, these effects of ionization potential may be of either initial or final state origin. Charge transfer from the zeolite support would presumably be labeled an initial state effect, but it is likely that relaxation energies are more dominant. For an isolated atom, the screening of a positive charge that results from ionization can only be accomplished by intra-atomic relaxation, but as a cluster is formed and grows in size, there will also be extra-atomic screening of the charge by conduction electrons and this relaxation energy may be of the order of 5–10 eV for metals [16] and leads to a decrease in the binding energy (ionization potential). Our measurements of $K_{t/b}$, which only sense the relative energetics of charge transfer between the aromatic molecule and the Pt particle, do not distinguish between initial state (charge accumulation on the Pt particle by interaction with the support) and final state (screening or distribution of charge transferred to the support following transfer to the particle by the aromatic molecule). The question is not just semantic since a fundamental understanding requires that they be distinguished. If one is primarily interested in the question of effect on catalysis, one must conclude that the electronic (initial or final state) effect of Pt particle interaction with zeolite support is significant, at least for the competitive adsorption of toluene and benzene, since $K_{t/b}$ varies by about an order of magnitude between Pt/Ce-Y and Pt/Ba-L.

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