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On the deactivation of Pt/L-zeolite catalysts

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Pt/L-zeolite catalysts have a unique activity for *n*-hexane aromatization to benzene. There have been proposals which attribute this to electronic and to geometric origins of the L-zeolite. Recently, the uniqueness of the L-zeolite support has been understood to derive from the ability to stabilize very small particles in a non-acidic environment and it has been proposed that a further stabilization against deactivation (by geometric constraint of bimolecular coke precursor reactions) is what distinguishes these catalysts relative to SiO_2 supported small Pt particles. We have investigated the initial deactivation rate of four Pt/L-zeolite catalysts and a Pt/SiO_2 reference during reaction of *n*-hexane, neopentane and 2-methyl-2-pentene. In all cases, the relative rates of deactivation correlate with the apparent acidity (as determined by competitive benzene/toluene hydrogenation) suggesting that the deactivation stabilization may have an electronic component.

Keywords: Pt; L-zeolite; deactivation; benzene/toluene hydrogenation; *n*-hexane; neopentane hydrogenolysis; 2-methyl-2-pentene coking; effect of zeolite acidity on deactivation

1. Introduction

The discovery of non-acidic reforming catalysts based on Pt particles supported in L-zeolite has stimulated two opposing hypotheses to explain the different aromatization selectivity of such catalysts relative to other supports [1]. The initial proposal was that the interaction of the Pt particle with the basic L-zeolite walls caused the particles to be electron rich [2,3]. Alternative proposals based on the confining structure of the undulating parallel channels of the L-zeolite were proposed by Tauster and Steger [4,5] and Derouane and Vanderveken [6]. The latter authors suggested that the L-zeolite channels might pre-orient reactant in such a way as to make 1, 6 adsorption more probable. The former proposal suggested that the narrowest portion of the channels collimated the reactant to make an end-on encounter probable and that this might give a propensity for terminal adsorption promoting 1, 6 ring closure and the competing reaction, terminal cracking. Tauster and Steger [3] provided extensive experimental evidence for the correlation of aromatization and terminal cracking on a large number of Pt/L-zeolites of varying dispersion, cation exchange and ratio of particles inside and outside the channels of the zeolite. Recently Mielczarski et al. [7] have confirmed the aromatization selectivity/terminal cracking correlation for Pt/L-zeolite catalysts, but find that Pt supported on a hexagonal faujasite, a microporous carbon and a silica also fit on the same correlation. They thus conclude that the high aromatization selectivities observed over monofunctional Pt catalysts are independent of support microporosity as long as the support is completely non-acidic. The counter proposal of Mielczarski et al. is that the uniqueness of Pt/KL catalysts for *n*-hexane aromatization lies not in the geometry of their channel structure but in their ability to stabilize extremely small Pt clusters in a non-acidic environment. They did not discuss the nature of the stabilizing property of L-zeolite, but by inference, it must have an electronic or bonding nature if it does not rely on geometry.

Two groups have observed that the L-zeolite ability to stabilize small Pt particles is lost in the presence of sulfur [8,9], i.e. that sulfur promotes Pt particle growth. We have confirmed this observation using TEM and EXAFS results that will be published elsewhere [10]. It is difficult to see how the *destabilization* of the Pt particles by sulfiding could be interpreted in terms of a geometric effect of the L-zeolite. However, if the stabilization of small Pt particles involved some sort of electronic interaction such that there were net charge transfer from the L-zeolite walls to the Pt particle, sulfur might compete with Pt as an electron acceptor.

Iglesia and Baumgartner [11–13] have presented the most compelling experimental evidence that it is inhibited deactivation of Pt sites within the one-dimensional channels of L-zeolite that most distinguishes the latter from mesoporous supports such as SiO_2 and Al_2O_3. Dehydrocyclization turnover rate and terminal hydrogenolysis selectivity are found to be similar on Pt/KL and fresh Pt/SiO_2, but both the rate and selectivity decrease rapidly on Pt/SiO_2 as it deactivates. A combination of H_2 chemisorption and particle size determination by TEM demonstrates that deactivation of Pt/SiO_2 is not dominated by particle growth but coking of the Pt particles. They propose that inhibited deactivation of Pt sites within one-dimensional zeolite channels, rather than previously proposed molecular-die or shape selectivity effects, accounts for the high dehydrocyclization rate and for selective terminal hydrogenolysis of Pt/KL-zeolite catalysts. They and Mielczarski et al. [7] concur that 1, 6 ring closure and terminal cracking are intrinsic properties of very small Pt particles and can be achieved on other supports as well as L-zeolite.

Iglesia and Baumgartner [11–13] propose that the inhibited deactivation is a protective effect of L-zeolite channels and reflects the shape-selective restriction on bimolecular transition states required in polymerization steps needed to form the coke. They further suggest that the probability of bimolecular encounters are particularly low in one-dimensional spaces such as the L-channels, a concept attributed to Kopelman [14]. Such bimolecular reactions to form deactivating coke would presumably involve olefin precursors. However, there are other possibilities that should be considered which might account for the Pt deactivation inhibition effect of L-zeolite. First, it is conceivable that catalyst deactivation by polymerization-like reactions of coke formation indeed take place, but primarily occur between gas phase precursors (typically olefins and/or aromatics) and condensed carbonaceous residues [15] thereby requiring little or no support three-dimensionality for them to occur. Second, other types of deactivation mechanisms such as unimolecular formation of carbon fragments may take place when the generation of dehydrogenated species is experimentally kept to a minimum.

We have recently studied the neopentane reaction with hydrogen on a variety of Pt/L-zeolite catalysts with a wide range of Pt particle sizes and support acidity [16]. Due to neopentane molecular inability to yield olefinic products, this catalytic probe has long been recognized as valuable as a purely metal-catalyzed reaction [17,18]. Even after proper adjustment of the experimental variables in order to guarantee operation under a primary product regime, it was observed that the deactivation of the hydrogenolysis (to isobutane + methane) pathway was a strong function of the L-zeolite support acidity. To test if this influence of the zeolite acid/base properties could be extended to other substantially different hydrocarbon reactions, the 2-methyl-2-pentene (2M2P) isomerization in the absence of hydrogen was also studied on the same set of catalysts. The deactivation results are correlated to the kinetically derived ratio of toluene to benzene adsorption coefficients, $K_{\text{toluene}}/K_{\text{benzene}} = K_{\text{t/b}}$, which is in turn known to be a very sensitive parameter of the electronic nature (support acidity) of small metal clusters [19,20]. We have also compared deactivation during dehydrocyclization of *n*-hexane at low pressures and high conversion on the same catalysts.

Both the reactions of neopentane and isomerization of 2M2P were carried out at temperatures substantially lower than required for aromatization. Because low temperature (or high H_2 pressure) inhibits rapid initial deactivation of Pt even under aromatization conditions [11], our deactivation results may not be mechanistically the same nor necessarily relevant to deactivation under commercial aromatization conditions. This may also be true for our *n*-hexane results to some extent because of the sub-atmospheric pressure used.

2. Experimental

Four catalysts with comparable dispersions (CO/Pt ratio) were employed. The preparation and reaction conditions are described in detail in ref. [16]. In brief, two catalysts were prepared using the incipient wetness technique on the KL-zeolite and a BaKL (prepared by exchange of the KL-zeolite, 6.2 wt% Ba^{2+}, Galbraith laboratories analysis) support with an appropriate solution of $Pt(NH_3)_4(NO_3)_2$ followed by calcination and reduction at 773 K. The catalysts are labeled 0.51% 773-Pt/KL-IM and 0.52% 773-Pt/BaKL-IM where the numbers preceding Pt are the calcination temperatures. An ion exchange preparation using the same precursor was obtained as described elsewhere (except that nitrate-based salts were used in every step for the current preparations) [20]. The catalyst (0.98% 693-Pt/K(H)L IE) was calcined at 693 K under O_2 flow and subsequently reduced with hydrogen at 773 K. The lower calcination temperature, relative to the impregnation preparation, was chosen to produce a comparable dispersion. A portion of the reduced IE sample was back-exchanged with a 0.3 M KNO_3 solution to partially eliminate the residual Brønsted acidity. The back-exchanged material was named 0.98% 693-Pt/KL IE-BE. A fifth catalyst from the same preparation as 0.51% 773-Pt/KL-IM, but calcined at 543 K and therefore of higher dispersion, was used to assess particle size effects. This catalyst is called 0.51% 543-Pt/KL-IM.

As a reference, we used a 1.92 wt% Pt/SiO_2 (100–200 mesh Davison 923 silica). After the SiO_2 was impregnated to incipient wetness (1.0 ml soln./g of support) the material was oven-dried at 383 K for 8 h. The dried catalyst was purged under flowing ultra high purity (uhp) He (32 ml/min) at 373 K. The flow was then switched to uhp H_2 and the reduction temperature (723 K) was reached at 2 K/min and held for 8 h.

Pyrex 0.8 mm i.d. U-tubes were used as flow reactors for the kinetic measurements at atmospheric pressure. Ultra high purity H_2 and He gases were further purified using H_2O and O_2 traps from Analabs. Pre-blended mixtures of uhp 9.8% neopentane/He, 2.0% benzene/He and 0.6% toluene/He were purchased from Matheson. Typically, a 0.5 g catalytic bed was reactivated under H_2 flow at the reduction temperature for 1 h. In all cases, neopentane activity measurements were carried out in the temperature range of 513–653 K. For the determination of apparent activation energies, the H_2, neopentane and He feed flows were adjusted with Brooks 5850 mass-flow controllers and the partial pressures set at 8.1, 1.6 and 91.6 kPa, respectively. Turnover frequencies were typically in the range of 10^{-3}–10^{-4} s^{-1} when normalized to CO chemisorption. Conversions below 1% were necessary in order to guarantee operation under primary product regimes.

The ratio of toluene to benzene adsorption coefficients, $K_{t/b}$, was kinetically determined at 353 K using the method of Tri et al. [19] as described previously [20]. Briefly, the procedure was as follows. Pyrex 0.8 mm i.d. U-tubes were used as flow reactors for the kinetic measurements at atmospheric pressure. The ratio of toluene to benzene adsorption coefficients was kinetically determined at 353 K by plotting the ratio of the rate of pure benzene hydrogenation to benzene hydrogenation in competition with toluene as a function of the ratio of the toluene and benzene partial pressures. If both the benzene and toluene are zero order such a plot is linear and has an intercept of 1.0 and a slope equal to the ratio of the toluene and benzene adsorption coefficients, $K_{t/b}$ [19]. The reactor effluent was analyzed by an on-line 5880 Hewlett-Packard gas chromatograph equipped with a 100 m capillary column coated with methylsilicone.

The reaction of *n*-hexane was investigated at below atmospheric pressure over a period of time on stream from 15 to 170 min at conversions that ranged from 13 to 40%. Reaction was carried out in the same reactor described above at $T = 753$ K with hydrogen and *n*-hexane partial pressures of $P_{H_2} = 33.8$ kPa and $P_{n\text{-}C_6} = 4.2$ kPa, respectively, and the balance He. 10–20 mg of catalyst was diluted with 100 mg α-Al_2O_3 (3 g of which was also used as a preheating bed). The total flow was 30 cm^3/min at STP. The analysis train was the same as described above.

3. Results and discussion

The catalyst description and chemisorption characterization is presented in table 1. The four L-zeolite catalysts were selected from a set of 24 catalysts where the dispersion in each of the four series had been varied by varying the calcination temperature. They have approximately the same average particle size as measured by CO chemisorption which is necessary to remove the particle size effect of reactions of neopentane. A fifth L-zeolite catalyst, 543-Pt/KL-IM, was used only for *n*-hexane reaction to test the effect of dispersion on activity, selectivity and deactivation.

We have tested for diffusion limitations using the Koros–Nowak test [21] in earlier experiments with the *n*-hexane reaction. These tests were limited, but of two kinds, i.e. increase in sites by increase in metal loading by a factor of four and decrease in sites by dilution with pure KL-zeolite by a factor of five. In all cases the Pt was introduced by ion exchange so the Pt/acidity ratio was constant. An error analysis indicates that the uncertainty of our rates is ±10% [22] and, within this uncertainty, the rate was proportional to the sites in the reactor for both the bed dilution and metal loading experiments indicating that these catalysts do not have serious transport control limitations. Because the rates of the neopentane and 2M2P reactions reported here are lower than in the *n*-hexane experiments, we assume the same conclusion applies. However, we admit that the lower temperatures used for the neopentane and 2M2P reactions will result in higher density of reactant in the L-zeolite pores so we cannot rule out effects of diffusion with the experiments in hand.

The turnover frequency (TF) for neopentane hydrogenolysis, based on CO site density, is plotted in fig. 1 for the four catalysts listed in table 1. Also shown is the result for a Pt/SiO_2 catalyst. The latter catalyst did not have comparable dispersion, i.e. $CO/Pt = 0.26$, but when this reference was compared to all members of a series of 24 catalysts with a range of dispersions, it fell between the ion exchange preparations, Pt/KHL-I, and impregnation preparations,

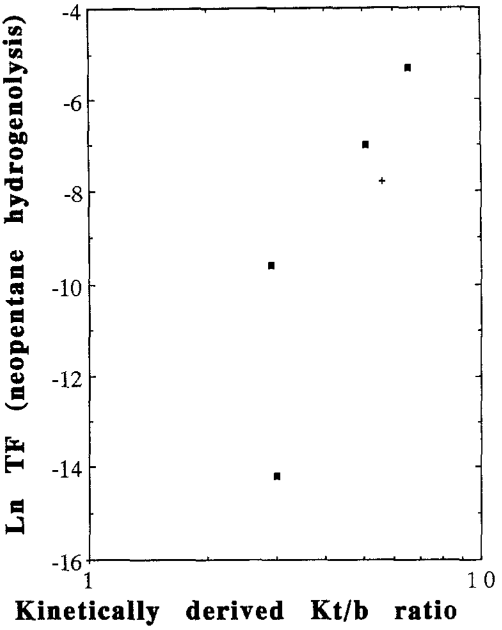

Fig. 1. Neopentane hydrogenolysis rates of catalysts (TF/s) versus the kinetic measure of acidity, $K_{t/b}$. $T_{reac} = 563$ K, $P_{H_2} = 8.1$ kPa, $P_{neoC_5} = 1.6$ kPa. Balance: He to atmospheric pressure. (■) Pt/L-zeolite, see table 1; (+) Pt/SiO_2.

Pt/KL-IM, for all dispersions. We assume that the $K_{t/b}$ is a kinetic measure of acidity of the support as demonstrated by a comparison across several supports [20]. The three supports which are primarily cation balanced by K^+ are ordered in decreasing acidity of the support by both $K_{t/b}$ and neopentane activity, 693-Pt/KHL > 693-Pt/KL (back-exchanged) > 773-Pt/KL (impregnated) and Pt/SiO_2 falls between the ion exchange and impregnation preparations. One can also understand the placement of 773-Pt/BaKL (impregnated) based on the recent results of Mielczarski et al. [7]. They showed (by NH_3 TPD) that impregnated BaKL has both weak and strong acidity when uncalcined and that

Table 1
Catalyst description

Name	Preparation procedure	Calcination T (K)	Pt (wt%)	CO/Pt	$K_{t/b}$ at 353 K
693-Pt/KHL-I	ion exchange	693	0.98	0.68	6.6
693-Pt/KL-I, BE	ion exchange	693	0.98	0.61	5.2
773-Pt/KL-IM	impregnation	773	0.51	0.63	3.0
773-Pt/BaK-IM	impregnation	773	0.52	0.71	2.9
543-Pt/KL-IM	impregnation	543	0.51	1.06	–
Pt/SiO_2	impregnation	383	1.92	0.26	5.6

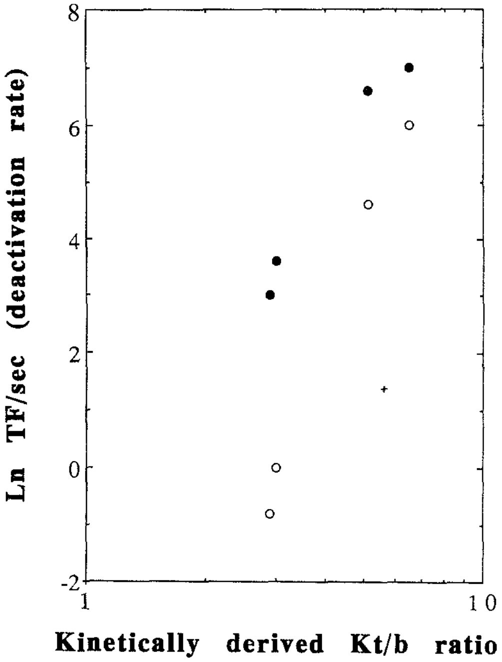

Fig. 2. Deactivation rates of catalysts (TF/s) versus the kinetic measure of acidity, $K_{t/b}$. Initial deactivation rates were calculated from TOF values after 5 min and 20 min time on stream by extrapolating to zero time. (○), Neopentane/H_2 hydrogenolysis reaction: TF/s × 10^8, T_{reac} = 563 K, P_{H_2} = 8.1 kPa, P_{neoC_5} = 1.6 kPa. Balance: He to atmospheric pressure. (●) 2M2P isomerization reaction: TF/s × 10^6, T_{reac} = 563 K, P_{2M2P} = 6.2 kPa. Balance: He to atmospheric pressure. (+) Pt/SiO_2.

all of the strong acidity is removed by calcination at 600 K but most of the weak acidity remains. Presumably both kinds of acidity are associated with water hydrolysis on the Ba^{2+} cations and the strong acidity is removed when the associated Ba^{2+} cations are moved to the locked sites after calcination. The weak acidity is associated with Ba^{2+} still in the main channels because it can be removed by simple exchange with K^+ at room temperature which does not involve cations not in the main channels [23]. A further implication of this interpretation is that $K_{t/b}$ senses only the support acidity as it is reflected through the Pt metal clusters (because $K_{t/b}$ is about the same for 773-Pt/KL-IM and 773-Pt/BaK-IM), but that neopentane is also sensitive to support acidity directly (that which can be detected by TPD of NH_3). One possible interpretation is that the proton is directly involved in the neopentane reaction (but not in aromatization hydrogenation) as recently suggested by Homeyer et al. for Pd–protons adducts in Y-zeolites [18]. This is potentially an interesting observation which deserves further study, but is not the main point we wish to make.

In fig. 2, the deactivation rates of all four catalysts listed in table 1 are expressed as sites lost/s are plotted against the corresponding $K_{t/b}$ values.

Table 2
Site time yield (STY) and benzene selectivity of *n*-hexane reaction at $T = 753$ K, $P_{H_2} = 33.8$ kPa and $P_{n\text{-}C_6} = 4.2$ kPa

Name	STY		Rel. rate, 50 min/15 min	Sel. at 50 min (%)
	15 min	50 min		
693-Pt/KHL-I	0.50	0.30	0.60	33 (17%) [a]
693-Pt/KL-I, BE	0.69	0.50	0.72	36 (24%) [a]
773-Pt/KL-IM	0.64	0.51	0.79	74 (27%) [a]
773-Pt/BaK-IM	0.69	0.53	0.76	63 (31%) [a]
543-Pt/KL-IM	0.34	0.31	0.91	72 (22%) [a]
Pt/SiO_2	0.16	0.12	0.72	56 (22%) [a]

[a] The conversion at 50 min is given in a parentheses because the selectivity increases more or less linearly with conversion [1].

Again, the Pt/SiO_2 is included as a reference, but only for the case of deactivation by neopentane. Interestingly, we have also found that at least 95% of the initial neopentane/H_2 and 2M2P isomerization activities are recovered after a second reduction cycle. No activity loss is detected on fresh catalysts during the benzene/toluene hydrogenation studies. In addition, we have measured the apparent activation energies for both deactivation processes on the 693-Pt/KL-IE-BE sample and these were found to be 19 ± 1 and 16 ± 1 kcal/mol for the neopentane/H_2 and the 2M2P isomerization reactions, respectively. None of the L-zeolite supports show significant blank activity for any of the four catalytic probe reactions used.

The results for *n*-hexane are reported (table 2) as site time yields (STY) based on total conversion and CO chemisorption site density because the conversions ranged between 20–40%, too large to calculate a TF. At the low H_2 pressure and short reaction times used here, the rapid deactivation of Pt/SiO_2 relative to a good Pt/L-zeolite catalyst is not obvious as it was in the work of Iglesia and Baumgartner [13]. It may be the large particle size of the Pt/SiO_2 also plays a role here. The comparison of 773-Pt/KL-IM and 543-Pt/KL-IM is interesting because they are the same preparation except for the calcination temperature. The obvious structural difference that results from the lower calcination temperture is the higher average dispersion, i.e. CO/Pt equal to 1.06 compared to 0.63. While the smaller particles might be expected to give smaller rates for a structure sensitive reaction, it is surprising that they also appear to be more stable. What is most obvious under these conditions is that deactivation is more sensitive to the acidity of the L-zeolite than to particle size or cations which balance charge on the zeolite lattice.

One important observation is that the deactivation of both neopentane and 2M2P reactions appear to be entirely confined to the metal which is suggested by the activity recovery measurements although we cannot rule out the possibility of spillover. A second and more significant consequence of this set of experiments is that the acidity of the support has a marked (indirect) effect on the Pt/L catalyst deactivation suggesting that factors other than zeolite channel geometry are of crucial importance for the activity loss processes at the conditions of our present study. Finally, it should be noted that the apparent activation energies for the deactivation of both reactions are more or less comparable. It might be expected that if deactivation proceeds via a bimolecular pathway, the activation energy will be lower than other unimolecular reaction channels. However, whatever the mechanism, the similar activation energy suggests it is of the same kind for both neopentane and 2M2P. Because the deactivation by 2M2P correlates with the kinetically determined acidity, $K_{t/b}$, in the same way as neopentane and has about the same activation energy, there appears to be a unimolecular deactivation path on the Pt clusters for olefins.

There may also be bimolecular deactivation pathways which directly involve the acid sites of the zeolite and this is particularly so at the higher reaction temperatures and conversion used by Iglesia and Baumgartner [11–13]. However, 2M2P is a very sensitive probe for both weak acidity (double bond isomerization) and strong acidity (structural isomerization by methyl shift) [24]. On the pure KL-zeolite, we find that not even the double bond isomerization is catalyzed, i.e. there would not appear to be available the strong acid sites needed for the bimolecular deactivation pathways on a good Pt/KL-zeolite non-acidic reforming catalyst. Moreover, it should be noted that the only product of 2M2P double bond isomerization in the absence of H_2 on all four of the catalysts listed in table 1, is 2M1P. This indicates that, like neopentane, reaction of 2M2P is restricted to the Pt particles influenced by the support since direct reaction of 2M2P on acid sites produces all possible double bond isomerization products.

Iglesia and Baumgartner have noted that not only undeactivated Pt/SiO_2 [12,13], but also Pt supported on Mg(Al)O [25] and dealuminated Y-zeolite [26] also catalyze selective dehydrocyclization. The latter was particularly emphasized because Pt clusters within the highly dealuminated Y-zeolite (Si/Al > 100) are more stable than on mesoporous SiO_2, show dehydrocyclization turnover rates similar to those on Pt/KL [12] and Iglesia and Buamgartner suggest that Pt clusters in such Y-zeolite may be electron-deficient by analogy to other Pt/Y-zeolite catalysts [27]. However, Pt in Y-zeolite has only been claimed to be electron deficient when the Si/Al is in the normal range and the zeolite has a high acid site density [27]. Because the acidity is a strong function of the Si/Al ratio, it is conceivable that these materials are nearly as basic as L-zeolite, i.e. that stabilization of Pt in dealuminated Y-zeolite might result from an interaction similar to L-zeolite.

From the above arguments, we speculate that the unidimensional L-zeolite framework does not inhibit coke formation in the general sense of shape-selectivity. Rather, it appears reasonable to think that the same interactions that stabilize the small size of Pt particles in L-zeolite [7,11–13] also stabilize these particles against unimolecular deactivation mechanisms that are available with non-acidic supports such as silica.

While we believe that these results call into question the proposal of Iglesia and Baumgartner suggesting that L-zeolite inhibits bimolecular deactivation [12], we do not wish to be too adamant on this point because our reaction conditions are far from those under which they compared the deactivation of Pt/KL-zeolite and Pt/SiO_2, with regard to both pressure and temperature of reaction and time on stream. That is, what we have observed at lower pressures and temperatures and at shorter reaction times may reflect only the metal deactivation and/or the initial deactivation step. There may be an additional zeolite deactivation that only becomes obvious under commercial reforming reaction conditions. However, even if this is the case our results do speak to the scientific question of Pt interaction with the L-zeolite and provide additional evidence that the acidity of the L-zeolite influences the reactivity of the small Pt particles. This is also the case for *n*-hexane conversion to benzene, at least at low pressure. Finally, we note that smaller particles (in an acid free L-zeolite) are less active but more stable than larger particles. If an interaction with the L-zeolite were the origin of the stabilization, it might be greater with small particles which have a greater fraction of the Pt atoms at the particle–zeolite interface.

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