JOURNAL OF CATALYSIS **156**, 304–306 (1995)

LETTER TO THE EDITOR

n-Hexane Conversion over Supported Pt Catalysts: Reply to Zoltán Paál

In the accompanying letter to the *Journal of Catalysis*, Paál (1) has questioned the findings and conclusions of our recently published paper (2). It is important to stress that many of our conclusions are based on the combined interpretation of the data from our recently published paper (2) with results from our spectroscopic and microcalorimetric studies of various supported platinum catalysts (3, 4). In short, we have shown that highly dispersed, cluster-sized platinum particles supported in L-zeolite have the same heats of H_2 and CO adsorption as larger platinum particles supported on silica; however, Pt/L-zeolite catalysts are more resistant to self-poisoning reactions, exhibit higher turnover frequencies, and show enhanced formation of benzene and methylcyclopentane (MCP) compared to larger particles of Pt supported on silica during *n*-hexane conversion at total pressures of 3 atm and hydrogen pressures near 276 kPa.

The main conclusion of our studies on Pt/L-zeolite catalysts is that cluster-sized platinum particles stabilized in the micropore structure of L-zeolite are at least partially responsible for the reduced rate of catalyst deactivation under the *n*-hexane reaction conditions used in our studies, thereby maintaining high catalytic activity and high yields of benzene and MCP. This conclusion does not follow simply from analysis of reaction kinetics data, but is deduced from the combined consideration of these data with results from related microcalorimetric and NMR spectroscopic studies. We also stress here that our conclusions relate to catalysts studied under conditions that do not favor olefin formation (i.e., higher total pressures and higher higher hydrogen pressures); therefore, these conclusions may not be directly related to catalyst performance under conditions typically employed by Paál and co-workers, where olefin production is significant (e.g., total pressures near 0.2 atm and hydrogen pressures near 16 kPa).

We thank Paál for his reading of our most recent paper (2), and we now address the main points raised by Paál in his Letter to the Editor.

Our presentation of catalytic performance data for *n*-hexane reactions (Table 2 in (2)), reporting benzene and methylcyclopentane as combined "dehydrocyclization" products, has been misinterpreted by Paál to mean that benzene and MCP formation proceed via a common reaction pathway. We agree with Paál that the C_5-cyclization (1,5-cyclization) mechanism proposed by Gault and co-workers (5, 6) is responsible for MCP formation and that this pathway is distinct from the route leading to benzene (1,6-cyclization). We have clearly stated this position in our discussion and have cited the appropriate literature references where necessary. We further agree that benzene is formed from more deeply dehydrogenated intermediates than either MCP or the hydrogenolysis products. This position is also stated in our discussion (2) and forms the basis for explaining the more negative hydrogen order measured for benzene formation versus MCP formation (2).

It also seems that Paál has misinterpreted our discussion regarding the similar activation energies measured for the two catalysts (Table 4 in (2)). The similar activation energies reported are between the two catalysts studied and not between reaction pathways which lead to MCP and benzene (C_5 and C_6 ring closure), as stated by Paál (1). Inspection of Table 4 in (2) clearly shows that the activation energy for benzene formation is more than two times greater than that for MCP over both catalysts. We agree that similarities in activation energies between the two catalysts are not sufficient to prove that similar mechanisms are responsible for product formation over both catalysts. However, we suggest that these similarities provide support for the notion that the factors controlling individual product formation may be similar for the two catalysts.

It should also be clarified that our definition of yield (Table 2 in (2)) is consistent with that used in kinetics textbooks (such as (7, 8)). Also, we have defined selectivity as the ratio of reaction rates in a manner similar to that of Boudart and Djéga-Mariadassou (9). We have clearly stated these definitions in the text. Also, the conversion levels for the kinetics data are given in the text and figure captions (i.e., 9–12%). We would like to take this opportunity to correct a typographical error regarding the measurement of hydrogen orders; the hydrogen partial pressure was varied between 270 and 370 kPa and not between 270 and 370 Torr as reported in the Results section.

0021-9517/95 $12.00

TABLE 1

Turnover Frequencies for *n*-Hexane Conversion over Various Catalysts

Catalyst	603 K	693 K
EUROPT-1[a] (6% Pt/SiO_2)	0.0142 s^{-1}	0.0164 s^{-1}
0.8% Pt/KL[b]	—	0.0306 s^{-1}
4% Pt/SiO_2[c]	—	0.19 s^{-1}
1% Pt/K(Ba)L[c]	—	1.2 s^{-1}

[a] Data taken for sample 30 from Table 2 of (13); 16 kPa H_2, 1.3 kPa *n*-hexane, 4% conversion.

[b] Data taken for sample 21 from Table 2 of (13); 16 kPa H_2, 1.3 kPa *n*-hexane, 4% conversion. Data for this sample were also used in the comparison presented in Table 1 of (1) (sample c).

[c] Data taken from Table 3 of (2); 276 kPa H_2, 27.6 kPa *n*-hexane, ca. 9–12% conversion.

The effects of hydrogen and temperature on reaction pathway selectivity for Pt/K(Ba)L have been considered and are summarized as hydrogen orders and reaction activation energies. For example, consider the effect that increasing temperature and decreasing hydrogen pressure would have on benzene selectivity. Since the benzene formation pathway has a higher activation energy and a more negative hydrogen order than the MCP formation pathway (2), an increase in temperature and a decrease in hydrogen pressure should increase the rate of benzene formation relative to the rate of MCP formation. This effect should result in increased benzene selectivity, in agreement with the statement of Paál that the benzene to MCP selectivity (benzene/MCP ratio) increases with increasing severity of the reaction conditions (1).

In addition to effects of hydrogen pressure on reaction kinetics, reaction selectivities are also affected by the availabilities of the active sites under reaction conditions. For example, the availability of a particular type of site under reaction conditions may depend on the extent of catalyst deactivation. During *n*-hexane transformation reactions, hydrogen partial pressure and total reaction pressure have a strong influence on catalyst deactivation. At high hydrogen and total pressures, catalyst deactivation is reduced since thermodynamic limits suppress the formation of unsaturated hydrocarbons, which promote catalyst deactivation. Comparison of *n*-hexane reaction product yields and selectivities under extremely different hydrogen and total pressure conditions, such as those presented in Table 1 (1), can be misleading if differences in extents of catalyst deactivation are not taken into account. For example, the turnover frequency (TOF) for *n*-hexane conversion over EUROPT-1 at 603 K is reported by Paál to be nearly equal to that measured at 693 K under the same reactant partial pressures and at the same conversion levels (see Table 1). However, *n*-hexane conversion reactions have significant activation energies (2) and should exhibit a significant temperature response. Thus, it is likely that the catalyst is more severely deactivated at the higher temperature, thereby reducing the number of exposed active sites. Furthermore, our 4% Pt/SiO_2 catalyst is an order of magnitude more active than EUROPT-1 at 693 K, despite the fact that benzene and MCP formation rates have negative hydrogen orders and our studies were conducted at higher hydrogen and total pressures. These differences are probably due to a smaller extent of catalyst deactivation at the higher hydrogen partial pressures used in our experiments. In addition, the Pt/K(Ba)L catalyst under our reaction conditions is more than an order of magnitude more active than our Pt/SiO_2 catalyst and nearly two orders of magnitude more active than the Pt/KL catalyst studied by Paál at lower pressures (see Table 1) and used in the comparison with our data in (1). These examples serve to highlight the possible effects of reaction conditions on catalyst deactivation and, consequently, on catalyst activity and selectivity.

The results of our studies suggest that differences in catalytic activity and selectivity between Pt/L-zeolite and Pt/SiO_2 catalysts are at least partially a consequence of the different degrees to which each catalyst deactivates under similar reaction conditions (2). At the high hydrogen and total reaction pressures (3–4 atm) used in our studies, Pt/K(Ba)L is more stable to deactivation than Pt/SiO_2. These differences in catalyst behavior cannot be explained simply by metal–support interactions that alter the metal, since our previous microcalorimetric studies do not provide experimental evidence for this conclusion (3). These studies have demonstrated that platinum particles supported in L-zeolite have strengths for hydrogen and carbon monoxide adsorption similar to those for Pt supported on other neutral supports such as silica (3). Indeed, our ex situ microcalorimetric studies over these catalysts have quantitatively illustrated that carbonaceous species deposited on the catalyst during *n*-hexane conversion reactions have a stronger effect on platinum adsorption properties (2) than metal–support interactions (3). It is precisely for this reason that effects of catalyst deactivation on reaction activity and selectivity must be considered in a discussion of this catalyst system.

The greater resistance of very highly dispersed, cluster-sized platinum particles to coke deposition is clearly demonstrated by our ex situ ^{13}C NMR studies (2). The resistance of small platinum particles to self-poisoning reactions has also been previously demonstrated (10, 11). Although our 4% Pt/SiO_2 catalyst is highly dispersed (dispersion ca. 76% (3)), platinum particles on this catalyst are still large compared to platinum particles supported in L-zeolite. The L-zeolite catalyst contains primarily diamagnetic, cluster-sized particles (containing five to six atoms (12)), while the silica-supported catalyst consists predominantly of larger metallic particles. We have developed a ^{13}C NMR technique that can be used to distinguish between these types of particles (4).

Importantly, we do not discount the possible effect that the L-zeolite framework may have on catalyst activity and selectivity. Our experimental results clearly demonstrate that Pt/L-zeolite catalysts stabilize highly dispersed, cluster-sized platinum particles under *n*-hexane reaction conditions. Also, our ex situ ^{13}C NMR studies have demonstrated the greater resistance of these cluster-sized particles to self-poisoning reactions. We believe that it is the combination of these cluster-sized particles in the micropore structure of the L-zeolite support that helps to keep the platinum clean under reaction conditions and helps to maintain high catalyst activity during *n*-hexane transformation reactions. We also acknowledge the possible relevance of hydrogen spillover effects on various catalysts. For example, we have pointed out that Pt/L-zeolite samples are able to adsorb large amounts of hydrogen, beyond the metal loading of the sample, on a relatively weak adsorption site (3). At present, there is insufficient information to determine if these weak hydrogen adsorption sites influence catalyst activity and stability.

In closing, we certainly agree with Paál that Pt/L-zeolite catalysts are fascinating materials that may demonstrate a variety of phenomena, e.g., interactions of acid or base sites with metal particles, availability of surface hydrogen, transport of hydrogen between metal and support. Many more studies of this catalyst system are needed. The main point of our studies is that Pt/L-zeolite catalysts stabilize highly dispersed, cluster-sized platinum particles that exhibit essentially the same characteristics for H_2 and CO adsorption shown by larger particles of platinum supported on silica, whereas these cluster-sized platinum particles are more resistant to self-poisoning reactions, exhibit higher turnover frequencies, and show enhanced formation of benzene and methylcyclopentane during *n*-hexane conversion at total pressures of 3 atm, temperatures of 700–750 K, and hydrogen pressures near 276 kPa. While we believe that the combination of these cluster-sized particles in the micropore structure of the L-zeolite support is at least partially responsible for maintaining a clean platinum surface under our reaction conditions for *n*-hexane conversion and thereby maintaining high catalyst activity and high yields of benzene and methylcyclopentane under these reaction conditions, we realize that other factors, such as those mentioned by Paál, may play contributing roles in this catalyst system. We especially stress that these other factors may be important under reaction conditions, such as those studied by Paál and co-workers, where olefin formation is significant.

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Received August 1, 1995