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LETTER TO THE EDITOR

Is *n*-Hexane Conversion on Supported Pt Catalysts So Simple (or Can We Learn More about the Active Sites from This Reaction)?

A paper in which some very refined techniques (such as microcalorimetry and ^{13}C NMR study) were used to characterize Pt catalysts on zeolitic and SiO_2 supports has appeared in the *Journal of Catalysis* (1). That work—as well as its companion paper presenting ^{13}C NMR results for fresh catalysts (2)—supplies important new information on the changes of surface energetics of supported Pt samples, giving unquestionable evidence that the adsorption properties of a Pt/zeolite—as indicated by the differential heats of CO adsorption—after catalytic runs with *n*-hexane at 673 K are much closer to those of the initial state than are those of Pt/SiO_2. I must agree with the approach of the authors that no surface physical information has real value unless it is compared with catalytic propensities; the authors also include results of *n*-hexane test reactions. The discussion of catalytic results is oversimplified, however, and may suggest false ideas as far as the reaction pathways and their evaluation are concerned.

Table 2 (Ref. 1, p. 237) presents the product distribution in terms of "dehydrocyclization," "isomerization," and "hydrogenolysis," combining benzene and methylcyclopentane (MCP) into one product group. Several arguments against this oversimplified assumption have been summarized in two review papers of the present author (3, 4). Briefly, the formation of a C_5 ring produces a *saturated* ring from *saturated* alkane(s) (probably involving not too deeply dehydrogenated surface intermediates), whereas a benzene ring is probably produced via polyunsaturated open-chain intermediates, dienes, trienes, etc. (5). Further, C_5 cyclization is *reversible;* its surface intermediate is able either to desorb as a cyclopentane derivative or to give skeletal isomers. This is the well-known C_5 cyclic isomerization route postulated by Gault's group (see, e.g., 5). Papers supporting both mechanisms are duly quoted in the Discussion [Refs. (25–27) cited on p. 240 of Ref. (1)] without making the above-mentioned necessary and proper distinction. [In addition, Table 2 contains a rather regrettable error of mixing selectivities with yields. The definition of "yield," as used there, is in fact what is generally called "selectivity" (6).]

Before commenting on the more exact selectivity data which can be extracted from Table 3 in Ref. (1), three features disregarded by Sharma *et al.* should be mentioned. First, with MCP formation and isomerization being related reactions, the amount of MCP decreases in parallel with the increase in the yields of isomers as the overall conversion increases. This follows from the kinetic scheme put forward by Amir-Ebrahimi and Gault (5). This correlation between these two product classes has been observed on both Pt/SiO_2 (7) and Pt/zeolite catalysts (8, 9). As a rule, the monotonically increasing selectivities of isomers as a function of the conversion cross that of MCP, which in turn exhibits a maximum-type curve, characteristic of intermediate products (see, for example, Fig. 5 of Ref. (7), Fig. 4 of Ref. (8), Fig. 3 of Ref. (9)).

Second, the ratio of MCP to isomers at steady state depends strongly on the abundance of surface hydrogen, which is controlled, in turn, by (i) the hydrogen pressure and (ii) the temperature (10). This ratio varied considerably during *deactivation* of the Pt catalyst (an enhanced C_5 cyclization being observed on a moderately deactivated Pt catalyst at the expense of skeletal isomers).

Third, benzene selectivity remained more or less the same on deactivating Pt/SiO_2 (11). Hence the formation of benzene seems to be independent of the C_5-cyclic family of reactions; the two processes probably require different active sites (12). Davis *et al.* reported higher and higher benzene/MCP ratios with increasing severity of the reaction conditions, i.e., with lower hydrogen excess and higher temperature (13). Obviously, a more deeply dehydrogenated surface intermediate leads to benzene and this reaction was assisted by hydrogen-depleted surfaces.

The effect of hydrogen is evaluated properly on p. 239 of Ref. (1). Not only hydrogenolysis reactions but *all* skeletal processes are hydrogen-controlled and can exhibit maxima as a function of $p(H_2)$, as confirmed by very detailed experiments on various Pt catalysts at different temperatures (7–9, 11, 14, 15) and discussed in a more general way in Refs. (4, 10).

The results presented by Sharma *et al.* obtained under one specific experimental condition reflect, in our view, just one rather arbitrary experimental point for both catalysts,

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TABLE 1

Selectivity Results Obtained from *n*-Hexane over Various Pt Catalysts

	4% Pt/SiO_2[a]	1% Pt/K(Ba)-L[a]	6% Pt/SiO_2[b]	0.8% Pt/KL[c]	0.8% Pt/KL[d]		0.8% Pt/NaY[e]
at conversion, X%:	?	?	28.5	4.5	6	13	4
$<C_6$	16.3[f]	8.5[f]	15.5[g]	5.5[g]	35[g]	32[g]	4[g]
Isomers	56.5	19.2	34.5	0	9	21	18
MCP	19.0	21.8	33.5	1.5	10	9	40
Benzene	8.2	50.5	10	23	16	14	38
Hexenes	<0.5[h]	<0.5[h]	6.5	68[i]	30	24	1

[a] Ref. (1), $T = 698$ K, $p(H_2) = 276$ kPa, $p(nH) = 27.6$ kPa.

[b] Ref. (11), $T = 633$ K, $p(H_2) = 64$ kPa, $p(nH) = 5.33$ kPa.

[c] Ref. (8), $T = 693$ K, $p(H_2) = 16$ kPa, $p(nH) = 1.33$ kPa.

[d] Paál, Z., and Xu, X. L., unpublished results; $T = 693$ K, $p(H_2) = 64$ kPa, $p(nH) = 1.33$ kPa. As in other cases, increasing isomer, decreasing olefin and MCP, and steady benzene selectivities were observed.

[e] Ref. (9), $T = 603$ K, $p(H_2) = 64$ kPa, $p(nH) = 5.33$ kPa.

[f] Calculated from the $C_3 + C_4 + C_5$ fragments only (others not given).

[g] Calculated from the sum of C_1–C_5 fragments.

[h] As given in the text in Ref. (1), not included in the table.

[i] Plus 2% chain growth products.

corresponding to a steady state after runs of 4 h. No overall conversion value is given to inform the reader whether the product compositions correspond to an initial, medium, or final stage of *n*-hexane transformation. More information could have been obtained by observing the response of the selectivities during the run or under various experimental conditions. The two Arrhenius plots (Figs. 5 and 6 of Ref. 1) resulting in similar activation energy values for C_5 and C_6 ring closure reactions represent, in our view, insufficient evidence that the pathways of these reactions are similar. Thus, the discussion on page 240 of Ref. (1), which considers the possible relative importance of C_5 and C_6 ring closure reactions but disregards several arguments in the literature, does not seem to have a sound experimental basis.

Table 1 compares selectivity data calculated from Ref. (1) with other results obtained by the author over different catalysts. The results reported for Pt/SiO_2 (1) compare well with those of Ref. (11), despite the different temperatures for the low benzene (8–10%) and high C_6 saturated selectivities (70–75%). Table 1 demonstrates also that the higher H_2 pressure used in Ref. (1) at a higher temperature could result in very similar selectivity values. It is obvious that the aromatic selectivities of Pt/zeolites are higher than those of Pt/SiO_2 catalysts. As opposed to Ref. (1), in which olefins "are equilibrated at all reaction temperatures" (p. 238), the lower $p(H_2)$ in Ref. (8) was not sufficient to hydrogenate the initially produced alkenes to equilibrium concentration at 693 K. Smaller amounts of hexenes were present with a higher hydrogen excess (selectivities in columns 5 and 6, Table 1). Thus, the table also gives some clues to the hydrogen, conversion, and temperature effects mentioned. The shift in selectivities in the runs of Ref. (1) should have been similar to those reported in Refs. (7–12). Was it really so?

It is stated in Ref. (1) that "the primary hydrogenolysis reactions of *n*-hexane produce $C_4 + C_2$ and $C_5 + C_1$ hydrocarbons." This originates from a misunderstanding of the reference quoted therein (16) and is, consequently, untrue. Garin *et al.* (16) reported results with 2-methylpentane and 3-methylpentane but *no results with n-hexane.* The tertiary C atom in those isohexanes influences the direction of rupture (17). Further, *no propane can be formed by the primary rupture of 3-methylpentane* and this gives a simple explanation as to why it is reported in such low amounts in Ref. (16). The rupture in the *middle of the n-hexane molecule* prevails over most disperse (and single-crystal) platinum catalysts when secondary splitting is negligible (7–9, 11, 14, 15). Decreasing the hydrogen pressure results in more and more $C_5 + C_1$ splitting at the expense of propane formation, with the importance of the $C_4 + C_2$ rupture remaining small (15). This may be due to accumulation of Pt–C ensembles that promote terminal splitting (18).

The statement correlating aromatization activity with "the number of strong adsorption sites" (Ref. 1, Abstract) is baffling until one reads p. 241, where it turns out that strong adsorption of *adsorbed CO* rather than of chemisorbed reactants is meant.

The effect of the zeolite support cannot be restricted to "stabilizing cluster-sized particles" (Ref. 1, p. 241). Small Pt crystallites of other catalysts may also be rather stable. For example, the very small particles in 6% Pt/SiO_2 (i.e., EUROPT-1, the catalyst used in Refs. 7, 11, 14) are surprisingly stable under oxidation–reduction cycles as well as under reaction conditions (19). More influence can be attributed to the peculiar framework structure of the zeolite as well as to the interactions of the basic or acidic (not only zeolitic) supports with small metal particles, as discussed in several papers (20–22). Another important factor may be the availability of hydrogen on various catalysts, which can determine whether primarily sorbed reactive species turn into polymers or leave the catalyst. This, in turn, can be controlled by several factors, including the exposed crystal faces, the facility of hydrogen "traffic" between metal and the support, etc. (10). The availability of hydrogen, like most other aspects of hydrogen pressure effects, has not been considered.

To conclude: one regrets that the authors of Ref. (1) missed several possibilities of properly correlating surface characterization and catalytic properties. The insufficient treatment of catalytic results has left interesting questions unanswered. Revisiting these problems, including the correlation of selectivity *variation* with the number of strong CO adsorbing sites as well as hydrogen effects on the temporal change in the concentration of these sites, could bring us closer to determining the ultimate reason why one catalyst is more active and/or more stable than another.

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