Journal of Catalysis **203,** 529–530 (2001)
doi:10.1006/jcat.2001.3353, available online at http://www.idealibrary.com on IDEAL®

# LETTER TO THE EDITOR

# Hydrogen Effects in *n*-Hexane Isomerization on Pt/Sulfated Zirconia. A Comment on the Paper by Duchet *et al.* (*J. Catal.* **198**, 328 (2001))

Duchet *et al.* (1) recently published a study that presented new information about the catalytic properties of Pt-promoted sulfated zirconia. This family of catalyst is important because of its high activity in low-temperature alkane isomerization (2). It has been suggested that platinum prevents rapid deactivation by supplying hydrogen to acidic sites where the isomerization reaction proper takes place (3). In general, Duchet *et al.* (1) agree with this suggestion. They reported maximum rates of isomerization as a function of hydrogen pressure. However, their paper gives the impression that such maximum curves are a novel phenomenon that was described first by this group of authors. Our comment is intended to correct this impression and to put the results into a broader, more general context.

Maximum rates of various alkane reactions (independent of whether they produce or consume hydrogen or are neutral) were reported as early as the 1960s (4). This and several subsequent observations were summarized by Paal and Menon (5, 6). Metal-catalyzed isomerization, $C_5$-cyclization, and aromatization of alkanes served as the main examples. The underlying idea was that, in the hydrogen-poor region, more hydrogen prevented excessive surface dissociation, leading to deactivation of the surface deposits, whereas at high $p(H_2)$, the "useful" dissociation (for example, to give $C_5$-cyclic or aromatic products, which require the loss of hydrogen atoms from the parent alkane) would be suppressed. Bond and Slaa (7) interpreted this in terms of the reactive intermediates competing for hydrogen in the positive hydrogen order range. Hydrogen thus has a promoting effect. In the negative hydrogen order range, the reacting molecules have to compete with hydrogen for the empty surface sites (and the overall process is, thus, impeded by hydrogen). Bond *et al.* derived a Langmuir–Hinshelwood-type equation for butane hydrogenolysis on metals such as Ru (8). This was a very close approximation of the experimental finding of curves with a maximum. The kinetic analysis by Bond and co-workers (7, 8) gave a quantitative description of all kinetic phenomena, of Arrhenius parameters, and of the likely coverage under various conditions.

The above phenomena are not only valid for reactions catalyzed by metallic sites alone. Maximum-type curves were first reported for butane isomerization over sulfated zirconia (9). Later studies (10, 11) pointed out that *n*-hexane reactions (isomerization with up to nearly 100% selectivity) showed, as a rule, maximum rates as a function of hydrogen pressure between 543 and 603 K. These results were interpreted in light of the work conducted by Iglesia *et al.* (3): hydrogen dissociation on Pt and migration of the hydrogen atoms to the isomerizing Lewis sites, although the temperatures in Refs. (10, 11) were higher than those reported by Duchet *et al.* (1). The position of the maxima shifted toward lower hydrogen pressure upon "reversible" deactivation (11), indicating that the Pt sites, which supply active hydrogen atoms, were poisoned first. Thus, there was insufficient hydrogen available on the Lewis sites to compete with carbenium species, and the negative hydrogen order branch was less steep than that observed with metal catalysts (5). The metal loading in Refs. (10, 11) was higher (3% Pt) than that reported by Duchet *et al.* (1); this enabled us to detect slight metallic activity. These metallic properties were monitored by the fragmentation pattern; smaller fragments disappeared first during reversible deactivation, confirming the above suggestion that Pt sites are poisoned first (11).

The shape of the maximum curves calculated on the basis of the Langmuir–Hinshelwood approximation has a rather steep section, increasing from $p(H_2) = 0$ to the highest rate followed by a longer, less steep decrease that approaches zero activity at moderate pressure. However, Fig. 6 in Ref. (1) showed that this equation, proposed first by Bond *et al.* (7, 8), did not show a good fit with the experimental results, especially in the negative hydrogen order branch, which exhibited a much shallower slope, approximating zero rate only at very high hydrogen pressure. These shapes were similar for very different $H_2$ pressures for a few hundred mbar (10, 11) as well as for values up to 50 bar (Figs. 3 and 9 in Ref. (1)). The qualitative explanation (Ref. (1)) that the positive hydrogen order branch indicates that higher hydrogen pressure accelerates the first step on Pt sites, while the negative hydrogen order branch "is simply due to a competition between protons and carbenium species on the Lewis base sites" (Ref. (1), p. 333), is correct and corroborates earlier results for *n*-hexane isomerization on Pt/sulfated zirconia (9, 10, 11), but it is not new.

Active surface Pt–acid entities (10) are created during the first calcination of Pt/sulfated zirconia. The way in which the catalyst is prepared will decide the optimum Pt loading. Keogh *et al.* (12) used Pt loadings between 0.03 and 5% and reported the highest activity for hexadecane conversion between 0.5 and 1% Pt loading. Duchet *et al.* compared catalysts containing 0.025 to 0.5% Pt (Ref. (1), Fig. 8). Less Pt resulted in shallower slopes at hydrogen pressure higher than the maximum. Apparently the competition between protons and carbenium ions becomes less important in the negative hydrogen order range with decreasing Pt, i.e., when the rate of supply of the primary dissociated H entities for the acidic sites is the limiting factor. The quantification of the hydrogen effect obviously requires further study. Apparently, the rate-determining character of the steps catalyzed by Pt may be more important than what was assumed. Final deactivation was accompanied by the disappearance of surface platinum (13).

In conclusion, apart from the otherwise valuable results of Duchet *et al.* (1), the observation of maximum curves as a function of $p(H_2)$ is not new; it is a common phenomenon in alkane catalysis and was also observed with Pt/sulfated zirconia. Furthermore, the equation used by Duchet *et al.* to describe this maximum has already been proposed elsewhere, although it does not fully describe the maximum curves.

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Zoltán Paál

*Hungary Academy of Science*
*Institute of Isotope and Surface Chemistry*
*Chemical Research Center*
*P.O. Box 77*
*Budapest H-1525, Hungary*

Received June 28, 2001; accepted June 29, 2001