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Disproportionation of Ethylbenzene: Reply to Guisnet

Guisnet (*1*) has commented on our paper "Disproportionation of Ethylbenzene: A Potential Test Reaction for Acidity of Bifunctional Zeolite Catalysts" (*2*). In our paper we reported a significant decrease in activity of (reduced) Pt/LaNaX catalysts toward ethylbenzene disproportionation when H_2 was admitted to the feed stream. Guisnet proposes as a possible explanation the decrease in concentration of intermediate carbenium ions, viz. $C_6H_5C^+HCH_3$, due to (*i*) *reaction with* H_2 (resulting in ethylbenzene and H^+) or (*ii*) *reaction with the product ethylcyclohexane* (resulting in ethylbenzene and the tertiary ethylcyclohexyl cation). Support for these explanations is inferred from earlier work by Minachev *et al.* (*3*) and Gnep *et al.* (*4, 5*).

First of all, it is important to note that the earlier studies (*3–5*) dealt with reactions of toluene or xylene where quite different mechanisms most probably apply as compared with the case of ethylbenzene disproportionation (*6, 7*). The main point is that methylaromatics are lacking the secondary carbon atom in the alkyl group.

Moreover, explanation (i) should also hold for disproportionation of ethylbenzene over an acidic catalyst not loaded with noble metal, since this case would require intermediate $C_6H_5C^+HCH_3$ carbenium ions as well. In contrast, we have shown that admission of hydrogen to the feed stream has no effect on the disproportionation activity in the case of Pt-free LaNaX or unreduced Pt/LaNaX catalysts (see Fig. 1, Table 1, and text of Ref. (*2*)).

Finally, in more recent experiments we have employed the same (reduced) 0.2 Pt/LaNaX catalyst for a very much different test reaction, viz. the dehydration of cyclohexanol (*8*). This reaction is also catalyzed by the acidic OH groups of the zeolite (*9*). Again, upon admission of hydrogen the activity decreases significantly. This finding provides further support for the assumption advanced in our paper (*2*) that admission of H_2 decreases the strength of the Brønsted acid sites of the catalysts. However, we wish to stress that we still consider this assumption as a hypothesis (cf. Ref. (*2*)). Confirmation of this hypothesis, which is related to earlier work by Chick *et al.* (*10*), requires further experimental evidence.

Guisnet's second suggestion (ii) is indeed an interesting approach. However, the inhibiting effect of admitted hydrocarbons with a tertiary carbon atom on the conversion rate of alkylaromatics is small, even if they are admitted in a concentration of 2% (*5*). In our experiments, the concentration of ethylcyclohexane formed from ethylbenzene was of the order of 0.1% (Fig. 1 in Ref. (*2*)). As expected, we have found in additional experiments that the admission of ethylcyclohexane does not affect the rate of ethylbenzene conversion over 0.2 Pt/LaNaX, at least up to the concentrations of cyclohexane that are typical of the experiments described in Ref. (*2*).

Likewise, in view of the abovementioned influence of *hydrogen* admission on the rate of cyclohexanol dehydration over Pt/LaNaX, Guisnet's suggestion (ii) cannot apply: upon hydrogen admission to the cyclohexanol feed the product, viz. cyclohexene, is partly hydrogenated to cyclohexane. The latter does not contain a tertiary carbon atom and hence no inhibiting effect related to (ii) should occur. Nevertheless, we did observe the decrease in activity (*vide supra*).

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In conclusion, Guisnet offers interesting alternative explanations for our results. However, we believe that a more detailed discussion of these alternatives reveals that they are inconsistent with several important findings, as shown in this reply.

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