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Reply to "Determination of Active Sites on Pd by CS_2 Titration"

The remarks of G. V. Smith and colleagues (preceding letter) about our dynamic study (*1*) of heterogeneous catalyst poisoning are useful additions. The identification of edge sites as active for hydrogen dissociation is compatible with our experiments showing an initial rapid decrease, followed by a slower decay, in hydrogenation activity. In his review of structure effects in heterogeneous catalysis, Boudart (*2*) has likewise observed the importance of edge and corner sites in catalytic hydrogenation. In our two other investigations of Pd/Al_2O_3 hydrogenation of α-methyl styrene (*3, 4*), we have provided further information on structure sensitivity and site activity that is compatible with this interpretation.

It should be noted that the dynamic technique employed in our work permits separation of the rate constants, k_a and k_r (per mass of catalyst), for the adsorption and surface reaction steps in the overall hydrogenation. In terms of the adsorption equilibrium coefficient K, the values of the ratio Kk_r/k_a, shown in Table 4 of our paper (*1*), indicate that the adsorption rate has a significant influence on the overall rate. On the other hand, steady-state experiments allow only the overall rate constant, $k_0 = 1/(1/k_a + 1/Kk_r)$, to be measured.

In (*3*) we considered the effect of catalyst reduction temperature on individual values of adsorption equilibrium, adsorption rate, and surface reaction rate coefficients. Increased reduction temperature caused a decrease in dispersion, but not an apparent decrease in site activity. This is an indication of structure insensitivity.

In (*4*) we examined adsorption on both poisoned and unpoisoned (reactive) sites. Equilibrium adsorption was the same on either poisoned or unpoisoned sites, corresponding to the concept (*2*) that hydrogen adsorbs on sites already occupied by olefin. The value of the surface rate constant, k_r, was independent of the number of poisoned sites. The adsorption rate constant, k_a, on the contrary, decreased with the amount of poison, in the same manner as the overall rate constant (*1*). That is, the adsorption rate decreased more sharply for initial poisoning.

The interpretation consistent with our findings is that the adsorption rate, not the adsorption equilibrium nor the surface reaction rate, declines with increased elimination of sites by poisoning.

It is interesting to consider why there are two linear regions for this decline. It is indeed likely that the large amount of catalyst used in our investigations allows a more sensitive determination of the activity of sites that are more difficult to poison. Butt (*5*), in a review of catalyst poisoning and deactivation, provided explanations for selective poisoning, for which increments of poison give a diminishing rate of change of activity. Explanations for this behavior include (a) nonuniform distribution of site strengths, (b) interactions between poison molecules on the catalyst surface, and (c) multiple site coverage by initial poison molecules with corresponding steric hindrance for larger amounts of poison. The data of (*1*) seem to be evidence of the existence of a distribution with two kinds of sites (hence, two straight lines for activity as a function of poisoning). But due to experimental uncertainties, we cannot rule out the possibility that a wider distribution of site activities is a more appropriate representation.

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B. J. McCoy
J. M. Smith

Department of Chemical Engineering
University of California
Davis, California 95616

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