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LETTERS TO THE EDITORS

Determination of Active Sites on Pd by CS_2 Titration

Using an elegant dynamic response technique, Chen *et al.* (*1*) examined the CS_2 poisoning of styrene hydrogenation over three Pd/Al_2O_3 catalysts with different loadings (0.05, 0.150, and 0.450%) but relatively similar low percentage exposed Pd atoms (11.4, 10.2, and 7.2% D, respectively). Their technique revealed two linear decreases in activity when CS_2 is added. The first, rapid, decrease reduces the original activity by 99.5% (0.05% Pd), 96.6% (0.15), and 91.3% (0.45%). The second, slow, decrease further reduces the activity to zero. The authors use the amount of CS_2 required to accomplish zero activity as the number of active Pd atoms. As a result, they find essentially the same fraction of exposed atoms (34.4 ± 2.8) to be active for each catalyst, and, therefore, different turnover frequencies per active site for each catalyst (0.26, 0.17, and 0.14, respectively).

On the other hand, if the authors were to use the endpoints for the first rapid decrease as the number of active sites they would find smaller fractions of exposed sites to be active and more constant turnover frequencies per active site for each catalyst (see Table 1). Such findings would be more in accord with recent single crystal results (*2*) and also in agreement with similar results from our laboratories.

Recently we have also been using CS_2 poisoning of hydrogenation reactions ((+)-apopinene, cyclohexene, 1-hexene, and 1-heptene) over several different Pd/SiO_2 catalysts to determine the fraction of exposed atoms which are active for addition and double-bond migration. Descriptions of our basic techniques and early results (not CS_2 poisoned) have appeared in this journal (*3, 4*). Since our CS_2 poisoning results are in substantial agreement with those of Chen *et al.* but add new dimensions not available to them (isomerization and steric factors), and our interpretation is different, we believe it is useful to call attention to these facts for comparison.

We have used mainly (+)-apopinene (6,6-dimethyl-1*R*-5*R*-bicyclo-[3.1.1]-heptene-2) as a surface probe molecule and determined the ratio of isomerization (double-bond migration) to addition, k_i/k_a, during hydrogenation for Pd/SiO_2 and Pt/SiO_2 catalysts over wide ranges of dispersion (*3, 4*). On both catalyst systems the ratio k_i/k_a and turnover frequency for addition go through maxima as a function of dispersion (*5, 6*). These maxima correspond approximately to the maxima in edge sites on octahedra as a function of dispersion.

When CS_2 is used to titrate the active sites on the Pd/SiO_2 catalysts, we also find an initial rapid decrease in addition but no second slow decrease as found by Chen *et al.* We believe our failure to observe the second slow decrease results from our use of very small amounts of catalyst (5 to 20 mg) compared to those of Chen *et al.*: 4750 to 20,000 times as much (95 to 100 g). Nevertheless, our CS_2 titrations agree with their titrations for the initial rapid decrease. For example, extrapolating our results to their lower values of dispersion, we would expect approximately 10% active sites for the initial rapid decrease portion (compare to Table 1). And, since the numbers of active sites found in our titrations go through the same maximum as edge sites as a function of dispersion, we believe CS_2 poisons edge sites.

Furthermore, we find no change in the ratio of k_i/k_a during CS_2 titration, so we con-

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TABLE 1

Number of Active Sites and Rate Parameters

Pd Content (wt%)	0.05	0.15	0.45
Dispersion (%)	11.4	10.2	7.2
CS_2/exposed Pd (%)	36.0	36.9	30.0
More act. CS_2/exp. Pd (%)	19.4	7.7	8.1
$N_i' \times 10^{-20}$ (active site/g Pd)	2.32	2.13	1.23
$N_i' \times 10^{-20}$ (more active site/g Pd)	1.25	0.45	0.33
$k_0^* \times 10^{+17}$ (cm^3/(active site)(s))	0.26	0.17	0.14
$k_0^* \times 10^{+17}$ (cm^3/(more active site)(s))	0.48	0.82	0.46

clude that both addition and isomerization are results of chemical events occurring on edge sites and each CS_2 molecule destroys an equivalent percentage of both isomerization and addition activity.

Adoption of the ideas that isomerization and hydrogen dissociation occur principally on edge sites and that addition occurs on plane sites through the interaction of chemisorbed alkene and hydrogen atoms which have migrated there following dissociation on edge sites (*7*) offers an explanation for both our results and those of Chen *et al.*

The initial rapid poisoning destroys both hydrogen dissociation sites and alkene isomerization sites. Addition activity decreases on the planes because the vast majority of hydrogen atoms originate from the edges which, for Pt (*2*), are seven times more active for hydrogen dissociation than the plane sites. After the edges are poisoned, hydrogen dissociation and addition occur on the planes. Hydrogen dissociation is much slower and therefore the rate of addition is much slower.

Concomitantly, the initial rapid poisoning destroys the most active isomerization sites. We presume that these sites include at least one edge site, that is, the same number as that required for hydrogen dissociation, and that they must be arranged in some special order together with other sites, perhaps adjacent plane sites. The latter is in agreement with our previous observation that Pd–Si metallic glasses do not yield as large a ratio of k_i/k_a as Pd/SiO_2 do (*8*). The glasses dissociate hydrogen well enough to accomplish addition but do not isomerize apopinene well. Since the glasses have no long-range order, it follows that at least one kind of isomerization mechanism requires an ordered cluster of atoms but hydrogen dissociation does not (*9*).

As for the particular intermediates involved, we suggest the π-allyl Anderson type mechanism (*10*) for isomerization on the edge-associated sites and the classical Horiuti–Polányi half-hydrogenated state mechanism for addition and isomerization on the planes.

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plane atoms as now suggested by our data. For the earliest proposal of adsorbed π-allyl species see Rooney, J. J., Gault, F. G., and Kemball, C., *Proc. Chem. Soc.*, 407 (1960) and Gault, F. G., Rooney, J. J., and Kemball, C., *J. Catal.* **1,** 255 (1962).

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