Determination of Specific Site Turnover Numbers for Cyclohexene Hydrogenation

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Single turnover analyses have shown that there are three different types of alkene saturation sites present on dispersed Pt catalysts, which have turnover numbers (TON) of 2.1, 18.2, and 5.2 in the solution phase hydrogenation of cyclohexene.

The rate of heterogeneously catalysed reactions is usually expressed in terms of the mass or surface area of the catalyst even though the turnover number has been defined as the number of molecules of product formed per catalytically active site per unit time under a given set of reaction conditions.[1] The difficulty with this definition, though, is that there is no apparent relationship between either the mass or surface area of the catalyst and the number of active sites present. Further, it is probable that there are different types of sites present, each promoting the reaction at a different rate so the observed rate is really only a composite of these specific site rates.[1]

We have previously shown that, at least for dispersed Pt catalysts, our single turnover (STO) reaction sequence provides data from which the densities of a number of different types of sites present on the metal surface can be determined.[2] For an alkene hydrogenation reaction there are two direct hydrogenation sites, one on which H_2 is strongly adsorbed and one on which it is more weakly, reversibly, adsorbed. There are also two-step alkene hydrogenation sites on which stable half-hydrogenated or metal–alkyl species are initially formed and then converted into alkane by adsorption of a second H_2 molecule. In addition to these saturation sites there are also isomerization sites and those which adsorb H_2 but do not take part in the alkene hydrogenation reaction. Following the reaction descriptions outlined by Siegel[3] we have termed those direct hydrogenation sites having strongly adsorbed H_2 as ^3M_I, those with reversibly adsorbed H_2 as ^3M_R, and the two-step saturation sites as ^2M_S. The isomerization sites are named ^2M_C and the unreactive surface sites as ^1M.[2]

Since there are three distinct hydrogenation sites present,[2] the overall rate of an alkene hydrogenation can be represented as in equation (1) where A, B, and C are the turnover numbers for each of these specific type of sites and the square brackets represent the site density.

$$\text{Rate} = A \times [^3M_I] + B \times [^3M_R] + C \times [^2M_S] \qquad (1)$$

We have also shown that the specific site densities on supported Pt catalysts vary with changing Pt load and reduction temperature,[4] so we have available a number of STO characterized Pt catalysts having a wide range of site densities.

Seven of these characterized Pt/CPG (Controlled Pore Glass) catalysts were used in the hydrogenation of cyclohexene in heptane solution at 10 °C. The site densities of these catalysts (mol/mol Pt), which are reproducible to within ±5%, are listed in Table 1. The hydrogenations were run in a jacketed reactor attached to a sloping manifold, atmospheric pressure hydrogenator,[5a] and agitated by vigorous shaking. The H_2 used was purified as described in ref. 6. The heptane was shaken under 3 atm of H_2 and Pd/C for 2—3 h and distilled from sodium immediately before use. The cyclohexene was purified by distillation and passed through a column of activated alumina immediately before use. The catalyst, 10 mg in 10 ml of heptane, was presaturated with H_2 for 15 min and then 0.5 ml (5 mmol) of cyclohexene was introduced into the reactor through a septum. Agitation was restarted and the rate of absorption of the first 10—12 ml (0.5 mmol) of H_2 was measured as described in ref. 5b. The temperature in the reactor was maintained at 10 ± 0.1 °C by a circulating refrigerated bath connected to the reactor jacket. The rate values (mol alkane/mol Pt/s) listed in Table 1 are the averages of several runs and were reproducible to within ±5%. To ascertain whether the reaction might have been diffusion controlled under the agitation conditions employed, catalyst 1 was used to hydrogenate cyclohexene at 30 °C. A rate of 0.359 mol alkane/mol Pt/s was obtained. The apparent activation energy for the reaction was, therefore, about 8 kcal/mol (cal = 4.184 J), near that expected for non-diffusion controlled hydrogenations.[7]

In order to determine the turnover numbers for the specific hydrogenation sites present, the site densities and experimental rate values shown in Table 1 were substituted into equation (1) and the resulting series of equations were solved using a multiple linear regression analysis. Values for A, B, and C of 2.1, 18.2, and 5.2 mol alkane/mol site/s respectively, were obtained. Rates calculated using equation (1) with these site turnover numbers are also listed in Table 1. The calculated

Table 1. Site densities and rate data for the hydrogenation of cyclohexene over Pt–CPG catalysts.

			Site densities[a]					
Catalyst	% Pt	Redn. temp./K	^3M_I	^3M_R	^2M_S	Exptl. rate[b]	Calc. rate	% Diff.[c]
1	6.2	400	0.027	0.002	0.008	0.141	0.135	+4.3
2	5.1	400	0.035	0.009	0.014	0.312	0.310	+0.6
3	5.1	300	0.083	0.001	0.026	0.359	0.328	+8.6
4	5.1	250	0.085	0.008	0.033	0.506	0.496	+2.0
5	4.5	300	0.082	0.015	0.022	0.549	0.560	−2.0
6	4.9	200	0.167	0.002	0.061	0.670	0.704	−5.1
7	4.3	200	0.203	0.002	0.082	0.891	0.889	+0.2

[a] moles site/mole Pt. [b] moles alkane/mole Pt/s. [c] [(exptl. − calc.)/exptl.] × 100.

and experimental values are all very close, certainly within the experimental errors associated with the site density and rate determinations. A plot of the experimental *vs.* the calculated rates has a slope of 1.03 (least squares), within experimental error of the desired value of 1.

The numerical values of these specific site turnover numbers are of interest in themselves. It is not surprising that those sites on which the H_2 is more loosely adsorbed (^3M_R) would be more active than the others. The observation that the two-step hydrogenation sites (^2M_S) are more active than the direct saturation sites (^3M_I) might not have been expected but this difference could also be due to the strong adsorption of H_2 on the ^3M_I sites slowing down the reaction at those sites.

We have presented here only our initial work in this area to show that once the densities of the various types of sites present on a catalyst surface were determined, the turnover numbers associated with each of these types of sites could also be measured. Further work in this area is currently underway.

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