

## CARBON DISULFIDE TITRATION OF ACTIVE SITES ON PLATINUM CATALYSTS

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### INTRODUCTION

The problem of determining the number of active centers on a catalytic surface is important in experimental catalytic investigations. The method of using an indicator reaction to monitor the poisoning of active sites was developed for determination of number of active centers. Several different kinds of poisons were used as titrants, and a number of test reactions as indicators. CS<sub>2</sub> was found to be the best titrant, and ethylene hydrogenation the best test reaction for Pt [1, 2]. We developed earlier (+)-apopinene as a molecular probe to characterize the catalyst surface [3]. The hydrogenation and isomerization of (+)-apopinene were sensitive to the different preparations of a series of Pt and Pd catalysts. In the present study we examined the effects of the poison CS<sub>2</sub> on the rates of hydrogenation and isomerization of (+)-apopinene on a series of Pt catalysts.

### EXPERIMENTAL

The method of measuring the hydrogenation and isomerization of (+)-apopinene was described previously [3]. Some of the Pt catalysts were donated by Burwell and Butt; detailed descriptions of these can be found in [4]. The other Pt catalysts were prepared in our laboratory using the AcAc method. The preparation and characterization of these catalysts was the same as described earlier [3]. A description of the catalysts can be found in Table 1.

In the poisoning experiments we used 20 mg of catalyst and 0.1% at 0.01% CS<sub>2</sub> in n-pentane solution. Two different procedures were used to determine the number of active sites and the

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Table 1. Preparation and characterization data on catalysts

catalyst	Pt(wt%)	D%	prep.meth.	Ref.
Pt/SiO <sub>2</sub>	0.48	62.1	ion exch.	4
Pt/SiO <sub>2</sub>	0.82	80.9	ion exch.	4
Pt/SiO <sub>2</sub>	1.17	40.7	impregnation	4
Pt/SiO <sub>2</sub>	1.48	21.5	ion exch.	4
Pt/SiO <sub>2</sub>	0.13	100.0	AcAc	5
Pt/Al <sub>2</sub> O <sub>3</sub>	0.15	100.0	AcAc	5
Pt/SiO <sub>2</sub>	1.48	27.0	ion exch.	4

change in the ratio  $k_i/k_a$  as a function of the amount of CS<sub>2</sub>. To determine the number of active sites, 200  $\mu$ l (+)-apopinene was injected onto the catalyst, which had been reduced at room temperature overnight, the initial rate of addition was measured and the reaction was then stopped. A definite amount of poisoning solution was added to the reaction mixture, a waiting period of 30 sec for the adsorption was observed ~~the~~ reaction was started again, and the rate of addition was measured. This procedure was repeated until <sup>no</sup> further addition reaction occurred. To determine the change in the ratio  $k_i/k_a$  as a function of the amount of CS<sub>2</sub>, the surface was poisoned in advance with definite amount of CS<sub>2</sub> in 200  $\mu$ l n-pentane. The reaction was then run using 500  $\mu$ l (+)-apopinene and the rates of addition and isomerization were measured. The ratio  $k_i/k_a$  was calculated as described earlier. [3].

#### RESULTS AND DISCUSSION

Barbier et al [6] studied the poisoning effects of different sulfur compounds on supported Pt catalysts. They observed selective poisoning due to the site-selective adsorption of the poison. They also found that sulfur compounds (thiophene, H<sub>2</sub>S and SO<sub>2</sub>) were non-selective poisons, while atomic sulfur was a selective poison [6, 7]. When CS<sub>2</sub> was used as a titrant, with ethylene hydrogenation as an indicator, it was found that the active sites comprised only a fraction of the total surface atoms [2]. As a result the turn-over frequencies (TOF) calculat-

ed on the basis of the number of active sites were more consistent than those calculated <sup>on</sup> the basis of the total number of atoms.

In our experiments, the initial rate of addition decreased in proportion to the amount of surface poisoned (see Fig. 1), Figure 1. Change in initial rate of addition vs. amount of CS<sub>2</sub>.

The "titration curve" for the Pt catalysts was a straight line in all cases. The intercept at zero rate gives the number of CS<sub>2</sub> molecules necessary to destroy the hydrogenation activity of the catalyst. The calculated number of active sites (1:1 stoichiometry) differed in every case. The number of active sites determined by CS<sub>2</sub> titration was a fraction of that determined by H<sub>2</sub> chemisorption.

Turkevich et al [2] examined the Pt catalyst donated by Burwell and Butt. They used a pulse microreactor, CS<sub>2</sub> as titrant, and ethylene hydrogenation as test reaction. In each case for they found a higher number of active sites for the same catalysts. The reason for this in our opinion is that in their system all of the CS<sub>2</sub> could not adsorb on the surface, due to the short contact time used. For comparison, Table 2 shows the two results on the same catalyst.

Table 2. Numbers of active sites on several Pt/SiO<sub>2</sub> catalysts, determined in the gas and liquid phases.

catalyst	D%	% of active sites in gas phase	% active sites in liquid phase
0.43% Pt/SiO <sub>2</sub>	62.1	58.3	34.0
1.17% Pt/SiO <sub>2</sub>	40.7	50.0	20.0
1.43% Pt/SiO <sub>2</sub>	21.5	37.0	9.0

Our earlier results on these Pt catalysts suggest that the isomerization of (+)-apopinene takes place on the edge sites and that the vertices are responsible for the addition.

For the same series of Pt catalysts, a plot of the number of active sites (determined by CS<sub>2</sub> titration) against the dispersion displays a maximum (see Fig. 2.)

Figure 2. Number of active sites vs. dispersion for Pt catalysts.

In the dispersion range 0-60% the number of active sites decreases gradually with decreasing D%. Moreover, when D=0% (where the % of vertices and edge sites = 0) the number of active sites is approximately 0. Thus, it is very likely that CS<sub>2</sub> adsorbs on the vertices and edge sites. As the calculated number of vertex and edge sites is approximately twice (assuming a fcc-octahedral crystal structure) the number of active sites, it is very likely that the stoichiometry on the surface is 1:2.

We also measured the change in the ratio  $k_1/k_a$  (the ratio of the isomerization to the addition) of (+)-apopinene as a function of the amount of CS<sub>2</sub>.

The selectivity did not change as the surface became more and more poisoned. It follows that CS<sub>2</sub> affects both reactions in the same way. In other words, in this case CS<sub>2</sub> is a "site-selective poison" [3] and adsorbs in the same way on the vertex and edge sites.

Using the CS<sub>2</sub> poisoning titration method to determine the number of active sites on Pt catalysts [1,2], Turkevich et al. found that these numbers are fractions of those determined by H<sub>2</sub> chemisorption. To explain this, they assumed that there are "atomically" dispersed Pt particles on the surface, due to decomposition of the platinum particles into an "atomic" form. These particles have lost their ability either to chemisorb H<sub>2</sub> or catalyse the hydrogenation of ethylene. They also suggested the existence of a number of platinum diads, which are able to chemisorb H<sub>2</sub>, but not to chemisorb ethylene. This would require at least four-atom clusters of platinum atoms.

A plot of the TOF of addition vs. dispersion yields a maximum curve (see Fig. 3).

Figure 3. TOF of addition vs. dispersion for Pt catalysts.

A comparison of Figs. 3 and 2 reveals that the curves show the same trend. We earlier found [5] that the isomerization and addition of (+)-apopinene take place on the edge and vertex sites. Thus, the increase in the number of active sites with increasing dispersion up to D= 60% could be explained by the increase of the number of edge and vertex sites.

Beyond this point the number of active sites decreases, because on the highly dispersed catalysts an increase at the dispersion gradually increases the number of small clusters not capable of hydrogenating olefins [2].  $\text{CS}_2$  does not adsorb on these small clusters. From the correlation between the TOF of addition and the number of active sites, it follows that the TOF calculated on the basis of the number of active sites is more consistent than that, calculated on the basis of total number of surface atoms. Our results permit the following conclusions:

1. The  $\text{CS}_2$  titration method is suitable for determination of the number of active sites in the hydrogenation of (+)- $\alpha$ -pinene.

2. On a series of Pt catalysts the number of active sites exhibits a maximum as a function of D%. The rising part of this curve can be characterized by an increasing number of active sites. The descending part corresponds to an increase in the number of small clusters not able to catalyse hydrogenation.

3.  $\text{CS}_2$  is a "site-selective" poison, which adsorbs on the edge and vertex sites and affects isomerization and addition in the same way.

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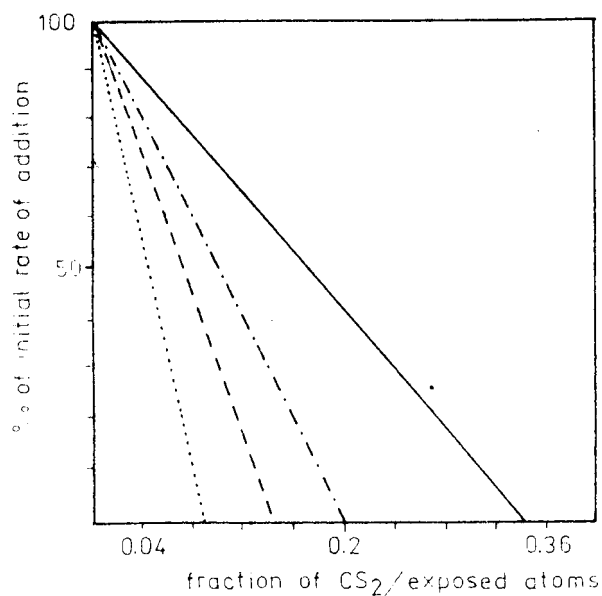


Fig. 1. Change in initial rate of addition vs. amount of CS<sub>2</sub>.

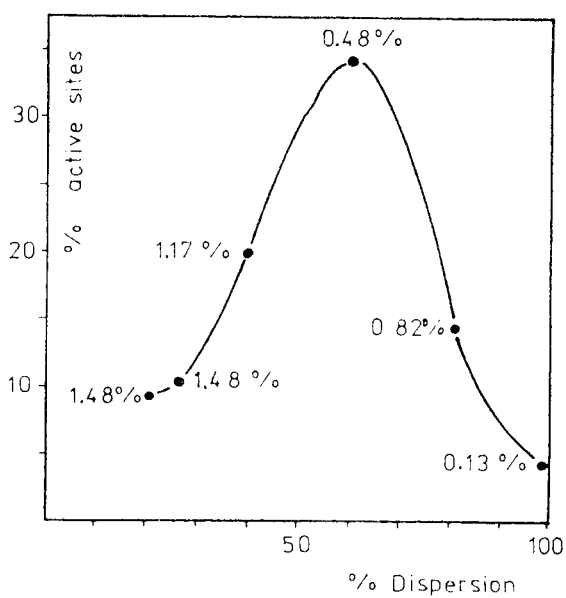


Fig. 2. Numbers of active sites vs. dispersion for Pt catalysts.

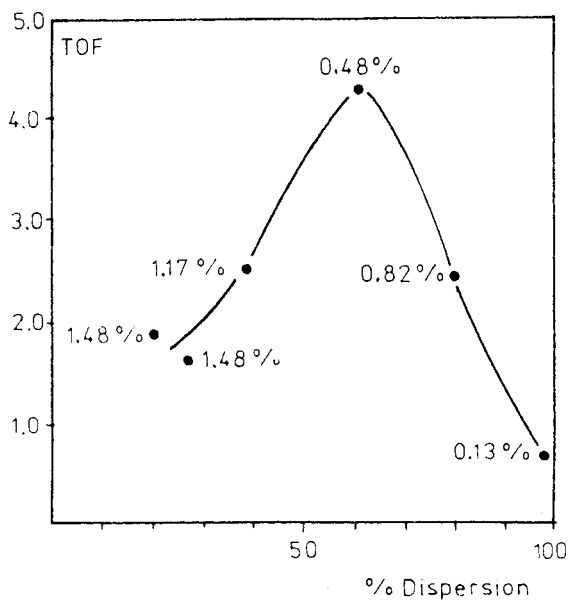


Fig. 3. TOF of addition vs. dispersion for Pt catalysts.