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Hydrogenation and Isomerization of (+)-Apopinene over Well-Characterized Pt/SiO_2 and over Pt/Al_2O_3

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Six Pt/SiO_2 and four Pt/Al_2O_3 catalysts were characterized by CO chemisorption and H_2–O_2 titration and by electron microscopy. Five of the Pt/SiO_2 catalysts originated at Northwestern University and had been similarly characterized before. Over these catalysts the hydrogenation reaction of the complex molecular probe (+)-apopinene (6,6-dimethyl-1*R*,5*R*-bicyclo[3.1.1]hept-2-ene) was used to evaluate the change in the mix of active sites as a function of percentage exposed Pt atoms (percentage dispersion, %*D*). The ratio of isomerization to addition, k_i/k_a, goes through a maximum at approximately 60% *D*, which corresponds to a maximum in edge sites (C_7 sites) on fcc octahedra. These sites are identified as Siegel type ^2M sites which catalyze essentially isomerization whereas adatoms and vertices (C_4 sites), Siegel type ^3M sites, catalyze addition and isomerization.

INTRODUCTION

In the elucidation of surface structure the use of chemical probes is enhanced by the use of surfaces which have been well characterized by several laboratories. Such well-characterized surfaces are a series of Pt/SiO_2 catalysts prepared with different dispersions (*1–7*). These catalysts have been extensively studied in several different laboratories.

Our use of these catalysts have been for the hydrogenation and isomerization of (+)-apopinene (6,6-dimethyl-1*R*,5*R*-bicyclo[3.1.1]hept-2-ene), a unique molecular probe which is extremely sensitive to different preparations of supported and unsupported palladium catalysts (*8*). In these studies on platinum we have measured the effect of dispersion on the rates of hydrogenation with deuterium and on the ratios of isomerization to hydrogenation. For comparison, we have prepared a series of Pt/Al_2O_3 catalysts of different dispersions.

Although less sensitive to changes in Pt dispersion than to changes in Pd dispersions (+)-apopinene exhibits adequate sensitivity to the method of preparation of the catalyst.

EXPERIMENTAL

Catalysts. We used two types of catalysts, Pt/SiO_2 and Pt/Al_2O_3. The 1.91, 1.48, 1.17, 0.48, and 0.83% Pt/SiO_2 catalysts originated from the laboratories of Burwell and Butt (*1–7*). They were prepared by either impregnating chloroplatinic acid or by ion exchanging $Pt(NH_3)_4Cl_2$ on Davison grade 62 wide-pore silica gel. These catalysts were reduced at a temperature of 353 K for 1 h, at temperatures rising to 391 K with a hold for 1 h, and then 478 K with a hold for 2 h. Percentage exposed Pt atoms were determined by H_2 chemisorption and H_2–O_2 titration (*1*); other details may be found in their papers (*2–7*).

The Pt/Al_2O_3 catalysts were supported on Katalco alumina (82-6931), 80–140 mesh, which had been washed five times with triple-distilled water and dried at 573 K for 22 h. The Davison grade 56 silica gel, 80–140 mesh, used in the preparation of the 0.13% Pt/SiO_2 catalyst was pretreated in the same

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manner as the Katalco alumina. Three different methods of preparation were used, and in each method the catalysts were reduced under a 10 ml/min flow of H_2 at the same temperatures and times as the Burwell and Butt catalysts.

The impregnation method was used to prepare the 1.17% Pt/Al_2O_3. In this method the alumina was stirred in a very slight excess of aqueous chloroplatinic acid solution for 24 h, and dried for 2 h under an infrared lamp. The dried catalyst was then heated for 24 h at 413 K in air, and reduced. This procedure resulted in a similar particle size distribution (1.3–6.7 nm) to that of the 1.17% Pt/SiO_2 (2.1–9.4 nm) (*1*).

The ion exchange method was used to prepare the 0.48% Pt/Al_2O_3 catalyst. The support was stirred in a 1.0 *N* NH_4OH solution for 24 h then, after adding chloroplatinic acid, stirred for another 24 h. The resulting mixture was filtered, washed repeatedly with triple-distilled water, dried at 413 K in air for 24 h, and reduced. The filtrate and all the wash solutions were kept for residual Pt analysis.

The third type of catalyst, the 0.16% Pt/Al_2O_3 and the 0.13% Pt/SiO_2, was prepared by stirring the support in a benzene solution of platinum acetyl acetonate for 48 h, after which the benzene solution was filtered off and kept for residual Pt analysis. The treated support was then dried in air at 413 K for 24 h, dried in air at 573 K for 24 more hours, and reduced. The 0.15% Pt/Al_2O_3 catalyst was also made by this method, but the support was not calcined (dried at 573 K for 22 h) prior to treatment with the platinum acetyl acetonate.

The percentages of exposed Pt atoms (%*D*) on each of the Pt/Al_2O_3 catalyst were determined by both CO chemisorption and H_2–O_2 titration. The 1.17% Pt/SiO_2 catalyst was examined in the same way, and the average percentage dispersion of two separate samples was 40.3 ± 0.9%. This is in good agreement with the value of 40.7% dispersion previously determined (*1*). Additionally, particle sizes for all catalysts were examined by electron microscopy on a Hitachi H500H transmission electron microscope. Data for all of the catalysts are shown in Table 1.

The particle sizes as calculated from dispersion values (based on chemisorption data) were generally close to the particle sizes obtained by electron microscopy. Only in three situations were there large deviations. The first situation occurred when the metal particles are very small and hard to distinguish from the support. Thus the overall average particle size was measured to be much higher than the real value due to the inability of the electron microscope to detect the smaller particles (0.83% Pt/SiO_2, 0.15 and 0.16% Pt/Al_2O_3). The second situation involved the 0.13% Pt/SiO_2 catalyst made with platinum acetyl acetonate. This catalyst has an average particle size of 22.3 nm, yet carbon monoxide chemisorption as well as H_2–O_2 titration measurements indicated that its dispersion is 100%. Because

TABLE 1

Preparation and Characterization Data for Catalysts

Catalyst	%*D* (nm)[a]	EM, nm (%*D*)[b]
Pt/SiO_2		
1.91% impreg.[c]	7.1 (22.0)	2.79 (40)
1.48% ion ex.[d]	21.5 (7.0)	4.24 (29)
1.17% impreg.	40.7 (2.8)	3.75 (32)
0.48% ion ex.	62.1 (1.5)	1.59 (60)
0.83% ion ex.	80.9 (0.9)	1.83 (55)
0.13% $Pt(AcAc)_2$[e]	100 (0.3)	22.3 (7.0)
Pt/Al_2O_3		
1.17% impreg.	29.3 (4.1)	3.49 (33)
0.48% ion ex.	35.6 (3.2)	3.08 (37)
0.15% $Pt(AcAc)_2$[f]	98.6 (0.4)	1.50 (62)
0.16% $Pt(AcAc)_2$[e]	100 (0.3)	1.21 (90)

[a] The particle size as calculated from the dispersion (obtained from chemisorption data) (*12*).

[b] The dispersion as calculated from particle size measurements taken from electron micrographs (*12*).

[c] Made by the impregnation method.

[d] Made by the ion exchange method.

[e] Made by the platinum acetyl acetonate method on a calcined support.

[f] Made by the platinum acetyl acetonate method on a support that was not calcined.

of this data we suspect that this catalyst consists of large monolayers of platinum, and would therefore not fit the calculations based on regular fcc octahedral crystallites. An alternate explanation suggested by one referee is that these large particles are clumps of Pt crystallites which look large in TEM but have high areas. The third situation involved the 1.91% Pt/SiO$_2$ catalyst for which we and others have found discrepancies between chemisorption and EM measurements. It will be discussed in greater detail later in this article.

Chemicals. (+)-Apopinene was prepared as previously described (*8*) but with an added purification step of percolating through freshly activated basic Al$_2$O$_3$ (Camag) similar to that previously described (*10*) but under Ar pressure. The gases were all high purity.

Hydrogenations. The hydrogenation and isomerization of (+)-apopinene were carried out with deuterium gas in the apparatus previously described (*9, 10*).

Analytical. Reaction mixtures were analyzed on a gas chromatograph and a polarimeter as previously described (*10*).

RESULTS

Results of the hydrogenation and isomerization of (+)-apopinene with deuterium over the various catalysts are shown in Table 2. The ratios k_i/k_a are determined from plots of ln(1-2Iso) vs ln(1-Add) shown in Fig. 1 where Iso is mole fraction of (+)-apopinene isomerized and Add is mole fraction of apopinene hydrogenated. The slope of these lines is 2 k_i/k_a P_H (*10*).

TABLE 2

Results of Hydrogenation of (+)-Apopinene over Pt/SiO$_2$ and Pt/Al$_2$O$_3$ Catalysts

Catalysts	Exp	%Add	%Or	k_i/k_a	Addn-TOF molecules/exp. Pt/sec
Pt/SiO$_2$ (1.91% D_H = 7.1)	17	5.9	97.9	0.22 ± 0.04	4.2 ± 0.4
	71	29.5	85.3		
	69	39.5	81.5		
	36	39.0	80.8		
	73	49.1	74.1		
	24	57.1	67.5		
Pt/SiO$_2$ (1.48% D_H = 21.5)	21	9.3	95.9	0.24 ± 0.01	1.8 ± 0.2
	23	26.1	85.8		
	41	26.3	83.5		
	35	37.9	80.6		
Pt/SiO$_2$ (1.17% D_{CO} = 40.7)	39	29.7	72.2	0.39 ± 0.03	2.4 + 0.2
	33	34.0	68.9		
	34	37.1	67.5		
	26	55.5	54.6		
Pt/SiO$_2$ (0.48% D_H = 62.1)	32	38.1	56.5	0.59 ± 0.01	6.0 ± 0.4
	28	53.5	41.0		
	27	56.4	37.9		
Pt/SiO$_2$ (0.83% D_H = 80.9)	417	23.6	77.9	0.51 + 0.03	2.4 ± 0.1
	416	34.0	64.5		
	531	38.0	60.7		
Pt/SiO$_2$ (0.13% D_{CO} = 100)	130	4.9	96.1	0.31 ± 0.01	0.4 ± 0.1
	131	15.5	90.0		
	132	2.1	99.7		
Pt/Al$_2$O$_3$ (1.17% D_{CO} = 29.3)	171	12.0	92.0	0.29 + 0.02	3.8 ± 0.4
	183	30.6	81.8		
	185	42.4	72.5		
	178	45.3	69.5		
Pt/Al$_2$O$_3$ (0.48% D_H = 35.6)	175	12.7	90.7	0.40 + 0.03	6.0 ± 0.9
	241	15.1	89.8		
	184	31.1	76.1		
	176	34.9	68.4		
	186	41.6	65.2		
Pt/Al$_2$O$_3$ (0.16% D_{CO} = 100)	252	34.5	72.1	0.37 ± 0.01	2.7 + 0.6
	255	46.6	63.2		
Pt/Al$_2$O$_3$ (0.15% D_{CO} = 98.6)	120	9.5	97.2	0.23 + 0.15	1.1 ± 0.1
	124	20.0	93.1		
	134	1.3	98.7		
	135	12.8	94.2		
	136	9.8	97.1		
PtO$_2$	12	16.2	89.3	0.33 ± 0.01	
	14	30.3	78.2		
	13	38.9	72.4		

Several potential experimental errors were examined. Shaking rate variations of 20% caused small variations in hydrogenation rates (7%). However, other studies in our laboratory have shown that the shaking rate of 1850 rpm used in this study results in little diffusion problems. Moreover, plots of sites densities (percentage dispersion multiplied by loading) vs k_i/k_a and vs turnover frequency per exposed Pt(TOF) reveal no correlation. In fact two catalysts with virtually identical site densities (Pt/SiO$_2$ 0.48 and 1.48) exhibit quite different values for k_i/k_a and for TOF.

In addition, an induction period occurred in all experiments even though the catalysts were pretreated in deuterium for 22 h (standard pretreatment). However, variations in the ratio of k_i/k_a do not correlate with variations in hydrogenation rates. The estimated maximum accumulated error for the ratio k_i/k_a is 5%, which is generally larger than that actually observed between experi-

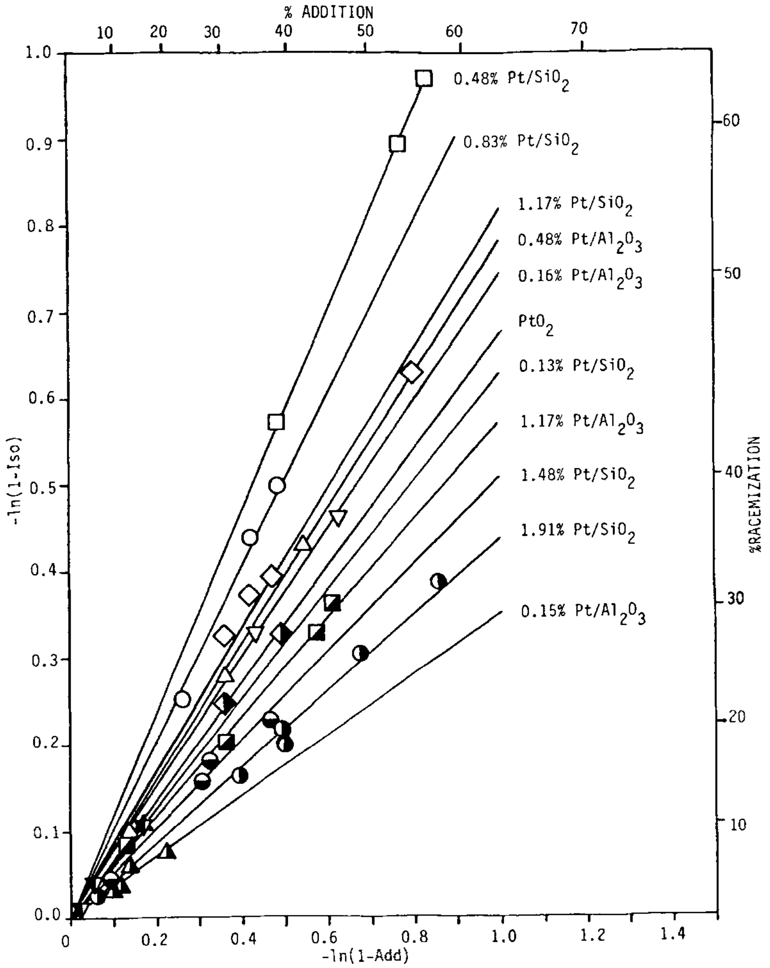

FIG. 1. Isomerization and addition data of (+)-apopinene on Pt/SiO_2 and Pt/Al_2O_3 catalysts.

ments. On the other hand, the TOF have higher experimental error.

DISCUSSION

The most striking result is the correlation between k_i/k_a and the %*D* (Fig. 2) which passes through a maximum around 60% *D*.

Only the 1.91% Pt/SiO_2 catalyst does not fit the correlation and we suggest that its dispersion is inaccurate because: (1) it does not correlate well with turnover numbers for propene (*11*), and (2) its %*D* has been questioned by others on the basis of electron microscopy (*7*). Based on its k_i/k_a value we suggest that its dispersion is about 19%, and that perhaps its actual percentage Pt is lower than 1.91%.

From the data in Fig. 2 it appears that the Pt/SiO_2 and the Pt/Al_2O_3 catalysts follow the same correlation.

When compared to similar Pd catalysts (*10*), the Pt catalysts exhibit smaller absolute values for k_i/k_a. This difference appears to be a function of the metal rather than the physical structure of the metal and may be related to the relative rates of desorption of alkenes from the two metals (*9*).

The correlation between k_i/k_a and dispersion reflects the relative abilities of the different kinds of active sites on the Pt crystallites to catalyze apopinene isomerization

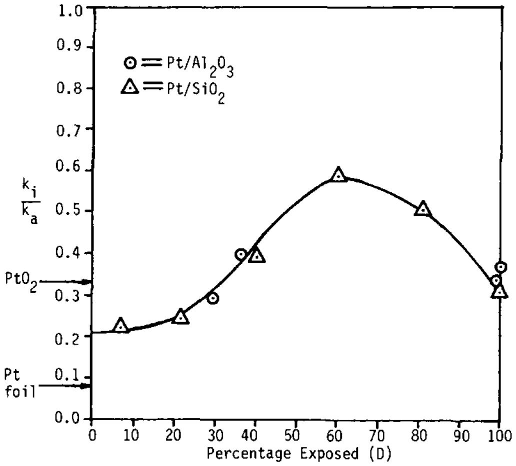

FIG. 2. Correlation between k_i/k_a and the percentage of exposed Pt atoms for (+)-apopinene on Pt/SiO$_2$ and Pt/Al$_2$O$_3$ catalysts.

and addition. Several investigators have proposed which kind of sites catalyze which reaction. Siegel has proposed specific types of sites which catalyze alkene hydrogenation (*13*). These are highly coordinatively unsaturated sites. Augustine has measured the relative amounts of the Siegel sites by a novel chemisorption–desorption procedure (*14*). Similarly, Ledoux has specified certain sites which are responsible for hydrogenation, exchange, and isomerization (*15*).

Although the exact structure of the individual active sites might be a subject for continued discussions we would like to adopt a simple model of the surface structure based on the general consensus that the more highly unsaturated sites are active for hydrogenation and isomerization. These sites are commonly referred to as vertices or adatoms or kinks (Siegel ^{3}M sites) and edges (Siegel ^{2}M sites) (*16*). The relative percentages of these sites have been calculated for a perfect fcc octahedron crystal and correlated with dispersion (*12*). Using this information we will assume that only adatoms and vertices (C_4 sites) and ledges (C_7 sites) are involved in isomerization (k_i) and addition (k_a). At low dispersion adatoms on planes and possibly kinks (C_6 sites) on plane steps catalyze both isomerization and addition whereas at high dispersion vertices do this. Edges catalyze mainly isomerization.

In Fig. 3 the relative fractions of edges and vertices (*12*) in relation to the total number of surface atoms for a fcc octahedron crystal are superimposed onto the data shown in Fig. 2. Up to 75% dispersion the ratio of C_7/C_4 increases linearly. Beyond this point the fraction of vertices increases more rapidly than edges. The ratio k_i/k_a correlates with C_7 sites for a perfect fcc octahedron.

The correlation of k_i/k_a with such a simple model of the surface may be fortuitous; however, it fits the generally accepted concepts without relying on a mechanism. Nevertheless, the mechanistic concepts also fit this model. That is, both hydrogenation and isomerization are possible on vertices (or adatoms or kinks) and essentially isomerization occurs on edges. Also, superimposed on Fig. 3 is the relative fraction of C_7 sites for a fcc octahedron max-B_5 crystal (*12*). The maximum in the k_i/k_a curve (D = 62.1%) lies between the two maxima for the relative fractions of C_7 sites on the fcc octahedra (D = approximately 84%) and on the

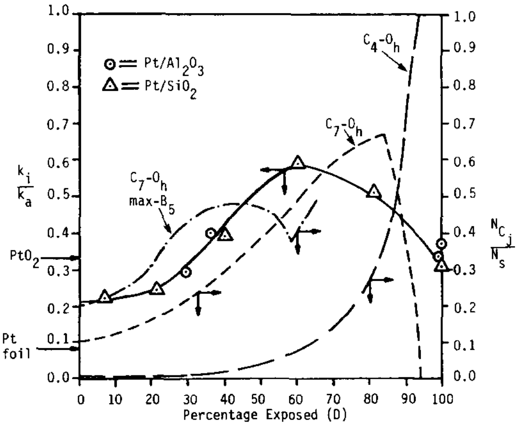

FIG. 3. Correlations of populations (N_{C_j}/N_s) for edge (C_7) and vertex (C_4) sites of fcc octahedra (O_h) and maximum B_5 (max-B_5) fcc octahedra superimposed on Fig. 2, showing that the experimental maximum in k_i/k_a falls between the maxima in C_7 sites for the perfect and max-B_5 structures.

max-B_5, fcc octahedra (D = approximately 45%). It should be expected that the structure of our supported Pt crystallites are neither perfect fcc octahedra nor max-B_5 fcc octahedra, but instead, a mixture of intermediate structures.

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