Catalysis Letters 26 (1994) 315–324

Structure sensitive hydrogen effect during Pt/SiO_2 catalyzed hydrogenolysis of methyloxirane: absence of effect with EuroPt-1

F. Notheisz [a,b], A. Zsigmond [a,b], D. Ostgard [b,a], M. Bartók [a] and G.V. Smith [b]

[a] *Department of Organic Chemistry, József Attila University, 6720 Szeged, Dóm tér 8, Hungary*
[b] *Molecular Science Program and Department of Chemistry and Biochemistry,*
Southern Illinois University, Carbondale, IL 62901, USA

Received 24 November 1993; accepted 31 March 1994

On Pt/SiO_2 catalysts, with the exception of EuroPt-1, rates of methyloxirane hydrogenolysis go through maxima at 33.3 kPa of hydrogen and the size of the maximum depends on platinum dispersion. Therefore, structure sensitivity is related not only to the clean metal surface, but also to the metal–hydrogen system. These relationships suggest that hydrogen- and/or methyloxirane-induced surface restructuring may occur and offer a method by which supported platinum catalysts may be characterized. Thus, carefully chosen chemical reactions distinguish among ambiguous and conflicting physical characterizations and are essential components in complete catalyst characterization. Additionally, optimum flexibility of 60%D particles explains the failure of EuroPt-1 to perform according to its dispersion and explains why diverse reactions exhibit rate maxima at approximately 60%D.

Keywords: structure sensitive hydrogen effect; surface restructuring; hydrogenolysis of methyloxirane; surface characterization; platinum; EuroPt-1

1. Introduction

Experimental chemists working with metal hydrogenation catalysts often encounter phenomena that may be called hydrogen effects. This term indicates that hydrogen, besides participating stoichiometrically in hydrogenation, also affects the reaction in known and unknown ways. Hydrogen effects in catalysis have been reviewed by Paál and Menon [1].

Two types of hydrogen effects are known. The first is the effect of varying hydrogen pressure. Such a variation either promotes or suppresses individual reactions and results from an optimum hydrogen coverage for each reaction [1–5]. The second is the effect of pretreating the catalyst with hydrogen, which may result in permanent changes in catalyst activity and selectivity [1]. In this work we report on the first effect: the effect of varying hydrogen pressure on the rate of hydrogenolysis of methyloxirane over a wide range of dispersions of silica-supported platinum catalysts.

2. Experimental

2.1. CATALYSTS

The silica-supported platinum catalysts shown in table 1 (except EuroPt-1 and 0.13% Pt/SiO_2 {100-SiO_2}) were from the laboratories of Burwell and Butt at Northwestern University. They were prepared on Davison silica gel either by impregnating with chloroplatinic acid or by ion exchange with $Pt(NH_3)_4Cl_2$, and their percent exposed (%D) Pt atoms were determined by hydrogen chemisorption, H_2–O_2 titration [6], and electron microscopy. We have confirmed the hydrogen chemisorption and electron microscopy results. Over the years, these catalysts have been characterized so thoroughly, using both physical and chemical methods, that they are now considered reference catalysts [7–13]. In addition to these, 100-SiO_2 was prepared in our laboratory using platinum acetyl acetonate (AcAc method) [14], and its dispersion was determined by CO chemisorption and H_2–O_2 titration. Finally, the well-known 6.3% Pt/SiO_2 reference catalyst (EuroPt-1) was prepared by Johnson Matthey by ion-exchange and has been well characterized [15–19]. X-ray diffraction shows the average size of the platinum particles as 1.7 nm and a dispersion of 65–70% [20], whereas hydrogen chemisorptions indicate dispersions of 44–91% (65% most likely) [21], and electron microscopy, 60% [17].

2.2. CONDITIONS

Rates were measured in a closed circulation reactor [22]. The partial pressure of methyloxirane (BDH, distilled before use) was 2 kPa, while the range of partial pressures of hydrogen was 1.8–54.1 kPa. Turnover frequencies (min^{-1}) were calculated from initial rates.

Before use, the Northwestern catalysts (5 mg) were pretreated in hydrogen

Table 1
Characteristic features of Pt/SiO_2 catalysts

Catalysts	Metal content (%)	Preparation method	Dispersion
7-SiO_2	1.91	impregnation	0.07
41-SiO_2	1.71	impregnation	0.41
62-SiO_2	0.48	ion exchange	0.62
EuroPt-1	6.3	ion exchange	0.65
80-SiO_2	0.825	ion exchange	0.80
100-SiO_2	0.13	AcAc	1.00

(Matheson H_2 generator) at 473 K for 30 min, and then cooled to the reaction temperature of 393 K. The EuroPt-1 catalyst (5 mg) was pretreated in hydrogen at 473 K (673 K gave identical results) for 30 min, then cooled to its reaction temperature of 423 K. This higher reaction temperature was used because EuroPt-1 exhibited lower activity than the other catalysts. The same results (structure insensitivity) were also observed over EuroPt-1 at 393 K but errors were higher due to lower yields.

For these reactions oxygen pretreatment at 300°C [23] was rejected for the Northwestern catalysts because we found little differences between oxygen pretreatment and hydrogen pretreatment. Additionally, oxygen pretreatment of EuroPt-1 gave a turnover frequency of only 3.5 min^{-1} at 20 kPa, which was slower than the 5 min^{-1} value obtained with only hydrogen pretreatment. Although oxygen pretreatment improved Pt catalytic activity for ethylene hydrogenation, presumably because it removed some unknown hydrocarbon contaminant(s) [23], it does not improve Pt activity for methyloxirane hydrogenolysis.

This lack of improvement may be due to several possible factors. First, the catalysts used in this study may not have been exposed to environments similar to those in the earlier study [23]; second, even if hydrocarbons are adsorbed on our catalysts, methyloxirane likely adsorbs so strongly that hydrocarbons preferentially desorb; and finally, oxygen pretreatment may rearrange Pt surfaces in ways favorable to ethylene hydrogenation but unfavorable for methyloxirane hydrogenolysis. Certainly, methyloxirane dissociates on Pt to produce adsorbed oxygen and hydrocarbons, and this adsorbed oxygen may have an effect similar to oxygen pretreatment. So methyloxirane adsorption may cause more changes in a Pt surface than mere oxygen pretreatment and result in the same active surface regardless of hydrogen or oxygen pretreatment. From the available data we are unable to differentiate among these several factors, or other unknown factors, and we conclude that hydrogen pretreatment alone is a reasonable pretreatment for methyloxirane hydrogenolysis studies.

3. Results

Plotting turnover frequencies against partial pressures of hydrogen (fig. 1), reveals maxima at 33.3 kPa. This plot also reveals the different effects of hydrogen pressure on the different catalysts, according to their dispersions. The largest effect occurs on 62-SiO_2, a smaller effect occurs on the other catalysts, and the smallest effect (none) occurs on 100-SiO_2. Very similar effects occur with turnover frequencies for formation of acetone and 2-propanol. Clearly, the effect of hydrogen pressure on the hydrogenolysis of methyloxirane is structure sensitive.

The extent of structure sensitivity is strongly influenced by hydrogen pressure. In fig. 2 the experimental data shown in fig. 1 are replotted as a function of dispersion. The curves represent data measured at different hydrogen pressures and

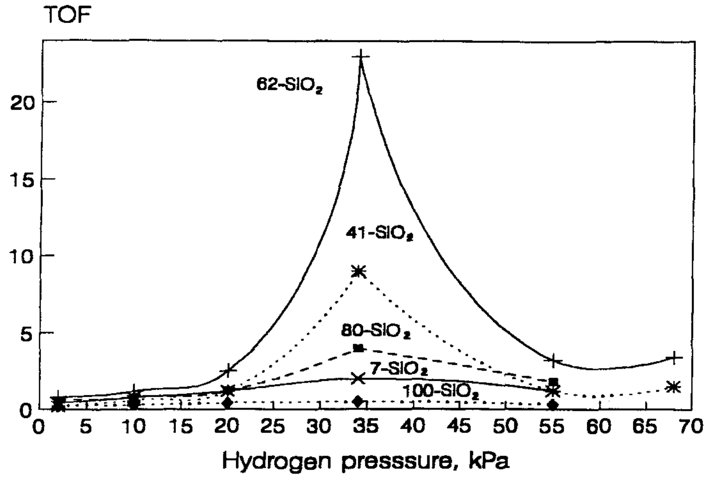

Fig. 1. Variations of methyloxirane hydrogenolysis turnover frequencies with hydrogen pressure over the different Pt/ SiO_2 catalysts at 393 K.

emphasize structure sensitivity. At low hydrogen pressures (1.8 and 9.0 kPa) structure sensitivity is slight, at 19.8 and 54.1 kPa it is moderate, and at 33.3 kPa, maximum. Therefore, structure sensitivity is related not only to the clean metal surface, but also to the metal–hydrogen system.

On the other hand, EuroPt-1 (65%D) exhibits only a slight hydrogen effect. This contrasts with 62- SiO_2, which has almost the same dispersion (62%D). Data for these two catalysts are compared in fig. 3. Clearly these results are affected not by dispersion alone but by a combination of dispersion and hydrogen effect.

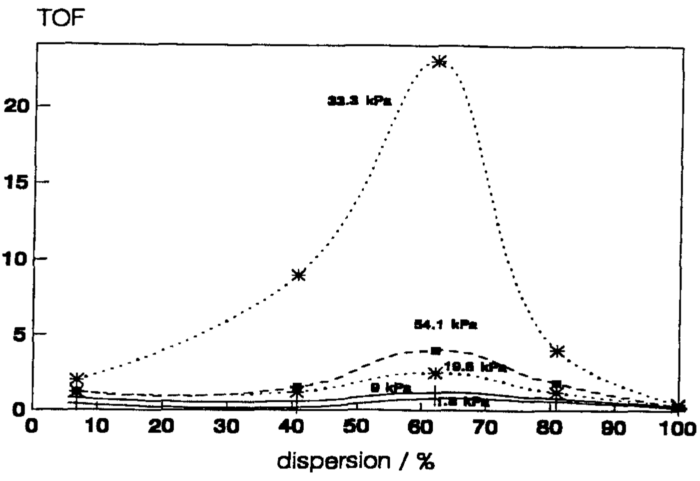

Fig. 2. Variations of methyloxirane hydrogenolysis turnover frequencies with dispersion for different pressures at 393 K.

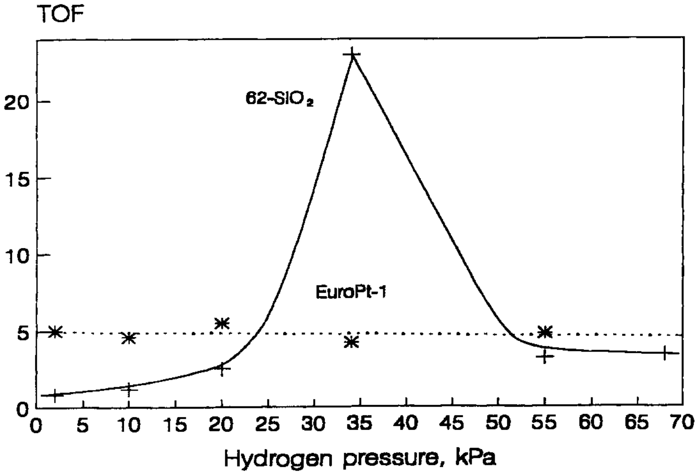

Fig. 3. Comparison of EuroPt-1 (423 K) and 62-SiO_2 (393 K) catalyzed methyloxirane hydrogenolysis turnover frequencies at different hydrogen pressures.

4. Discussion

We have frequently studied the transformations of oxacycloalkanes on transition metal catalysts [24]. Especially, we have studied the mechanisms of their hydrogenolysis and isomerization [25–27]. During these studies we assumed that two different mechanisms occur simultaneously: in the first, hydrogen is involved in the rate determining step, while in the second, it is not. In the first, hydrogenolysis and isomerization require the simultaneous adsorption of oxirane and hydrogen, while in the second, ring opening requires only adsorption of oxirane and no participation of hydrogen. The first is a structure sensitive mechanism that occurs on planes too [24,27].

This structure sensitive hydrogen effect can be used to characterize supported platinum catalysts. For example, a large hydrogen effect should indicate an abundance of edge sites, and, in contrast, a small hydrogen effect should indicate a dearth of these sites. Accordingly, the small hydrogen effect on EuroPt-1 indicates a smaller fraction of ^2M (edge) sites on that catalyst than on the 62-SiO_2 Northwestern catalyst.

Both EuroPt-1 and 62-SiO_2 have also been characterized by Augustine and coworkers by 1-butene hydrogenation under hydrogen deficient conditions [28]. Instead of finding similar site densities for both, they found site densities of 27% and 49%, respectively, for EuroPt-1 and 62-SiO_2. Moreover, they found identical site densities (27%) for EuroPt-1 and another Northwestern catalyst, 21.5-SiO_2. Despite their different dispersions, EuroPt-1 and 21.5-SiO_2 appear to have a similar surface structure which is different from that of 62-SiO_2.

Differences between EuroPt-1 and 62-SiO_2 also occur in alcohol selectivity from methyloxirane hydrogenolysis. For example, table 2 shows that alcohol selec-

Table 2
Selectivities of methyloxirane transformation (2-propanol/(acetone + 2-propanal) on EuroPt-1 (443 K) and 62-SiO_2 (393 K) catalysts, as a function of hydrogen pressure

	H_2 pressure (kPa)				
	1.8	9.0	19.8	33.3	54.1
EuroPt-1					
alcohol selectivity	0.0	0.12	0.14	0.073	0.15
62-SiO_2					
alcohol selectivity	0.38	0.48	0.51	0.55	0.65

tivity is lower on EuroPt-1 than on 62-SiO_2. We found earlier [25], that this lower alcohol selectivity is determined by hydrogen availability on the surface. Since the dissociation of hydrogen is attributed to edge structures [21,30], and since a high alcohol selectivity should indicate an abundance of edge sites, it follows that EuroPt-1 possesses fewer edge sites than 62-SiO_2. This dearth of edge structures on EuroPt-1 is likewise supported by its low hydrogenolysis selectivity of alkanes [27,30], a reaction for which step structures have been identified [31]. Therefore, one explanation of the difference between EuroPt-1 and 62-SiO_2 is a kinetic effect resulting from different concentrations of edge sites.

Another kind of kinetic effect may partly explain the maximum at 33 kPa. For example, the classic explanation would have chemisorbed methyloxirane, chemisorbed hydrogen, and free sites dominating the surface at low hydrogen pressures. As hydrogen pressure increases, the rate would increase until all surface sites are occupied by hydrogen. Further increase in hydrogen coverage would result in a decrease of methyloxirane coverage and would result in a rate decrease; however, two factors argue against this as the only explanation. First, methyloxirane adsorbs strongly on Pt surfaces; in all probability few vacant sites exist and both hydrogen and methyloxirane compete for available sites. Second, the 33.3 kPa structure sensitive rate maximum on the Northwestern catalysts and the lack thereof on EuroPt-1 are unexplained.

On the other hand, some process other than a simple kinetic effect, such as surface restructuring, may be occurring. Recent evidence shows that catalyst surfaces are not rigid but their atoms can change equilibrium positions by forming strong chemical bonds with adsorbed molecules [32]. Indeed, chemisorbed hydrogen reconstructs the surfaces of transition metals [33]. And chemisorbed carbon monoxide restructures the surfaces of platinum [34,35] and palladium [36]. In this way, adsorbed molecules elevate metal atoms above the metal crystallite surface [37] to create ridges of edges or protuberances. These *transient active sites* affect reaction rates.

According to the dynamic restructuring model [38,39], rates of surface reactions are determined by rates of dynamic surface restructurings. That is, surfaces are flexible and their flexibility influences rates of reconstruction and, therefore, influences rates of catalytic reactions. Furthermore, surfaces can be divided into groups according to their flexibility [40]. The more open the surface, the more flexible the surface atoms. Atoms in a close packed surface have the most neighbors and, consequently, are fairly rigid, while atoms in small clusters have the fewest neighbors and, therefore, are the most flexible.

However, the overall three-dimensional size of the crystallites may not be as important catalytically as the two-dimensional size of its sides. This was demonstrated by Zuburtikudis and Saltsburg [41], who found a rate maximum in the hydrogenolysis of ethane as a function of the nickel layer thickness in a layered synthetic microstructure (LSM) system. That is, the rate maximized at a certain surface width regardless of the surface length. Thus neither the surface-to-volume ratio nor the number of atoms in the catalytic entity is the only controlling source of size effects (structure sensitivity). More likely, surface reactions cause size-constrained surface reconstructions, and nonequilibrium surface structures in a certain range of sizes [42] (width, in the case of ethane hydrogenolysis) have especially high sensitivity for surface restructuring.

This type of surface restructuring should occur, of course, not only on LSMs, but also on supported crystallites. For example the height of the crystallite may be critical but not its girth. In fact, recent calculations suggest real surface structures are significantly different from those previously calculated [43]. Tunneling electron microscopy studies suggest that nonideal structures exist in supported cluster catalysts [44]. Clusters within a certain range of sizes that have nonequilibrium surface structures may be most susceptible to surface restructuring.

We suggest that atomic clusters of approximately 60% dispersion (approximately 1.7 nm) may be most suitable for restructuring into the largest fraction of active sites per exposed atom. Indeed, in this work we found that the largest hydrogen effect occurs around 60%D. And we have reported hydrogenation [45] and decarbonylation [46] activity maxima at approximately 60%D. Crystallites of approximately 60%D may be composed of a critical number of atoms which, upon chemisorption of hydrogen and/or methyloxirane (as well as other substrates), can rearrange to a maximum fraction of active sites per exposed atom.

In this 60%D region, crystallites containing 147 atoms (62%D) should be the most abundant species, assuming a cubooctahedral shape and a relatively Gaussian distribution. This particle size may be the smallest on which steps can be created. Although smaller sizes, 55 and 13 atoms, are more flexible, they are too small to accommodate steps or even edges of more than one atom. Moreover, these smaller crystallites may be so flexible that their easy restructuring causes instability of the catalyst structure [39] and decreases the turnover frequency. In contrast, larger sizes, 309 and 561 atoms, can accommodate steps but are too inflexible to restructure and create many steps, so their fractions of active sites per exposed atom (and their turnover frequencies) are low. Particles containing intermediate numbers of atoms should behave intermediate to particles containing closed shell numbers of atoms (for cubooctahedra: 13, 55, 147, 309, 561, ...). *The size of the particle is important but optimum flexibility is essential.*

Given the above reasoning, it is difficult to rationalize the marked difference between EuroPt-1 and 62-SiO_2 on the basis of surface restructuring. Why should two catalysts with the same dispersion show such different catalytic activities? Perhaps the EuroPt-1 catalyst is not as homogeneous as claimed. Certainly, chemisorption characterizations testify to that suspicion [21]. Perhaps its high loading brings into play some hitherto overlooked mechanism. Or perhaps some property of the silica support causes the difference [21]. Notwithstanding these possibilities, we suggest that the works of Gnutzman and Vogel [20] and Candy, Fouilloux, and Renouprez [47] suggest an answer.

Gnutzman and Vogel [20] found that 90% of the Pt in EuroPt-1 is in 55 atom crystallites (76%D) at 300°C and the remainder of the particles are larger, bringing the average dispersion to approximately 65%. But the larger particles at 300°C are mostly 309 atom crystallites with few 147 atom crystallites. Even at 24°C most of the crystallites are 55 and 13 atom with few 147 atom clusters. Thus, at our reaction temperature of 150°C, even though the average dispersion is 65%, the vast majority of the surface atoms are on 55 and 13 atom particles which are too flexible to maintain stable active sites as well as too small to accommodate steps. A large number of the remainder of the surface atoms are on particles of 309 or more atoms, which are too inflexible to allow much reconstruction to steps. Only a small number of surface atoms are on 147 atom clusters. Candy, Fouilloux, and Renouprez [47] found similar particle size distributions for EuroPt-1.

In contrast, no such deficiency of 147 atom clusters have been observed in 62-SiO_2. Therefore, assuming 147 atom clusters dominate 62-SiO_2 and other 60%D catalysts, these particle size distributions may explain the difference between EuroPt-1 and 62-SiO_2 in these methyloxirane hydrogenolyses as well as differences between EuroPt-1 and other catalysts in other experiments.

We believe such specialized chemical probes as methyloxirane and (+)- and (−)-apopinene [13,14,29] furnish valuable partners with physical methods for catalyst characterizations. In the present case the chemical reaction characterizes EuroPt-1 as different from other 60% dispersed Pt/SiO_2 catalysts and, combined with physical characterizations, suggests an explanation for the difference.

Acknowledgement

Financial support from OTKA (1885/91 and 4182/92), NSF INT-8403357, and US–Hungarian Joint Fund (No. 177) is gratefully acknowledged. The authors thank Z. Paál (Institute of Isotopes, Hungarian Academy of Sciences) for valuable discussions.

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