JOURNAL OF CATALYSIS **89**, 462–469 (1984)

Determination of Support and Reduction Effects for Pt/Al_2O_3 and Pt/SiO_2 by X-Ray Absorption Spectroscopy

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Received November 25, 1983; revised April 30, 1984

By use of a recently developed technique to quantitatively determine the number of unfilled *d* states in a material from measurements of the L_{II} and L_{III} X-ray absorption edge spectra, the electronic properties were examined in terms of the change in the number of unfilled *d* states of Pt/Al_2O_3 and Pt/SiO_2 as a function of reduction conditions and of the support relative to that of the bulk metal. Pt/SiO_2 is fully reduced after 473 K H_2 reduction and undergoes no further measurable changes in electronic properties with higher-temperature reduction. Pt/Al_2O_3 still exhibits a significant extent of electron deficiency after 473 K H_2 reduction; this is largely eliminated by H_2 reduction at 723 K.

INTRODUCTION

Supported metal catalysts in the form of very small crystallites (less than 3.0 nm) are a very important class of heterogeneous catalysts finding application in catalyzing hydrogenation, dehydrogenation, oxidation, isomerization, reforming, and CO hydrogenation (*1–7*). The specific catalytic activity of supported Pt, which for some reactions can vary by orders of magnitude, has been studied as a function of metal particle size (*8–11*), as a function of preparation procedures (*12*), and of support (*13, 14*) in an attempt to better understand the factors affecting catalytic behavior. Particle size, geometric, and electronic factors have been implicated, but the true cause of the effect on catalytic behavior remains unclear. Recent studies of Pt/TiO_2 and other group VB oxides have led to interesting speculation about the role of electronic interactions between the metal and the support on chemisorption (*15–17*).

Lewis (*18*) concluded that the L_{III} X-ray absorption edge characteristics of small, well-reduced Pt crystallites (14–26 Å) supported on Al_2O_3 were similar to those of large Pt crystals, that the small crystallites were metallic, and that the 6*s*, 6*p*, and 6*d* band characteristics were those of bulk platinum. Studies of calcined Pt/Al_2O_3 (*18–22*) give evidence for the presence of two platinum oxide phases for high metal loadings on Al_2O_3. One is a two-dimensional complex platinum oxide phase (either $Pt–Al_2O_3–Cl$ or $PtO_2–Al_2O_3$), which interacts strongly with the support; the other is a three-dimensional oxide phase which does not interact with the support. For low metal loadings the three-dimensional phase does not occur. This would suggest that the ease of reduction of the Pt would be variable and be dependent on its exact nature in the oxide state.

Highly dispersed Pt/SiO_2 and Pt/Al_2O_3 were studied as a function of reduction temperature by means of L_{II} and L_{III} X-ray absorption edge spectroscopy. Using a technique recently developed by Mansour *et al.* (*23*) the data were analyzed to determine quantitative changes in the *d* electron prop-

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0021-9517/84 $3.00

erties of the Pt as a function of support and reduction conditions, and to compare the supported Pt with bulk Pt. Observed differences are related to the degree of interaction between the metal and the support and to changes of the electronic band structure which may be due to very small metal particles.

EXPERIMENTAL TECHNIQUES

The Pt/Al_2O_3 and Pt/SiO_2 were prepared by the wet impregnation method (*24*). The tetrammine platinous hydroxide ($Pt(NH_3)_4(OH)_2$) was supplied by Matthey Bishop, Inc. (Lot 30877—60.31 mg of Pt per ml of solution). The Al_2O_3 was obtained from Harshaw Chemical Company (Al-0104-5-1/8) and the silica gel support by Davidson Chemical Company (Grade 59, mesh size 3–8).

Each support was prepared separately using the same procedure. The support was ground and screened to between 28 and 60 mesh. It was then washed in a 20% HNO_3 solution and set aside for one-half hour. Finally, the support was rinsed several times with deionized water, dried at 393 K for 3 h, and calcined by passing air over the support at a flow rate of 300 cm^3/min, as the temperature was slowly raised to 973 K.

A known mass of the support was put into a flask and enough deionized water was added to just submerge the support. A small volume of $Pt(NH_3)_4(OH)_2$ containing sufficient Pt to make 1 wt% Pt on the support was added to the flask over a period of one-half hour. The flask was allowed to stand in the dark for 12 days to allow uniform distribution of the Pt. The catalyst mixture was then dried at 338 K for 1 day and at 393 K for another day.

The Pt/Al_2O_3 and Pt/SiO_2 were then heated in flowing O_2 slowly to 623 K and held there for 1 h to decompose the Pt tetrammine complex and oxidize the Pt to a uniform state. H_2 chemisorption was carried out on portions of the Pt/Al_2O_3 and Pt/SiO_2 after reduction in flowing H_2 at 623 K following slow heating to this temperature. Chemical analysis gave 1.0 wt% Pt/Al_2O_3 and 0.7 wt% Pt/SiO_2 as prepared. The dispersion of the Pt/Al_2O_3 was $H/Pt \cong 1.0$ indicating very small clusters of Pt atoms <10 Å; that of the Pt/SiO_2 was $H/Pt = 0.87$ indicating Pt particles about ~ 12 Å in overall dimension. Electron micrographs of these materials indicated that the Pt was very highly dispersed <15 Å particles; no further quantification was possible.

Portions of preoxidized Pt/Al_2O_3 and Pt/SiO_2 were ground to a fine powder and pressed into separate wafers, sized to give an incident intensity to transmitted X-ray beam intensity ratio of three to five. Samples were placed in a controlled-atmosphere X-ray spectroscopy cell, which could be heated to 823 K under flowing H_2 for reduction, evacuated, and cooled to liquid N_2 temperature (80 K) for X-ray absorption measurements. Samples were reduced *in situ* in the cells just prior to taking the X-ray absorption spectra by heating at <3 K/min under flowing H_2 to the desired reduction temperature and holding for 2 h. On occasion the cell was evacuated at reduction temperature to $<10^{-3}$ Torr and backfilled with some He before cooling to 80 K; more frequently the H_2 pressure was reduced to about 100 Torr and then the sample was cooled to 80 K. A 2.5-μm-thick Pt foil was used as a reference and standard.

The data were collected in February 1980 on beam line I-5 at the Stanford Synchrotron Radiation Laboratory (SSRL). The storage ring energy was approximately 3 GeV and the current in the stored beam varied between 50 and 90 ma.

RESULTS

Analysis of the near edge region for the absorption data was done using the technique of Mansour *et al.* (*23*), as briefly described below. First, a Victoreen function was fit to the energy region below the edge and extrapolated through the region above the edge to remove the contributions from all other X-ray absorption edges. The data were scaled to an absolute cross section by

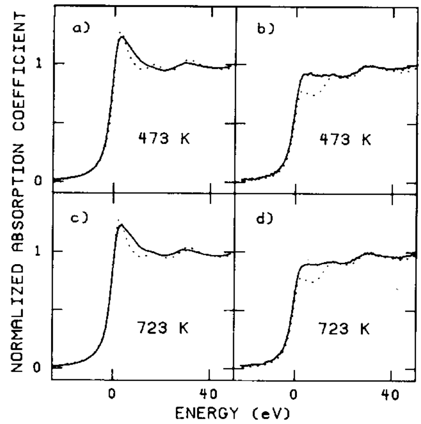

FIG. 1. Effect of dispersion, support, and reduction temperature on X-ray absorption edge structure for 1 wt% Pt/SiO_2. (a) L_{III} edge of Pt/SiO_2 reduced at 473 K (solid line) compared with L_{III} edge of bulk Pt (dotted line). (b) L_{II} edge of Pt/SiO_2 reduced at 473 K (solid line) compared with the L_{II} edge of bulk Pt (dotted line). (c) L_{III} edge of Pt/SiO_2 reduced at 723 K (solid line) compared with L_{III} edge of bulk Pt (dotted line). (d) L_{II} edge of Pt/SiO_2 reduced at 723 K (solid line) compared with L_{II} edge of bulk Pt (dotted line).

systematically selecting a point above the edge to normalize the data using the tabulated X-ray edge cross sections (*25*). Finally, the L_{III} and L_{II} edges were both aligned so that they symmetrically overlapped at energies greater than 40 eV above the edges, i.e., so that the fine structure from one edge exactly overlayed that of the other edge. The L_{II} and L_{III} edges of Pt foil were aligned with the corresponding edges in the catalyst sample in the same manner and the areas used to calculate the change in unoccupied *d* states were determined by integrating the area between the Pt foil curves and the catalyst curves. The areas were evaluated using Simpson's Rule and were done over a range of −10 to approximately 13 eV depending on the first crossing of the sample edge and the reference edge.

The effect of the support, of the high dispersion (very small cluster size) of Pt, and of reduction temperature on the L_{II} and L_{III} edge structure of Pt/SiO_2 as compared with bulk Pt is shown in Fig. 1. The L_{III} edge peak (Figs. 1a and c) is slightly less high but considerably broader for the Pt/SiO_2 than for bulk Pt. The area under the L_{III} edge peak, which is a measure of the integrated total-energy-range intraatomic $2p_{3/2}$ core states to unoccupied $5d_{3/2}$ and $5d_{5/2}$ states transition probability, is clearly larger for the highly dispersed Pt/SiO_2 than for bulk Pt. These results could be due to a broadening of the energy range occupied by the *d* states and a reduced occupancy of 5*d* states caused either by a hybridization-type change or by a transfer of electron density to the SiO_2. These spectra were taken under a low pressure of H_2; chemisorbed H_2 contributes to a broadening of the high-energy side of the edge peak. However, even after high-temperature evacuation, the peak is still broader than that of bulk Pt and still has a larger integrated area than that of bulk Pt (*6*). The area under the L_{II} edge, which is a measure of integrated total-energy-range intraatomic $2p_{1/2}$ core states to unoccupied $5d_{3/2}$ states transition probability is again clearly larger for the Pt/SiO_2 than for bulk Pt (Figs. 1b and d). In this case the major differences appear immediately behind the edge rather than at higher energies, as was observed for the L_{III} edge. The absorption edge structures of the Pt/SiO_2 were little changed by H_2 reduction at the higher temperature (Figs. 1a and b vs c and d).

Figure 2 shows the absorption edge data for Pt/Al_2O_3 reduced at 473, 573, and 723 K and compares them with the respective absorption edges of bulk Pt. Again, the absorption edges of the Pt/Al_2O_3 are broader and have larger areas than those of bulk Pt, indicative of an enhanced intraatomic electron transition probability relative to bulk Pt. There is an apparent change in the absorption edge structure with reduction temperature for the Pt/Al_2O_3.

The position of the absorption edge can be related to the charge on the absorbing atom as can the binding energy obtained from core-level electron spectroscopy (XPS). Table 1 gives the L_{III} and L_{II} edge

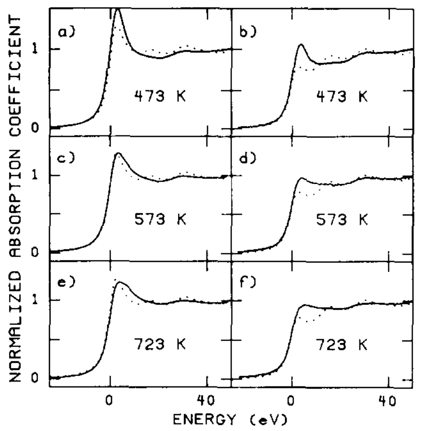

FIG. 2. Effect of dispersion, support and reduction temperature on X-ray absorption edge for 1 wt% Pt/Al$_2$O$_3$. (a) L_{III} edge of Pt/Al$_2$O$_3$ reduced at 473 K (solid line) compared with the L_{III} edge of bulk Pt (dotted line). (b) L_{II} edge of Pt/Al$_2$O$_3$ reduced at 473 K (solid line) compared with the L_{II} edge of bulk Pt (dotted line). (c) L_{III} edge of Pt/Al$_2$O$_3$ reduced at 573 K (solid line) compared with the L_{III} edge of bulk Pt (dotted line). (d) L_{II} edge of Pt/Al$_2$O$_3$ reduced at 573 K (solid line) compared with the L_{II} edge of bulk Pt (dotted line). (e) L_{III} edge of Pt/Al$_2$O$_3$ reduced at 723 K (solid line) compared with the L_{III} edge of bulk Pt (dotted line). (f) L_{II} edge of Pt/Al$_2$O$_3$ reduced at 723 K (solid line) compared with the L_{II} edge of bulk Pt (dotted line).

shifts relative to bulk Pt observed for the samples studied; the absorption edges for all the supported Pt samples are shifted to higher energy relative to bulk Pt. The enhanced p to d intraatomic transition probability and the edge shifts to higher energy both suggest that the highly dispersed Pt/SiO$_2$ and Pt/Al$_2$O$_3$ are electron deficient when compared to Pt foil. This is inferred to be due to electron transfer from the Pt to the support.

For Pt/SiO$_2$ there was little effect of H$_2$ reduction at 723 K relative to that at 473 K on the X-ray absorption edges (Fig. 3). The Pt in the case of Pt/SiO$_2$ is as fully reduced after 473 K H$_2$ reduction as after 723 K reduction; there is no measurable difference in the electronic properties as a function of reduction temperature. In contrast, increased reduction temperature causes a marked reduction in the height of and area under both the L_{III} and L_{II} absorption edges of Pt/Al$_2$O$_3$ (Fig. 3). The L_{III} absorption edge of Pt/Al$_2$O$_3$ shifts to significantly lower energy with increasing H$_2$ reduction temperature reaching essentially the same location as for Pt/SiO$_2$ after 723 K H$_2$ reduction. This suggests a shift in electron density toward the Pt atoms with increased H$_2$ reduction temperature. The electronic properties and the average extent of electron transfer to the support is a significant function of H$_2$ reduction temperature for Pt/Al$_2$O$_3$. The X-ray absorption edge structure, and thus the

TABLE 1

H$_2$ Reduction Temperature and Support Effects for Pt/SiO$_2$ and Pt/Al$_2$O$_3$

Catalyst	Pt particle size (Å)	Reduction temp.[a] (K)	L_{III} Edge shift[b] (eV)	L_{II} Edge shift[b] (eV)	fd[c]	No. of unfilled d states per Pt atom[d]
0.7% Pt/SiO$_2$	~12	473	1.3	0.9	0.19	0.357
0.7% Pt/SiO$_2$	~12	723	0.9	0.9	0.17	0.351
1% Pt/Al$_2$O$_3$	<10	473	1.7	0.9	0.31	0.393
1% Pt/Al$_2$O$_3$	<10	573	1.3	0.9	0.22	0.366
1% Pt/Al$_2$O$_3$	<10	723	0.9	0.9	0.19	0.357
Pt foil	—	—	0.0	0.0	0.00	0.30

[a] Reduced *in situ* in flowing H$_2$ in the EXAFS cell by heating at 3 K per min to indicated temperature and holding for 2 h.

[b] Edge shift is relative to that of bulk Pt; estimated error in edge shift is ±0.2 eV.

[c] Calculated using Eq. (1); estimated error is ±0.01.

[d] Calculated using Eq. (2) assuming there are 0.30 unfilled d states per Pt atom in bulk Pt.

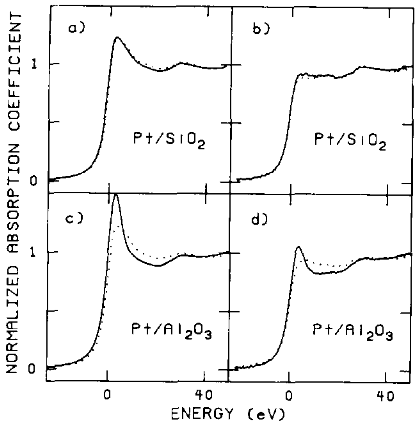

FIG. 3. Effect of H_2 reduction temperature on the X-ray absorption edge structure. (a) L_{III} edge of Pt/SiO_2 reduced at 473 K (solid line) compared with L_{III} edge of Pt/SiO_2 reduced at 723 K (dotted line). (b) L_{II} edge of Pt/SiO_2 reduced at 473 K (solid line) compared with L_{II} edge of Pt/SiO_2 reduced at 723 K (dotted line). (c) L_{III} edge of Pt/Al_2O_3 reduced at 473 K (solid line) compared with L_{III} edge of Pt/Al_2O_3 reduced at 723 K (dotted line). (d) L_{II} edge of Pt/Al_2O_3 reduced at 473 K (solid line) compared with L_{II} edge of Pt/Al_2O_3 reduced at 723 K (dotted line).

electronic properties of Pt/Al_2O_3 are significantly different from those of Pt/SiO_2 after a 473 K H_2 reduction (Fig. 4); but after 723 K reduction there is little or no significant difference in measurable electronic properties between them (Fig. 4).

Following the work of Mansour *et al.* (*23*), the fractional change in the number of *d* band vacancies (unfilled *d* states) from that of bulk Pt, f_d, can be defined as

$$f_d = \frac{\Delta(h_T)}{(h_T)_{Pt}} = \frac{(\Delta A_3 + 1.11\Delta A_2)}{(A_3 + 1.11A_2)_{Pt}} \qquad (1)$$

where

$\Delta(h_T) = (h_T)_{sample} - (h_T)_{Pt}$
$\Delta A_3 = (A_3')_{sample} - (A_3')_{Pt}$
$\Delta A_2 = (A_2')_{sample} - (A_2')_{Pt}$
h_T = total number of unoccupied *d* states
A_i' = total edge peak area for the *i*th edge
A_i = contribution to the total area due to enhanced absorption by *d* states
Pt = bulk Pt.

Table 1 gives the calculated f_d values for the catalysts studied; the values are all positive indicating that the highly dispersed supported Pt has a larger number of unfilled *d* states than the bulk Pt. Equation (1) can be rearranged to give

$$(h_T)_{sample} = [1.0 + f_d](h_T)_{Pt} \qquad (2)$$

from which the number of unfilled or vacant *d* states for the supported Pt samples can be calculated if the number of unfilled *d* states is known for bulk Pt. Band structure calculations suggest that there are between 0.3 and 0.4 vacant *d* states per Pt atom for bulk Pt (*26–28*). Assuming 0.30 unfilled *d* states per Pt atom for bulk Pt, the number of unfilled *d* states per Pt atom for the samples was calculated (Table 1).

For both samples there is a decrease in f_d and in the number of unfilled (vacant) *d* states with increasing temperature of H_2 reduction, although the decrease for the Pt/SiO_2 is within the reproducibility of the data and is probably not significant. There is a significant decrease in f_d and in the number

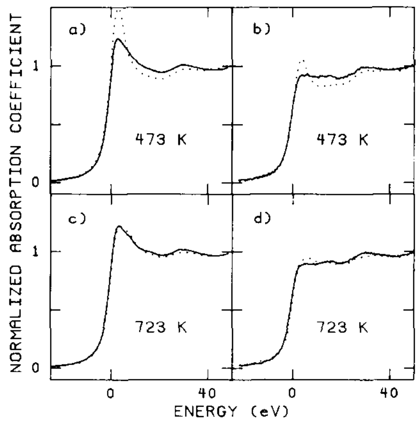

FIG. 4. Effect of the support on X-ray absorption edge structure. (a) L_{III} edge of Pt/SiO_2 reduced at 473 K (solid line) compared with L_{III} edge of Pt/Al_2O_3 reduced at 473 K (dotted line). (b) L_{II} edge of Pt/SiO_2 reduced at 473 K (solid line) compared with L_{II} edge of Pt/Al_2O_3 reduced at 473 K (dotted line). (c) L_{III} edge of Pt/SiO_2 reduced at 723 K (solid line) compared with L_{III} edge of Pt/Al_2O_3 reduced at 723 K (dotted line). (d) L_{II} edge of Pt/SiO_2 reduced at 723 K (solid line) compared with L_{II} edge of Pt/Al_2O_3 reduced at 723 K (dotted line).

of unfilled *d* states with increasing H_2 reduction temperature; after 723 K reduction the Pt/SiO_2 has a somewhat smaller f_d value than Pt/Al_2O_3 (Table 1).

DISCUSSION

The results strongly suggest that highly dispersed Pt/SiO_2 and Pt/Al_2O_3 in the presence of H_2 are electron deficient relative to bulk Pt even after high-temperature H_2 reduction. The extent of electron deficiency in the presence of H_2 is about 0.06 electrons per Pt atom for Pt/SiO_2 relative to bulk Pt and is 0.09 electrons per Pt atom for Pt/Al_2O_3 reduced at 473 K relative to bulk Pt (Table 1). The number of unfilled *d* states for Pt/Al_2O_3 decreased by 0.03 electrons per Pt atom with increased H_2 reduction temperature to 723 K. The presence of H_2 enhances this apparent electron deficiency; high-temperature evacuation to remove chemisorbed hydrogen results in a significant reduction in the additional edge peak area relative to that of bulk Pt after high-temperature H_2 reduction (*29*). Of the two supports, SiO_2 appears to induce the least perturbation in the electronic properties of the supported Pt; the Pt/Al_2O_3 shows much more pronounced effects of reduction temperature (Figs. 3 and 4). For Pt/SiO_2 the effect is 0.06 electrons per atom under H_2 and less than that with chemisorbed hydrogen removed.

For Pt/Al_2O_3 on average, because the X-ray absorption edge data are an ensemble average, the Pt, in the presence of chemisorbed hydrogen is about 0.09 electrons deficient per Pt atom after 473 K H_2 reduction. This deficiency is decreased by about 0.03 electrons per Pt atom for 723 K reduction. There are two possible models that can explain the behavior observed (Fig. 5); charges are to be taken as arbitrary but direction of charge changes are important. In one model (Fig. 5A) a fraction of the Pt may undergo reduction to clusters of zero-valent Pt atoms, and a small fraction of the Pt atoms on specific surface sites may undergo no or only partial reduction to a low-valent cationic species. This latter fraction is reduced at higher temperatures. In the other model (Fig. 5B) all of the Pt is reduced by the low-temperature H_2 reduction but is very highly dispersed as clusters of small numbers of Pt atoms which interact with the support more extensively because of their very high degree of dispersion. Higher-temperature H_2 reduction results in movement and the aggregation of the very small clusters to form larger clusters such that the ensemble average of the interactions per Pt atom is reduced. With X-ray absorption data alone it is not possible to distinguish between the two models. If model A were to apply, about 10% of the Pt would be in the unreduced state.

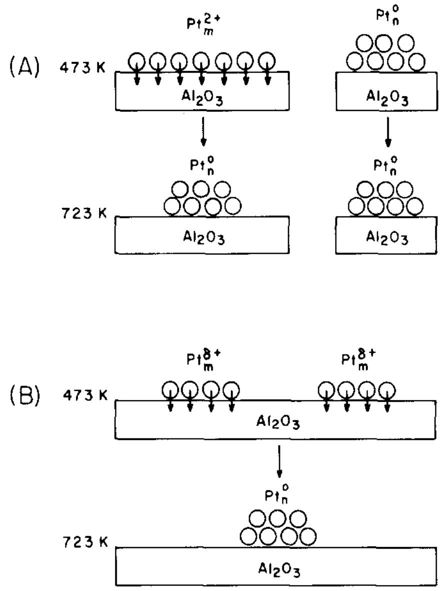

FIG. 5. Schematic model of interactions between small Pt clusters and Al_2O_3, illustrating the range of metal–support interactions involved.

Other studies suggest that Pt/Al_2O_3 is present as a dispersed phase interacting with and stabilized by the Al_2O_3 (*19–21*) and as a separate Pt oxide phase which appears and increases in amount with increasing Pt content (*21*). Temperature-programmed reduction showed that unsupported PtO_2 is reduced around 298 K; at 7.4 wt% Pt/Al_2O_3 Pt reduction occurred distinctly at 298 and at 463 K (*21*). For 0.78 wt% Pt/Al_2O_3 reduction occurred between 453 K and 583 K (temperature increase 8 K/min) (*21*), indicating Pt stabilized to different extents and undergoing reduction at different temperatures. These results suggest that 473 K reduction for 2 h should reduce most but not all of the Pt/Al_2O_3 and therefore strongly support Model A (Fig. 5).

Clearly there are support effects present in the system studied here, particularly for Pt/Al_2O_3. SiO_2 appears to produce a minimum interaction with the Pt, and thus the Pt is readily and fully reduced at 473 K. The Pt atoms would appear to also move around more readily and form somewhat larger clusters of Pt, thus the lower dispersion for the Pt/SiO_2. Highly dispersed Pt/SiO_2 is 10-fold more active on a specific catalytic activity basis than Pt/Al_2O_3 in NH_3 oxidation (*30*). The results suggest, although do not prove, that the reduction conditions should also affect the catalytic behavior particularly for structure sensitive reactions. Further, since Al_2O_3 has a significant effect on Pt, different types of Al_2O_3 and different pretreatment conditions for the Al_2O_3 preparation could be expected to affect the specific catalytic behavior of supported Pt. It is inferred that many successful commercial Pt catalysts have been developed to take advantage of such interactions although their exact nature is as yet not understood. This work illustrated the presence of significant metal–support interactions on nonreducible oxides which we feel is part of the larger question of the nature of the interactions observed for reducible oxides, e.g., TiO_2 (*15–17*).

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Grant DMR 80-11946. Some of the materials incorporated in this work were developed at SSRL with the financial support of the National Science Foundation (under Contract DMR 77-27489), in cooperation with the Department of Energy.

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