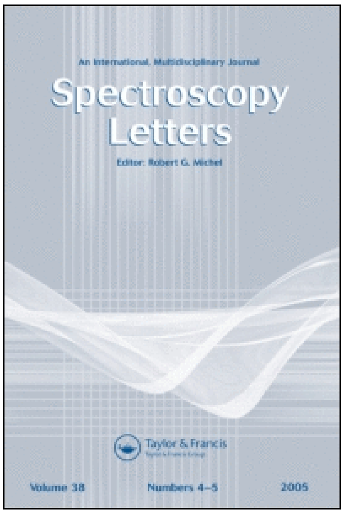

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Jun-ying, Yang and Swartz Jr., W. E.(1984) 'An XPS Study of the Effect of La_2O_3 Dopant on the Dispersion and Thermal Stability of Pt/Al_2O_3 Catalysts', Spectroscopy Letters, 17: 6, 331 — 343
To link to this Article: DOI: 10.1080/00387018408062691
URL: http://dx.doi.org/10.1080/00387018408062691

SPECTROSCOPY LETTERS, 17(6&7), 331-343 (1984)

AN XPS STUDY OF THE EFFECT OF La_2O_3 DOPANT ON THE DISPERSION AND THERMAL STABILITY OF Pt/Al_2O_3 CATALYSTS

KEY WORDS: X-ray photoelectron spectroscopy, platinum, catalyst, dispersion, lanthanum oxide dopant

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ABSTRACT

The Pt(4d)/Al(2s) XPS intensity ratio for Pt/Al_2O_3 catalysts increases with the addition of La_2O_3 as a dopant. The Pt(311) line in the X-ray diffraction pattern also broadens with the addition of La_2O_3. These data imply that doping the Pt/Al_2O_3 catalyst with La_2O_3 increases the dispersion of the platinum which in turn would be expected to increase the activity and thermal stability of the catalyst.

0038-7010/84/1706-0331$3.50/0

INTRODUCTION

Supported platinum group metals have been employed as important catalysts in the chemical and petroleum industries for years. However, the catalysts are sensitive to partial or total deactivation by increasing metal crystallite size during use and/or regeneration at high temperature. Numerous results have been reported in which dopants have been used to increase the catalytic activity and thermal stability of the catalysts. Ernest (1) has reported that catalysts prepared from the platinum group metals achieve stability at very high temperature when they are doped with CeO_2 and La_2O_3. With the addition of the dopant, the activity of the catalyst was retained. McVicker, et al. (2) added Group IIA oxides to Ir/Al_2O_3 and Pt/Al_2O_3 catalysts. The doped catalysts retained activity after calcination at 600°C. No agglomerated crystals were found on the catalytic surface. The authors speculate that the Group IIA oxide and iridium interact to form a stable surface iridate. Reduction of the iridate with H_2 forms a highly dispersed, active metallic iridium. Xie, et al (3,4) added La_2O_3 to a $Ni/\gamma\text{-}Al_2O_3$ catalyst to improve the catalytic activity. They used X-ray powder diffraction to prove that the La_2O_3 in the doped catalyst was dispersed as a monolayer. The La_2O_3 alters the support and produces a higher degree of metal dispersion.

In this investigation, the Pt(4d)/Al(2s) intensity ratio in the X-ray photoelectron spectrum (XPS) and X-ray diffraction line broadening are employed to determine the relative dispersion for a series of La_2O_3 doped Pt/Al_2O_3 catalysts. The effect of the La_2O_3 dopant on dispersion and thermal stability are discussed.

EXPERIMENTAL SECTION

i. Reagents and Catalysts: The chloroplatinic acid and lanthanum nitrate employed for catalyst preparation were of analytical purity grade. The γ-alumina employed as the support was of 100% purity as determined by X-ray powder diffraction. It's BET surface area was determined to be 201 m^2/g. The γ-Al_2O_3 was dried at 140°C for four hours prior to use.

The Pt/Al_2O_3 catalysts were prepared by the wet impregnation technique. The γ-Al_2O_3 was treated with an amount of $H_2[PtCl_6]\cdot 6H_2O$ stock solution to yield the desired weight percent of platinum. The system was mixed very well and dried at 80-90°C. The material was then decomposed at 500°C for four hours in air. The impregnated catalyst was then reduced with pure H_2 at numerous, desired temperatures.

The lanthanum dopant was introduced by impregnating the γ-alumina with appropriate amounts of $La(NO_3)_3\cdot 6H_2O$ solution. The material was then dried at 80-90°C. The lanthanum was oxidized to La_2O_3 by heating in air at 580°C for forty hours. The La_2O_3/γ-Al_2O_3 was then treated with $H_2[PtCl_6]\cdot 6H_2O$ as described above to yield the desired catalysts.

ii. XPS Spectra: X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA 36 photoelectron spectrometer. Mg(kα)(E_x=1253.6 eV) or Al(kα)(E_x=1486.6 eV) X-rays were employed to excite the spectra at a tube power of 320 W. The base pressure in the sample chamber was typically 2×10^{-7} torr. Analysis of the residual sample chamber gases with a spectromass 80 RGA indicated that the pressure was mostly due to H_2O and CO/N_2. Typical spectra were recorded over a 20 eV binding energy range. The C(1s) signal from the ubiquitous hydrocarbon contaminant was used to correct for charging of the insulating samples. Since the binding energies of the Pt($4f_{7/2}$) and Al(2p) electrons are approximately identical, it was necessary to determine the areas of the Pt($4d_{5/2}$) and Al(2s) electron signals to obtain intensity data. The peak areas were measured by using standard planimeter techniques on normalized spectra. The powdered samples were mounted on double sided cellophane tape for analysis.

iii. X-ray Diffractometry: X-ray diffraction data were obtained on a Phillips X-ray gonimeter equipped with a crystal monochromator and proportional detector. The Cu(kα) X-rays were obtained at a tube power of 680 W. The diffraction patterns were obtained at a scan rate of 0.5° 2θ/min. Since the primary platinum and alumina lines overlap, it was necessary to use the weak Pt(311) line.

Scherrer's equation (1) was used for the (311) line.

$$D_{311} = \frac{\kappa\lambda}{(B^2-b^2)^{1/2}\cos\theta} \qquad (1)$$

The constant κ is equal to 0.89, B and b are the half widths of the diffraction lines from the sample and a quartz standard, respectively, and D_{311} is the average crystallite size.

RESULTS AND DISCUSSION

The dispersion of a supported metal is routinely measured by selective chemisorption (5) or X-ray line broadening (6). However, the applicability of these techniques are often limited by the nature and particle size of the catalyst. The signal from XPS is limited to a surface region whose thickness is less than the mean free path of the photoelectron (∿50 Å). Therefore, XPS has become widely used to measure the dispersion of supported transition metal catalysts. If the metal loading on the support is small, the metal covers only a small fraction of the surface area of the support. In this case the XPS signal from the support ($I_{support}$) is almost constant. The XPS signal from the metal (I_{metal}) depends on its degree of loading and on its praticle size. The larger (thicker) the size of the metal at constant loading, the weaker the XPS signal intensity. Therefore, the ratio of metal and support XPS signal intensities (R_d)

$$R_d = {}^{I_{metal}}/I_{support} \qquad (2)$$

will be related to the extent of metal dispersion.

Scharpen (7) studied the Pt/SiO_2 system and found a good correlation between the XPS intensity ratio and the dispersion as determined by hydrogen chemisorption. He reported an empirical relationship which related dispersion (d) to R_d in which W is the weight percent of total metal in the catalyst and κ is a constant.

$$d = \kappa \frac{R_d}{W} \qquad (3)$$

When W is constant, there is a linear relationship between R_d and the dispersion (d).

A series of $Pt/\gamma\text{-}Al_2O_3$ catalysts with 3% metal loading but varying amounts of La_2O_3 dopant (expressed as g La_2O_3/g Al_2O_3). The catalysts were reduced in pure H_2 at 250°C, 400°C and 550°C. The $Pt(4d_{5/2})/Al(2s)$ intensity ratios are tabulated in Table I and the data are plotted in Figure 1.

TABLE 1

Effect of La_2O_3 Concentration and Temperature on the $Pt(4d_{5/2})Al(2s)$ Ratio and Crystallite Size for a 3% Pt/Al_2O_3 Catalyst.

g La_2O_3/g Al_2O_3	$Pt(4d_{5/2})/Al(2s)$ Intensity Ratio			D_{311}(Å)*
	T = 250°C	T = 400°C	T = 550°C	
0.00	0.092	0.075	0.069	143
0.10	0.135	0.110	0.088_5	113
0.25	0.205	0.159	0.126	∿96
0.40	0.261	0.221	0.167	
0.60		0.349	0.209	

*Crystallite size after treatment at 550°C.

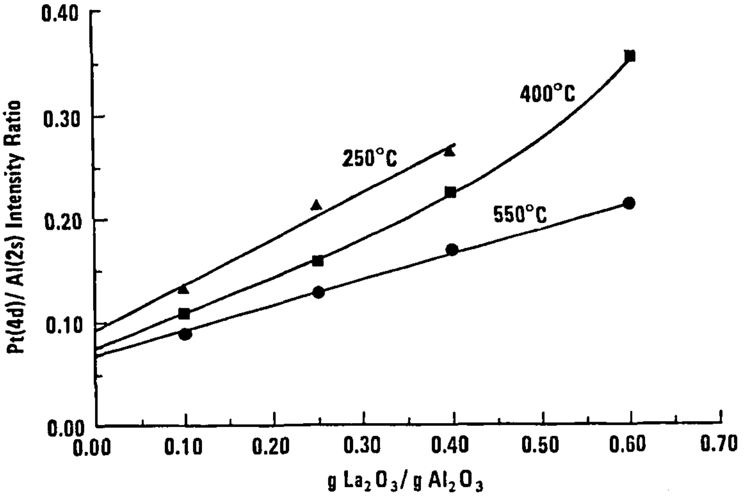

Fig. 1: Pt(4d)/Al(2s) intensity ratio as a function of La_2O_3 content for a 3% Pt/Al_2O_3 catalyst after heating to 250°C, 400°C and 550°C.

The $Pt(4d_{5/2})/Al(2s)$ ratio increases with increasing lanthanum content at each temperature. The Pt(311) XRD lines are shown in Figure 2 and the resulting crystallite sizes are tabulated in Table 1. With increasing La_2O_3 content the Pt (311) line becomes weaker and broader. This indicates that the platinum crystallites become smaller as the dispersion increases with increasing La_2O_3 content.

Figure 3 is a plot of $Pt(4d_{5/2})/Al(2s)$ ratios for the 3% Pt/Al_2O_3 catalysts as a function of temperature. The data clearly indicate that R_d decreases with increasing temperature as the result of the formation of larger crystallites. It must be pointed out that with the addition of only 0.1 g La_2O_3/g Al_2O_3, the dispersion of a doped catalyst that has been heated to 550°C remains higher than that of an undoped catalyst that has been heated to only 250°C. Thus, the addition of La_2O_3 to the catalyst increases the thermal stability of the system.

A series of catalysts were prepared with 0.10 g La_2O_3/g Al_2O_3 in which the platinum loading varied. The $Pt(4d_{5/2})/Al(2s)$ intensities are tabulated in Table 2 and plotted vs weight % platinum in Figure 4. The data clearly indicate that the addition of La_2O_3 to the Pt/Al_2O_3 system universally increases the dispersion of the platinum up to at least 10% weight percent.

The question of the mechanism by which a La_2O_3 dopant increases the platinum dispersion must be addressed. The XRD patterns as a function of La_2O_3 content are shown in Figure 5. Note that the lines due to La_2O_3 are not observed until 0.6g of La_2O_3 have been added per 1 g of Al_2O_3.

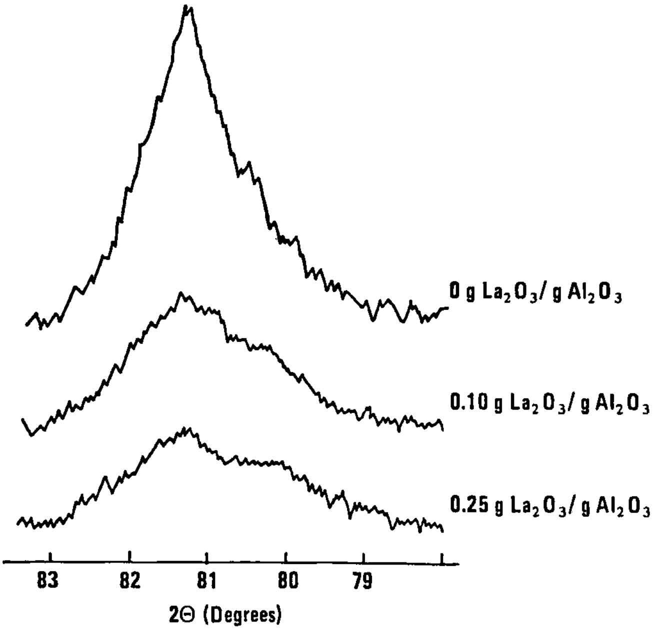

Fig. 2: The effect of La_2O_3 on the Pt(311) X-ray diffraction line.

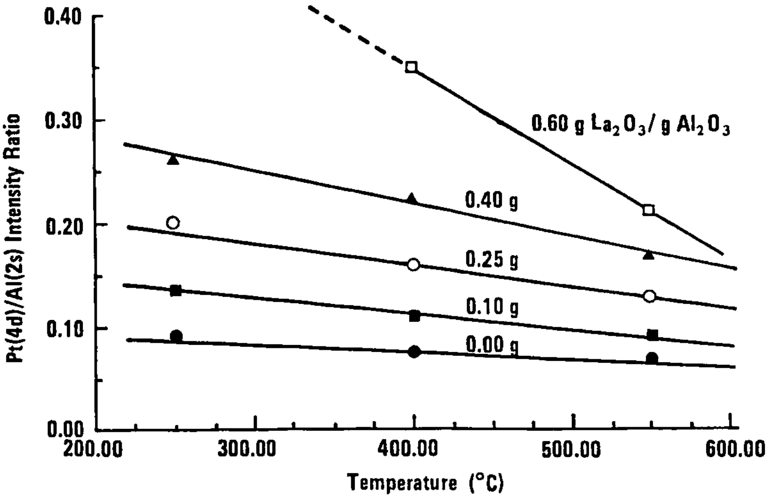

Fig. 3: Pt(4d)/Al(2s) intensity ratio as a function of temperature for a 3% Pt/Al_2O_3 catalyst with varying La_2O_3 loading.

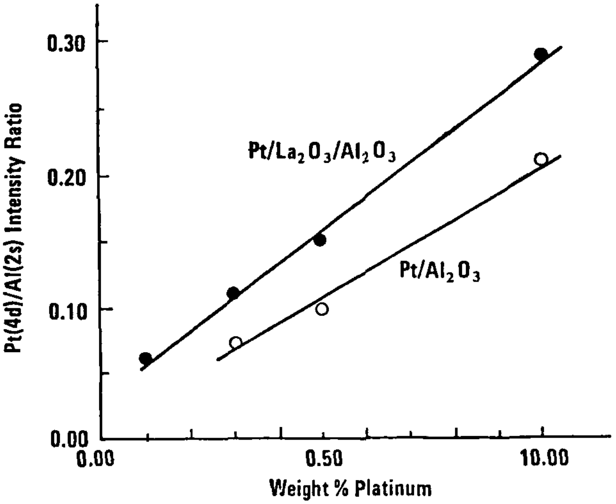

Fig. 4: Pt(4d)/Al(2s) intensity ratio as a function of metal loadinq for Pt/Al_2O_3 and Pt/La_2O_3/Al_2O_3 catalysts.

TABLE 2

Effect of Pt metal Loading on the Pt($4d_{5/12}$)/Al(2s) Intensity Ratio for Pt/Al_2O_3 and Pt/0.10g La_2O_3/Al_2O_3 Catalysts

W % pt	Pt/Al_2O_3	Pt/0.10g La_2O_3/Al_2O_3
	Pt($4d_{5/2}$)/Al(2s)	Pt($4d_{5/2}$)/Al(2s)
1		0.0625
3	0.0752	0.110
5	0.102	0.148
10	0.210.	0.290

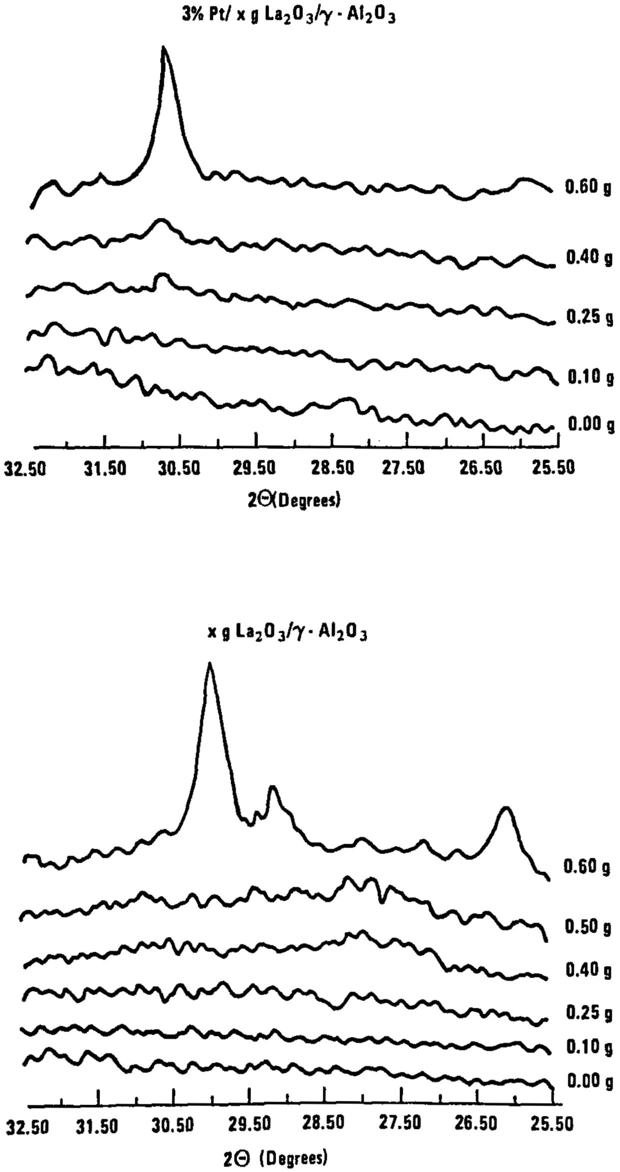

Fig. 5: X-ray diffraction patterns as a function of La_2O_3 content for doped γ-Al_2O_3 and 3% Pt/La_2O_3/γ-Al_2O_3 catalysts.

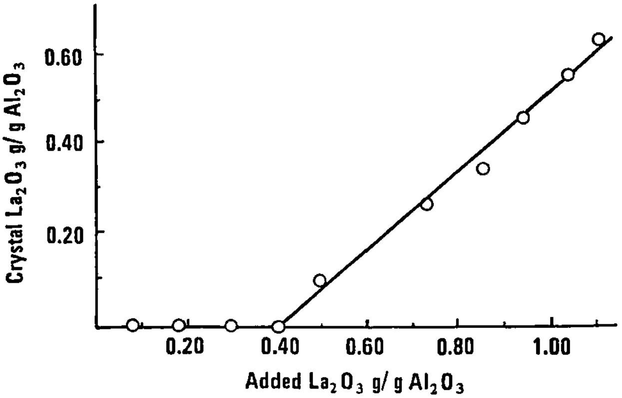

Fig. 6: Relative crystallinity for La_2O_3 doped γ-Al_2O_3 (BET Surface area of r-Al_2O_3=141 m2/g)

These data suggest that there are no La_2O_3 crystallites on the surface which are large enough to yield an XRD signal below 0.60g La_2O_3/g Al_2O_3. This corresponds to a threshold value of 0.30g La_2O_3/100m^2 of γ-Al_2O_3.

Xie (3,4) has reported that XRD phase analysis of La_2O_3 doped Ni/γ-Al_2O_3 catalysts yields a threshold for the La_2O_3 signal of 0.28g La_2O_3/100 m^2 of γ-Al_2O_3. By treating the La_2O_3 as a dispersed close-packed monolayer, Xie has calculated that 0.27g La_2O_3/100 m^2 Al_2O_3 is required for monolayer coverage. Therefore, Xie concludes that the La_2O_3, like other inorganic oxides and salts, is loaded onto the surface of alumina as a monolayer. As long as the La_2O_3 content is less than 0.28g La_2O_3/100 m^2 Al_2O_3, the La_2O_3 disperses a monolayer and no XRD signal is observed.

Our threshold value of 0.30g La_2O_3/100 m^2 Al_2O_3 is certainly within experimental error of the 0.27g La_2O_3/100 m^2 Al_2O_3 monolayer value. Thus it is likely that the La_2O_3 dopant in the present study is dispersed as a monolayer on the γ-Al_2O_3.

CONSLUSIONS

The utility of X-ray photoelectron spectroscopy and X-ray diffraction to determine the relative dispersion for supported platinum catalysts has been demonstrated. When La_2O_3 is added as a dopant to γ-Al_2O_3 it disperses as a monolayer. This monolayer of La_2O_3 changes the surface properties of the support and thereby effects the dispersion and crystallite size of the supported metal. This in turn improves the activity and thermal stability of the Pt/Al_2O_3 catalyst.

ACKNOWLEDGEMENT

The authors wish to acknowledge the generous assistance of Dr. R. Strom and Dr. A. Rosenzweig of the Department of Geology for their assistance with the XRD measurements.

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Received 1-20-84
Accepted 4-16-84