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The state of platinum in Pt–Al_2O_3 catalysts containing high chloride loading

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XPS data indicate that Pt in a highly chlorided (5–10% Cl) Pt–Al_2O_3 catalyst is present in a metallic form, and is not chlorided. Surface chloride concentration decreases following reduction in hydrogen; exposure to oxygen increases the surface chloride concentration. In contrast, reduction of chloride containing Pt–SiO_2 catalyst dramatically reduces the chloride level; in addition, treatment with CCl_4 appears to reoxidize at least some of the Pt in the Pt–SiO_2 catalyst.

Keywords: Platinum; platinum–alumina catalysts; isomerization catalyst; chlorided Pt–Al_2O_3; XPS; ESCA

1. Introduction

The introduction of the bifunctional chlorided Pt–alumina catalyst for naphtha reforming provided one of the revolutions in catalysis [1]. This catalyst system has been extensively investigated. A common view is that the platinum is present as Pt^0 and, depending on a number of factors, may be highly dispersed and even approach atomic dispersion. In the highly dispersed state, there does not appear to be a unanimous agreement on the state of Pt. Some authors supported the view that Pt was present as a chloro complex [2–6], while others questioned this conclusion [7,8]. Chloride, being very electronegative, was also believed to enhance the acidity of the isolated Al–O–H bonds. This was accomplished by the nearby Cl^-, withdrawing electrons from the O of the OH group, and thereby making a stronger acid.

In the 1960s, the heavily chlorided Pt–alumina catalyst received much attention for alkane isomerization, especially of the lower carbon number fraction of naphtha [9,10]. The need to eliminate lead as an octane enhancer led to gasolines rich in aromatics and alkenes. The current and future need to decrease the aromatic and olefin content of gasoline has led to a renewed interest in paraffin isomerization as a way to obtain the necessary octane rating of gasoline [11].

The state of platinum in these heavily chlorided catalysts is of interest. X-ray photoelectron spectroscopy (XPS or ESCA) provides one of the few techniques available for directly assessing the chemical valence of an element in a complex catalyst formulation. However, in the case of the Pt–alumina catalyst, the Al 2p and the Pt 4f peaks overlap; when platinum is present in low concentrations the Pt 4f peak is masked by the lower-energy tail of the Al 2p peak. Other approaches have been utilized to obtain direct evidence for the valence of platinum. For example, in an effort to obtain information about the valence state of platinum in a Pt–Sn–Al_2O_3 catalyst, it was shown that Rh in an analogous Rh–Sn–Al_2O_3 catalyst was present as Rh^0 and that platinum in a Pt–Sn–carbon catalyst was present as Pt^0 [12]. It was therefore concluded that platinum was present as Pt^0 in the Pt–Sn–Al_2O_3 catalyst.

In the present study we have utilized catalysts containing sufficient platinum so that the Al 2p peak does not entirely mask the Pt^0 4f peak. The catalysts were examined following in situ reduction and chlorination.

2. Experimental

2.1. CATALYSTS

Two materials, prepared for utilization for other investigations, were characterized in this study. A high surface area (230 m^2/g) alumina (United Catalysts, Inc.) was impregnated with an acetone solution of chloroplatinic acid to produce a catalyst containing 4 wt% Pt.

An alumina precipitated by bubbling carbon dioxide into a potassium aluminate solution after calcination at 600°C in air; this alumina had a surface area of 200 m^2/g and contained about 0.5 wt% K. The alumina was impregnated with chloroplatinic acid to produce a material containing 10 wt% Pt.

2.2. SURFACE CHARACTERIZATION BY XPS

The XPS analyses were carried out in Leybold-Hereaus LH-11 spectrometer equipped with a heatable sample probe and reaction chamber. The catalyst was pressed into a thin wafer and studied in the as-received state, following reduction in flowing H_2 at 300° for 1 h and following chloridation by a flow of He saturated with CCl_4 at the same conditions, and in that order. The Al 2p, Pt 4f, C 1s, O 1s, Cl 2p regions of the samples were monitored. The alumina support was also examined for any discernible surface species modification on exposure to chlorine. The data were acquired using Mg Kα (1253.6 eV) excitation with a pass energy of 20 eV, were corrected for background and subsequently smoothed using the Savitsky–Golay algorithm. The smoothed spectra were curve-fitted to elucidate the relative area of the various chemical species by using Gaussian peak shapes and a nonlinear least squares method [13]. The sensitivity factors employed in quantitation have been calculated for the instrument with typical analyzer settings and operating conditions.

3. Results and discussion

For the 10% Pt catalyst the XPS spectrum for the Al 2p and Pt 4f region is very broad and is readily deconvoluted to show the presence of Pt in the chlorided form (fig. 1A, left). However following reduction in an in situ reactor at 300°C for 1 h in flowing hydrogen, an XPS spectrum is obtained that shows peaks that are characteristic of Al 2p in alumina and Pt 4f in the zero valence state (fig. 1B, left and 1B, right). Thus, Pt can be distinguished in both the chlorided and the metallic state at this high Pt loading. Following in situ chloriding at 300°C for 1 h in a flow of helium saturated with CCl_4, there is essentially no change in the Pt 4f peak (fig. 1C, left and right). Thus, chloriding did not convert the Pt^0 to an oxidized state; the Pt remained reduced to the zero valence state. Subsequent reduction of the chlorided sample did not alter the Pt 4p peak (fig. 1D, left) to a measurable extent.

The overlap of the chlorided Pt 4f and the Al 2p of alumina makes it difficult to obtain an accurate measure of full width at half maximum (FWHM) of the Al 2p peak. However, this can be done for spectra for the reduced and the chlorided sample. For the reduced sample the FWHM is 1.94 eV. For the sample chlorided following reduction, the Al 2p peak FWHM is 3.25 eV (or 2.29 eV if the measurement is based upon the deconvoluted peak), and following reduction again the FWHM is 2.45 eV. It is clear that the linewidth is consistent with Pt not being reoxidized by chloridation.

The 10 wt% Pt alumina catalyst was reduced in flowing hydrogen at 450°C and was then chlorided in a flow-through reactor at 300°C in a nitrogen stream saturated with CCl_4. The reaction was continued until the CO_2 evolution had reached a maximum and then declined to a low value. CCl_4 is a very selective chloriding agent that produces CO_2 with only trace deposition of carbon, of any [12]. Bulk chemical analysis indicated that the chloride level was about 7 wt%. The chlorided sample was pelleted and transferred to the XPS sample holder in a glovebox and subsequently studied by XPS with minimum exposure to air. The FWHM for the Al 2p peak is 2.20 eV, in good agreement with the deconvoluted peak for the sample chlorided in the reactor chamber attached to the XPS instrument. The peak corresponding to Pt^0 is clearly evident in this sample. From XPS measurements, the Cl fraction of the elements is 0.035 for the sample chlorided in the plug flow reactor and for the sample chlorided in situ, this fraction is 0.03.

For 10 wt% Pt/Al_2O_3 catalyst, it is observed that the fraction of Cl on the surface is 0.035 for the chlorided sample but the fraction decreases to 0.013 following treatment in hydrogen for 1 h at 300°C (table 1). We have reported previously that the surface chloride concentration decreases upon reduction with hydrogen [13], and the current data are in agreement with this observation.

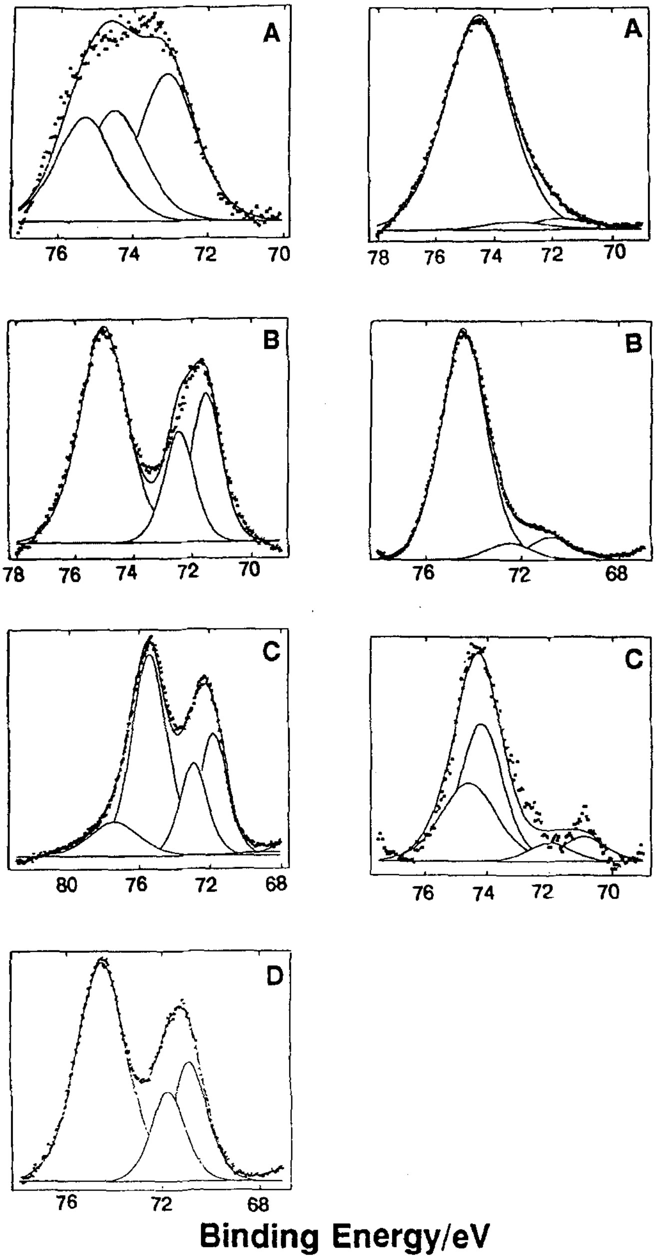

Fig. 1. XPS spectra for the Al 2p/Pt 4f region for Pt–Al_2O_3 catalysts following various treatments. Spectra on the left are for the catalyst containing 10 wt% Pt: A, as prepared; B, following reduction in hydrogen at 300°C for 1 h; C, following chloriding with CCl_4 at 300°C for 1 h; C, following reduction in hydrogen at 300°C for 1 h. Spectra on the right are for the catalyst containing 4 wt% Pt: A, as prepared; B, following reduction at 300°C for 1 h; and C, following chloriding with CCl_4 at 300°C for 1 h.

Table 1
Surface compositions of the 4 and 10 wt% Pt–alumina catalysts following various treatments

Catalyst	Pretreatment	Element (at%)			
		Pt	Al[a]	O	Cl
4 wt% Pt	none, as prepared	0.27	36.6 (2.27)	59.9	3.3
4 wt% Pt	H_2/300°C/1 h	0.22	42.0 (2.31)	58.0	nd[b]
4 wt% Pt	CCl_4/300°C/25 min	0.24	23.1 (1.84)	73.6	3.1
10 wt% Pt	CCl_4/300°C/ ~ 14 h[c]	0.41	42.0 (2.20)	53.1	4.5
10 wt% Pt	as prepared[d]	1.2	13.6 (2.43)	85.2	nd[b]
10 wt% Pt	H_2/300°C/1 h[d]	1.7	62.3 (1.94)	36.1	nd[b]
10 wt% Pt	CCl_4/300°C/1 h[d]	2.07	67.8 (3.25)	26.6	3.47
10 wt% Pt	H_2/300°C/1 h[d]	1.60	66.9 (2.45)	30.2	1.29

[a] Full width at half maximum intensity is given in parentheses.
[b] nd = not determined.
[c] Chlorided in plug flow reactor and transferred to XPS chamber.
[d] Sample treated succesfully in order from top to bottom.

The XPS spectrum of the as-prepared 4 wt% Pt catalyst indicated that the Pt was present in an oxidized state and that it was included in the larger Al 2p peak (fig. 1A, right). Thus, the Pt was presumably present as $PtCl_6^{2+}$, or a similar compound of related stoichiometry. Following in situ reduction in flowing hydrogen for 1 h at 300°C, a peak corresponding to Pt^0 was observed (fig. 1B, right). In situ chloriding of the sample in the XPS did not eliminate the peak corresponding to Pt^0 (fig. 1C, right). The data with the 4 wt% Pt catalyst are similar to that obtained with the 10 wt% Pt catalyst.

Our earlier studies [14] and the deconvoluted Cl 2p peaks in fig. 2 indicate that the chloride is present in at least two chemical states in the as-prepared, the chlorided, and in the re-reduced samples (e.g., fig. 2B, left). It also appears that reduction in hydrogen following the chloriding step reduces the surface concentration of the lower-binding, i.e., more negative chloride. Thus, the present data are consistent with our earlier observation of a significant reduction in the surface chloride concentration following hydrogen reduction [14]. Bulk analysis of the sample does not show a significant decrease in the chloride concentration following two oxidation and reduction cycles. These observations suggest that the more negative chloride ion migrates into the bulk of the alumina support with hydrogen reduction and diffuses to the surface in an oxygen atmosphere. Since chloride was not added during the oxidation portion of a cycle, it is clear that chloride migrates from the interior during oxidation; however, many cycles of oxidation and reduction would be required to distinguish between the removal of chloride to the gas phase and the migration into the bulk during hydrogen reduction.

When chloroplatinic acid was added to a silica support, the data indicated that

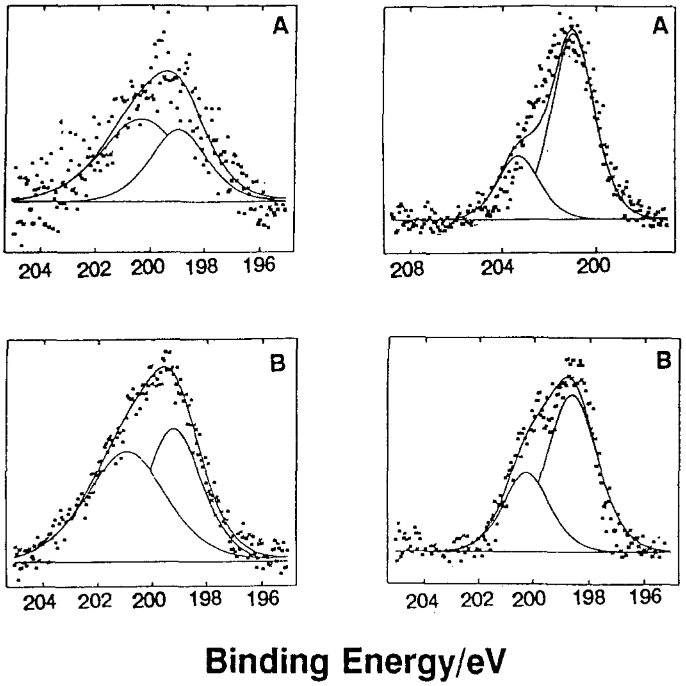

Fig. 2. XPS spectra for the Cl 2p region following various treatments. Spectra on left are for the 10 wt% Pt catalyst: A, following reduction in flowing hydrogen at 300°C for 1 h, and then CCl_4 at 300°C for 1 h; B, sample used to record spectrum A following reduction in flowing hydrogen at 300°C for 1 h. Spectra on right are for the 4 wt% Pt catalyst: A, following preparation and calcination in air; B, following reduction in flowing hydrogen at 300°C for 1 h and then chloriding in flowing He saturated with CCl_4 at 300°C for 1 h.

the chloroplatinum complex survived drying. However, reduction in hydrogen at 400°C converted the platinum to Pt^0. Subsequent treatment with CCl_4 converted part of the platinum to a more positive form, presumably a chloroplatinum compound. In the present study, the aluminum peak of the support prevents making an accurate measure of the amount of platinum that is present in an oxidized state and as Pt^0. However, it does not appear that the addition of chloride from CCl_4 and the subsequent reduction causes a measurable change in the amount of Pt^0 from that of a reduced form of the catalyst.

In summary, it appears that in the heavily chlorided (3 wt% and higher) Pt–alumina catalysts the Pt is present as Pt^0, and not as a chloride. It also appears that the chloride is present in at least two chemical environments; furthermore, the chloride present on the lower binding energy form appears to be mobile. Thus, treatment of the chlorided catalyst causes the lower binding energy chloride concentration to decrease on the surface; subsequent treatment in oxygen causes bulk chloride to migrate to the surface. Silica is less amenable to chloriding so that on this support, in contrast to alumina, the treatment with CCl_4 results in chloridation of the platinum.

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