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REACTIONS OF H_2PtCl_6 ON HY ZEOLITE

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ABSTRACT

The reactions of H_2PtCl_6 supported on HY zeolite were studied by X-ray photoelectron spectroscopy and diffuse reflectance spectroscopy. During impregnation, $[PtCl_6]^{2-}$ is anchored on the surface via chloride bridging. On the basis of the spectroscopic results, the feature of the thermal decomposition of H_2PtCl_6 on HY zeolite may be represented as follows:

$$[PtCl_6]_s^{2-} \xrightarrow[\approx 330\,^\circ C]{-Cl_2} [PtCl_4]_s^{2-} \xrightarrow[\approx 450\,^\circ C]{air} \left[PtCl_xO_{(2-x)/2}\right]_s \xrightarrow[\approx 500\,^\circ C]{+H_2O,\ -HCl} [PtO_2]_s$$

where the subscript s denotes surface. The decomposition reactions are different from those of the unsupported compound as a result of interaction between the complex and the support.

INTRODUCTION

The search for the means of preparing small platinum particles on various supports has for many years been motivated by both practical and theoretical interests. The methods of preparation have been described extensively in different reviews [1,2]. Relatively little attention has been paid so far to the preparation process. The reactions of platinum in oxygen- and hydrogen-treated Pt/Al_2O_3 catalysts have been studied by temperature-programmed reduction (TPR) and diffuse reflectance spectrometry (DRS) [3]. Thermal decomposition of H_2PtCl_6–$SnCl_2/Al_2O_3$ has been investigated by DRS, and the redox reactions of the surface complexes have been elucidated in terms of coordination chemistry [4]. Recently, the structural transformation in V_2O_3 during the preparation of Pt/V_2O_3 catalysts has been reported [5].

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X-ray photoelectron spectroscopy (XPS) can be used to investigate all metals and elements except hydrogen, especially to determine the metal valency. For inorganic platinum complexes, for example, the chemical shift of the binding energy of $Pt(3d_{5/2})$ varies within a range of 4 eV [6]. The transition metal ions exhibit optical properties which are characteristic of their oxidation state and local symmetry, and a UV–visible diffuse reflectance spectrum of transition metal ions on the support surface contains information about the energy levels of the electronic ground and excited states [7].

On the basis of XPS and DRS determinations, in the present report we give a detailed account of the reactions of H_2PtCl_6 on the surface of HY zeolite at different temperatures. Special attention is focused on the surface process, on the identification of surface species during thermal decomposition, and on the effects of the support. It is hoped that such an evaluation of the surface reactions may contribute to a better understanding of the formation of Pt/HY catalysts.

EXPERIMENTAL DETAILS

Materials

The H_2PtCl_6, K_2PtCl_6 and K_2PtCl_4 were of analytical grade; $PtO_2 \cdot H_2O$ was prepared by the method of Adams et al. [8]. NaY zeolite was produced by Nanjing Inorganic Chemical Factory. NH_4Y zeolite was prepared by exchange of NaY zeolite with NH_4Cl aqueous solution, and HY zeolite was obtained by heating NH_4Y zeolite with SiO_2/Al_2O_3 in a ratio of 5 : 4. H_2PtCl_6/HY with 1.0 wt.% of Pt was prepared by impregnation of HY zeolite with a solution of H_2PtCl_6 in dilute hydrochloric acid, and was dried in vacuo at 60 °C. K_2PtCl_4/HY with 1.0 wt.% of Pt was prepared by treatment of the support with an aqueous solution of K_2PtCl_4. After drying, H_2PtCl_6 was calcined in air at different temperatures. The samples were analyzed for platinum by atomic absorption spectrophotometry following heating and reduction in hydrogen at 450 °C.

Instrumentation

The X-ray photoelectron spectra were obtained using a Perkin–Elmer PH5300 photoelectron spectrometer. The Mg $K\alpha$ X-ray line (1253.6 eV) was used for photoelectron excitation. In order to compensate for the charging of insulating samples during the photoelectron ejection process, all the spectra were referenced to the photoelectron line Si(2p) $E_b = 103.5$ eV. This reference was found to yield more reproducible E_b values than the more commonly used reference, C(1s) at 285.0 eV. The UV–VIS diffuse reflectance spectra were recorded with a Hitachi UV-330 spectrophotometer. The reference standard in the spectrometer, Pt-free HY, was always treated in the same way as the supported sample.

RESULTS

X-ray photoelectron spectroscopy

As shown in Fig. 1 and Table 1 the change of E_b (Pt, $3d_{5/2}$) of H_2PtCl_6/HY was not noticeable as compared with that of K_2PtCl_6, indicating that six Cl^- ions coordinated with a Pt^{IV} ion and the effect of the support was sufficiently weak. The binding energy of the decomposition product of H_2PtCl_6/HY at 330 °C was identical with that of K_2PtCl_4 or K_2PtCl_4/HY, implying that $[PtCl_4]_s^{2-}$ (s = surface) was formed on the support. The product at 450 °C gave a typical binding energy of Pt^{IV}; however, the E_b was slightly lower than that of undecomposed K_2PtCl_6/HY, and this would mean that a portion of the Cl^- ions was replaced by oxygen

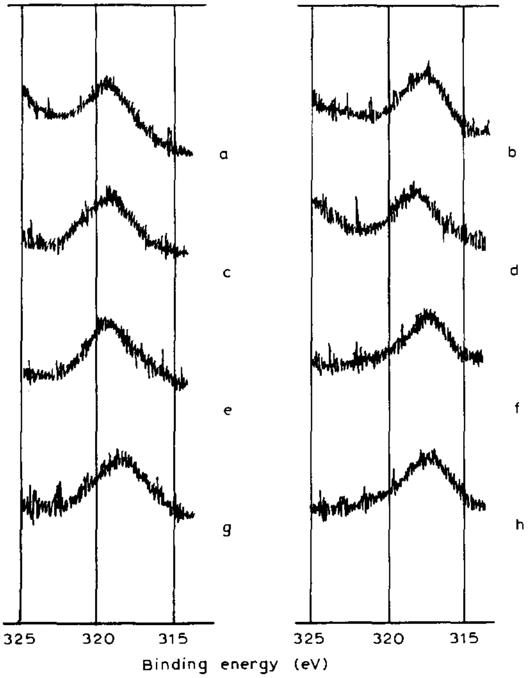

Fig. 1. X-ray photoelectron spectra (Pt, $3d_{5/2}$): H_2PtCl_6/HY (a) and its decomposition products at 330 °C (b), 450 °C (c), and treated with steam at 500 °C (d); K_2PtCl_6 (e), K_2PtCl_4 (f), $PtO_2 \cdot H_2O$ (g), K_2PtCl_4/HY (h).

TABLE 1

XPS data (eV)

Sample	Heating temperature (° C)	Pt($3d_{5/2}$)
H_2PtCl_6/HY	60	319.4
	330	317.5
	450	319.0
	500 [a]	318.5
K_2PtCl_6	–	319.3
K_2PtCl_4	–	317.5
K_2PtCl_4/HY	–	317.5
$PtO_2 \cdot H_2O$	–	318.1

[a] Treated with steam.

ions. After heating at 450 ° C, the supported sample was treated with steam at 500 ° C, and a lower binding energy of 318.5 eV was measured.

Diffuse reflectance spectroscopy

The results are listed in Table 2 and shown in Fig. 2. Assignments were made based on the values for Pt complexes in aqueous solution [9,10]. The absorption character of H_2PtCl_6/HY was close to that of K_2PtCl_6 with d–d transition bands at 360 and 457 nm; these may be assigned to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^3T_{1g}$ or ${}^1A_{1g} \rightarrow {}^3T_{2g}$ transitions, respectively. This suggests that a Pt^{IV} complex with six Cl^- ligands was preserved on the surface. The charge transfer band of H_2PtCl_6/HY at 278 nm was shifted to higher wavelengths as compared with that of K_2PtCl_6 as a result of the interaction between the complex and the support. The reflectance spectrum of the decomposition product of H_2PtCl_6/HY at 330 ° C was similar to that of K_2PtCl_4 or K_2PtCl_4/HY, giving three d–d bands at 331 (${}^1A_{1g} \rightarrow {}^1E_g$), 392 (${}^1A_{1g} \rightarrow {}^1A_{2g}$) and 464 nm (${}^1A_{1g} \rightarrow {}^3E_g$). The transitions arising from the

TABLE 2

DRS results

Sample	Heating temperature (° C)	Bands (nm)
H_2PtCl_6/HY	60	278, 360, 457
	330	330, 392, 464
K_2PtCl_6	–	270, 362, 458
K_2PtCl_4	–	330, 389, 465
K_2PtCl_4/HY	–	331, 389, 465

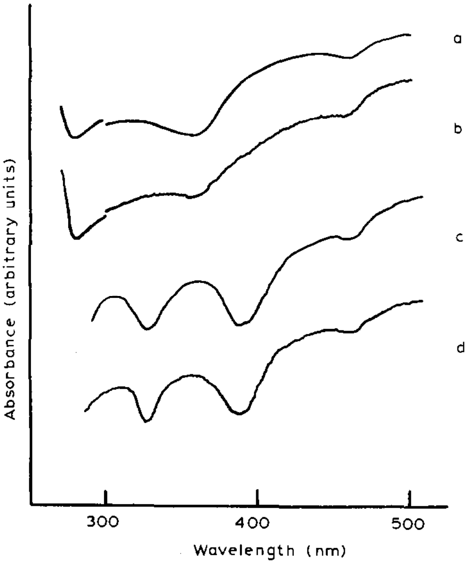

Fig. 2. Diffuse reflectance spectra: K_2PtCl_6 (a), H_2PtCl_6/HY (b), K_2PtCl_4 (c), product of H_2PtCl_6/HY at 330 °C (d).

singlet to the triplet were very weak since they were spin forbidden. The DRS results are in good agreement with those of XPS measurements.

DISCUSSION

The decomposition process of unsupported H_2PtCl_6 may be considered to proceed according to the following scheme [4]

$$H_2PtCl_6 \cdot 6H_2O \xrightarrow[\approx 100\,^\circ C]{-6H_2O} H_2PtCl_6 \xrightarrow[\approx 160\,^\circ C]{-2HCl} PtCl_4 \xrightarrow[\approx 300\,^\circ C]{-Cl_2} PtCl_2 \xrightarrow[> 500\,^\circ C]{-Cl_2} Pt$$

However, the decomposition of H_2PtCl_6/HY is quite different from that of the unsupported compound, since $PtCl_4$, $PtCl_2$ and Pt were not found on the surface of the zeolite.

The XPS and DRS results show that, after impregnation, the local symmetry of the Pt^{IV} complex is preserved and the change of the charge transfer band is the result of the effect of Al^{III} on the surface of the zeolite. During impregnation, $[PtCl_6]^{2-}$ ions are anchored on the surface via Cl^- bridging and surface polynuclear complexes are formed (Fig. 3).

According to XPS and DRS of the product at 330 °C, the first stage of decomposition of H_2PtCl_6/HY is found to be the evolution of Cl_2, resulting in the reduction of Pt^{IV}

$$[PtCl_6]_s^{2-} \rightarrow [PtCl_4]_s^{2-} + Cl_2$$

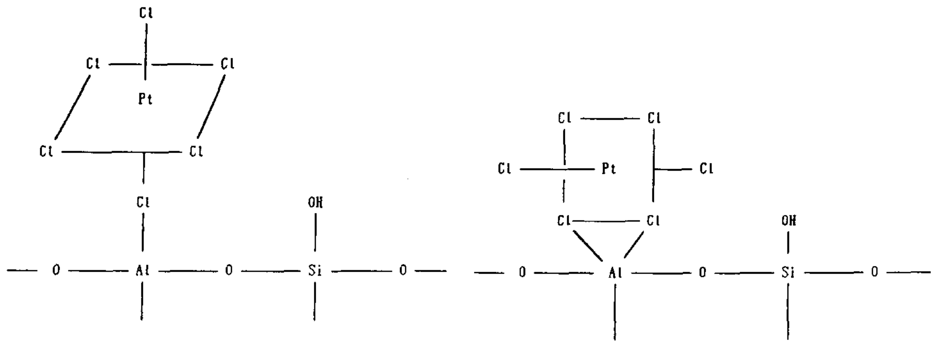

Fig. 3. Surface complex $[PtCl_6]_s^{2-}$.

At higher temperatures Pt^{II} is oxidized in air and a new surface species is formed:

$$[PtCl_4]_s^{2-} \xrightarrow{air} [PtCl_xO_{(2-x)/2}]_s$$

It is expected that the binding energy (Pt, $3d_{5/2}$) of $[PtCl_xO_{(2-x)/2}]_s$ is low relative to that of $[PtCl_6]_s^{2-}$, as indicated in the XPS study.

Treatment with steam at 500 °C leads to the formation of $[PtO_2]_s$:

$$[PtCl_xO_{(2-x)/2}]_s + x/2\ H_2O \rightarrow [PtO_2]_s + xHCl$$

In conclusion, the decomposition process of the H_2PtCl_6/HY system may be represented as follows

$$[PtCl_6^{2-}]_s \xrightarrow[\approx 330\,°C]{-Cl_2} [PtCl_4^{2-}]_s \xrightarrow[\approx 450\,°C]{air} [PtCl_xO_{(2-x)/2}]_s \xrightarrow[\approx 500\,°C]{H_2O,\ -HCl} [PtO_2]_s$$

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