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Short Communication

Influence of the method of platinum deposition on activity and stability of Pt/TiO_2 photocatalysts in the photocatalytic oxidation of dimethyl methylphosphonate

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ABSTRACT

Gas-phase photocatalytic oxidation of organophosphorous compound dimethyl methylphosphonate was carried out in a flow reactor on platinized TiO_2 Degussa P25. Platinization was performed by soft chemical reduction (SCR) and photodeposition (PD) techniques. Dispersion and chemical state of platinum were studied by X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). It was found that SCR gave mostly metallic platinum, whereas PD gave only Pt^{2+} form. During the oxidation, the state of platinum on a SCR catalyst remained unchanged, which determined its good stability. The catalyst with PD platinum deactivated quite fast due to aggregation of Pt particles. The SCR technique was found to provide better stability and activity.

1. Introduction

Heterogeneous photocatalysis on the basis of semiconductors has attracted considerable attention in recent years for the destruction of undesirable organic pollutants both in liquid [1–4] and gaseous phases [5–8] with the help of solar or artificial light. A large variety of pollutants like insecticides, pesticides, detergents as well as several chemical warfare agents (CWA) are organophosphorous compounds. This research is aimed at the gas-phase photocatalytic oxidation of dimethyl methylphosphonate (DMMP) which is a simulant compound of other organophosphorous CWA.

TiO_2 is the most widely used heterogeneous photocatalyst for efficient decomposition of organic compounds both in air and water under irradiation by mild UV light [2–8]. The specific advantages of TiO_2 are in high chemical stability, low cost and low toxicity [3,5,6,8]. However, its photocatalytic activity in the oxidation of many target pollutants is too low to be of practical interest [2]. Correspondingly, considerable efforts have been made to improve the photocatalytic activity of TiO_2 [9,10]. One of the most effective techniques appears to be the modification of TiO_2 with platinum [11,12]. The addition of noble metals to titanium dioxide is known to significantly increase its photocatalytic activity. Supporting platinum over TiO_2 is thought to enhance charge separation inside the semiconductor and to decrease the electron–hole pair recombination. Besides, platinum is one of the best catalysts for the conventional thermal oxidation [13,14], and Pt particles can also increase the adsorption constants for organic compounds [14].

Among many known techniques of platinum deposition, most researchers recommend photodeposition [2,15,16]. However, it was observed that catalysts with platinum deposited on TiO_2 by H_2PtCl_6 impregnation with further soft chemical reduction with $NaBH_4$ (the SCR technique) in some cases are more active in comparison to catalysts with photodeposited platinum [14,17]. In contrast, some authors showed [17] that platinum deposited on titania by both the SCR and PD techniques increases the activity of titania. Indeed, the data on the platinum oxidation state and dispersion are required for the explanation of respective catalytic properties.

In the present study, TiO_2-based catalysts with 2 wt.% Pt were prepared and characterized by X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) in order to find the difference in the dispersion and the chemical state of platinum in fresh and used catalysts. Platinum was deposited on commercial Degussa P25 titania. The rate of the gas-phase photocatalytic oxidation of DMMP was measured in a flow reactor. This reactor allows one to measure both the reaction rate and the stability of the photocatalyst. For the first time, electron and catalytic properties of the photocatalysts with platinum deposited by different techniques are compared.

2. Experimental

2.1. Chemicals

All chemical reagents used in our experiments were obtained from commercial sources as guaranteed-grade reagents and were used without further purification and treatment. DMMP (98%) was

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purchased from Aldrich; sodium borohydride (98%) was received from ACROS (Russia). Chloroplatinic acid hexahydrate (98%) was received from Reakhim (Russia). Deionized distilled water was used in all experiments. Commercial TiO_2 Degussa P25 (80% anatase and 20% rutile, SSA 57 m^2/g, Degussa AG) was used for platinum deposition.

2.2. Pt/TiO_2 catalyst preparation

We used two methods of platinum deposition. The SCR method was described in detail elsewhere [17]. In this case, titania was impregnated with an H_2PtCl_6 solution and then a $NaBH_4$ solution was added for reducing Pt^{4+}. The other method was PD of platinum [17]. A deaerated suspension, which consisted of TiO_2 Degussa P25, H_2PtCl_6 in a proper amount, an excess of isopropanol and water, was illuminated with the radiation of a high-pressure mercury lamp DRSh-1000 W (Russia). During the illumination, electron and hole pairs are generated on the surface of titania; photo-generated electrons are able to reduce Pt^{4+} to Pt^0, whereas the holes oxidize isopropanol. Below, the above photocatalysts are denoted as SCR and PD catalysts, respectively. The content of platinum was 2 wt.% for all photocatalysts.

2.3. Catalyst characterization

The BET surface area (S_{BET} in m^2g^{-1}) was derived from nitrogen adsorption isotherms measured at liquid nitrogen temperature, using an automatic ASAP-2400 Sorptometer (Micromeritics, USA). The oxidation state and dispersion of platinum were evaluated by X-ray photoelectron spectroscopy. XPS measurements were performed on a SPECS's photoelectron spectrometer equipped with a hemispherical electron energy analyzer PHOIBOS-150, and an X-ray source XR-50 with a double Al/Mg anode. The core-level spectra were obtained using non-monochromatic Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV). All binding energies were referenced to the Ti$2p_{3/2}$ peak at 458.6 eV. In this case the main peak in the C*1s* spectra of the fresh and used catalysts was observed at 284.8 and 285.2 eV, respectively.

Investigation of the surface morphology by HRTEM was carried out with a JEM-2010 electron microscope (JEOL, Japan) at the accelerating voltage of 200 kV and a lattice resolution of 0.14 nm. The samples for microscopy were prepared by suspending the photocatalyst powders in ethanol followed with its ultrasound treatment; then, they were deposited onto holey amorphous carbon films supported on standard copper grids.

2.4. Catalytic activity measurements

Catalytic activity for both photocatalysts was measured in a gas-phase photocatalytic oxidation of DMMP. Fig. 1 shows a scheme of a setup for these studies. A luminescence lamp OSRAM Dulux L (11 W) was used as a mild UV light source. The intensity of the incident radiation was 4.5 mW/cm^2. The gas mixture flow rate was about 15 ml/min. DMMP was injected into a chromatograph by means of a syringe pump with the rate 0.5 µl/h; this rate corresponds to the DMMP concentration of 100 ppm in the initial gas flow. The humidity of the gas mixture was 50%. The reactor was thermostated at 40 °C. The photocatalyst (30 mg) was deposited on a glass slide; the area of the catalyst spot was 2.5 × 2.5 cm. We measured the rate of carbon dioxide production in the flow system for 24 h. CO_2 was detected with a gas-chromatograph equipped with a mass-spectrometer detector and a Plot Fused Silica column (25 m × 0.32 mm) coated with CP Paraplot QHT. The reaction temperature was 40 °C.

3. Results and discussion

3.1. Catalyst characterization

Table 1 represents some textural and structural characteristics of bare and platinized titania photocatalysts before and after their catalytic testing in the DMMP oxidation. Fig. 2 shows the XPS Pt*4f* core-level spectra of the SCR and PD photocatalysts also before and after the catalytic testing. The analysis of these spectra was complicated due to overlapping of the Pt*4f* spectrum with the plasmon loss peak of the Ti*3s* spectrum at 75 eV. Thus, for the

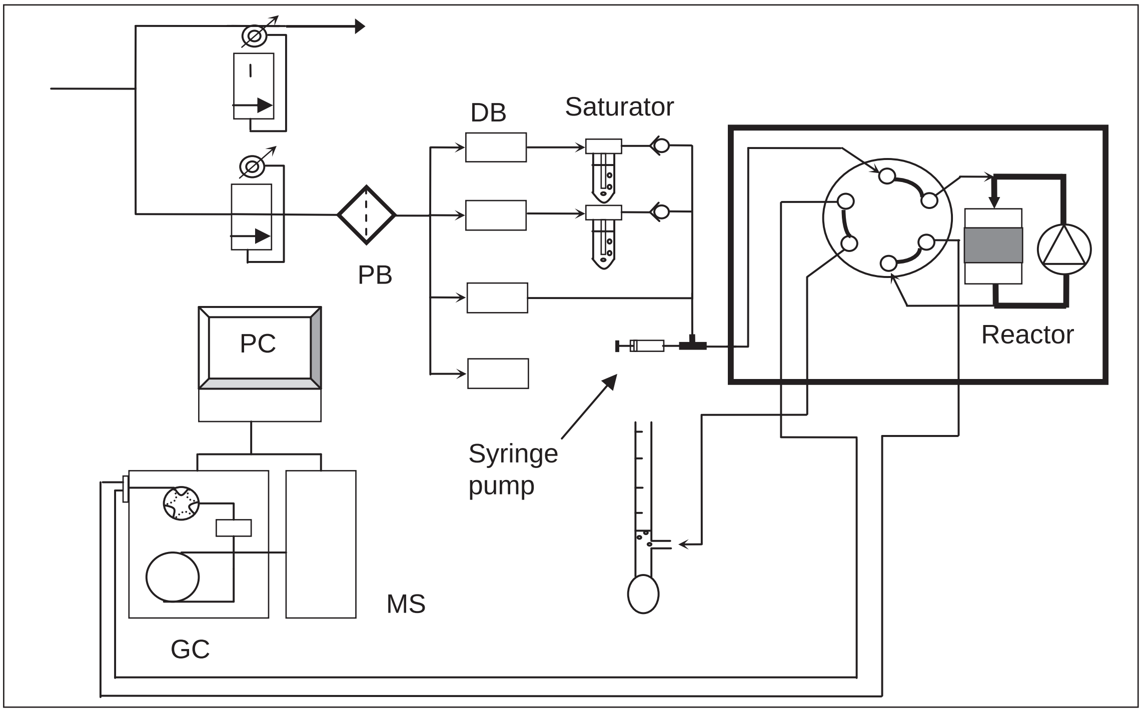

Fig. 1. Experimental setup: GC is a gas chromatograph; MS is a mass-spectrometer; PC is a personal computer; PB is a gas purification block; DB is a gas dosage block.