

Effect of photocatalytic activity of CO oxidation on Pt/TiO₂ by strong interaction between Pt and TiO₂ under oxidizing atmosphere

Qiuye Li, Ke Wang, Shunli Zhang, Min Zhang, Jianjun Yang, Zhensheng Jin*

Key Laboratory of Special Functional Materials, Henan University, Kaifeng 475001, China

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Abstract

The effect of photocatalytic activity of CO oxidation on Pt/TiO₂ catalysts under oxidizing atmosphere was investigated. A strong metal-support interaction (SMSI) between Pt and TiO₂ have been found by means of XPS and in situ Ar⁺ sputtering test after Pt/TiO₂ films being calcinated at 673 K under oxygen for 2 h, which was also corroborated by the photoelectrochemical measurement. When Pt/TiO₂ catalysts were calcinated at 673 K in air, the SMSI between Pt and TiO₂ occurred. Pt atoms on the surface thermally diffuse into the lattice of TiO₂ grains, and then the contact resistance on the interface decreases. The migration velocity of the photo-generated electrons from the surface of TiO₂ to Pt particles increases, which may bring out the enhancement of the photocatalytic activity of CO oxidation.

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1. Introduction

The activity of a supported catalyst has a close relationship with conditions in the post-treatment. For example, after being prepared, Pt/TiO₂ catalyst often needs oxidation or reduction treatment under a proper temperature [1–5]. In the past two decades, the strong interaction between Pt and TiO₂ at the interface under reducing-gas (H₂) atmosphere has been studied by many scientists [6–14]. The principle characteristic of strong metal-support interaction (SMSI) catalysts is the almost complete suppression of H₂ and CO chemisorption on the supported noble metal. Recently, Zhang et al. [1] found that the strong interaction will also happen if Pt/TiO₂ is treated in oxygen ambience at a high temperature. In the paper, since the Pt colloid is prepared using poly (*N*-vinyl-2-pyrrolidone) (PVP) as a stabilizing agent, the protected PVP that affected the photocatalytic activity can decompose only through annealing. Therefore, the effect of SMSI on photocatalytic activity cannot be determined using a PVP-Pt⁰/TiO₂ catalyst.

In this paper, we used the method of sodium citrate reduction of H₂PtCl₆ [15] to prepare Pt colloid, and investigated the pho-

toelectrochemical properties and photocatalytic activity of CO oxidation on catalyst Pt/TiO₂ under UV irradiation, and related them with the results of Ar⁺ sputtering tests.

2. Experimental

2.1. Preparation of Pt/TiO₂ photocatalysts

TiO₂ powder HR3 (Zhoushan Mingri Nanometer Material Company, China) was used as the precursor. Before deposition, raw TiO₂ was pretreated at 773 K for 4 h in air to stabilized its surface area (from 267 decreased to 102 m² g⁻¹) and the anatase crystal form. The Pt colloid was prepared using the method of sodium citrate reduction of H₂PtCl₆, Fig. 1 shows the TEM image of Pt colloid, its size is homogeneous distributed, and the average size is about 4–5 nm.

Pt/TiO₂ powder catalysts were prepared as follows: 0.4 g of pre-treated TiO₂ powder was put in a beaker, then appropriate Pt colloid and NaCl were added. After evaporated at 80 °C, the mixture was washed with distilled water, until no Cl⁻ was detected. The samples had Pt contents of 0.5, 1.0, and 2.0 wt.% (ESCA results: 0.25, 0.47, 0.66 at.%), respectively. All Pt/TiO₂ catalysts were stabilized at 423 K under nitrogen atmosphere.

A well-dispersed suspension (5 mg ml⁻¹) of Pt/TiO₂ was repeatedly spread on both sides of a 0.9 cm × 11 cm surface-

* Corresponding author. Tel.: +86 378 2852533; fax: +86 378 2852533.
E-mail address: zhenshengjin@henu.edu.cn (Z. Jin).

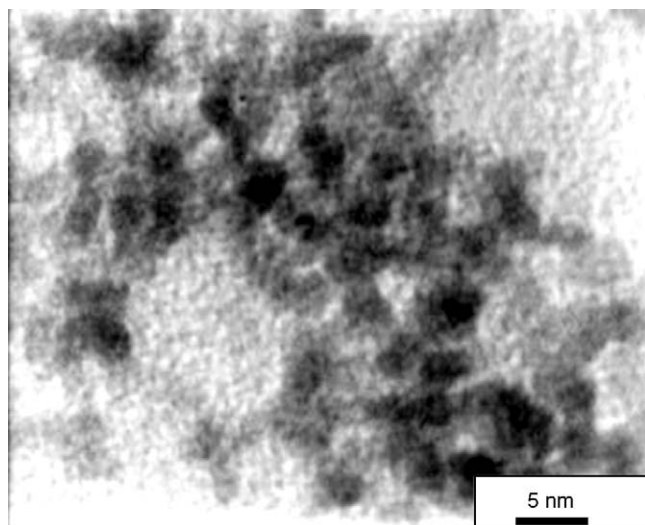


Fig. 1. TEM image of Pt colloid.

roughened glass plate and then heated at 423 K in nitrogen for 2 h, the sample was noted as A; the mass of Pt/TiO₂ deposited on the plate was ca. 30 mg. After examined the photocatalytic activity of CO oxidation, sample A was annealed at 673 K in air for 2 h, the sample obtained was noted as B.

2.2. Photocatalytic experiments

The photocatalytic reactor was made of a flat quartz tube, the dead space of the tube with a glass plate (0.9 cm × 11 cm × 0.2 cm) in it to support the catalyst was 14 mL. Two 4 W black light lamps ($\lambda = 365$ nm, $h\nu = 3.40$ eV) from the Beijing Institute of Electric Light Source were located outside the flat quartz reactor (the distance between the lamps and the glass plate were 1.5 cm), with a 3 mW cm⁻² for each light intensity illuminated on the catalyst. The results obtained using this equipment can be treated with a plug flow model [2,16].

A feed gas of ca. 200 ppmV CO was made up of CO (purity 99.99%) and air, and was stored in a high-pressure cylinder. The change in CO concentrations before and after reaction was determined by a chromatographic method. Before entering into a 13X molecular sieve column, the gas sample was first passed through a small tube filled with soda asbestos to absorb the formed CO₂. After passing through the 13X molecular sieve separating column, CO was methanized on the Ni catalyst and was detected by a gas chromatograph (Type-3420, Beijing Factory of Analytical Instruments) using a hydrogen flame detector. By standardization with known concentration of CO in air, a linear relation between CO concentration and integral signal intensity in the range of 0–1000 ppm V was obtained. The sensitivity of analysis for CO was 1 ppm V.

2.3. Photoelectrochemical measurements

The photoelectrochemical measurements were carried out in a photoelectro-chemical cell with a quartz window in three-electrode mode, by which a saturated calomel electrode was used

as the reference electrode and a platinum patch as the auxiliary electrode. The supporting electrolyte was a 0.1 mol l⁻¹ Na₂SO₄ solution. The working electrodes were prepared as follows: the well-dispersed suspension (5 mg ml⁻¹) of Pt/TiO₂ was put on the conducting indium–tin oxide (ITO) glasses (1 cm × 1 cm, $R = (80 \pm 10)$ Ω/sq, AnHui Huaguang Glass Group Corporation) using a five-time dip-coating method, and was treated at 423 K under nitrogen atmosphere and 673 K in air for 2 h, respectively. After cooled down, Pt/TiO₂/ITOs were fabricated into electrodes [17]. The photocurrent–voltage curve was investigated on a DJS292-type potentiostat. The lamp-house was a 8 W black light lamp, with the light intensity of 0.6 mW/cm² illuminated on the electrode surface.

2.4. Preparation of Pt/TiO₂ film sample

X-ray photoelectron spectroscopy (XPS) is an effective tool to determine the surface concentration of solid and the valence state of atom. When XPS analyses combine with in situ Ar⁺ ion sputtering tests, the change of the component of surface and the valence state of atom can be obtained. When only sputtering in situ by Ar⁺ ion is used, the information of the strong interaction between Pt and TiO₂ cannot be acquired due to the distribution of disordered Pt particles on the TiO₂ powder. Therefore, a Pt/TiO₂ film sample is necessary. A TiO₂ film was first prepared using a sol–gel method [18], and then the Pt colloid was deposited on it. For the convenience of investigating, the conditions for the treatment of Pt/TiO₂ film were the same as those used for Pt/TiO₂ powder catalyst.

2.5. Characterization of photocatalysts

Transmission electron microscopic (TEM) patterns were taken on a JEM-2010 electron microscope. X-ray photoelectron spectroscopic characterizations and Ar⁺ ion sputtering in situ tests were performed using an ESCALAB210 X-ray photoelectron spectrometer (C1s = 284.8 eV was used as the reference, X-ray beam area = 300 μm × 700 μm).

3. Results and discussion

3.1. CO photocatalytic oxidation on Pt/TiO₂ catalysts

The catalytic oxidation of CO with O₂ is one of the simple bimolecular surface reactions and often used as a model for the research of the photocatalytic-oxidation reaction [19–22]. It is well known that the reaction rate of CO oxidation on platinum metals is of first order with respect to CO at low CO concentration. The effect of calcination temperature and Pt contents of Pt/TiO₂ on CO photocatalytic activity was investigated. The results of CO photocatalytic activity of Pt/TiO₂ at 423 K under nitrogen atmosphere and 673 K in air are shown in Fig. 2a and b, respectively, and the kinetic constants were calculated. Fig. 3 displays the relationship between the kinetic constants (k) and the contents of platinum. Both results of Figs. 2 and 3 indicate that the photocatalytic activity of CO oxidation increases when different Pt loaded Pt/TiO₂ calcinated at 673 K in air are used.

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