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Effect of photocatalytic activity of CO oxidation on Pt/TiO_2 by strong interaction between Pt and TiO_2 under oxidizing atmosphere

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Abstract

The effect of photocatalytic activity of CO oxidation on Pt/TiO_2 catalysts under oxidizing atmosphere was investigated. A strong metal-support interaction (SMSI) between Pt and TiO_2 have been found by means of XPS and in situ Ar^+ sputtering test after Pt/TiO_2 films being calcinated at 673 K under oxygen for 2 h, which was also corroborated by the photoelectrochemical measurement. When Pt/TiO_2 catalysts were calcinated at 673 K in air, the SMSI between Pt and TiO_2 occurred. Pt atoms on the surface thermally diffuse into the lattice of TiO_2 grains, and then the contact resistance on the interface decreases. The migration velocity of the photo-generated electrons from the surface of TiO_2 to Pt particles increases, which may bring out the enhancement of the photocatalytic activity of CO oxidation.

Keywords: Photocatalysis; CO oxidation; Strong interaction; Pt/TiO_2

1. Introduction

The activity of a supported catalyst has a close relationship with conditions in the post-treatment. For example, after being prepared, Pt/TiO_2 catalyst often needs oxidation or reduction treatment under a proper temperature [1–5]. In the past two decades, the strong interaction between Pt and TiO_2 at the interface under reducing-gas (H_2) 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 H_2 and CO chemisorption on the supported noble metal. Recently, Zhang et al. [1] found that the strong interaction will also happen if Pt/TiO_2 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-Pt^0/TiO_2 catalyst.

In this paper, we used the method of sodium citrate reduction of H_2PtCl_6 [15] to prepare Pt colloid, and investigated the photoelectrochemical properties and photocatalytic activity of CO oxidation on catalyst Pt/TiO_2 under UV irradiation, and related them with the results of Ar^+ sputtering tests.

2. Experimental

2.1. Preparation of Pt/TiO_2 photcatalysts

TiO_2 powder HR3 (Zhoushan Mingri Nanometer Material Company, China) was used as the precursor. Before deposition, raw TiO_2 was pretreated at 773 K for 4 h in air to stabilized its surface area (from 267 decreased to 102 $m^2\,g^{-1}$) and the anatase crystal form. The Pt colloid was prepared using the method of sodium citrate reduction of H_2PtCl_6, Fig. 1 shows the TEM image of Pt colloid, its size is homogeneous distributed, and the average size is about 4–5 nm.

Pt/TiO_2 powder catalysts were prepared as follows: 0.4 g of pre-treated TiO_2 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/TiO_2 catalysts were stabilized at 423 K under nitrogen atmosphere.

A well-dispersed suspension (5 $mg\,ml^{-1}$) of Pt/TiO_2 was repeatedly spread on both sides of a 0.9 cm × 11 cm surface-

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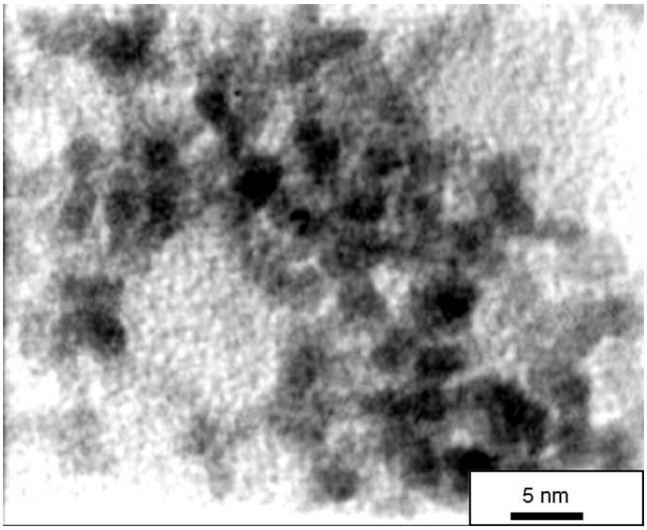

Fig. 1. TEM image of Pt colloid.

roughened glass plate and then heated at 423 K in nitrogen for 2 h, the sample was noted as A; the mass of Pt/TiO_2 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 CO_2. 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} Na_2SO_4 solution. The working electrodes were prepared as follows: the well-dispersed suspension (5 mg ml^{-1}) of Pt/TiO_2 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/TiO_2/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/cm^2 illuminated on the electrode surface.

2.4. Preparation of Pt/TiO_2 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 TiO_2 cannot be acquired due to the distribution of disordered Pt particles on the TiO_2 powder. Therefore, a Pt/TiO_2 film sample is necessary. A TiO_2 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/TiO_2 film were the same as those used for Pt/TiO_2 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/TiO_2 catalysts

The catalytic oxidation of CO with O_2 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/TiO_2 on CO photocatalytic activity was investigated. The results of CO photocatalytic activity of Pt/TiO_2 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/TiO_2 calcinated at 673 K in air are used.

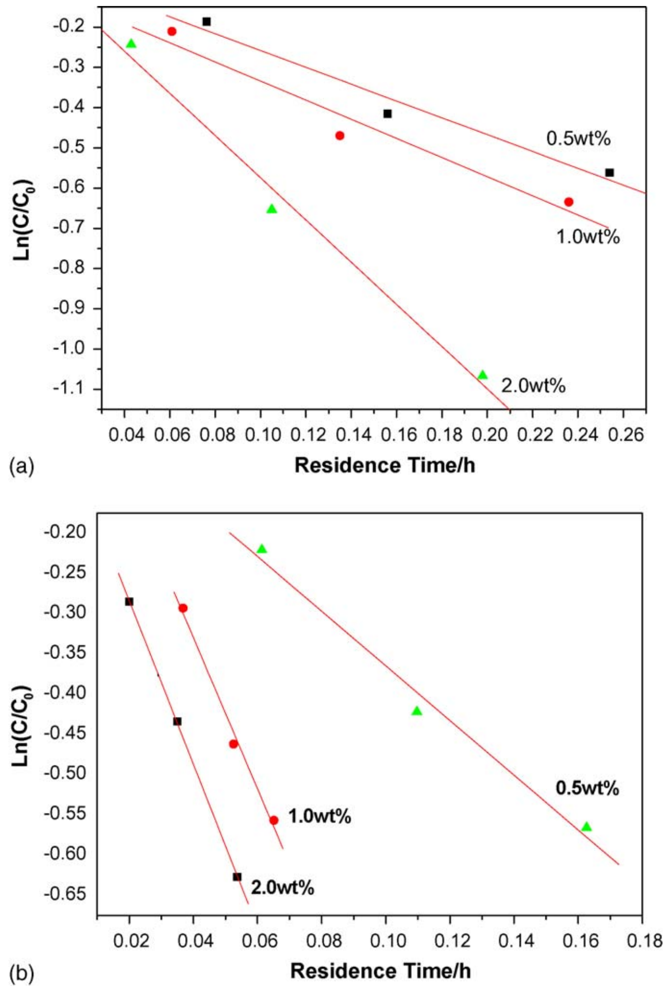

Fig. 2. Effect of different Pt loadings on photocatalytic activity of CO oxidation on Pt/TiO_2 (C_0: CO concentration of feed gas, C: CO concentration after reaction): (a) Pt/TiO_2 stabilized under nitrogen atmosphere at 423 K for 2 h. (b) Pt/TiO_2 first stabilized under nitrogen atmosphere at 423 K for 2 h and then annealed at 673 K in air for 2 h.

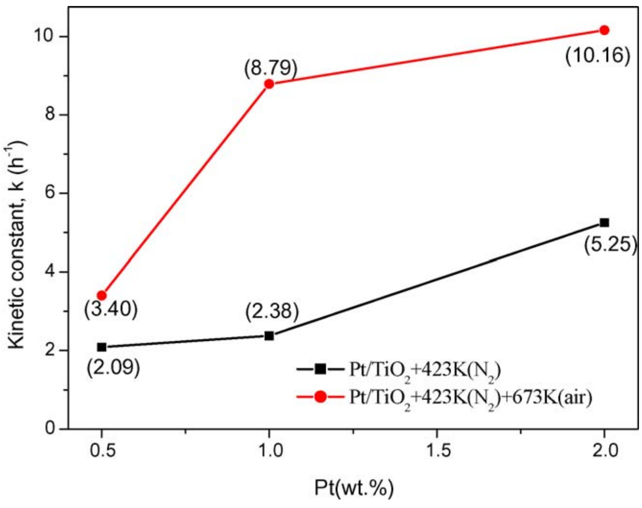

Fig. 3. Relationship between kinetic constants (k) and contents of Pt loadings (k in bracket is calculated according to Fig. 2).

The CO photocatalytic activity improves with the increase of Pt contents within 0.5–2 wt.%.

In the process of CO photocatalytic-oxidation, the dissociative chemisorption of O_2 is the pre-requisite for CO catalytic oxidation on platinum metals. The mechanism of CO oxidation on platinum is as follows [23–25]:

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+) \tag{1}$$

$$O_2 \xrightarrow{Pt} O_{2(a)} \xrightarrow{+e^-} O_{2^-(a)} \rightarrow O_{(a)} + O^-_{(a)} \tag{2}$$

$$CO \rightarrow CO_{(a)} \tag{3}$$

$$O^-_{(a)} + CO \rightarrow CO_2 \tag{4}$$

$$CO_2 + h^+ \rightarrow CO_2 \uparrow \tag{5}$$

$$O^-_{(a)} + h^+ \rightarrow O_{(a)} \tag{6}$$

$$CO_{(a)} + O_{(a)} \rightarrow CO_{2(a)} \rightarrow CO_2\uparrow \tag{7}$$

From formula (7), the velocity of product (CO_2) can be displayed as:

$$d[CO_2]/dt \quad [CO_{(a)}]\,[O_{(a)}] = k\,[O_{(a)}] \tag{8}$$

Eq. (8) indicates that the reaction velocity, d[CO_2]/dt, is in proportion to the concentration of oxygen atom on the surface. When the other experimental conditions are the same, the first order kinetic constant (k) will improve with the increase of concentration of $O_{(a)}$. The bond energy of $O_2{}^-$ is lower than that of O_2 (the former is 94.5 kcal/mol, while the latter is 118 kcal/mol), so $O_2{}^-$ is easier than O_2 to decompose to oxygen atom. Therefore, the concentration of oxygen atom on the surface will increase when the velocity of the photo-generated electron transfer from TiO_2 to Pt metal is accelerated.

3.2. Photoelectrochemical properties of Pt/TiO_2 electrodes

In the process of photocatalytical reaction, the velocity of photo-generated electron transfer from the bulk to surface is often the control step of the reaction velocity. Using a photoelectrochemical method, the transfer velocity of electron can be estimated. Fig. 4 shows the photocurrent–potential curve of Pt/TiO_2 electrodes. The potential at the point of zero photocurrent is the flat band potential (E_{fb}), where no band bending occurs, and the product velocity of photo-generated electron–hole pairs is equal to the recombination velocity, so the photocurrent equals to zero. At the zero photocurrent point, all the curves almost intersect at one dot, indicating that no change occurs after Pt being loaded on the surface of TiO_2. The photocurrent of Pt/TiO_2 electrodes treated at 673 K in air is higher than that treated at 423 K under nitrogen atmosphere and the photocurrent gradually increases with the increase of the contents of the loaded Pt. Fig. 5 shows the relationship between the balance photocurrent and the contents of the loaded Pt. The pattern of the curves in Fig. 5 conforms to that of Fig. 3. Photocurrent represents the transfer velocity of photo-generated charges, the larger the photocurrent, the more the charge transfer, the oxygen dissociative chemisorption on

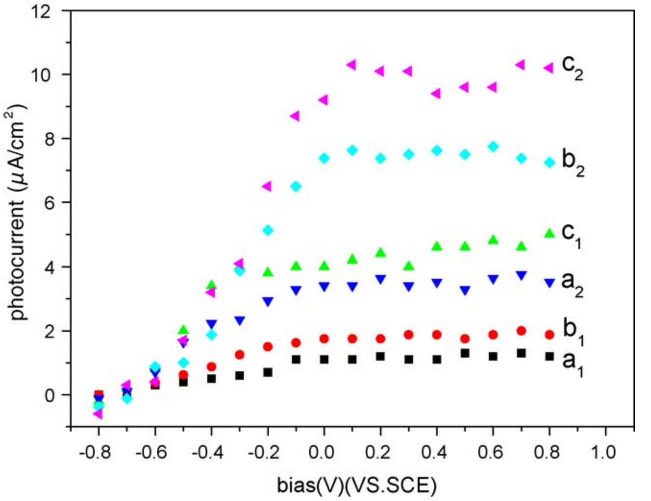

Fig. 4. Photocurrent–voltage curves of Pt/TiO_2 electrodes: a_1, b_1, c_1 denote Pt (0.5 wt.%)/TiO_2, Pt (1 wt.%)/TiO_2, Pt (2 wt.%)/TiO_2 stabilized under nitrogen atmosphere at 423 K for 2 h, respectively. a_2, b_2, c_2 denote Pt (0.5 wt.%)/TiO_2, Pt (1 wt.%)/TiO_2, Pt (2 wt.%)/TiO_2 annealed at 673 K in air for 2 h, respectively.

the surface will be accelerated, which will help to improve the photocatalytic activity of CO oxidation.

3.3. Strong interaction on Pt/TiO_2 after treatment at 673 K under oxygen atmosphere

After the treatment of the different Pt-loaded TiO_2 electrodes at 673 K in air, we analyzed the reason for the increase in the transferring velocity of the photo-generated charges from the bulk to the surface. XPS analyses were carried out to determine the surface concentration and valence state of Pt (2 wt.%)/TiO_2 film sample under different treating conditions. Figs. 6 and 7 show the dependence of Pt_{4f} spectra on sputtering time (t). Before calcination, the valence state of Pt is zero [$E_b(Pt_{4f7/2}) = 70.7 \pm 0.1$ eV] (Fig. 8). After Pt/TiO_2 being stabilized at 423 K under nitrogen atmosphere, the E_b value of $Pt_{4f7/2}$ peak increases with t ($\Delta E_b = 0.37$ eV between $t = 0$ and 13 min);

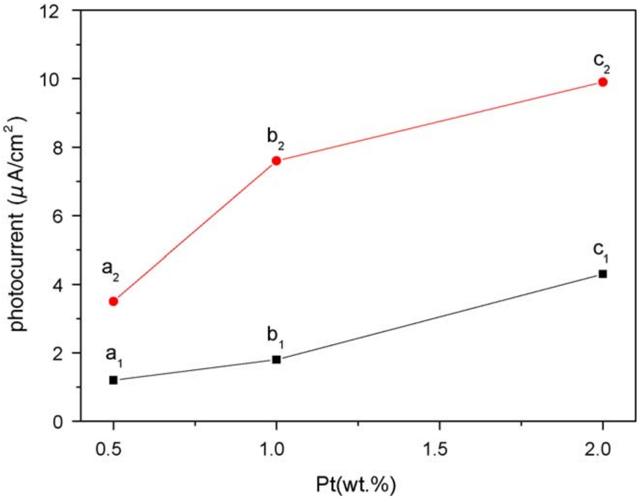

Fig. 5. The relationship between the balanced photocurrent of Pt/TiO_2 and the contents of Pt (the balanced photocurrent was calculated according to Fig. 4).

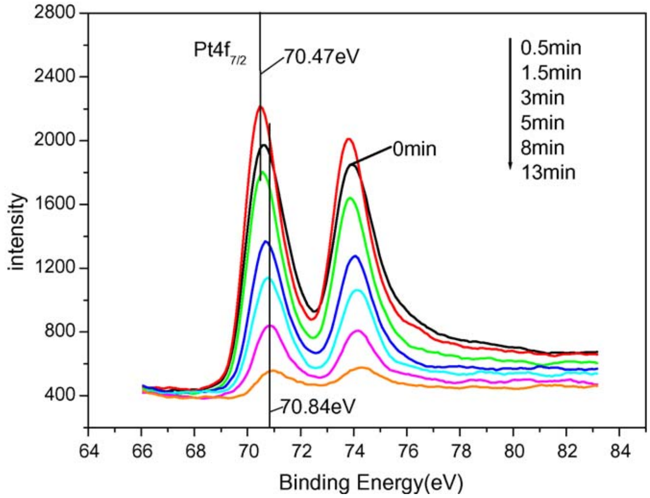

Fig. 6. Dependence of Pt 4f spectra on sputtering time for Pt (2 wt.%)/TiO_2 at 423 K under nitrogen atmosphere ($\Delta E_b = 0.37$ eV).

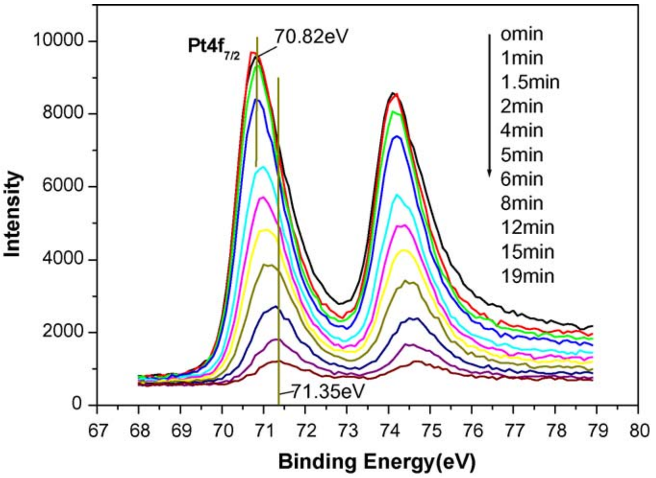

Fig. 7. Dependence of Pt 4f spectra on sputtering time for Pt (2 wt.%)/TiO_2 at 673 K in air ($\Delta E_b = 0.60$ eV).

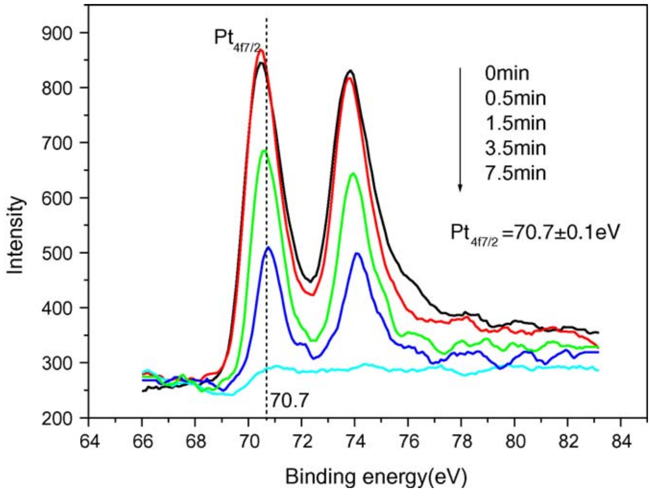

Fig. 8. Dependence of Pt 4f spectra on sputtering time for Pt (2 wt.%)/TiO_2 untreated.

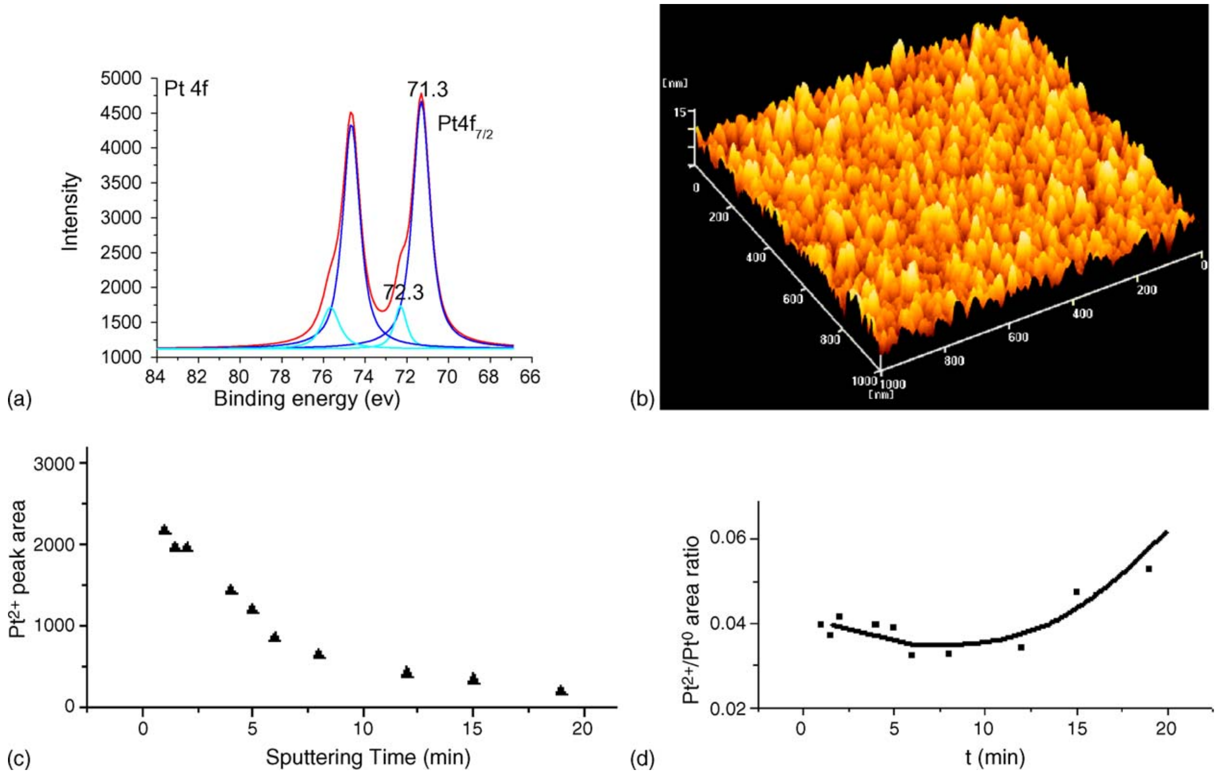

Fig. 9. Sputtering tests for Pt (2 wt.%)/TiO_2 calcinated at 673 K in air for 2 h: (a) deconvolution of Pt 4f spectrum at $t = 6$ min; (b) Pt^{+2}–t curve; (c) AFM picture (before calcination); (d) Pt^{+2}/Pt^0–t curve.

and after Pt/TiO_2 being calcined at 673 K in air, the E_b value of $Pt_{4f7/2}$ peak also increases with t ($\Delta E_b = 0.6$ eV between $t = 0$ and 19 min). This is an important phenomenon. Fig. 9a is a typical deconvolution spectrum of the sample calcined at 673 K in air at $t = 6$ min. The deconvolution of Pt_{4f} spectrum reveals that in addition to Pt^0 (E_b of $Pt_{4f7/2}$ is 71.0 eV) there is still a $Pt_{4f7/2}$ peak of $E_b = 72.3$ eV, which corresponds to Pt^{2+}. Before calcination of Pt/TiO_2 sample the sputtering tests show that E_b(Pt4f7/2) does not change with t (Fig. 8) and keeps at 70.7 ± 0.1 eV (i.e. Pt^0), which proves that no Pt^{2+} exists in the interior of the Pt particles prepared by the method of sodium citrate reduction of H_2PtCl_6. As well known, Pt^0 metal cannot be oxidized to PtO in air even at high temperature. Through the dissociative adsorption of O_2, only one Pt–O monolayer can be formed on the surface of Pt^0 metal [24]. So we infer that Pt^{2+} must exist in the TiO_2 grains. The Pt^{+2}–t curve (Fig. 9b) represents the change of Pt^{2+} concentration verses depth for TiO_2 grains. Due to the Pt^0 particles are spherical (Fig. 1) and randomly distributed on TiO_2 film (RMS = 1.8 nm) (Fig. 9c), the Pt^{+2}/Pt^0–t curve first slightly decreases (at $t = 1$–5 min), then increases (at $t = 5$ min) (Fig. 9d). These facts evidence that during the process of calcination the Pt atoms thermally diffuse from Pt particles into the lattice of TiO_2 grains and substitute for Ti^{4+} to form Pt^{2+}. Therefore, the photoelectrochemical properties of the semiconductor TiO_2 changed. As a result, the contacted resistance on the interface decreases, which is beneficial for the transfer of the photo-generated electron. And this is the reason of why the balanced photocurrent of Pt/TiO_2 electrode improves and the photocatalytic activity of CO oxidation increases after calcination at 673 K in air.

4. Conclusions

The effect of photocatalytic activity of CO oxidation on Pt/TiO_2 catalysts under oxidizing atmosphere was investigated. A SMSI between Pt and TiO_2 have been found by means of XPS and in situ Ar^+ sputtering test after Pt/TiO_2 films being calcinated at 673 K under oxygen for 2 h. A similar kind of interaction can quicken the migration velocity of the photo-generated electrons, which can be corroborated by the electrochemical measurement performed on Pt/TiO_2 catalysts. Moreover, a SMSI between Pt and TiO_2 can also be the reason for the increase of photocatalytic activity of CO oxidation.

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