# Effect of calcination and reduction treatment on the photocatalytic activity of CO oxidation on Pt/TiO$_2$

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## Abstract

The effect of calcination and reduction treatment on the photocatalytic activity of CO oxidation on Pt/TiO$_2$ was investigated at room temperature. The results showed that an optimum calcination temperature of CO photocatalytic activity was at 673 K for 2 h in air and the higher temperature detrimental to the enhancement of CO photocatalytic activity. The decreased photocatalytic activity of CO oxidation can be restored by the reduction in H$_2$ atmosphere at 773 K. The X-ray photoelectron spectroscopy (XPS) results show the Pt doped into TiO$_2$ particles when it was calcinated at 673 K for 2 h, which may bring about the enhancement of photocatalytic activity of CO oxidation.
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*Keywords:* Pt/TiO$_2$; X-ray photoelectron spectroscopy; CO photocatalytic activity

## 1. Introduction

TiO$_2$ photocatalysis has been the focus of numerous investigations in recent years [1–2], particularly because its application for the destruction of harmful contaminants appears to be a promising process for water and air pollution control [3]. In order to enhance the photocatalytic activity, the properties of TiO$_2$ have been modified by selective surface treatments, e.g. platinization [4–6].

Being a model reaction, the photocatalytic oxidation of CO using platinized TiO$_2$ has been studied by many scientists [7–10]. It is well known that Pt deposits on TiO$_2$ not only increase the photo-induced electron transfer rate at the interface but also provide catalytic sites. Hwang et al. concluded that Pt nanoparticles deposited on TiO$_2$ in enhancing the CO photooxidation rate provides surface sites on which active oxygen species photogenerated from adsorbed O$_2$ are stabilized [7]. Vorontsov et al. found that CO photocatalytic activity increases with lowering of Pt oxidation state (highest

with Pt$^0$/TiO$_2$) [8]. Gan et al. observed that both TiO$_2$ surface structure and Pt nanocluster size have profound effects on CO surface chemistry [9]. Although CO photocatalytic oxidation on Pt/TiO$_2$ was investigated by many scientists, the report on the effects of calcination and reduction treatment on CO photocatalytic oxidation is few. In this paper, it was found that after calcinating at 673 K, Pt doped into TiO$_2$ lattice which can greatly enhance the activity of CO photocatalytic oxidation.

## 2. Experimental

### 2.1. Preparation of Pt/TiO$_2$ photocatalysts

TiO$_2$ powder (Zhoushan Mingri Nanometer Material Company, HR3) was used as the precursor and the reference. Before deposition, All TiO$_2$ sample was pretreated at 773 K for 4 h in air which makes its specific BET surface areas decrease from 267 to 102 m$^2$ g$^{-1}$, but the anatase crystal form remain unchanged. TiO$_2$ film was deposited on a glass plate

using a dip-coating technique. A well-dispersed suspension (5 mg ml$^{-1}$) of TiO$_2$ was repeatedly spread on both sides of a 0.9 × 11 cm$^2$ surface-roughened glass plate then heated at 473 K in air for 2 h. The mass of TiO$_2$ deposited on the plate was ca. 30 mg.

The Pt/TiO$_2$ was prepared as follows: a mixture of 120 ml anhydrous ethanol, 13 ml deionized water, 15 ml 6.0 mM H$_2$PtCl$_6$ (AR, Changchun Fine Chemical Industry Plant, China) aqueous solution and 0.01 g poly(*N*-vinyl-2-pyrrolidone) (PVP) (AR, Shanghai Chemical Reagent Company of China National Medicine Group) were added into a flask and refluxed for 3 h under magnetically stirring, then the dark-brown PVP-protected Pt$^0$ sol was obtained [11]. TiO$_2$ powder was added into a beaker with PVP-Pt$^0$ sol solution to form a suspension, then the suspension was repeatedly spread on both sides of a 0.9 × 11 cm$^2$ surface-roughened glass plate, then the plate was calcinated for 2 h at 673 K in air. The loaded Pt amount increased with increase of the amount of PVP-Pt$^0$ sol. The samples had the Pt contents of 0.5, 1.0, and 2.0 wt.%, respectively. The mass of Pt/TiO$_2$ deposited on the plate was ca. 30 mg.

### 2.2. Characterization of photocatalysts

X-ray photoelectron spectroscopy (XPS) characterizations and Ar$^+$ ion sputtering tests in situ were performed using an ESCALAB210 X-ray photoelectron spectrometer (taking C$_{1s}$ = 284.8 eV as reference, X-ray beam area = 300 µm × 700 µm). The Brunauer–Emmett–Teller (BET) surface areas of the TiO$_2$ powder before and after calcination were measured by ASAP-2010.

### 2.3. 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 (λ = 365 nm, *hν* = 3.40 eV) of Beijing Institute of Electric Light Source were located outside the flat quartz reactor (the distance between the lamp and glass plate was 1.5 cm), light intensity illuminated on the catalyst was 3 mW cm$^{-2}$ for each one. The results obtained using this equipment can be treated with a plug flow model.

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 of CO concentration before and after reaction was determined by chromatographic method. Before entering into a 13X molecular sieve column, the gas sample went through a small tube filled with soda asbestos first to absorb the formed CO$_2$. After passing through the separating column of 13X molecular sieve, CO was methanized on Ni catalyst and was detected by 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
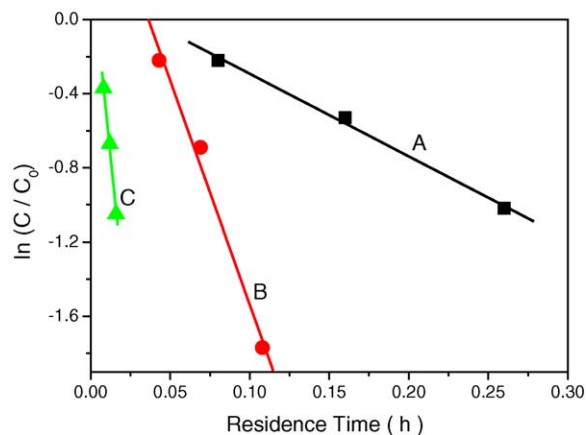


Fig. 1. The effect of different Pt loadings on the photocatalytic activity of CO oxidation on Pt/TiO$_2$ ($C_0$ is the CO concentration of feed gas and $C$ the CO concentration after reaction): (A) 0.5 wt.%; (B) 1.0 wt.%; (C) 2.0 wt.%.

intensity in the range of 0–1000 ppmv was obtained. The sensitivity of analysis for CO is 1 ppmv.

## 3. Results and discussion

### 3.1. CO photocatalytic oxidation on TiO$_2$ and Pt/TiO$_2$

For evaluating the photocatalytic activity of Pt/TiO$_2$ and determining the optimum content of deposited Pt, photocatalytic oxidation of CO was investigated under UV light irradiation (λ = 365 nm). First, TiO$_2$ and Pt/TiO$_2$ were compared for their photocatalytic activity of CO oxidation at room temperature. The results showed that no CO photocatalytic oxidation takes place on TiO$_2$ under UV light irradiation, which is consistent with the previous report [12–13]. When Pt nanoparticles were deposited on TiO$_2$ surface and calcinated in air at 673 K for 2 h, it exhibits great photocatalytic activity of CO oxidation under UV light irradiation, and CO
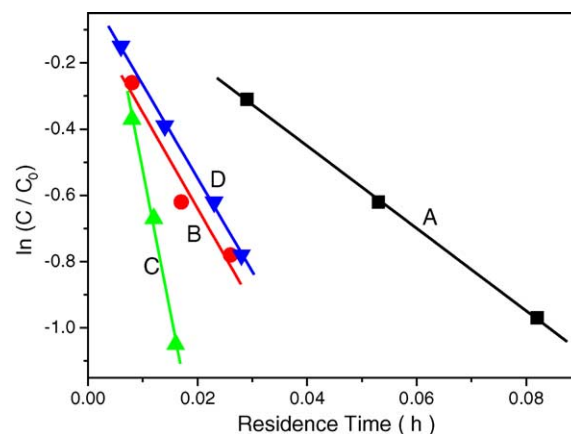


Fig. 2. The effect of different calcination temperatures on the photocatalytic activity of CO oxidation on Pt (2 wt.%)/TiO$_2$ ($C_0$ is the CO concentration of feed gas and $C$ the CO concentration after reaction): (A) untreated; (B) 573 K; (C) 673 K; (D) 773 K.

Table 1
The kinetic constants of CO photocatalytic oxidation of Pt (2 wt.%)/TiO$_2$ at different calcination temperatures

| Calcination temperature (K) | Kinetic constant, $k$ (h$^{-1}$) | Correlation coefficient, $R$ |
|---|---|---|
| Untreated | 12.4 | 0.9998 |
| 573 | 28.9 | 0.9762 |
| 673 | 85.0 | 0.9977 |
| 773 | 28.2 | 0.9993 |

photocatalytic activity increases with the increase of Pt contents within 0.5–2 wt.% (Fig. 1). It is known that the reaction rate of CO oxidation on platinum metals is first order with respect to CO at low CO concentration. The results indicate that the first-order kinetic constants of Pt (0.5 wt.%)/TiO$_2$, Pt (1 wt.%)/TiO$_2$ and Pt (2 wt.%)/TiO$_2$ are 4.5, 24.1, and 85.0 h$^{-1}$, respectively. The constant of Pt (2 wt.%)/TiO$_2$ is about 19 times that of Pt (0.5 wt.%)/TiO$_2$. The rates of CO photocatalytic oxidation show no maximum with increasing

the Pt loading, which is consistent with the Hwang' report [7]. But this is in contrast with the fact the most photocatalytic reactivity of Pt/TiO$_2$ is optimized at a few percent of Pt concentration [14]. This result shows that Pt is main active sites in CO photocatalytic oxidation.

### 3.2. The effect of calcination and reduction treatment of Pt (2 wt.%)/TiO$_2$ on CO photocatalytic oxidation

The effect of calcination temperature of Pt (2 wt.%)/TiO$_2$ on CO photocatalytic oxidation was investigated. All studies were carried out on one Pt (2 wt.%)/TiO$_2$ sample. The results of CO photocatalytic activity of Pt (2 wt.%)/TiO$_2$ at different calcinating temperature (573, 673 and 773 K) are shown in Fig. 2 and Table 1. The kinetic constants were calculated (Table 1). The constant increased with the increase of calcinating temperature when it was calcinated below 673 K, and decreased when it was calcinated higher than 673 K. This suggests that an optimum calcination temperature was at 673 K
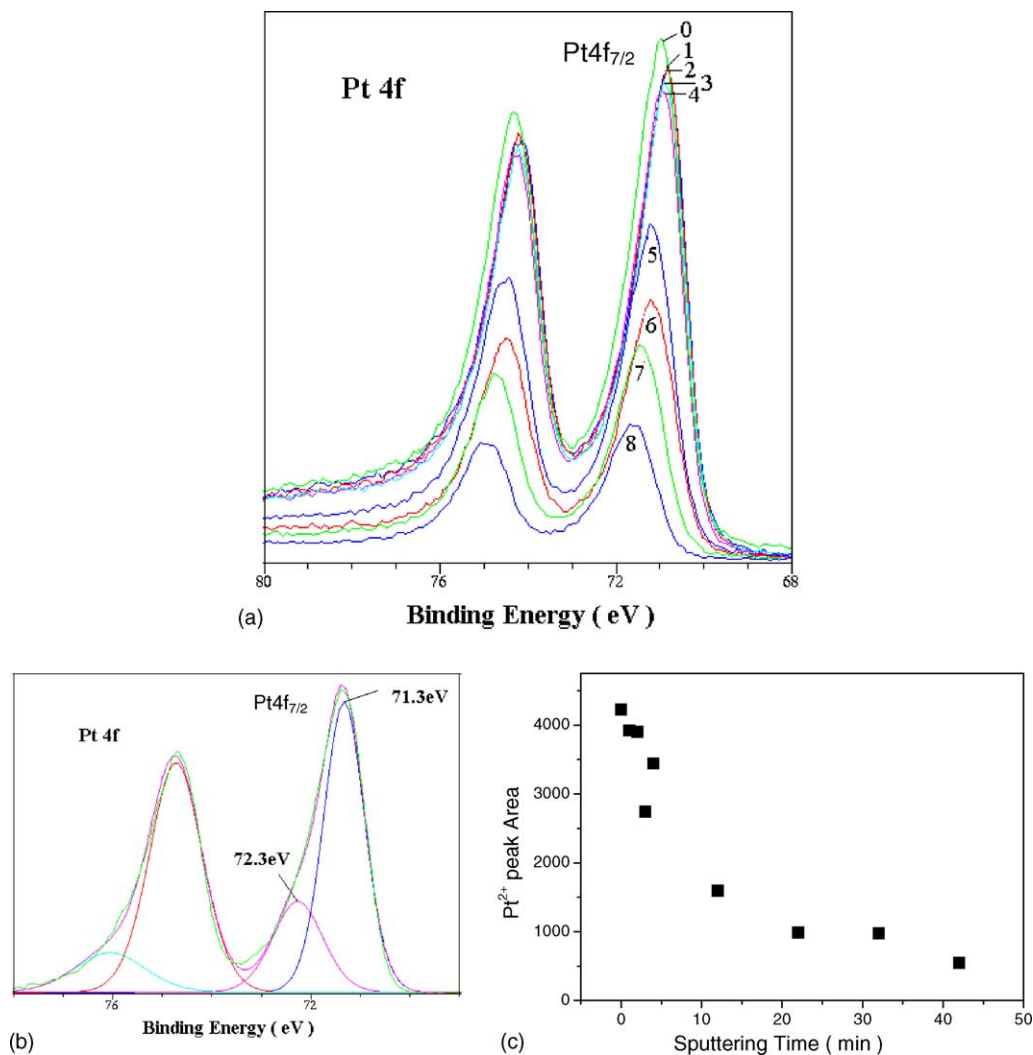


Fig. 3. Sputtering tests for Pt (2 wt.%)/TiO$_2$ calcinated at 673 K: (a) dependence of Pt 4f spectra on $t$; (b) devolution of Pt 4f spectrum at $t = 4$ min; (c) $S$–$t$ curve.

Table 2
The kinetic constants of CO photocatalytic oxidation of Pt (2 wt.%)/TiO$_2$ at different reduction temperatures

| Reduction temperature (K) | Kinetic constant, $k$ (h$^{-1}$) | Correlation coefficient, $R$ |
|---|---|---|
| 473 | 26.2 | 0.9958 |
| 573 | 34.3 | 0.9842 |
| 673 | 58.5 | 0.9639 |
| 773 | 71.4 | 0.9637 |

and the higher temperature detrimental to the enhancement of CO photocatalytic activity.

XPS analyses were carried out to determine the surface concentration and valence state of Pt (2 wt.%)/TiO$_2$ calcinated at 673 K for 2 h. Fig. 3a show the dependence of Pt$_{4f7/2}$ spectra on sputtering time ($t$). Before calcination, the valence state of Pt is zero ($E_b$ = 71.2 eV) [11]. After calcination, at $t \geq 2$ min, $E_b$ value of Pt$_{4f7/2}$ peaks increases with $t$ ($\Delta E_b$ = +0.7 eV between $t$ = 2 and 42 min) (Fig. 3a). The deconvolution results of Pt$_{4f\,7/2}$ spectra reveal that in addition to Pt$^0$ ($E_b$ of Pt$_{4f7/2}$ is 71.3 eV) there is a Pt$_{4f7/2}$ peak of $E_b$ = 72.3 eV yet, which corresponds to Pt$^{2+}$ [15], Fig. 3b is a typical devolution for $t$ = 4 min. Pt$_{4f7/2}$ peak area ($S$) of Pt$^{2+}$ decreases with $t$ (Fig. 3c). Calcinating in air, the inner part of Pt$^0$ particles is impossibly oxidized to form Pt$^{2+}$, so the $S$–$t$ curve shown in Fig. 3c should represent the change of Pt$^{2+}$ concentration versus depth for TiO$_2$ grains. Why at $t$ = 1 min, the $E_b$ value of Pt$_{4f7/2}$ peak shifts to the higher side ca. 0.1 eV (see Fig. 3a), it can be explained by the dissociative chemisorption of oxygen on Pt particle surface to form a monolayer of Pt–O in the course of air calcinations [16]. After sputtering for one minute, this monolayer Pt–O diminished. Above results prove that the Pt doping into TiO$_2$ happened. Calcinating at 673 K, the Pt atoms thermally diffused into lattice of TiO$_2$ grains.

Before calcination, the photocatalytic activity of CO is very low because Pt was covered by PVP which inhibit the CO photocatalytic oxidation on Pt (2 wt.%)/TiO$_2$. When the calcination temperature is higher than the decomposing temperature of PVP, photocatalytic activity of CO oxidation are greatly enhanced on Pt (2 wt.%)/TiO$_2$. After calcination at 673 K, the rate of photocatalytic activity of CO oxidation attains the optimum due to Pt doped into TiO$_2$ particles which may be facilitated the transfer of photo-generated electrons from TiO$_2$ to Pt particles. But the CO photocatalytic activity evidently decreases with the increase of calcination temperature up to 773 K, which may be due to the decrease of surface Pt concentration while a great deal of Pt atoms doped into TiO$_2$ particles. The decrease of the amount of Pt active sites greatly reduces the photocatalytic activity of CO oxidation.

The effect of H$_2$ reduction treatment at different temperatures of 473, 573, 673 and 773 K on CO photocatalytic activity of above Pt (2 wt.%)/TiO$_2$ sample (calcinated at 773 K) was also studied. The results showed that the CO photocatalytic activity increased with the increase of reduction temperature (Fig. 4 and Table 2). Treated in H$_2$ atmosphere, both
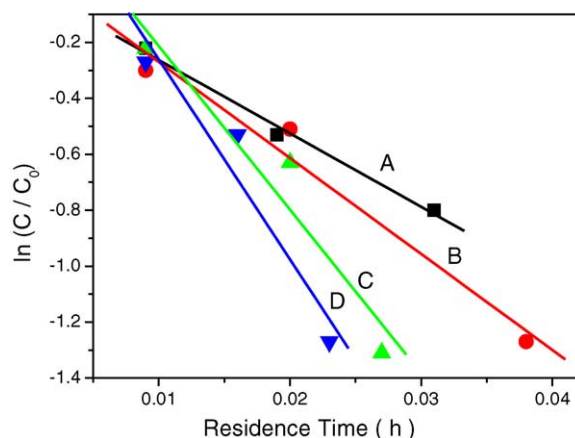


Fig. 4. The effect of different reduction temperatures on the photocatalytic activity of CO oxidation on Pt (2 wt.%)/TiO$_2$ ($C_0$ is the CO concentration of feed gas and $C$ the CO concentration after reaction): (A) 473 K; (B) 573 K; (C) 673 K; (D) 773 K.

TiO$_2$ and Pt$^{2+}$ doped can be reduced at the same time which makes the photocatalytic activity of CO oxidation restored.

## 4. Conclusions

The effect of calcination and reduction treatment on the photocatalytic activity of CO oxidation on Pt/TiO$_2$ was studied under UV light irradiation at room temperature. The XPS results showed that Pt doped into TiO$_2$ grains after calcination at 673 K for 2 h which makes the photocatalytic activity of CO oxidation enhanced. But the higher temperature is detrimental to the enhancement of CO photocatalytic activity. We also found the decreased photocatalytic activity of Pt (2 wt.%)/TiO$_2$ sample (calcinated at 773 K) can be restored by the reduction in H$_2$ atmosphere at 773 K.

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