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Article

Characterization of Pt-TiO₂ film used in three formaldehyde photocatalytic degradation systems: UV_{254 nm}, O₃+UV_{254 nm} and UV_{254+185 nm} via X-ray photoelectron spectroscopy

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ABSTRACT

Photocatalytic degradation of gaseous formaldehyde for 35 h was performed using Pt-TiO₂ film in the following irradiation systems: UV_{254 nm}, O₃+UV_{254 nm}, and UV_{254+185 nm}. Concurrent improvements in formaldehyde degradation and O₃ removal were achieved by modifying TiO₂ with Pt nanoparticles, resulting in a 3.1–3.4-fold O₃ elimination increase. X-ray photoelectron spectroscopy (XPS) of the Pt-TiO₂ film was carried out to assess the electronic states of the Pt nanoparticles and accumulated organic species. The deconvoluted C 1s and O 1s XPS spectra revealed that the content of carbonyl and carboxyl groups on Pt-TiO₂ and degree of catalyst deactivation in the systems studied decreased in the following order: UV_{254 nm} > O₃+UV_{254 nm} > UV_{254+185 nm}. Metallic Pt⁰ was oxidized to a mixture of PtO_{ads} and Pt⁴⁺ species under O₃+UV_{254 nm} and UV_{254+185 nm} irradiation owing to the presence of O₃ and hydroxyl radicals, but remained stable under UV_{254 nm} irradiation. Pt species at higher oxidation states can act as electron trapping centers, and improve the photocatalytic activity of Pt-TiO₂ and provide reactive sites for O₃ decomposition under UV irradiation, resulting in a faster O₃ removal rate than that displayed by TiO₂. The XPS studies provided valuable information to elucidate the beneficial role of Pt species and the reduction of catalyst deactivation under UV_{254+185 nm} irradiation.

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1. Introduction

TiO₂-based heterogeneous photocatalytic oxidation (PCO) is cost-effective and can operate at room temperature and atmospheric pressure. Hence, it has been widely investigated to decompose gaseous pollutants such as volatile organic compounds (VOCs) [1–4]. Formaldehyde (HCHO) is a major indoor pollutant, and efficient removal of it in air has attracted great attention [5–7]. However, some key problems, such as catalyst

deactivation [8,9] and inhibition effect of other molecules (e.g., H₂O, NO) [10,11], hinder the practical application of PCO. Various approaches have been employed to overcome these drawbacks such as combination of PCO with microwave [12], ozone [13,14], and adsorption [15,16].

Vacuum ultraviolet (VUV, $\lambda < 200$ nm) with high-energy photons can dissociate oxygen and water molecules into reactive oxygen species (e.g., O(¹D), O(³P), and O₃) and hydroxyl radicals ([•]OH), which can readily react with various VOCs in

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gas phase [17–19]. The photocatalytic efficiency in removing indoor VOCs remarkably increases under UV_{254+185 nm} irradiation (UV with $\lambda_{\max}$ = 254 nm and minor VUV λ = 185 nm) compared with that achieved under common UV_{254 nm} or UV_{365 nm} irradiation [17–20]. Furthermore, catalyst deactivation is reduced by effective decomposition of nonvolatile intermediates on the catalyst surface [18,19]. Therefore, photocatalysis under UV_{254+185 nm} irradiation is a facile and effective PCO technique for indoor air purification. However, hazardous contaminant O₃ is also generated via dissociation of O₂ with VUV [17,18]. In general, removal of O₃ byproduct, generated during photocatalysis under UV_{254+185 nm} irradiation, has been attempted using two routes: photocatalysis followed by ozone destruction catalysis [18,20], and in situ catalytic destruction using modified photocatalysts, e.g., TiO₂ modified with noble metals [21]. We previously found that Pd-modified TiO₂ films could simultaneously increase the formaldehyde degradation and O₃ elimination under UV_{254+185 nm} irradiation [21]. Additionally, the redox processes of Pd species under UV_{254+185 nm} irradiation were critical for the simultaneous decomposition of formaldehyde and O₃. The electronic states of the noble metal are likely to remarkably differ when noble metal-modified photocatalysts are applied in UV_{254 nm} and UV_{254+185 nm} irradiation photocatalytic systems owing to the presence of VUV-photochemically generated reactive species. Therefore, it is necessary to identify the electronic states of metal species when noble metal-modified photocatalysts are applied in the UV_{254+185 nm} irradiation photocatalytic system.

Lowering of catalyst deactivation was reported for the photocatalytic decomposition of formaldehyde [21], toluene [17,20], and benzene [18] under UV_{254+185 nm} irradiation. Gaseous reaction intermediates were measured to compare the photocatalytic degradation performance under UV_{254 nm} and UV_{254+185 nm} irradiation [18,22], thus to indirectly elucidate the decrease in catalyst deactivation under UV_{254+185 nm} irradiation compared to UV_{254 nm} irradiation. It is well known that accumulation of reaction intermediates on the catalyst surface is a key factor resulting in catalyst deactivation. Hence, quantification of accumulated intermediates could provide direct evidence for assessing degree of catalyst deactivation. However, little information on surface properties of photocatalysts has been reported to directly explain the low degree of catalyst deactivation under UV_{254+185 nm} irradiation.

In this work, we investigated the performance of Pt-modified TiO₂ films (Pt-TiO₂) to photocatalytically remove formaldehyde and O₃ under UV_{254+185 nm} irradiation. To illustrate the mechanism of reduction of catalyst deactivation and elucidate the role of deposited Pt nanoparticles on decomposing O₃, a comparative X-ray photoelectron spectroscopy (XPS) study was conducted to assess the accumulation of organic species on the catalyst surface and changes of the Pt valence states in the Pt-TiO₂ films under three irradiation systems: UV_{254 nm}, O₃+UV_{254 nm}, and UV_{254+185 nm}.

2. Experimental

2.1. Fabrication and characterization of Pt-TiO₂ films

TiO₂ films coated on a Ti wire net (40 mesh) (TiO₂/Ti) were fabricated via a sol-gel dip coating method [23]. Pt nanoparticles (NPs) were deposited on the TiO₂/Ti wire net using a low-temperature electrostatic self-assembly method, as described elsewhere [21,24]. H₂PtCl₆ solution (100 mL, 0.3 mmol/L) containing polyvinyl alcohol (PVA, 300 mg) was cooled in an ice water bath, to which a fresh NaBH₄ solution (4 mL, 0.07 mol/L) was rapidly added under sonication to obtain a reduced Pt colloidal solution. A piece of TiO₂/Ti wire net ($L \times W$ = 80 mm $\times$ 80 mm) was then immersed into the fresh Pt colloidal solution. The negatively charged Pt NPs were spontaneously adsorbed onto the positively charged TiO₂ surface via electrostatic interactions at pH $\approx$ 4. The self-assembly time was 30 min. The TiO₂/Ti wire net was removed from the solution and washed with boiling water to remove adsorbed chloride ions. The dried TiO₂/Ti wire net was then annealed in air at 300 °C for 1.5 h to fabricate the Pt-TiO₂ film.

The morphology of the samples was observed using an ultra-high-resolution field-emission scanning electron microscope (FESEM, S-5500, Hitachi). X-ray diffraction (XRD) analysis was carried out on a Rigaku D/max-RB using Cu K_{α} radiation (λ = 0.15418 nm), operating at 40 kV and 100 mA. The surface properties of the Pt-TiO₂ films were investigated by XPS (PHI-5300, ESCA) at a pass energy of 50 eV, using Al K_{α} as an exciting X-ray source. The base pressure in the measurement chamber was 4.53×10^{-7} Pa. The spectra were calibrated with respect to the C 1s line of graphitic carbon at 284.8 eV. Prior to individual elemental scans, a survey scan was conducted to detect all of the present elements. XPSPEAK software (version 4.1) with a Gaussian-Lorentzian mixed function and Shirley background subtraction was employed to deconvolute the XPS spectra. The peak positions were reproducible as well as the fixed Lorentz/Gaussian ratio of 1:4 and FWHM of the peaks.

2.2. Photocatalytic decomposition studies

The experimental setup is the same as that used in our previous work [21]. All UV lamps were purchased from Guangdong Cnlght Company. Two UV_{254+185 nm} lamps (2 $\times$ 3 W), i.e., ozone-producing low-pressure mercury lamps with $\lambda_{\max}$ at 254 nm and a minor emission (ca. 5%) at λ = 185 nm, were placed in the center of the flow-through reactor with an effective volume of 0.628 L. Two pieces of Pt-TiO₂/Ti wire nets were fixed at both sides of the lamp, respectively. The flow rate was fixed at 1.8 L/min. The inlet concentration of HCHO was set at ca. 0.52 mg/m³. After the inlet and outlet HCHO concentrations reached equilibrium, the UV_{254+185 nm} lamps were turned on. All photocatalytic experiments ran for 35 h. The UV lamps were then turned off to allow the system to equilibrate again. For the O₃-enhanced UV_{254 nm} (O₃+UV_{254 nm}) photocatalysis setup, two low-pressure mercury lamps ($\lambda_{\max}$ = 254 nm, 2 $\times$ 3 W), which do not produce O₃, were used. A mixture of HCHO and O₃ gases was introduced into the reactor. The concentration of added O₃ (ca. 22.5 mg/m³) is comparable with that generated by the two UV_{254+185 nm} lamps. The subsequent steps were the same as those employed in the UV_{254+185 nm} irradiation photocatalytic system. Photocatalysis under UV_{254 nm} irradiation was carried

out in the same manner as photocatalysis under $O_3 + UV_{254\text{ nm}}$ irradiation except that no O_3 was added.

The O_3 concentration was monitored with an online O_3 analyzer (Model 49i, Thermo Electron). The formaldehyde concentration was analyzed by the MBTH method (GB/T18204.28, China). A KI-coated annular denuder was used to remove O_3 for possible interference with formaldehyde analysis.

The HCHO reaction rate (R_{HCHO} , $\text{mg}/(\text{m}^3 \cdot \text{min})$) and O_3 decomposition rate (R_{O_3} , $\text{mg}/(\text{m}^3 \cdot \text{min})$) were calculated as follows:

$$R_{\text{HCHO}} = [Q \times ([\text{HCHO}]_{\text{initial}} - [\text{HCHO}]_{\text{steady}})]/V \quad (1)$$

$$R_{O_3} = [Q \times ([O_3]_{\text{VUV}} - [O_3]_{\text{steady}})]/V \quad (2)$$

where $[\text{HCHO}]_{\text{initial}}$ is the equilibrium concentration of HCHO before irradiation; $[\text{HCHO}]_{\text{steady}}$ is the steady-state outlet concentration of HCHO following the 35-h photocatalytic reaction; $[O_3]_{\text{VUV}}$ is the outlet concentration of the VUV-generated O_3 (in the absence of photocatalysts) or the added O_3 ($22.5\text{ mg}/\text{m}^3$); $[O_3]_{\text{steady}}$ is the steady-state concentration of O_3 in the $O_3 + UV_{254\text{ nm}}$ and $UV_{254+185\text{ nm}}$ irradiation photocatalytic systems; Q (m^3/min) is the flow rate of HCHO gas; and V (m^3) is the effective volume of the reactor.

3. Results and discussion

3.1. Characterization of Pt-TiO₂ films

An ultra-high-resolution FESEM image of the Pt-TiO₂ film is shown in Fig. 1. Pt NPs (white dots) were uniformly dispersed on the TiO₂ surface. The average size of the Pt NPs was 1.9 nm, indicating the presence of a large amount of surface unsaturated atoms in Pt NPs. The surface density of the Pt NPs was 1.43×10^{12} NPs/ cm^2 , which was almost one order of magnitude higher than that of deposited Pd NPs in our previous work [21]. As shown in Fig. 1 inset, approximately 4–8 Pt NPs were deposited onto each TiO₂ particle. The uniform dispersion of ultrafine Pt NPs is beneficial for increasing the amount of reactive sites and metal-TiO₂ contact area.

XRD patterns (Fig. 2) suggest that the as-synthesized TiO₂ film has a well-organized crystal structure, comprising 62.5% anatase and 37.5% rutile. Following the self-assembly process,

Fig. 1. Ultra high-resolution FESEM image of TiO₂ film modified with Pt nanoparticles.

Fig. 2. XRD patterns of as-prepared TiO₂ (1) and Pt-TiO₂ film (2) (in the absence of the Ti wire net support).

the resulting crystalline structure of TiO₂ showed no notable changes. The presence of Pt NPs in the Pt-TiO₂ film is indicated by the diffraction peaks at $2\theta = 39.9^\circ$, 46.4° , 67.5° , and 81.3° (Fig. 2) that can be attributed to the (111), (200), (220), and (311) reflections of metallic Pt (JCPDS 4-0802), respectively. The broad diffraction peaks strongly indicate the nanocrystalline nature of the deposited Pt NPs. The XRD result reveals that the metallic form of the deposited Pt NPs was maintained following annealing in air at 300°C .

3.2. Photocatalytic HCHO degradation and O_3 elimination

The performance of HCHO degradation and O_3 elimination using pure TiO₂ and Pt-TiO₂ photocatalysts was assessed under $UV_{254\text{ nm}}$, $O_3 + UV_{254\text{ nm}}$, and $UV_{254+185\text{ nm}}$ irradiation. Figure 3 presents the HCHO reaction rate as a function of irradiation time over TiO₂ and Pt-TiO₂ photocatalysts under the three irradiation processes. The degradation rate of HCHO decreased in the order of $UV_{254+185\text{ nm}} > O_3 + UV_{254\text{ nm}} > UV_{254\text{ nm}}$ for both photocatalysts studied. As HCHO can be easily degraded in gas phase via photochemical processes under 185-nm VUV irradiation, the HCHO degradation rate under $UV_{254+185\text{ nm}}$ irradiation was the highest among the three processes. Deactivation of the pure TiO₂ and Pt-TiO₂ did not take place under $UV_{254+185\text{ nm}}$ irradiation, as indicated by the absence of a decreased HCHO reaction rate during the 35-h photocatalytic process. However, reduced HCHO reaction rates were noted in both $O_3 + UV_{254\text{ nm}}$ and $UV_{254\text{ nm}}$ irradiation systems at reaction time above 25 h, resulting in catalyst deactivation. Nevertheless, a lower degree of catalyst deactivation could be observed in the $O_3 + UV_{254\text{ nm}}$ irradiation system relative to the $UV_{254\text{ nm}}$ irradiation system owing to the addition of O_3 .

In the $UV_{254\text{ nm}}$ photocatalytic system, the steady-state HCHO reaction rate over Pt-TiO₂ was ca. 1.3-fold higher than that over pure TiO₂, thereby indicating the positive effect of Pt NPs in improving the photocatalytic activity of Pt-TiO₂. In addition, the HCHO reaction rate decreased much faster in the case of pure

Fig. 3. Degradation rate of HCHO as a function of irradiation time under UV₂₅₄ nm, O₃+UV₂₅₄ nm, and UV₂₅₄+185 nm irradiation over pure TiO₂ (a) and Pt-TiO₂ films (b).

TiO₂, showing that modification with Pt NPs was beneficial to reducing catalyst deactivation. Furthermore, as shown in Fig. 3, under O₃+UV₂₅₄ nm and UV₂₅₄+185 nm irradiation, the HCHO reaction rate obtained over the Pt-TiO₂ films was higher than that over pure TiO₂. These results indicate that deposition of Pt NPs on TiO₂ is beneficial to increasing the photocatalytic degradation efficiency of HCHO in all three processes.

Figure 4 shows the O₃ decomposition performance under O₃+UV₂₅₄ nm and UV₂₅₄+185 nm irradiation. Despite the very low decrease in the O₃ decomposition rates observed over both pure TiO₂ and Pt-TiO₂ films in the early stages of the process, in general, the reaction rate was relatively constant throughout the 35-h photocatalytic process, indicating that both TiO₂ and Pt-TiO₂ did not deactivate under O₃+UV₂₅₄ nm or UV₂₅₄+185 nm irradiation. The O₃ decomposition rate over the Pt-TiO₂ films was much higher than that over pure TiO₂, resulting in a 3.1–3.4-fold enhancement regardless of whether the O₃ was introduced or generated in situ. The results clearly indicate that deposition of Pt NPs on TiO₂ remarkably enhances the O₃ decomposition. The O₃ decomposition rate over Pt-TiO₂ was 1.4-fold higher relative to that over previously reported

Pd-TiO₂ films under UV₂₅₄+185 nm irradiation [21].

3.3. C 1s and O 1s XPS study of Pt-TiO₂ films

The chemical states of carbon (oxygen)-containing functional groups of Pt-TiO₂ films were characterized by high-resolution XPS. XPS spectra of C 1s and O 1s of the Pt-TiO₂ films before and after the 35-h photocatalytic process are shown in Fig. 5, and the corresponding relative content and binding energy (BE) of the functional groups are listed in Table 1. The O 1s peak at 529.8–530.2 eV can be assigned to lattice oxygen of the Ti–O bond [25]. The as-prepared Pt-TiO₂ films displayed graphitic carbon (C 1s at 284.8 eV), C–O of alcoholic hydroxyls (C 1s at 285.9 eV), and surface hydroxyl groups (O 1s at 532.1 eV) features [26,27]. The alcoholic hydroxyl groups likely correspond to residual PVA on the TiO₂ surface after the annealing treatment. For the Pt-TiO₂ films, subjected to a 35-h UV₂₅₄ nm irradiation photocatalytic process, the broad C 1s peak can be deconvoluted into three bands. The C 1s peaks at 287.1 and 288.5 eV correspond to carbon from carbonyl groups of aldehydes (37.9%) and carboxyl groups (10.6%), respectively [26,28]. The deconvoluted O 1s peaks at 531.8 and 534.3 eV are assigned to carbonyl oxygen of aldehydes (32.1%) and oxygen atoms in carboxyl groups (12.9%), respectively [26]. Both the C 1s and O 1s XPS spectra indicate the presence of carbonyl and carboxyl groups on the Pt-TiO₂ surface. Previous studies have shown that the oxidation intermediates, generated during the photocatalytic decomposition of formaldehyde, are CO and formic acid; the latter tends to be strongly adsorbed on the catalyst surface [29,30]. Therefore, the carbonyl and carboxyl groups in this case can be assigned to corresponding groups in formaldehyde and formic acid adsorbed on Pt-TiO₂, respectively. It is clear that a large amount of formaldehyde and formic acid molecules have been accumulated on the Pt-TiO₂ films during the UV₂₅₄ nm photocatalytic process. This result is consistent with the fast deactivation of Pt-TiO₂ under UV₂₅₄ nm irradiation as the reaction time extends over 25 h (Fig. 3(b)).

Both C 1s and O 1s peaks of the resulting Pt-TiO₂ films, following O₃+UV₂₅₄ nm photocatalytic process for 35 h, were nar-

Fig. 4. Photocatalytic decomposition rate of O₃ as a function of irradiation time under O₃+UV₂₅₄ nm and UV₂₅₄+185 nm irradiation over pure TiO₂ and Pt-TiO₂ film.

Fig. 5. High-resolution XPS spectra and fitting curves of C 1s (a) and O 1s (b) of Pt-TiO₂ film photocatalysts. (1) Before reaction; (2)–(4) After 35-h UV₂₅₄ nm, 35-h O₃+UV₂₅₄ nm, and 35-h UV₂₅₄+185 nm photocatalytic processes.

Table 1

Relative content and corresponding binding energy of functional groups determined from XPS analysis for Pt-TiO₂ film before and after 35-h photocatalytic process.

Photocatalytic system	Relative content and binding energy of O 1s*				Relative content and binding energy of C 1s**			
	Peak 1	Peak 2	Peak 3	Peak 4	Peak I	Peak II	Peak III	Peak IV
Before reaction	81.5%		18.5%		88.9%	11.1%		
	530.1 eV		532.1 eV		284.7 eV	285.9 eV		
UV ₂₅₄ nm	49.9%	32.1%	5.1%	12.9%	51.5%		37.9%	10.6%
	529.9 eV	531.8 eV	532.9 eV	534.3 eV	284.8 eV		287.1 eV	288.5 eV
O ₃ +UV ₂₅₄ nm	60.5%	21.6%	12.2%	5.7%	91.7%		8.3%	
	529.8 eV	531.1 eV	532.6 eV	534.7 eV	284.8 eV		287.8 eV	
UV ₂₅₄ +185 nm	71.8%	16.9%	11.3%		86.8%		13.2%	
	530.2 eV	531.2 eV	532.3 eV		284.8 eV		286.1 eV	

*Peak 1: oxygen in Ti–O bond; Peak 2: carbonyl oxygen in aldehyde; Peak 3: oxygen in hydroxyl groups; Peak 4: oxygen in carboxyl groups.

**Peak I: graphitic carbon; Peak II: C–O in alcoholic hydroxyls; Peak III: carbonyl groups in aldehyde; Peak IV: carboxyl groups.

rower relative to those produced following UV₂₅₄ nm photocatalytic process. The C 1s peak at 287.8 eV corresponds to carbonyl groups (8.3%) of adsorbed formaldehyde. The O 1s peaks at 531.1 and 534.7 eV can be assigned to carbonyl oxygen (21.6%) of formaldehyde and oxygen atoms (5.7%) in carboxyl groups of formic acid, respectively [26,28]. The fitting results in Table 1 reveal that the accumulation of formaldehyde and formic acid on Pt-TiO₂ decreased in the presence of O₃. This may be attributed to the higher decomposition rates of formaldehyde and formic acid under O₃+UV₂₅₄ nm irradiation when compared with those under UV₂₅₄ nm irradiation. The C 1s and O 1s XPS findings are consistent with the observed higher HCHO reaction rate under O₃+UV₂₅₄ nm irradiation relative to that under UV₂₅₄ nm irradiation. Therefore, the lower degree of catalyst deactivation under O₃+UV₂₅₄ nm irradiation is ascribed to lower amounts of adsorbed formaldehyde and formic acid on Pt-TiO₂. Addition of O₃ has been reported to enhance the degradation of hydrophobic VOCs, and inhibits the deactivation of photocatalysts in a TiO₂/UV/O₃ reaction system [31,32].

The C 1s and O 1s XPS spectra of Pt-TiO₂ film subjected to UV₂₅₄+185 nm irradiation photocatalytic process for 35 h are shown in Fig. 5. The deconvoluted C 1s peak at 286.1 eV can be assigned to carbonyl groups (13.2%) of adsorbed formalde-

hyde. The deconvoluted O 1s peak at 531.2 eV corresponds to carbonyl oxygen (16.9%) of formaldehyde [26,28]. It can be inferred that only a small amount of formaldehyde was accumulated on the Pt-TiO₂ surface after the 35-h UV₂₅₄+185 nm photocatalytic process. Thus, formaldehyde was effectively decomposed to final products (e.g., CO₂ and H₂O) without accumulation of detectable oxidation intermediates.

The relative atomic content of C, O, Ti, and Pt on the surface of Pt-TiO₂ films before and after 35-h photocatalytic process was calculated from the corresponding peak areas of the XPS spectra (Table 2). The C content significantly increased from 33.21% (before photocatalytic reaction) to 39.77% and 38.89% after the Pt-TiO₂ films were subjected to 35-h UV₂₅₄ nm and O₃+UV₂₅₄ nm photocatalytic processes, respectively. A corresponding increase in the relative O content was also observed, as listed in Table 2. The significant increase in C and O contents is directly related to the accumulation of organic species on Pt-TiO₂ after the 35-h UV₂₅₄ nm and O₃+UV₂₅₄ nm photocatalytic processes. However, only a slight increase in the C and O relative atomic content was observed after the 35-h UV₂₅₄+185 nm photocatalytic process, which is indicative of the lowest amount of accumulated organic species among the three types of photocatalytic systems.

Table 2

Relative atomic content of C, O, Ti, and Pt on the surface of Pt-TiO₂ film before and after 35-h photocatalytic process.

Photocatalytic system	Relative atomic content (%)			
	C	O	Ti	Pt
Before reaction	33.21	45.88	16.40	4.51
UV ₂₅₄ nm	39.77	47.42	10.77	2.04
O ₃ +UV ₂₅₄ nm	38.89	46.90	11.82	2.39
UV ₂₅₄ +185 nm	35.10	46.09	14.85	3.96

3.4. Pt 4f XPS study of Pt-TiO₂ films

XPS spectra of the Pt 4f core level region of the Pt-TiO₂ films before and after the 35-h photocatalytic process are presented in Fig. 6. Several peaks that correspond to multiple oxidation states of Pt were observed. Pt 4f_{7/2} and 4f_{5/2} peaks were deconvoluted into two sets of spin-orbit doublet. The BE, relative content, and peak FWHM of the different Pt species in the Pt-TiO₂ before and after the 35-h photocatalytic processes are listed in Table 3. The BE of Pt 4f_{7/2} in the as-prepared Pt-TiO₂ at 71.2 and 72.4 eV can be assigned to metallic Pt⁰ (81.7%) and Pt²⁺ (18.3%), respectively [33–35]. The Pt 4f_{7/2} peak, observed at 72.4 eV, has a lower BE than that associated with PtO species (i.e., 73.4 eV); thus the oxidized Pt²⁺ species were assigned to PtO_{ads} (Pt²⁺ with adsorbed oxygen) [34]. However, no oxidized Pt species appeared in the XRD analysis (Fig. 2) owing to the relatively small amount of PtO_{ads} in Pt NPs. Because of the large amount of unsaturated surface atoms, as featured by the Pt NPs, it is highly likely that Pt NPs partially were oxidized to PtO_{ads} during annealing in air at 300 °C.

Following the 35-h UV₂₅₄ nm photocatalytic process, the Pt-TiO₂ films displayed Pt 4f_{7/2} peaks at 71.1 and 72.1 eV, which can be assigned to metallic Pt⁰ (79.9%) and PtO_{ads} (20.1%), respectively [33–36]. This shows that both metallic Pt⁰ and PtO_{ads} are stable under UV₂₅₄ nm irradiation. In contrast, Pt 4f_{7/2} peaks of the Pt-TiO₂ films, following a 35-h O₃+UV₂₅₄ nm photocatalytic process, were shifted to 72.3 and 74.2 eV, which cor-

Table 3

Binding energy, relative content, and FWHM of deconvoluted Pt 4f_{7/2} peaks of Pt-TiO₂ films before and after 35-h photocatalytic process.

Photocatalytic system	Pt species	Binding energy (eV)	Relative content (%)	FWHM (eV)
Before reaction	Pt ⁰	71.2	81.7	2.14
	Pt ²⁺ (PtO _{ads})	72.4	18.3	2.49
UV ₂₅₄ nm	Pt ⁰	71.1	79.9	2.27
	Pt ²⁺ (PtO _{ads})	72.1	20.1	2.77
O ₃ +UV ₂₅₄ nm	Pt ²⁺ (PtO _{ads})	72.3	76.9	2.11
	Pt ⁴⁺	74.2	23.1	2.34
UV ₂₅₄ +185 nm	Pt ²⁺ (PtO _{ads})	72.4	57.4	2.13
	Pt ⁴⁺	74.5	42.6	2.54

respond to PtO_{ads} (76.9%) and Pt⁴⁺ species (23.1%), respectively [33]. Thus, oxidation of the metallic Pt⁰ to Pt species with higher oxidation states occurred during the O₃+UV₂₅₄ nm photocatalytic process.

Following the 35-h UV₂₅₄+185 nm photocatalytic process, the Pt-TiO₂ displayed Pt 4f_{7/2} peaks at 72.4 and 74.5 eV, which were assigned to PtO_{ads} (57.4%) and Pt⁴⁺ species (42.6%), respectively [33,34]. Thus, under UV₂₅₄+185 nm irradiation, metallic Pt⁰ was no longer apparent and more Pt species were oxidized to Pt⁴⁺. Because the light intensity of the UV₂₅₄ nm irradiation and concentration of O₃ in the O₃+UV₂₅₄ nm photocatalytic system were comparable to those in the UV₂₅₄+185 nm photocatalytic system, the VUV-photochemically generated atomic oxygen species (O(¹D), O(³P)) and hydroxyl radicals (•OH) were likely to also contribute to the oxidation of the Pt species, thereby resulting in a large amount of Pt⁴⁺ species in the UV₂₅₄+185 nm photocatalytic system.

3.5. Effect of oxidized dispersed Pt species

As discussed from the above comparative XPS study for the Pt-TiO₂ films, the Pt species were significantly oxidized in the O₃+UV₂₅₄ nm photocatalytic system (PtO_{ads} (76.9%) and Pt⁴⁺ species (23.1%)) whereas subtle changes were noted in the UV₂₅₄ nm photocatalytic system. This clearly indicates that the added O₃ should be involved in the oxidation of the Pt species. Falconer et al. [37] reported that Pt particles on TiO₂ could serve as adsorption and reaction active sites for O₃ decomposition. Thus, in the O₃+UV₂₅₄ nm photocatalytic system, Pt NPs can act as centers for capturing O₃; the adsorbed O₃ can then be readily reduced to ozonide radical anion (O₃^{•−}) by reaction with the photogenerated electrons from TiO₂ (Eq. (3)) [21,38,39]. The unstable O₃^{•−} radicals rapidly split to form O₂ and O^{•−} radicals under UV irradiation (Eq. (4)), as confirmed by ESR measurements [40,41]. The adsorbed water molecules on the Pt NPs can be oxidized by the O₃^{•−} and O^{•−} radicals to form •OH radicals (Eqs. (5) and (6)), resulting in abundant •OH radicals on the surface of the Pt NPs. Owing to the strong oxidizing power of •OH radicals, the •OH radicals adsorbed on the Pt NPs are expected to oxidize metallic Pt⁰ to Pt species with higher oxidation states during the O₃+UV₂₅₄ nm photocatalytic process (Eqs. (7) and (8)) [21].

Fig. 6. High-resolution XPS spectra and fitting curves of Pt 4f for Pt-TiO₂ film photocatalysts. (1) Before reaction; (2)–(4) After 35-h UV₂₅₄ nm, 35-h O₃+UV₂₅₄ nm, and 35-h UV₂₅₄+185 nm photocatalytic processes.

Pt species with high oxidation states have stronger electron affinities. Therefore, PtO_{ads} and Pt^{4+} species can act as electron trapping centers for the Pt-TiO₂ nanocomposites in the O₃+UV_{254 nm} photocatalytic system. This will result in a more efficient photogenerated electron-hole pair separation, consequently resulting in a prolonged electron and hole lifetime. After trapping of the photogenerated electrons, the oxidized Pt species are reduced to Pt species with lower oxidation states (Eqs. (9) and (10)). The reduction of PtO_2 to Pt^0 in a reported photo-irradiated alcoholic suspension solution supports this assumption [42]. Thus, Pt species comprising both PtO_{ads} and Pt^{4+} species can steadily form on the TiO₂ surface during the O₃+UV_{254 nm} photocatalytic process.

In this work, the O₃ concentration and light intensity of the UV_{254 nm} irradiation in the UV_{254+185 nm} photocatalytic system were comparable to those in the O₃+UV_{254 nm} photocatalytic system. Therefore, the reactions given in Eqs. (3)–(6) are also expected to occur, leading to a large amount of $\bullet\text{OH}$ radicals on the Pt NPs in the UV_{254+185 nm} photocatalytic system. Additionally, the VUV-photochemically generated $\bullet\text{OH}$ radicals must be present in gas phase and adsorb on active sites of the Pt-TiO₂ surface. Therefore, higher amounts of $\bullet\text{OH}$ radicals are generated under UV_{254+185 nm} irradiation relative to O₃+UV_{254 nm} irradiation, leading to enhanced oxidation of Pt species to Pt^{4+} species (Eq. (8)). The higher amount of Pt^{4+} species, as determined by Pt 4fXPS, supports the above discussion relating to reaction process under UV_{254+185 nm} irradiation. The Pt species at higher oxidation states can be also reduced according to Eqs. (9) and (10) to form mixed Pt species in the UV_{254+185 nm} photocatalytic system.

As mentioned above, the dispersed Pt species can effectively trap photogenerated electrons from the conduction band of TiO₂, which helps to produce further $\bullet\text{OH}$ radicals on TiO₂ (Eqs. (11)–(13)). The surface unsaturated Pt atoms on the Pt NPs are highly active, and can act as reactive sites for adsorption and degradation of HCHO. Therefore, a larger number of $\bullet\text{OH}$ radicals and reaction sites were observed on the Pt-TiO₂ surface than on pure TiO₂ in the O₃+UV_{254 nm} and UV_{254+185 nm} photocatalytic systems, which resulted in a higher HCHO degradation rate, as observed in Fig. 3.

Compared with pure TiO₂, oxidized Pt species, acting as effective redox catalysts, can provide more reactive sites for capturing O₃ molecules [38], thus enhancing O₃ decomposition. The adsorbed O₃ molecules on the Pt NPs can be decomposed via the reactions given in Eqs. (3)–(6) by trapping the electrons generated upon UV irradiation. Additionally, thermal catalysis decomposition of O₃ should be effective on oxidized Pt species [38]. Therefore, the higher O₃ decomposition rate over the

Pt-TiO₂ films relative to that over pure TiO₂ under O₃+UV_{254 nm} and UV_{254+185 nm} irradiation, as shown in Fig. 4, agrees with the reported study whereby Pt-loaded TiO₂ accelerated the photocatalytic degradation of gaseous ozone [43].

4. Conclusions

XPS was used to assess the electronic states of Pt-TiO₂ films employed for the photocatalytic degradation of formaldehyde under UV_{254 nm}, O₃+UV_{254 nm}, and UV_{254+185 nm} irradiation conditions. The formation of carbonyl and carboxyl groups, corresponding to formaldehyde and formic acid on the Pt-TiO₂ films following photocatalytic reactions, was determined by deconvolution of the C1s and O1s XPS spectra. The content of the organic species on the Pt-TiO₂ and degree of catalyst deactivation under the studied conditions decreased in the order of UV_{254 nm} > O₃+UV_{254 nm} > UV_{254+185 nm}. More specifically, catalyst deactivation was negligible under UV_{254+185 nm} irradiation. The accumulation of organic species on Pt-TiO₂, as determined by XPS, gives direct evidence to elucidate the degree of catalyst deactivation.

The deconvoluted Pt 4fXPS spectra revealed that metallic Pt NPs were stable under UV_{254 nm} irradiation; however, they were oxidized to a mixture of PtO_{ads} and Pt^{4+} species under O₃+UV_{254 nm} and UV_{254+185 nm} irradiation conditions. The $\bullet\text{OH}$ radicals adsorbed on Pt NPs, generated during the O₃ decomposition process or dissociation of water under 185-nm VUV, are expected to be involved in the oxidation of Pt species. Pt species with high oxidation states can readily trap the photogenerated electrons to increase the photocatalytic activity of Pt-TiO₂. Ultrafine Pt NPs with a strong electron affinity can provide numerous reactive sites for O₃ decomposition. Therefore, formaldehyde degradation and O₃ elimination can be simultaneously enhanced in the O₃+UV_{254 nm} and UV_{254+185 nm} irradiation photocatalytic systems by modifying TiO₂ with Pt.

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Graphical Abstract

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Characterization of Pt-TiO₂ film used in three formaldehyde photocatalytic degradation systems: UV₂₅₄ nm, O₃+UV₂₅₄ nm and UV₂₅₄+185 nm via X-ray photoelectron spectroscopy

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O₃ byproduct can be photocatalytically decomposed on both TiO₂ substrate and Pt nanoparticles under UV₂₅₄+185 nm irradiation. The oxidized Pt species can trap the photogenerated electrons to increase the photocatalytic activity of Pt-TiO₂.

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X射线光电子能谱法研究UV₂₅₄ nm光催化、O₃强化UV₂₅₄ nm光催化和真空紫外光催化降解甲醛中Pt-TiO₂薄膜的表面性质

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摘要: 以Pt-TiO₂为光催化剂, 研究了气相甲醛分别在35 h连续UV₂₅₄ nm光催化、O₃强化UV₂₅₄ nm(O₃+UV₂₅₄ nm)光催化和真空紫外(UV₂₅₄+185 nm)光催化中的降解效率, 考察了副产物O₃的去除率, 采用X射线光电子能谱(XPS)法分析Pt-TiO₂在不同光催化前后Pt的电子态和累积有机产物, 研究纳米Pt对甲醛降解和O₃去除的强化机理. 连续光催化降解实验表明, 以纳米Pt改性TiO₂可以同时增

强甲醛和 O_3 的去除率,特别是 O_3 的去除率可提高3.1–3.4倍. 对催化剂C 1s和O 1s峰分别经分峰拟合处理后,发现Pt-TiO₂上累积的含羰基和羟基的有机物含量按以下顺序减少: UV_{254 nm}光催化 > O_3 强化UV_{254 nm}光催化 > 真空紫外光催化,而在连续35 h光催化降解过程中,催化剂的失活现象却按相反的方向变得越来越不明显. 负载的金属Pt在 O_3 +UV_{254 nm}和UV_{254+185nm}光催化过程中被氧化成PtO_{ads}和Pt⁴⁺物种,而在UV_{254 nm}光催化过程中金属Pt未被氧化,所以推测是气相中的 O_3 和羟基自由基参与金属Pt的氧化过程. Pt-TiO₂表面高价态的Pt氧化物物种可作为光生电子捕获中心,强化光生载流子的分离过程,增强Pt-TiO₂的光催化活性. Pt氧化物物种可作为 O_3 分解的活化中心,使Pt-TiO₂对 O_3 的分解效率远高于纯TiO₂. 以XPS对比研究在三种不同光催化环境中Pt-TiO₂表面性质,可以解释在UV_{254+185 nm}光催化过程中纳米Pt对甲醛和 O_3 同时去除的强化机理,并说明了催化剂不失活的内在原因.

关键词: 纳米铂; 真空紫外光; 光催化; 臭氧分解; 催化剂失活

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