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A study of the photocatalytic oxidation of formaldehyde on $Pt/Fe_2O_3/TiO_2$ [☆]

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Abstract

Preparation of TiO_2 photocatalysts loaded with noble metal or transition-metal oxide and the influences of preparing procedures on the photocatalytic activity for degradation of formaldehyde are reported. The products and intermediates in the photocatalytic oxidation of formaldehyde were detected, and a reasonable mechanism of reaction was suggested.

Keywords: Photocatalytic oxidation; Formaldehyde degradation; Titanium dioxide; Iron trioxide

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1. Introduction

In recent years, the application of heterogeneous photocatalysis on the removal of contaminants in air and wastewater has aroused great interest [1–4]. In particular, the removal of pollutants in indoor air is more important because they are strongly harmful to human health. The formaldehyde as a typical pollutant, which comes from the furnishing and decorating materials, frequently causes cancer. Therefore, the development of catalyst for photocatalytic degradation of formaldehyde and the investigation of reaction mechanism has not only the theoretical but also the practical significances.

2. Experimental

2.1. Preparation of photocatalysts

Three MO_x (metal or metal oxide)-loaded TiO_2 photocatalysts have been prepared and compared.

1. *Fe_2O_3/TiO_2 photocatalyst*. Raw TiO_2 (anatase, Analytical reagent, Fluka, AG, CH-9470, Buchs, packed in Switzerland) was calcined in pure N_2 flow at 700°C for 3 h prior to impregnation. A required amount of TiO_2 powder was slowly added into the $Fe(NO_3)_3$ aqueous solution under magnetic stirring. Then the powder was filtered up from solution and heated at 350°C for 3 h.
2. *Pt/TiO_2 photocatalyst*. The treated TiO_2 powder (4 g) and aqueous H_2PtCl_6 solution (0.077 M; 1.32 ml) were added into 40 ml of distilled water. The slurry was bubbled by using high purity N_2 for 15 min. The whole system was then sealed and irradiated with UV light for 1 h. After irradiation, the powder was filtered and washed to remove residual Cl^- ions and finally dried in vacuum oven at 120°C for 4 h.
3. *$Pt/Fe_2O_3/TiO_2$ photocatalyst*. The $Pt/Fe_2O_3/TiO_2$ photocatalyst was prepared according to the procedures mentioned in Section 2, with the exception of Fe_2O_3/TiO_2 instead of TiO_2 powder.

2.2. Measurement of photocatalytic activity

A closed reactor with the volume of 8.712 l is described in Fig. 1. An inert cylinder catalyst-bed was mounted upon the top of the frame and an electric fan was fixed below the cylinder. A 4 W UV lamp ($\lambda = 253.7$ nm) was co-axially installed inside the cylinder. Two grams of catalyst was uniformly coated on the inner wall of the cylinder. A required amount of gaseous formaldehyde was injected into the reactor and then stirred for 15 min in the dark. The initial concentration of formaldehyde was kept at 100 ppm for all of experiments. The photocatalytic oxidation of formaldehyde was carried out under the illumination in ambient temperature for 1 h. The concentration of formaldehyde was determined in terms of the colorimetric method and the conversion efficiency of formaldehyde for 1 h of reacting time was defined as the evaluation of photoactivity of the catalysts.

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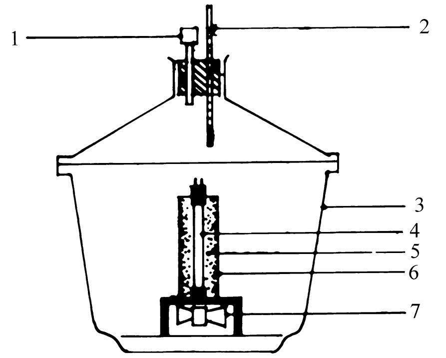

Fig. 1. Schematic diagram of gaseous photocatalytic reactor: (1) sampler, (2) thermometer, (3) reactor, (4) UV lamp, (5) catalyst, (6) catalyst bed, (7) fan.

2.3. *Determination of intermediate species and end products*

The measurements of the end products of photocatalytic oxidation of formaldehyde and adsorption species were performed by means of temperature programmed desorption (TPD) over 0.3 g of fresh Pt/Fe_2O_3/TiO_2 catalyst. The thermal programmed desorption products were detected online and continuously monitored at *m*/*e* 46.47 for HCOOH, *m*/*e* 44 for CO_2 and *m*/*e* 32 for oxygen, respectively, by using Finnigan-MAT 700ITD mass spectrometer with carrying gas He (30 ml/min), temperature rate 30°C/min, and terminal temperature 600°C.

The electron spin resonance (ESR) spectra for determination of intermediates were recorded with a Varian E-115 ESR spectrometer operating in the X-band mode (~9.5 GHz) with 5 mW of microwave power and 100 kHz of modulation frequency. The sample tube contained the dispersion of Pt/TiO_2in aqueous HCHO and DMPO solution. The ESR parameters were calibrated by spectroscopic splitting factor of DPPH (diphenyl picryl hydrazyl), $g = 2.0036$, and the distance between the third and fourth ESR lines of ZnS $^{\bullet}Mn^{2+}$(67.7 G).

XPS spectral measurements were performed on PHI-550 multifunctional spectrometer (Perkin-Elmer, USA) with Mg Kα radiation.

3. Results and discussion

3.1. *Effects of surface modification of photocatalyst on photocatalytic activity*

In heterogeneous photocatalysis, the photocatalytic activity of catalyst not only depends on properties of loading species but also on the amount of loaded compound (i.e. surface coverage) [3]. Fig. 2 shows the dependence of photocatalytic conversion efficiency of formaldehyde on the content of Fe_2O_3 deposited on TiO_2 surface. It can be seen that the efficiency is raised with increasing the content of Fe_2O_3 and the highest efficiency (66%) corresponds to a content of 5 wt.% Fe_2O_3. The photocatalytic conversion efficiency of formaldehyde at raw TiO_2 is 39%. The similar behavior was found in Pt/TiO_2 photocatalyst (63% efficiency corresponds to 1 wt.% Pt). When two photocatalysts Fe_2O_3/TiO_2 and Pt/TiO_2 were combined, a new photocatalyst Pt/Fe_2O_3/TiO_2 showed more high efficiency (74%) compared with Fe_2O_3/TiO_2 and Pt/TiO_2, respectively, which can be practically used to remove formaldehyde pollution in the indoor air.

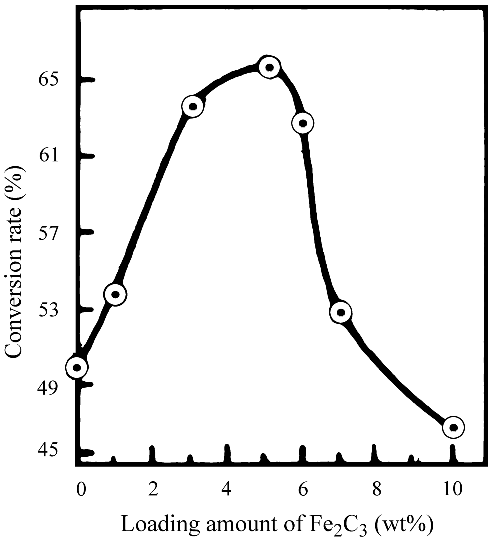

Fig. 2. Dependence of photocatalytic conversion rate of HCHO over Fe_2O_3/TiO_2 catalyst on the content of Fe_2O_3 deposited on TiO_2 surface.

The studies of XPS revealed that iron species at TiO_2 surface in the form of Fe_2O_3 ($E_b = 711.3$ eV) (Fig. 3). But platinum species existed at TiO_2 surface in two states Pt^0 ($E_b = 71.1$ eV) and PtO_2 ($E_b = 74.2$ eV) (Fig. 4) [5]. The PtO_2 could be decomposed into Pt^0 and O_2 after it

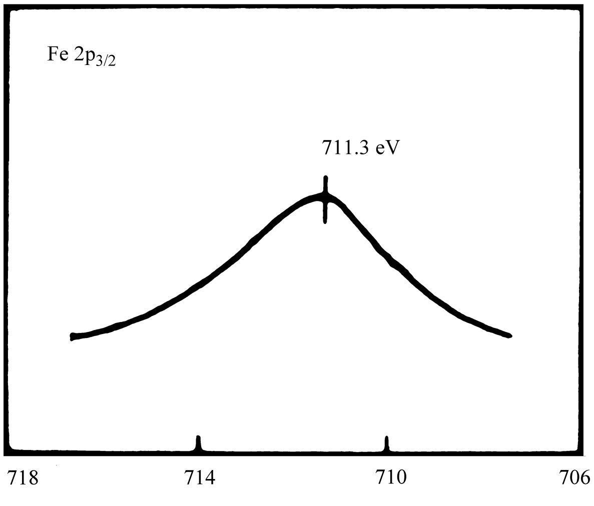

Fig. 3. XPS (Fe2$p_{3/2}$) spectrum of iron species deposited on TiO_2 surface.

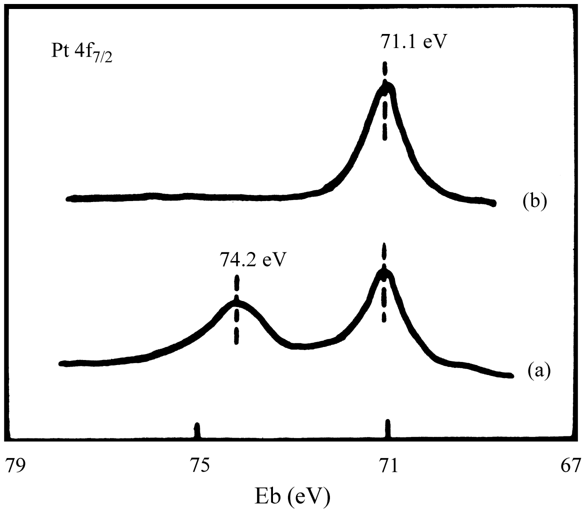

Fig. 4. XPS (Pt4f) spectra of $Pt/Fe_2O_3/TiO_2$ catalyst untreated (a) and retreated in N_2 flow at 550°C for 1 h (b).

was calcined at 550°C in N_2 flow and correspondingly, the peak at 74.2 eV disappeared in Fig. 4 [6]. A lot of study has recognized that Pt^0 on the catalyst surface functioned not only as the electron trap center but also as the adsorption center of O_2 in photocatalysis [7–9].

Fig. 5 compared the Ti2p XPS spectra of raw TiO_2(anatase) (a), calcined raw TiO_2 in N_2 flow at 700°C for 1 h (b), retreated Fe_2O_3/TiO_2 (c) and $Pt/Fe_2O_3/TiO_2$ (d) in N_2 flow at 550°C for 1 h. The experiments indicated that if Fe_2O_3/TiO_2 or $Pt/Fe_2O_3/TiO_2$ was retreated in N_2 flow at 550°C for 1 h, a new peak at 454.5 eV appeared in Ti2p XPS spectrum. This peak presents Ti^{3+} formed in surface layer of TiO_2 and which can reduce adsorbed O_2 into $^\bullet O_2^-$ radical [10]. As for the action of Fe_2O_3 loaded on the catalyst surface, it possibly played a role of promoting the formation of Ti^{3+}.

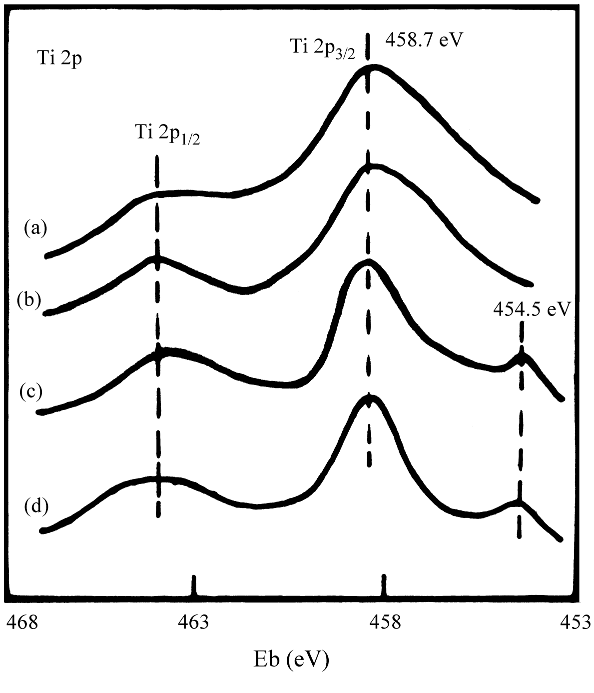

Fig. 5. XPS (Ti2p) spectra of raw TiO_2 (a), treated raw TiO_2 in N_2 flow at 700°C for 3 h (b), treated Fe_2O_3/TiO_2 catalyst (c), and $Pt/Fe_2O_3/TiO_2$ catalyst (d), in N_2 flow at 550°C for 1 h.

Above experiments illustrated that the procedure of re-treatment of $Pt/Fe_2O_3/TiO_2$ in N_2 flow at high temperature is necessary to promote electron transfer and consequently enhance the photocatalytic degradation of formaldehyde.

3.2. Mechanism of photocatalytic oxidation of formaldehyde

A number of works have been published on the photocatalytic mineralization of organic contaminates in aqueous suspension system [11–13]. However, the studies of photocatalytic removal of pollutants in gas phase were only focused on a few compounds, such as trichloroethylene (TCE) [14], 2-propanol [15] and acetone [16]. We attempted to investigate the influence of adsorbed oxygen and water at the gas–solid interface on the photocatalytic degradation of formaldehyde on $Pt/Fe_2O_3/TiO_2$ and identify the reaction intermediates formed in the process of photocatalytic oxidation of formaldehyde.

3.2.1. Oxygen adsorption

The oxygen adsorption behaviors on $Pt/Fe_2O_3/TiO_2$ surface were determined in the case of with or without UV light illumination after the adsorption of oxygen. Fig. 6(a) shows the TPD spectrum measured in the dark case, in which a thermal desorption peak appeared at 114°C which corresponded to the physisorption. When the adsorption of oxygen occurred under UV light irradiation, the TPD peak was measured at 175°C (Fig. 6(b)) and this peak area is obviously larger than the former. This result demonstrated that the adsorption intensity at 175°C is stronger than that at 114°C. Thereby, the peak at 175°C could be attributed to chemisorption of oxygen and usually named photosorption.

The adsorption states of oxygen on TiO_2 surface commonly can be described as O_2^-, O^-, and O_3^- [17,18]. They are caused from the transfer of photogenerated electrons to adsorbed oxygen molecule. Tanaka and Blyholder [19] studied the photosorption of O_2 on the surface of ZnO. The result showed that O_2^- was desorbed at 185°C, while O^- was desorbed at 290°C. Beck et al. [20] found that the thermal desorption of O_2^- appeared at 445 K (172°C). Ishibashi et al. [21] have employed a chemiluminescence technique to study the behavior of active oxygen species formed on photoirradiated TiO_2 films in air and observed a long-lived species, which may correspond to O_2^-. Referring to above literatures, we can conclude that the peak at 175°C can be reasonably attributed to O_2^- in this work.

As for the adsorption sites on TiO_2 surface, Gopel et al. [22] proposed that the formation of O_2^- required the

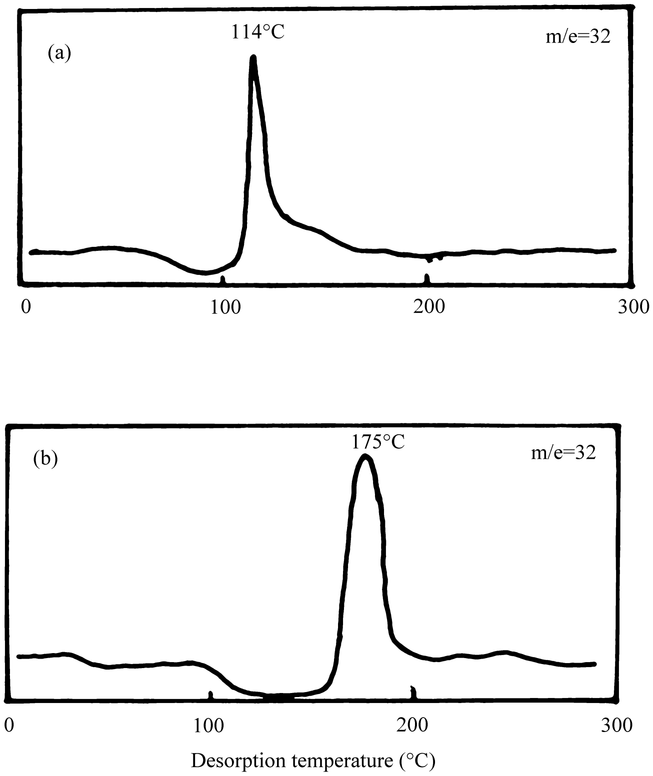

Fig. 6. TPD spectra of O_2 adsorbed on $Pt/Fe_2O_3/TiO_2$ at room temperature in the dark (a) and after UV illumination for 5 min (b).

presence of surface defect sites (i.e. surface oxygen vacancy sites [23] or surface Ti^{3+} sites [24]). XPS experiments have verified the existence of Ti^{3+} ($E_b = 454.5$ eV) on $Pt/Fe_2O_3/TiO_2$ surface (Fig. 5). In addition, it should be emphasized that Pt^0 deposited on $Pt/Fe_2O_3/TiO_2$ surface play an important role of the trapping center of photogenerated electron and oxygen adsorption center. Consequently, it may promote the formation of $O_2{}^-$.

3.2.2. Determination of $^\bullet$OH radical and intermediates

Studies of hydroxyl radical have aroused much interest, because it frequently behaved as an active oxidant in photocatalytic degradation of organic pollutants.

The hydroxyl free radicals and reaction intermediates were determined in an aqueous dispersion of Pt/TiO_2 powders containing the spin-trapping agent DMPO and formaldehyde. The spin trapping ESR spectra were measured after irradiation of whole system under UV light for 5 min.

The spectra shown in Fig. 7 could be analyzed as follows: the weaker quartet signal (labeled by Δ) with ESR parameters of $g = 2.0054$, $a_N = a_H{}^\beta = 14.8$ G can be attributed to the signal of $^\bullet$OH radical adduct of DMPO [25]. This result implies that water adsorbed on catalyst surface was oxidized into $^\bullet$OH by photogenerated hole (h^+), whereas the stronger sextet signal (labeled by $*$) with the ESR parameters of $g = 2.0054$, $a_N = 15.8$ G. $a_H{}^\beta = 21.1$ G was possibly originated from the adduct of DMPO and $^\bullet$CHO radical. It is worth to point out that when ESR experiments were performed in the same system with the exception of TiO_2 instead of Pt/TiO_2, the signal intensity of $^\bullet$OH is much higher than in the former case (Fig. 8). These results indicated that formaldehyde molecule was oxidized into $^\bullet$CHO by $^\bullet$OH radical in the first step of reaction at Pt^0 site on TiO_2 surface. As a result, the $^\bullet$OH radical was partially exhausted and ESR signal intensity of $^\bullet$OH on Pt/TiO_2 must be lowered. The reaction can be expressed by the following equation:

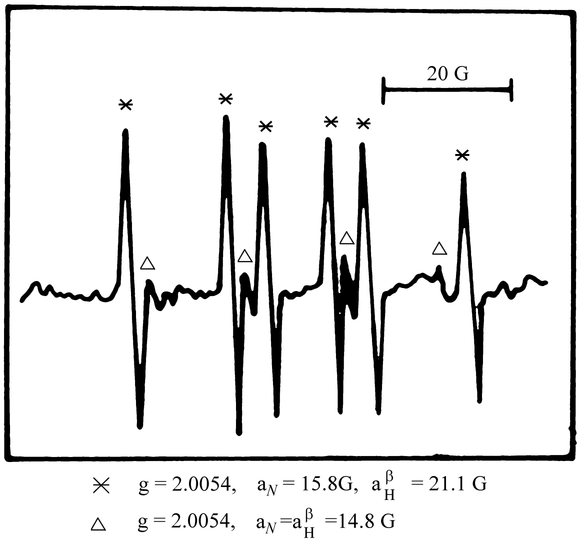

Fig. 7. ESR spectra of spin-trapped hydroxyl radical (labeled by $\triangle$) and $^\bullet$CHO radical (labeled by $*$) adducts of DMPO obtained by irradiation (5 min) of aqueous dispersion of Pt/TiO_2 containing HCHO and DMPO.

$$HCHO + {}^\bullet OH \rightarrow {}^\bullet CHO + H_2O$$

The signal which has $g = 2.0058$, $a_N = 15.8$ G, $a_H{}^\beta = 19.0$ G was also observed in same system (Fig. 9). It can be assigned to the $^\bullet CO_2{}^-$ free radical adduct of DMPO [26].

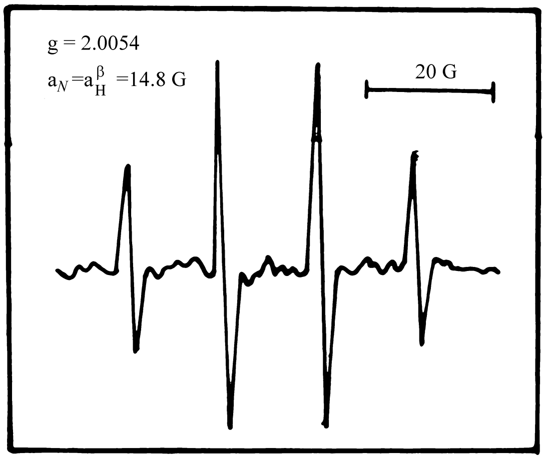

Fig. 8. ESR spectrum of $^\bullet$OH adduct of DMPO obtained by irradiation (5 min) of aqueous dispersion of TiO_2 containing HCHO and DMPO.

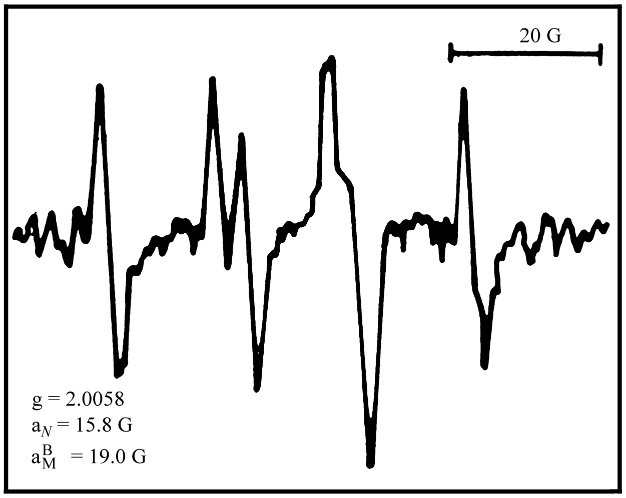

Fig. 9. ESR spectrum of $^{\bullet}CO_2$ adduct of DMPO measured from the illuminated dispersion of Pt/TiO_2 in the aqueous solution of HCHO and DMPO.

The products of photocatalytic oxidation of formaldehyde on Pt/Fe_2O_3/TiO_2 were detected in the mixture of gaseous HCHO and air by using the method of TPD. Fig. 10 shows that when the catalyst exposed in the mixture without UV light illumination, only one thermal desorption peak at 150°C was detected which corresponded to the adsorbed trace CO_2 ($m/e = 44$) from the air. However, after the system was irradiated under UV light, the desorption peak of HCOOH ($m/e = 46.47$) at 159°C was determined and two peaks of CO_2 appeared at 159 and 252°C, respectively (Fig. 11). It can be affirmed that the stronger desorption peak of CO_2 at 252°C was attributed to oxidizing product of HCHO owing to the fact that the interaction between product CO_2 and catalyst is more strong than the physisorbed CO_2. It must be noted that no more compounds were detected except of CO_2 and water in the end products.

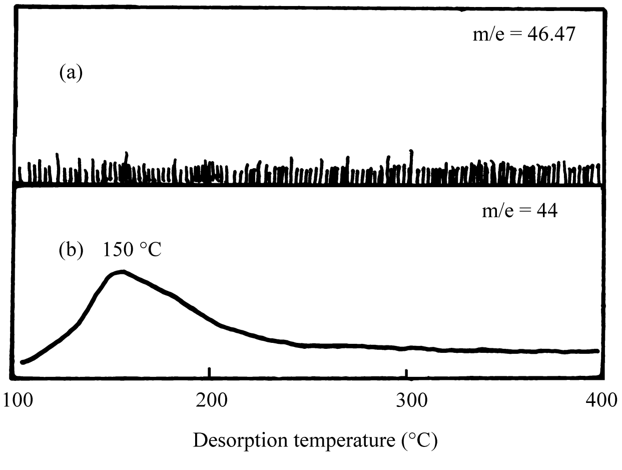

Fig. 10. TPD spectra of HCOOH ($m/e = 46.47$) (a) and CO_2 ($m/e = 44$) (b) adsorbed on Pt/Fe_2O_3/TiO_2 in the dark.

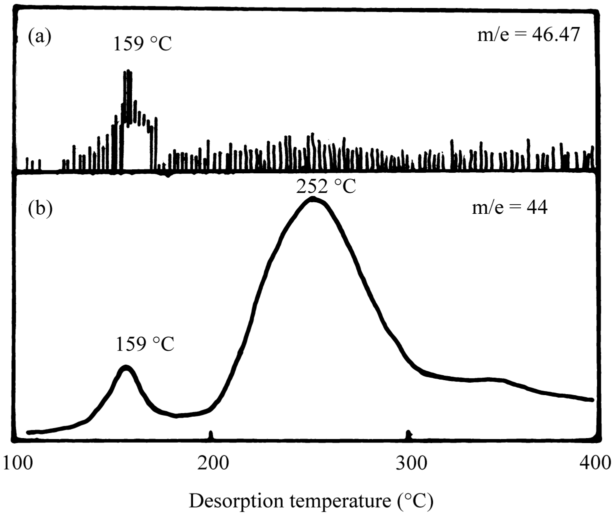

Fig. 11. TPD spectra of HCOOH (a) and CO_2 (b) adsorbed on Pt/Fe_2O_3/TiO_2 after UV illumination for 5 min.

Based on above experiments, a possible mechanism of photocatalytic oxidation of formaldehyde on the Pt/Fe_2O_3/TiO_2 is suggested as follows:

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

$$h^+ + OH^-_{(ads)} \to {}^{\bullet}OH \quad \text{or} \quad h^+ + H_2O_{(ads)} \to {}^{\bullet}OH + H^+ \tag{2}$$

$$e^- + O_{2(ads)} \to {}^{\bullet}O_2{}^- \tag{3}$$

$$HCHO + {}^{\bullet}OH \to {}^{\bullet}CHO + H_2O \tag{4}$$

$${}^{\bullet}CHO + {}^{\bullet}OH \to HCOOH \tag{5}$$

$${}^{\bullet}CHO + {}^{\bullet}O_2{}^- \to HCO_3{}^- \xrightarrow{+H^+} HCOOOH \xrightarrow{HCHO} HCOOH \tag{6}$$

$$HCOOH \xrightarrow{-H^+} HCOO^- \xrightarrow{{}^{\bullet}OH} H_2O + {}^{\bullet}CO_2{}^- \quad \text{or}$$

$$HCOO^- \xrightarrow{h^+} H^+ + {}^{\bullet}CO_2{}^- \tag{7}$$

$${}^{\bullet}CO_2{}^- \xrightarrow{[O],\ {}^{\bullet}OH,\ h^+} CO_2 \tag{8}$$

4. Conclusions

The experiments showed that Pt/Fe_2O_3/TiO_2 exhibited an applicable photoactivity with the photochemical conversion efficiency of 74% in the degradation of formaldehyde. The procedure of re-treatment of Pt/Fe_2O_3/TiO_2 in N_2 flow at high temperature is necessary to promote electron transfer and consequently enhance the photocatalytic degradation rate of formaldehyde. The photocatalytic oxidation of HCHO is carried out with two steps: firstly, HCHO was oxidized into HCOOH, then HCOOH was converted into final product of CO_2. The free radicals of $^{\bullet}OH$ and $^{\bullet}CHO$ were also detected in the experiments.

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