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Photocatalytic performance of Pt-loaded TiO_2 in the decomposition of gaseous ozone

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Abstract

Gas-phase catalytic and photocatalytic decomposition of ozone (O_3) was investigated using TiO_2 and Pt-loaded TiO_2 (Pt/TiO_2) at room temperature and atmospheric pressure. The nominal weight loading of Pt was less than 1 wt.%. Results of this study indicate that both the overall conversion of O_3 to O_2 and other products with UV irradiation and without UV irradiation (dark reaction) can be improved by using Pt-loaded TiO_2. Photocatalytic conversion of O_3 on pure TiO_2 decreased with increasing water vapor. In contrast, Pt/TiO_2 was active for the decomposition of ozone under the humidity condition at room temperature.

Keywords: Pt/TiO_2; Photocatalytic reaction; UV irradiation; Decomposition of ozone

1. Introduction

Because of absorbing ultraviolet radiation, the presence of ozone (O_3) in the stratosphere is beneficial, but close to the ground it is harmful, causing respiratory illness and enhancing photochemical pollution. Therefore, reducing the concentration of environmental O_3 is recently attracted. The most commonly used technique for removal of O_3 was adsorption and reaction with activated charcoal and catalytic decomposition over a metal such as Pt, Pd, Rh, etc. and/or a metal oxide catalyst including Mn, Co, Cu, Fe, Ni, Au and Ag. In these cases, γ-Al_2O_3, SiO_2, Fe_2O_3, TiO_2 and activated carbon are used [1–6].

The addition of metal particles to semiconductor photocatalyst for increasing the light-absorption efficiency and photocatalytic activity is of great interest [7–10]. It has been reported that the efficiency of the photoreaction over TiO_2 increased with the loading of transition metals, which has been explained either the suppression of hole–electron recombination or the electron trapping by the metal [11].

There are several studies reported on Pt-loaded TiO_2. They studied about photooxidation of several compounds such as formaldehyde, trichloroethylene, EDTA, oxalic acid, phenol, *t*-butylhydroquinone, acetaldehyde, ethylene, ethanol, etc. [12–19]. No result, however, for the decomposition of gaseous O_3 over Pt/TiO_2 has been published. It has been reported that the most active metals for photocatalytic enhancement is platinum, which can produce the highest Schottky barrier among the metals that facilitate electron capture [20]. The capture of electrons by Pt is postulated to make a longer electron–hole pair separation lifetime, and therefore hinder the recombination of electron–hole pairs and enhance the transfer of holes and possibly electrons to O_2 adsorbed on the TiO_2 surface. Afterwards, excited electrons migrate to the metal and they become trapped. Thus the electron–hole pair recombination is suppressed [20].

In the present work, TiO_2 photocatalysts were modified by depositing three different amounts of platinum on their surface. Two different photodepositing methods were used in order to investigate the difference in photocatalytic behavior and the influence of increasing the amounts of platinum under with/without UV light and the water vapor in air stream.

Our catalyst is expected to have good photocatalytic performance for O_3 decomposition under such conditions as a room temperature and the presence of water vapor. The catalyst may also be effective for decomposition of gaseous O_3 in the dark condition.

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2. Experimental

2.1. Preparation of photocatalysts

A supporting material employed to prepare Pt-loaded photocatalysts in this present study was TiO_2 (P25; 80% anatase, crystallite size of 25 nm, specific surface area of 50 m^2/g, Nippon Aerosil). Pt/TiO_2 was prepared by photodeposition. The treated TiO_2 powder and aqueous $H_2PtCl_6{\cdot}6H_2O$ were added into 75 ml of distilled water in a pyrex vessel with vigorous stirring. The pH of the suspension was adjusted to 6.8–7.0 by addition of 0.1 N KOH solution. The suspension was bubbled by using high purity nitrogen in order to remove the dissolved O_2 and irradiated with UV light (Ushio, USH-500D, 500 W, high pressure Hg lamp) for 30 min. After the irradiation, the solution containing Pt/TiO_2 catalysts were centrifuged, washed with distilled water until no Cl^- was detected in rinsing water and dried overnight at about 383 K. The contents of Pt loaded on TiO_2 were 0.05, 0.2 and 1.0 wt.%. Pt/TiO_2–EtOH was prepared in the same way as above, except that 45 ml of ethanol was added to the suspension before photodeposition.

2.2. Apparatus and procedure

Decomposition of O_3 was carried out in the flow-type photochemical reaction system (50 mm width, 300 mm in length and 5 mm in height) using three 10 W black light lamps (300–400 nm, FL10NBL, Toshiba) as a light source. The catalysts was coated onto the surface of glass plate (50 mm width and 100 mm in length, 1 mg/cm^2 of catalyst loading density) using an aqueous slurry and dried overnight at 383 K. Reactions were carried out at room temperature (293–298 K) under atmospheric pressure. In the experiment, purified air was employed (SGPU-22, STEC). Humidified air was prepared by bubbling purified air through a glass saturator containing deionized water. The gas flow rate and relative humidity were varied from 1000 to 2500 ml/min and from 0 to 80%, respectively. The initial concentration of gaseous O_3 in air stream was fixed to 1.0 ppmv for effect of flow rate and water vapor.

In a typical decomposition experiment, air containing a specific concentration of O_3 was passed through a photoreactor in the absence of UV irradiation until O_3 concentration in the effluent becomes 90% of initial concentration.

2.3. Analysis

O_3 concentration at the influent and effluent of the reactor was determined by ozone analyzer with internal and external zero and span (ML 9811, Monitor Labs). The O_3 concentrations were continuously monitored every 10 s with on-line ozone analyzer.

The chemical state of Pt and the Pt/Ti atomic ratio in the resulted nanocomposites were examined using a X-ray photoelectron spectroscopy with Al Kα radiation (Fisons Instruments, Escalab220i-XL). The charging effects were corrected by adjusting the C 1s peak to a position of 284.6 eV.

3. Results and discussion

3.1. Chemical and electronic structure of Pt/TiO_2

X-ray photoelectron spectra (XPS) analyses were carried out to determine the chemical and electronic structure of photocatalysts used in this work. Fig. 1 shows the typical XPS spectra of the Pt-loaded TiO_2 samples in the region of Pt 4f levels. As shown in Fig. 1(i), a binding energy of around 70.2 and 73.6 eV were observed as $4f_{7/2}$ and $4f_{5/2}$ electrons of the Pt metal (Pt^0), respectively, indicating that Pt photodeposited on TiO_2 surface is a metallic state [21–23], of which Pt^0 deposited on the catalyst surface functioned not only as the electron trap center but also as the adsorption center of O_2 in photocatalysis [12,24].

In the case of adding ethanol to the suspension (as shown in Fig. 1(ii)), however, binding energies ($4f_{7/2}$: 72.3 eV; $4f_{5/2}$: 75.6 eV) were higher than those of the two peaks of Pt, suggesting that Pt has an absorbed oxygen (PtO_{ads}).

3.2. Effect of photodeposited platinum in the O_3 decomposition on Pt/TiO_2 without UV light

Fig. 2 illustrates a representative time course for O_3 decomposition without UV light. The high relative conversion of O_3 could be obtained at the beginning because the surface of catalysts is initially covered with a monolayer of reactant, but conversion gradually decreases at longer reaction times. Conversion of O_3 abruptly decreases in case of pure TiO_2. The deactivation, however, on Pt/TiO_2 was much slower than on pure TiO_2 as shown in Fig. 2. In case of Pt/TiO_2, the higher is loading weight of Pt, the slower is the

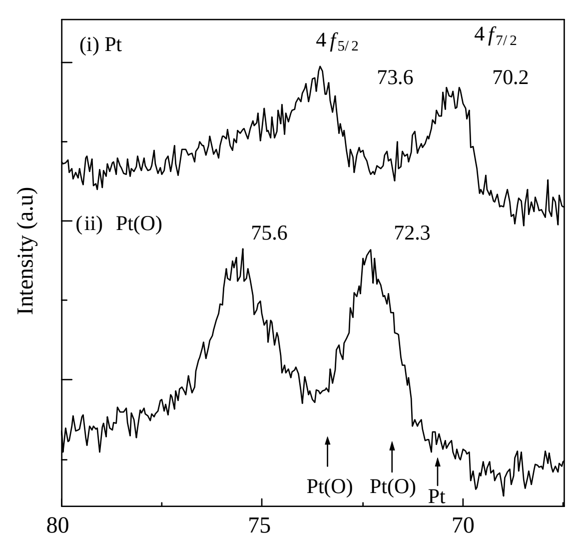

Fig. 1. XPS of Pt-loaded photocatalysts: (i) 1 wt.% Pt/TiO_2; (ii) 1 wt.% Pt/TiO_2–EtOH.

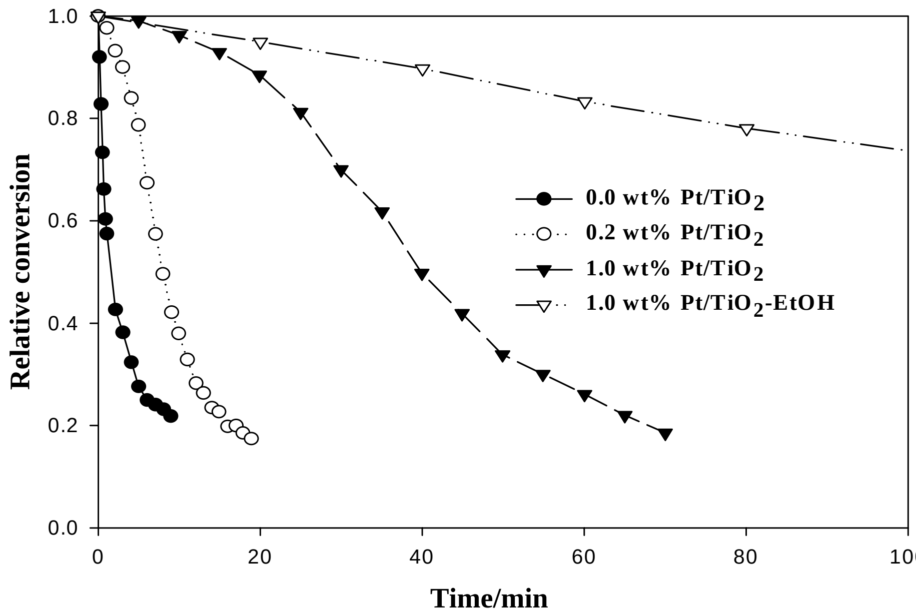

Fig. 2. Effect of amount of loaded Pt on conversion of O_3 without UV irradiation ($[O_3]_0 = 1$ ppmv; flow rate: 1.0 l/min).

deactivation rate as reaction time. As suggested by Li et al. [5], conversion decreasing as time is due to the coverage of the surface with reaction intermediates. They reported that O_3 adsorbs dissociatively on the catalyst surface to form an oxygen molecule and an atomic oxygen species. The atomic species reacts with another gaseous O_3 to form a peroxide species and a gas-phase oxygen molecule. The adsorbed peroxide species, the most abundant reaction intermediate, decomposes to form a gas-phase oxygen molecule.

As shown in Fig. 2, the relative conversion increased in the order of pure TiO_2 < 0.2 wt.% Pt/TiO_2 < 1.0 wt.% Pt/TiO_2 < 1.0 wt.% Pt/TiO_2–EtOH. Falconer and Magrini-Bair [25] reported that Pt supplies spillover oxygen onto the TiO_2 and the oxygen further oxidize the acetaldehyde products in the dark reaction. Therefore deactivation is dramatically slowed and oxidation of the acetaldehyde occurs efficiently even in the dark.

Imamura et al. [26] reported, in the decomposition of O_3 on a silver catalyst, that the activity of the metal oxide catalysts increased roughly in the order of the increase in their surface area and in the amount of surface oxygen on them. The synergistic effect of catalyst depends on how the catalysts were prepared. Vorontsov et al. [20] found that TiO_2 with various forms of photodeposited platinum particles has turned out to have different photocatalytic activity. These findings indicate that different reactive species responsible for the O_3 decomposition in the dark were formed on the photodeposited TiO_2 catalyst made in our study.

3.3. Photocatalytic performance of Pt/TiO_2 for O_3 decomposition

Table 1 shows dependence of the amount of Pt on photocatalytic decomposition of O_3. As shown in Table 1, the overall conversion efficiency for photocatalytic decomposition of O_3 was almost constant regardless of the amount of loaded Pt under the UV irradiation. Similar results have been observed in other photocatalytic systems up to 1 wt.% platinum loading [15,21]. In these cases, the amount of loaded Pt on a supporting material did not influence the activity.

The Pt/TiO_2 catalysts showed higher conversion efficiency for gaseous O_3 than pure TiO_2 catalyst. Pt may increase the O_2 concentration on the TiO_2 surface and thus accelerate photocatalytic oxidation. Even a low loading of Pt may be sufficient to slow deactivation significantly with UV light.

It was found that the decomposition products of O_3 can be removed from the Pt/TiO_2 surface under UV light.

3.4. Effect of flow rate on photocatalytic decomposition of O_3

Fig. 3 shows a time profile for the photocatalytic decomposition of gaseous O_3 observed by changing the flow rate. After the initial concentration of O_3 became stable at 1.0 ppm, the gas flow was switched to the photoreactor

Table 1
Dependence of the amount of Pt on photocatalytic decomposition of O_3 over Pt/TiO_2 catalyst (flow rate: 1.5 l/min; $[O_3]_0$: 1.0 ppmv; relative humidity: 0%)

	Amount of Pt loading (wt.%)				
	0	0.05	0.2	1.0	1.0[a]
Conversion of O_3 (%)	59.0	61.8	62.2	62.1	62.0

[a] Pt/TiO_2–EtOH.

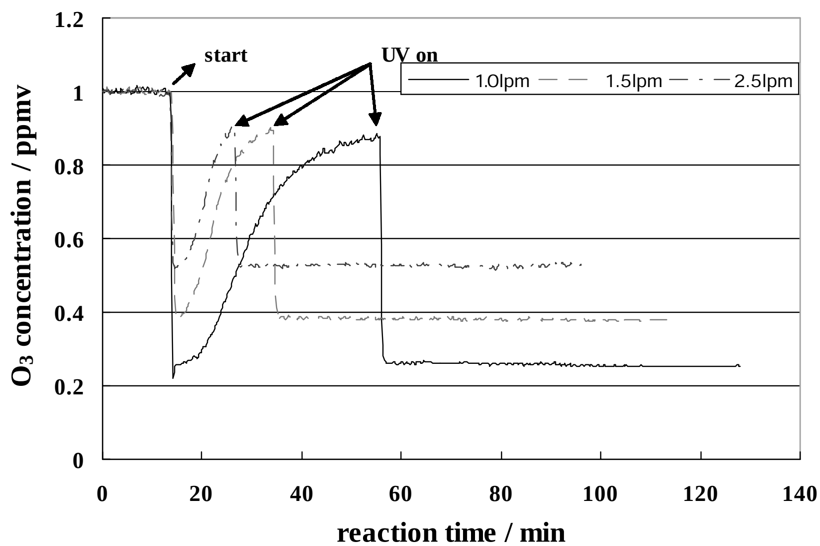

Fig. 3. Representative time profile for the photocatalytic decomposition of O_3 under different flow rates (Pt/TiO_2: 0.2 wt.%; $[O_3]_0 = 1.0$ ppmv; relative humidity: 0%; UV intensity: 0.49 mW/cm^2 at 300–400 nm).

(marked start in Fig. 3) and the UV lamp was turned on when the outlet concentration of O_3 reached about 90% of initial that of O_3. Just after the gas flow was switched to the reactor, the O_3 level rapidly decreased and then gradually increased when the UV lamp was off. However, the outlet O_3 level rapidly decreased to a sustained constant level when the UV light was illuminated. The oxidation rate was determined only after the outlet O_3 concentration reached a constant and sustained level under UV irradiation. As shown in Fig. 3, decomposition of O_3 decreases with increasing the flow rate. This is expected because a better gas–solid contact can be obtained with lower flow rate.

3.5. Effect of water vapor on photocatalytic decomposition of O_3

Many authors have reported a significant effect of humidity on the rate of photocatlytic degradation for gaseous air pollutants [27–29] and have observed that water vapor in the reaction gas affects the photocatalytic degradation reaction of gaseous air pollutants positively and negatively. In this study, different volume percentages of water vapor were added to a fixed O_3 concentration level of 1.0 ppmv in order to examine the effect of water vapor on the photocatalytic decomposition of gaseous O_3.

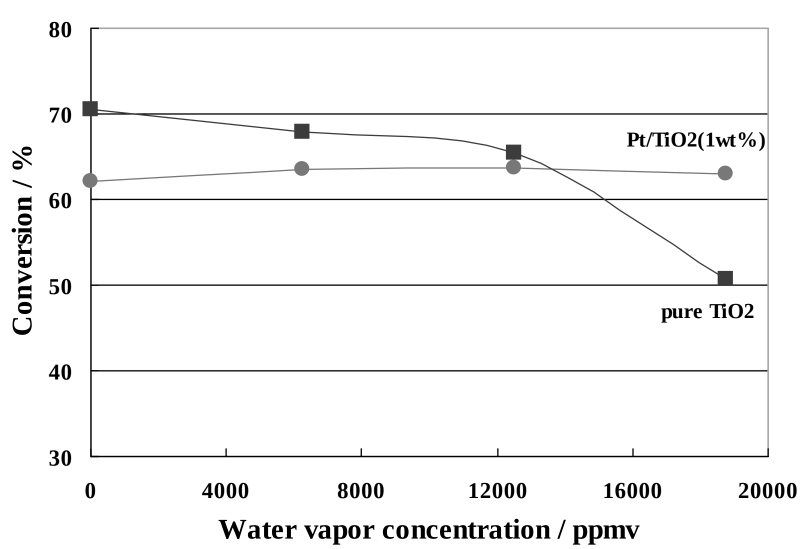

Fig. 4. Effect of water vapor concentration on photocatalytic conversion of O_3 (flow rate: 1.5 l/min (1 wt.% Pt/TiO_2) and 1.0 l/min (pure TiO_2); $[O_3]_0 = 1.0$ ppmv; UV intensity: 0.49 mW/cm^2 at 300–400 nm).

As shown in Fig. 4, Pure TiO_2 showed a decreased in the conversion of O_3 with increasing in water vapor in the feed stream. This result may indicate that the surface of the TiO_2 catalysts is strongly hydrophilic and the preferential adsorption of water on the surface is responsible for low degradation rate at high humidity [30]. Anpo et al. [31] have claimed that the addition of water onto oxides (TiO_2 and ZnO) causes structural changes in surface band bending, which enhances the efficiency of electron–hole recombination, and thus reduces photoefficiency.

For platinum loaded TiO_2, however, the O_3 conversion level was almost constant with increasing the water vapor concentration (Fig. 4) and maintained constants for the entire 5 days duration of the test, indicating that very little or no deactivation occurred. The role of water vapor has not been clarified yet. It has been reported that water vapor enhances the photoadsorption of oxygen by trapping the photogenerated holes at OH^- sites. Therefore, a possible explanation may be that water vapor inhibits the recombination of photogenerated holes and electrons, and facilitates the formation of stabilized active oxygen species on Pt/TiO_2 surface [13]. Kim and Hong [32] reported an important role of water vapor for regeneration of catalysts. They observed that the increase of toluene reaction rate under the presence of water vapor could lead to desorption or degradation of carboxylate molecules which were accumulated on the surface of catalysts. Ameen and Raupp [33] suggested that high water vapor concentrations result in high concentrations of adsorbed hydroxyls, which scavenge adsorbed organic intermediates and reduce the accumulation of inactive surface species.

Some authors have quantitatively reported the effect of humidity on photocatalytic reaction. Peral and Ollis [34] reported that the dependence of rate on the water concentration is expressed as

$$r = \frac{r_0}{1 + K_H[H_2O]^\beta} \tag{1}$$

where r_0 is the reaction rate under the condition that the feed stream is absolutely free of water, and K_H an influential factor related to water vapor in the flowing stream. Fig. 5 shows that the experimental data can be fitted by Eq. (2), which is the inverse of Eq. (1):

$$\frac{1}{r} = \frac{1}{r_0} + \frac{K_H}{r_0}[H_2O]^\beta \tag{2}$$

From plotting $1/r$ against $[H_2O]$, we can obtain $\beta = 1.714$, $r_0 = 0.0389\ \mu mol/cm^2\ h$, and $K_H = 1.8 \times 10^{-8}\ ppm^{-1}$.

3.6. *Effect of initial concentration on photocatalytic decomposition of O_3*

In general, for gas–solid reaction, the kinetics would follow the Langmuir–Hinshelwood (L–H) model, in which the reaction rate varies proportionally with the surface coverage (θ) as

$$r = k\theta = \frac{kKC}{1 + KC} \tag{3}$$

where k is the rate constant, related to the limiting rate of reaction at maximum coverage for the experimental conditions, K the adsorption equilibrium constant and reflects the proportion of solute molecules which adhere to the catalyst surface and C the concentration of the O_3. After substituting this rate expression into a mass balance on a plug flow

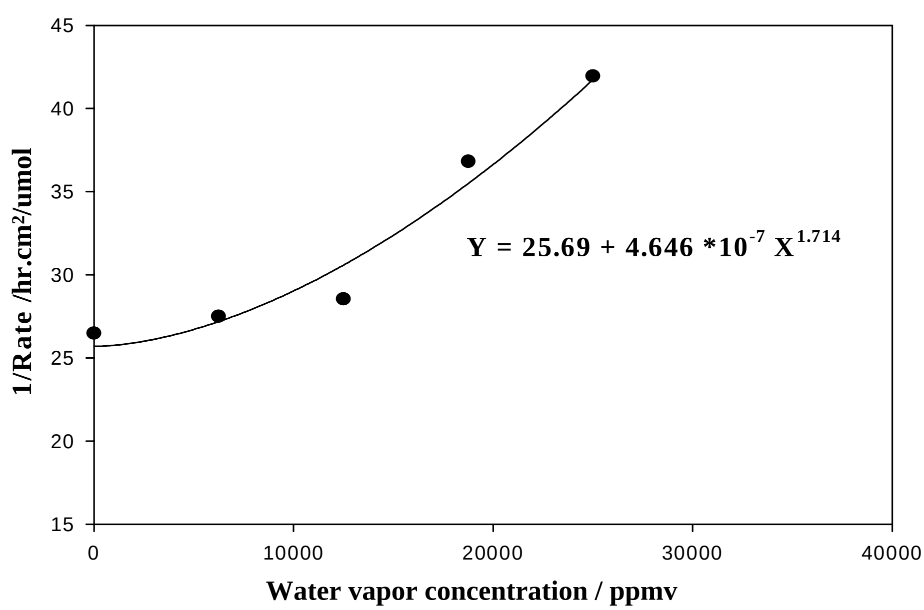

Fig. 5. Inverse of reaction rate of O_3 photooxidation vs. water vapor concentration in the gas phase (catalyst: pure TiO_2; $[O_3]_0 = 1$ ppmv; flow rate: 1.0 l/min; UV intensity: 0.49 mW/cm^2 at 300–400 nm).

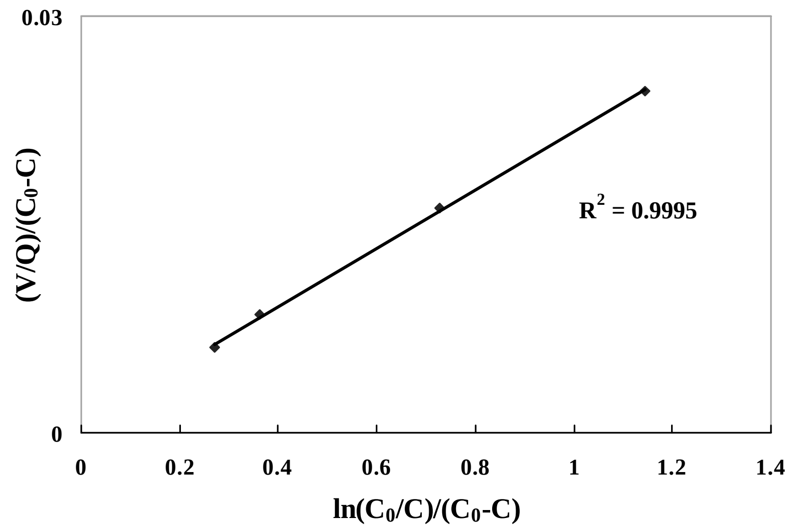

Fig. 6. L–H plots for O_3 decomposition (catalyst: 1 wt.% Pt/TiO_2; flow rate: 1.5 l/min; UV intensity: 0.49 mW/cm^2 at 300–400 nm).

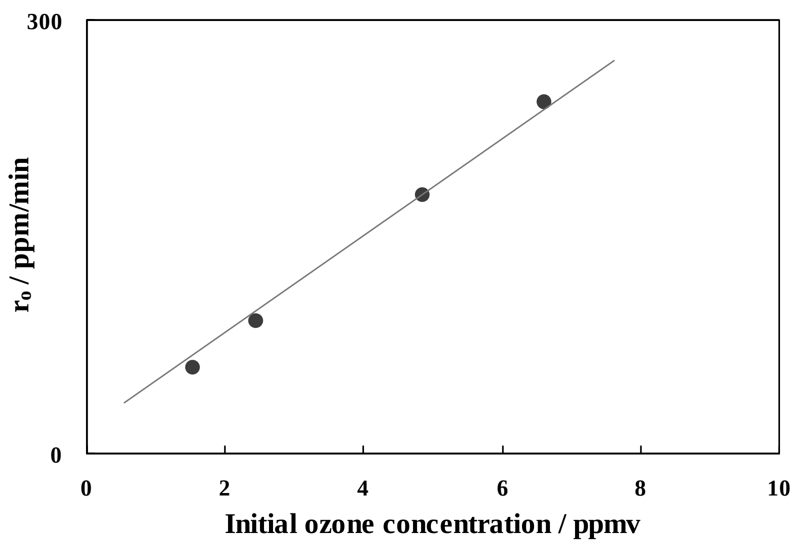

Fig. 7. O_3 oxidation rate dependence on initial O_3 concentration (catalyst: 1 wt.% Pt/TiO_2; flow rate: 1.5 l/min; UV intensity: 0.49 mW/cm^2 at 300–400 nm).

reactor, the following expression is obtained [35]:

$$\frac{V}{Q} = \frac{1}{kK}\ln\left(\frac{C_0}{C}\right) + \frac{1}{k}(C_0 - C) \quad (4)$$

where V is the volume of the reactor, Q the flow rate through the photoreactor and C_0 the initial concentration of O_3. The quantity, V/Q is known as the contact time for the reaction or average time that a molecule passes through the reactor.

The linear characteristic of Eq. (2) was used for fitting the experimental data after changing the form as follows:

$$\frac{V/Q}{C_0 - C} = \frac{1}{k} + \frac{1}{kK}\frac{\ln(C_0/C)}{C_0 - C} \quad (5)$$

If one assumes that L–H kinetics hold for a plug flow reactor, then a plot of $(V/Q)(C_0-C)^{-1}$ vs. $\ln(C_0/C)(C_0-C)^{-1}$ should be linear. Eq. (3) can be tested using different values of C_0 and C. Fig. 6 indicates that the experimental data are in good agreement with this integral rate-raw analysis. Values of k and K were obtained using linear least squares analysis. Values of $k = 1250$ ppm/min and $K = 0.038$ ppm^{-1} were then calculated from the intercept and slope in Fig. 6. In our preliminary experiments for decomposition of O_3 on pure TiO_2, values of $k = 357$ ppm/min and $K = 0.16$ ppm^{-1} were obtained. As shown in Fig. 7 the resulting correspondence between the L–H correlation and the experimental data was good.

4. Conclusions

In this study, we found that O_3 decomposition was promoted by the loading of Pt on TiO_2. The deactivation occurs much slower on Pt/TiO_2 than on pure TiO_2 in the dark reaction. The overall conversion efficiency of photocatalytic reactions was almost constant irrespective of the amount of loaded Pt under the UV irradiation. The conversion of O_3 decreased with an increase in water vapor in the feed stream for the photocatalytic decomposition of gaseous O_3 on pure TiO_2, while for Pt loaded on TiO_2, the O_3 conversion level was almost constant with increasing the water vapor. The photocatalytic decomposition rate of O_3 increased with increasing initial concentration of O_3 and the L–H kinetic model was successfully applied to correlate the obtained data.

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