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Titanium Dioxide/Zeolite Catalytic Adsorbent for the Removal of NO and Acetone Vapors

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ABSTRACT

This study delineates a simple and versatile approach for the removal of nitrogen monoxide (NO) and volatile organic vapors over composites of titanium dioxide (TiO₂) catalyst/zeolite adsorbent under ultraviolet (UV) irradiation at ambient temperature. The catalytic adsorbents with different TiO₂/H-ZSM-5 zeolite ratios were prepared by a simple insipient wetness impregnation method. It was found that a 60%/40% weight ratio of TiO₂/H-ZSM-5 composite is most effective and can achieve over 90% efficiency for the removal of NO and acetone vapors. This composite also showed a better long-term activity than that of bulk TiO₂ photocatalyst or zeolite adsorbent. The experimental results revealed that photocatalytic decomposition of NO was dramatically enhanced in the presence of acetone. NO also promoted the acetone oxidation under humid conditions. Furthermore, the co-existence of acetone and NO in the gaseous stream could reduce acid accumulation on the surface of the catalyst as confirmed by Fourier-transform infrared spectroscopy. Thus, the TiO₂/zeolite catalytic adsorbent could have a high potential for the removal of multiple air pollutants in the indoor air environment.

INTRODUCTION

Indoor air pollution has been recognized as one of the most important environmental problems.¹ Indoor air pollutants are emitted from various sources such as combustion processes, cooking stoves, office equipment, construction materials, consumer products, etc.^{1,2} Various kinds of air pollutants may be presented in the indoor air because of different sources of indoor air pollution, but nitrogen oxides (NO_x) and volatile organic compounds

(VOCs) have always been two of the most common air pollutants.

For the protection of indoor air quality, adsorption is one of the traditional pollutant control techniques. Adsorbent such as activated carbon is most commonly used for the removal of air pollutants because of its high adsorption capacity and low operation cost. However, the adsorbent merely transfers pollutants from the gaseous phase to the solid phase.^{3–5}

For the past 2 decades, it has been recognized that photocatalytic oxidation (PCO) using titanium dioxide (TiO₂) semiconductors is one of the attractive and efficient techniques for the complete destruction of harmful pollutants into nontoxic final products.^{6,7} Furthermore, the semiconductor catalysts are inexpensive and capable of effectively destroying the gaseous pollutants. In this regard, numerous investigations have been conducted on TiO₂ semiconductors for the photocatalytic destruction of various air pollutants such as VOCs^{8–10} and NO_x.^{11–13}

Several studies have been investigated on the photochemical reaction and photodegradation mechanism of VOCs and NO_x. For example, Atkinson^{14–16} reviewed the gas-phase reaction and photodegradation mechanism of VOCs and NO_x in the troposphere. Ao et al.^{3,17–19} have also demonstrated that the photoreaction and mechanism of nitrogen monoxide (NO); benzene, toluene, ethyl benzene, and xylenes (BTEX); NO; nitrogen dioxide (NO₂); and carbon monoxide (CO) at typical indoor air levels using TiO₂ as a photocatalyst. Although it is not possible to evaluate the interactions of all indoor air pollutants by photocatalysis, a study of the interactions between the major and common air pollutants using photocatalysis is feasible and valuable.

Most of the studies in the literature have mainly described removal of air contaminants by adsorption or photocatalytic destruction methods. The research works of Ao and co-workers^{3,17–20} have been the few references that have conducted the enhancement or inhibition effects due to the simultaneous presence of multiple air pollutants. The composite materials of photocatalyst/adsorbent they used were TiO₂ supported on activated carbon (AC). Tao and co-workers^{21,22} have investigated the photocatalytic removal of methanol over a dual functional TiO₂/AC composite material. They found that a well dispersion of TiO₂ particles on AC composite material prepared by dry impregnation method has a high photocatalytic activity for methanol removal. However,

IMPLICATIONS

Indoor air pollution has always been a problem that involves more than one air pollutant. However, there is usually only one air cleaner for removing several air pollutants, so the combination of effective adsorbents/catalysts in one air cleaning device is a viable method to achieve this goal. In this study, the composite of TiO₂/H-ZSM-5 as photocatalytic sorbent under UV irradiation has been used to study its effectiveness in removing common air pollutants of NO and volatile organic compounds. The promotion effect on the removal of these two air pollutants has been observed, and this composite material has shown its high potential application to indoor air cleaning.

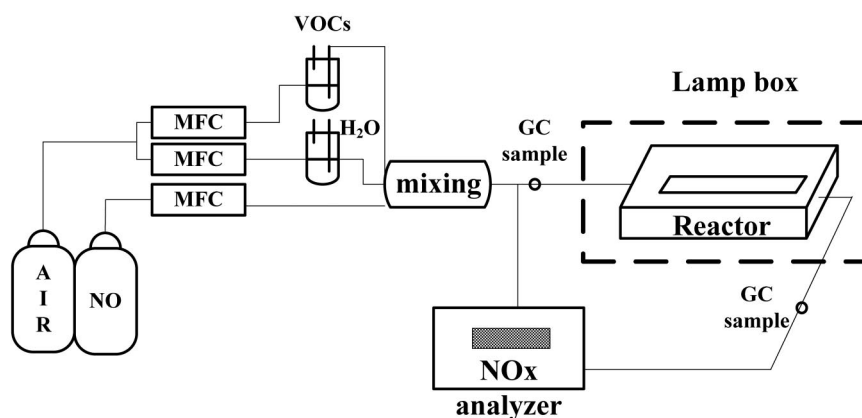


Figure 1. Schematic diagram of the continuous gas flow photoreactor system.

Thevenet et al.²³ conducted the photocatalytic enhancement of acetylene on TiO_2/AC and $\text{TiO}_2/\text{zeolite}$ and compared with the bulk TiO_2 , they found that zeolite significantly improved the photoactivity, whereas AC was only identified as a pollutant pool.

TiO_2 -supported zeolites have attracted research interest as an active composite photocatalyst for the removal of toxic contaminants.^{24,25} However, there is still limited information available on the photochemical interactions between VOCs and NO_x during the simultaneous adsorption and PCO process. In this regard, the purpose of this study was to evaluate the combined effects of TiO_2 catalyst and zeolite adsorbent for the removal of NO and acetone vapors under ultraviolet (UV) irradiation at ambient temperature. The removal efficiency of the catalyst/adsorbent composites was compared with those of bulk TiO_2 (ST-01) catalyst and zeolite (H-ZSM-5) adsorbent, and optimal catalyst/adsorbent composition was obtained. Furthermore, the promotion effects of NO and acetone removal efficiencies because of the co-presence of the two pollutants were addressed.

EXPERIMENTAL PROCEDURES

Preparation of $\text{TiO}_2/\text{Zeolite}$ Composite Materials

The Na-form of ZSM-5 zeolite (silicon/aluminum ratio 50, particle size 1.5–2 μm ; Zeotyst, Ltd.) was converted into the H-form by repeated ion exchange. The zeolite and 0.05 M ammonium nitrate solution (15 mL/g of zeolite) were stirred at 80 °C for 12 hr. Then the material was filtered and washed with distilled water. The resulting filtered material was dried at 120 °C for 6 hr and subsequently calcined at 550 °C for 6 hr. This H-form of ZSM-5 zeolite was used as an adsorbent and support in this study. The $\text{TiO}_2/\text{zeolite}$ -based composite photocatalysts were prepared by a simple incipient wetness impregnation method. An appropriate amount of TiO_2 (ST-01, particle size 7 nm, Ishihara Sangyo Kaisha, Ltd.) was added into 20 mL of deionized (DI) water and stirred for 1 hr. Then H-ZSM-5 zeolite was added into the aqueous colloidal suspension of TiO_2 . The above colloidal mixture was thoroughly stirred for additional 1 hr and agitated with sonication bath (Tohama DC-400) for 10 min. Then the above mixture was sprayed on a heating glass plate of 110 °C. The total weight of all samples for comparison tests was fixed at 0.1 g regardless of the weight percentage

of TiO_2 or zeolite. Repeated spraying, cooling, and weighting of the composite samples confirmed the total weight of sample.

Characterization of $\text{TiO}_2/\text{Zeolite}$ Composite Materials

The crystalline nature of the calcined samples was obtained with Rigaku X-ray diffractometer equipped with nickel-filtered $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation. The diffractograms of the calcined samples were recorded in the 2θ range between 2° and 60° in steps of 1° with a count time of 60 sec at each point. The BET (Brunauer-Emmett-Teller) specific surface areas of the samples were measured by nitrogen gas (N_2) adsorption-desorption isotherms at 77 K using a surface area analyzer (Micromeritics, ASAP 2000). All of the samples were degassed for 6 hr at 350 °C under vacuum (10^{-6} mbar) before the adsorption experiments. The elemental titanium in the samples was analyzed by a SCIEX ELAN 5000 inductively coupled plasma mass spectrometer (ICP-MS). The infrared (IR) spectra of the samples were obtained from a Fourier-transform IR (FTIR; FT-730) spectrophotometer using a potassium bromide pellet technique.

Adsorption and Photocatalytic Experiments

A photoreactor (dimensions of 5.5-cm height \times 63-cm length \times 10-cm width) was made up of acrylic resin-type material and a glass plate with 300 mm of length, 50 mm of width, and 1 mm of thickness was used as a coating substrate that was placed inside of the photoreactor. The photocatalysts were dispersed in DI water by using sonication method. The photocatalytic degradation of NO and acetone vapors was carried out using a continuous flow photoreactor under UV irradiation at ambient temperature. Figure 1 shows a schematic diagram of the experimental setup used in this study.

A feed gas of reactant mixture containing NO (10 parts per million by volume [ppmv]), acetone (110 ppmv), and air (balance) were passed through two different mass flow controllers to the photoreactor. It is noted that typical concentrations of indoor air pollutants such as VOCs and NO_x are usually in a few parts per million (ppm) to sub-ppm levels.^{26,27} However, for the sake of analytical quantification of the deterioration of photocatalyst due to

the formation of nitric acid and to speed up the adsorption breakthrough time, NO and acetone vapors were tested at relatively higher concentration levels in this study. The concentration of acetone was selected to be much higher than that of NO because the total concentration of volatile organic vapors in ambient air is usually much higher than that of the NO_x . The source of NO gas was supplied from cylinder and diluted by a separate airstream. The concentration of acetone (VOC) vapors was controlled by passing carrier gas through an impinger containing acetone and the impinger was kept in a constant-temperature controller maintained at -10°C . The diluted air was controlled by a mass flow controller and passed into an impinger containing DI water to adjust the relative humidity (RH) to be approximately $55 \pm 5\%$ in the outlet gas flow, which corresponds to a water vapor concentration of around 17,500 ppmv under 25°C and 1 atm. The level of RH used in this study was in the range of recommended levels by the American Society of Heating, Refrigerating and Air-Conditioning Engineers²⁸ (30–60%) and by the Taiwan Indoor Air Association²⁹ (40–70%).

The desired flow of gas stream of NO, acetone, and water vapors was controlled by a mass flow controller and the gas stream was premixed by using a stainless steel mixer. The concentrations of the gas mixture were measured before each experimental test to ensure the desired stable concentrations. The total flow rate of gas mixture was set at two different flow rates of 180 and 500 mL/min, which correspond to residence times of 75 and 27 sec, respectively. The photocatalytic decomposition reaction was carried out under UV irradiation with a 365-nm UV lamp (Sparkie UVA-S; 10 W) being used as a light source. The UV lamp was horizontally placed at the upper part of the reactor, and the photocatalyst-coated glass plate was horizontally fixed at the lower part of the reactor at a vertical distance of approximately 20 cm from the UV lamp. UV intensity measured in all experiments was 2.5 mW/cm^2 as measured on the surface of the photocatalysts. The inlet and outlet concentrations of NO and NO_2 were continuously monitored by an online NO_x (SIR Model S5012) analyzer, which monitors NO, NO_2 , and NO_x , and then the selectivity of NO_2 was calculated. The inlet and outlet concentrations of acetone samples were taken at designated time intervals during the experiment using a microsyringe, and the samples were analyzed by a gas chromatograph (GC; Model-SRI 8610) using a capillary column (30 m) equipped with a flame-ionization detector (FID).

Table 1. Physicochemical characterization of the photocatalytic sorbents.

Photocatalytic Sorbent	Catalyst/Sorbent Content (wt%)		ICP-MS Titanium Contents (wt%)	Surface Area (m^2/g)
	TiO_2 (ST-01)	Zeolite (H-ZSM-5)		
H-ZSM-5	–	100	–	410
$\text{TiO}_2/\text{H-ZSM-5}$	20	80	9.42	343
$\text{TiO}_2/\text{H-ZSM-5}$	40	60	19.47	292
$\text{TiO}_2/\text{H-ZSM-5}$	60	40	30.24	224
$\text{TiO}_2/\text{H-ZSM-5}$	80	20	40.53	158
TiO_2	100	–	–	82

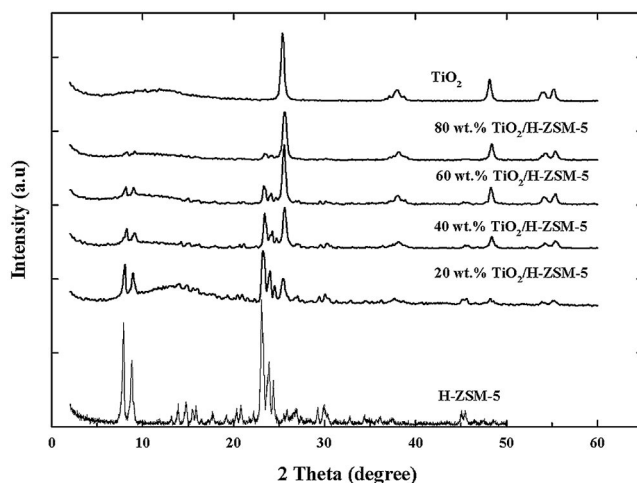


Figure 2. XRD patterns of the bulk TiO_2 , H-ZSM-5, and $\text{TiO}_2/\text{H-ZSM-5}$ composite catalysts.

RESULTS AND DISCUSSION

X-Ray Diffraction and BET Analysis

The crystalline nature of H-ZSM-5, TiO_2 (ST-01), and $\text{TiO}_2/\text{H-ZSM-5}$ composite materials was confirmed by X-ray diffraction (XRD) analysis and the results are depicted in Figure 2. It can be seen that the XRD pattern of TiO_2 clearly indicates characteristic peaks of the anatase form of TiO_2 crystals.³⁰ The major peaks that appeared in the 2θ range between 22° and 25° and 7° and 9° correspond to the specific peaks of H-ZSM-5 zeolite.³¹ As the content of H-ZSM-5 zeolite is increased in the $\text{TiO}_2/\text{zeolite}$ composites, the gradual increase in the intensity of the zeolite peaks and the decrease in the intensity of the TiO_2 peaks are clearly observed.

To confirm the accuracy of the weight percentage mixing of the $\text{TiO}_2/\text{zeolite}$ composites, the titanium contents of the $\text{TiO}_2/\text{H-ZSM-5}$ composite materials were analyzed by ICP-MS, and the specific surface areas of H-ZSM-5, TiO_2 , and $\text{TiO}_2/\text{H-ZSM-5}$ composites were analyzed by nitrogen adsorption-desorption measurements. ICP-MS and BET results of the samples are presented in Table 1. Because the surface area of H-ZSM-5 zeolite ($410 \text{ m}^2/\text{g}$) is much higher than that of bulk TiO_2 ($82 \text{ m}^2/\text{g}$), the specific surface area of the $\text{TiO}_2/\text{H-ZSM-5}$ composites gradually decreased with increasing TiO_2 loading. One can see that the surface area of the $\text{TiO}_2/\text{H-ZSM-5}$ composites and the titanium content corresponded well to the weight percentage of the composites.

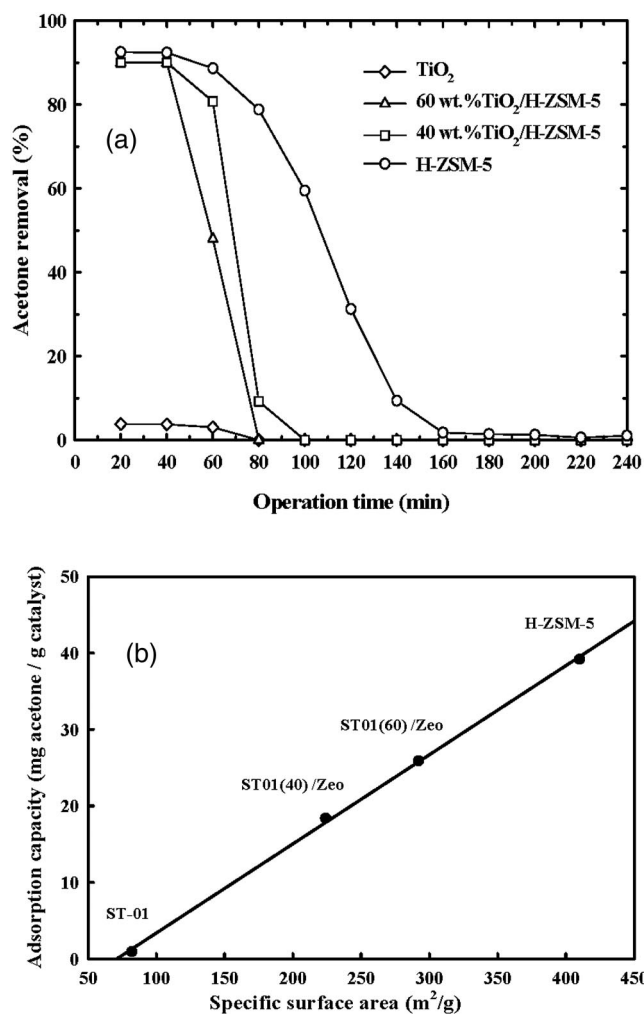


Figure 3. (a) The acetone removal from streams of NO + acetone mixture as a function of operation time without UV irradiation under a flow residence time of 75 sec. (b) The correlation between specific surface area of the material and the saturated adsorption capacity of acetone.

Removal of NO and Acetone Vapors

Blank tests on the removal of NO and acetone vapors were conducted first. The photochemical reaction was tested in the absence of catalyst and zeolite. The blank test results indicated that there was no photochemical reaction under UV irradiation in the absence of catalyst for NO and acetone vapors; hence, the results are not shown. Furthermore, blank tests were also conducted on TiO₂/zeolite composites in the absence of UV irradiation to evaluate the acetone and NO removal via pure adsorption. The adsorption results indicated that there was no adsorption of NO on the surface of the TiO₂/zeolite composites, but the acetone vapors were predominately adsorbed on the surface of the catalysts.

Figure 3a shows the acetone removal efficiency over H-ZSM-5, TiO₂, and 40 and 60 wt % TiO₂/H-ZSM-5 composites as a function of operation time. It can be seen that the acetone removal efficiencies are in the order of H-ZSM-5 zeolite > 40 wt % TiO₂/H-ZSM-5 > 60 wt % TiO₂/H-ZSM-5 > TiO₂. The higher acetone removal efficiency of H-ZSM-5 zeolite as compared with that of TiO₂ could be due to its higher BET surface area. This was confirmed by

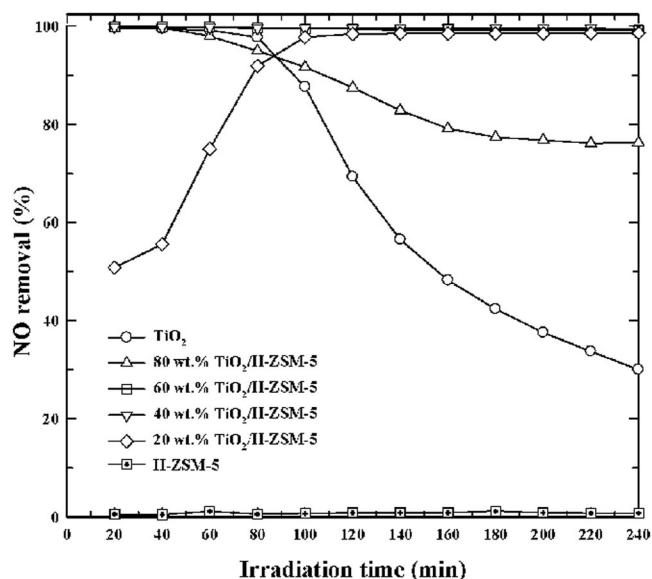


Figure 4. Effect of TiO₂ content in the TiO₂/zeolite composites on the NO removal from streams of NO + acetone mixture under a flow residence time of 75 sec.

the correlation between specific surface area of the material and the saturated adsorption capacity of acetone as shown in Figure 3b. It can be clearly seen that the adsorption capacity of acetone is linearly correlated to the specific surface area of the material.

Adsorption and Photocatalytic Effects

The adsorption and photocatalytic degradation for mixture of NO and acetone vapors were carried out in the continuous flow photoreactor system under UV irradiation at ambient temperature. Figure 4 shows the NO removal over bulk TiO₂, H-ZSM-5, and TiO₂-supported zeolite composites as a function of irradiation time. As can be expected, when no TiO₂ was present, there was no photocatalytic reaction at all. As the weight percentage of TiO₂ on the H-ZSM-5 zeolite was increased to 20% (w/w), the initial NO removal rate was gradually increased with increasing irradiation time and it reached approximately 100% removal after 100 min of irradiation time. On the other hand, at high TiO₂ loading of 80 wt % TiO₂/H-ZSM-5 composite and bulk TiO₂ catalyst, they showed quite high initial NO removal of approximately 100% up to 80 min, then the NO removal decreased with increasing irradiation time. This could be ascribed to the deactivation of the catalyst by accumulation of unreactive by-products. The deactivation rate is much faster as the TiO₂ content increases. As a result, the best TiO₂/zeolite composites appeared to be 40 and 60 wt % TiO₂/zeolite, the NO removal of which was near 100% for all irradiation time.

The adsorption and PCO of acetone vapors from streams of NO and acetone mixture by H-ZSM-5, bulk TiO₂, and TiO₂/H-ZSM-5 composites are depicted in Figure 5. The acetone vapor removal by H-ZSM-5 zeolite, which is expected to be due to its adsorption effect, was around 90% up to 60 min and then decreased to 0% because of saturated adsorption. On the other hand, the removal efficiency of acetone over bulk TiO₂ catalyst,

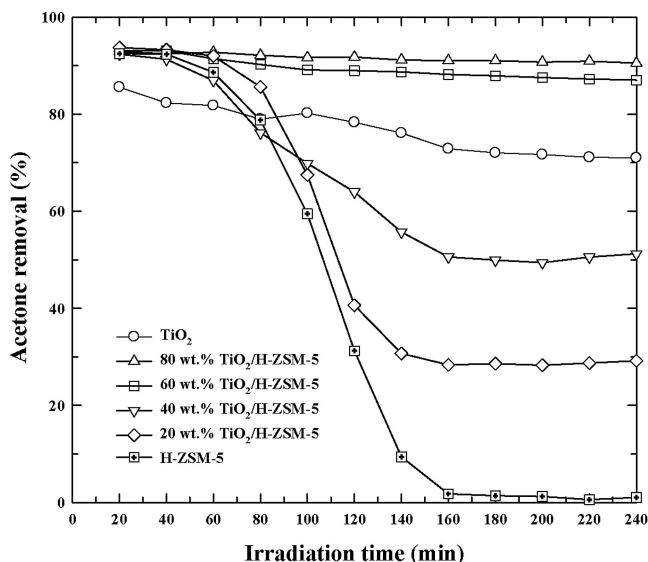


Figure 5. Effect of TiO₂ content in the TiO₂/zeolite composites on the acetone removal from streams of NO + acetone mixture under a flow residence time of 75 sec.

which is expected to be due to photocatalytic effect, was above 80% initially then gradually decreased to around 70%. For the TiO₂/zeolite composites, it showed that 20 and 40 wt % TiO₂-supported zeolites have less acetone removal efficiency as compared with those of 60 and 80 wt % TiO₂-supported zeolite and even bulk TiO₂ catalyst. This could be because the TiO₂ loading is not enough so that the adsorption process dominates and the photocatalytic reaction can proceed only to some extent. The results reveal that the optimal composite ratio seems to be 60–80 wt % TiO₂/H-ZSM-5 composites. Therefore it seems that combining a small amount of H-ZSM-5 zeolite with the TiO₂ photocatalyst can help to enhance acetone removal and prevent the deactivation of the photocatalysts.

Effect of Residence Time on the Optimal TiO₂/Zeolite Composite Ratio

Figure 6 shows the influence of residence time on removal of NO and acetone over TiO₂, H-ZSM-5, and TiO₂/H-ZSM-5 composites. In this study, two residence times of 75 and 27 sec were chosen to evaluate the removal efficiency of the catalysts. When decreasing the residence time from 75 to 27 sec, the acetone removal was drastically decreased over all catalysts. On the other hand, the removal of NO does not seem to be significantly affected by the residence time. It implies that the acetone molecules might first be adsorbed on the surface of the catalyst and then the photocatalytic decomposition of acetone takes place. But the NO molecule might be immediately photodecomposed into N₂ or oxidized to NO₂.^{32,33} The best TiO₂/zeolite composites appeared to be 20–60 wt % TiO₂ supported on H-ZSM-5 zeolite for the removal of NO, and 80 wt % TiO₂ supported on H-ZSM-5 zeolite for the removal of acetone vapors. For the removal of NO and acetone vapors, 60 wt % TiO₂/H-ZSM-5 composite was found to be the most effective and optimal catalyst/adsorbent composite.

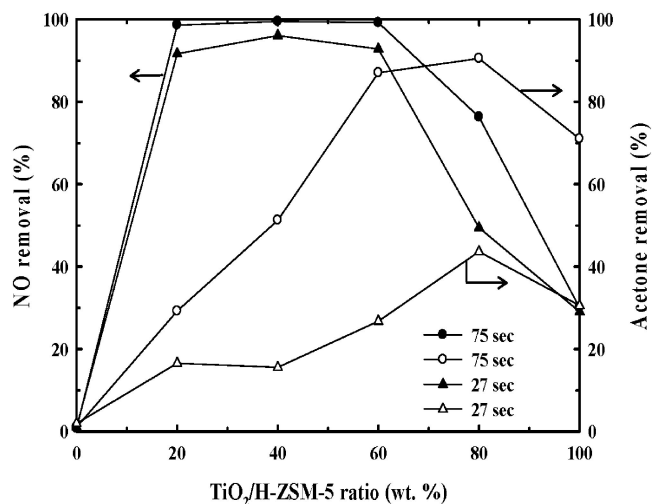


Figure 6. Effect of flow residence time on NO and acetone removal from streams of NO + acetone mixture at an irradiation time of 240 min.

Effect of NO on Acetone Removal

Figure 7 illustrates the removal of acetone in the presence and absence of NO in the gaseous stream using 60 wt % TiO₂/H-ZSM-5 composite at a flow residence time of 75 sec. It was found that the PCO of acetone was dramatically enhanced in the presence of NO and the photocatalytic activity was almost the same up to 240 min of irradiation time. On the other hand, the acetone removal under the absence of NO was initially very high at 100%, but it then decreased drastically to around 60–65% after 60 min.

On the basis of the results, it is possible to propose that the formation of some intermediate species from NO oxidation could react immediately with acetone molecules. Therefore, the oxidation of acetone is strongly promoted by some intermediate species formed from NO. During the photocatalytic reaction, NO is generally continuously oxidized to form NO₂, and then NO₂ is further

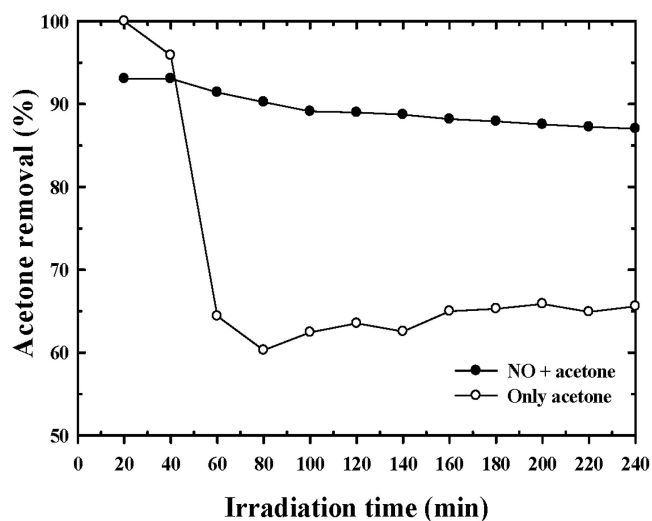


Figure 7. PCO of acetone in the presence and absence of NO over 60 wt % TiO₂/H-ZSM-5 composite.

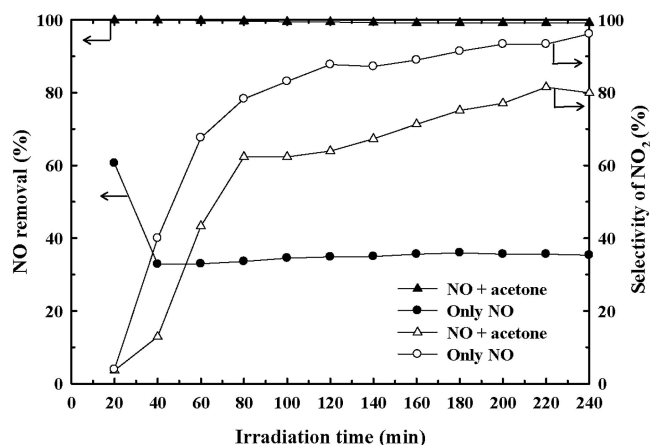
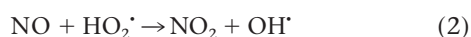


Figure 8. Removal of NO and the corresponding NO₂ selectivity in the presence and absence of acetone over 60 wt % TiO₂/H-ZSM-5 composite. The flow residence time was 75 sec.

converted into nitric acid (HNO₃) under PCO in the atmosphere. The general reactions of NO oxidation by photocatalysis are given in the following equations:



Atkinson and co-workers^{14–16} demonstrated the rate constant and mechanism for the combination reaction of the OH radical with NO₂ to form HNO₃ in the troposphere. They also calculated the rate constant for the gas-phase reactions of OH radical with acetone molecules with various temperature ranges.¹⁵ The calculated room temperature rate constants for the reactions of OH radicals with acetone molecule and NO₂ is around $0.22 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$ and $1.42 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$, respectively.^{14,34} Furthermore, methods also exist for estimating rate constants for the reactions of VOCs with OH and NO_x radicals, which can be used when data are not available.^{14–16}

Under the simultaneous presence of NO and acetone, the acetone could take up the OH radical formed in eq 2; hence, the acetone removal is enhanced. On the other hand, HNO₃ is usually formed as a final byproduct.³⁵ This HNO₃ species is strongly adsorbed on the surface of the catalyst, which causes catalyst deactivation and hence decreased photocatalytic activity with respect to irradiation time.^{13,33} But if the OH radical is taken up by acetone, then the HNO₃ formation of eq 3 should be hindered.

Effect of Acetone on NO Removal

To further understand the mutual effect of NO and acetone, the experiment was also conducted over 60 wt % TiO₂/H-ZSM-5 composite in the presence and absence of acetone in the gas mixtures under UV irradiation. The effects of acetone on the NO removal and on the selectivity of NO₂ are shown in Figure 8. It can be seen that the

photocatalytic decomposition of NO was significantly enhanced in the presence of acetone. Thus, from Figures 7 and 8 it was found that the photocatalytic decomposition of acetone and NO was enhanced under the simultaneous presence of NO and acetone vapors. Similar results have also been identified by Higashimoto et al.³⁶ for the photocatalytic decomposition of NO in the presence of propane (C₃H₈) over VS-1 zeolite used as a catalyst.

The photocatalytic decomposition of NO in the absence of acetone was found to be less efficient, as seen in Figure 8. This may be due to the rapid photooxidation of NO into NO₂ and the active NO₂ species reacting immediately with OH radical to form HNO₃, as shown in eq 3. Hence, the nitrate ions (NO₃⁻) from acid could be adsorbed on the surface active sites of the catalyst, which causes the catalyst deactivation.^{13,35} On the other hand, the enhancement in NO removal in the presence of acetone could be expected from the rapid formation of OH radical that can be utilized for the simultaneous oxidation of NO and acetone. Therefore, the formation of HNO₃ could be reduced with the co-existence of acetone and NO, and hence the photocatalytic decomposition of NO and acetone vapors could be maintained without any significant deactivation by HNO₃.

As also observed in Figure 8, the selectivity of NO₂ was increased with increasing irradiation time in the presence and absence of acetone vapors. However, it is interesting to note that the selectivity of NO₂ in the presence of acetone was lower than the selectivity of NO₂ in the absence of acetone. Therefore eq 2 may not be the only pathway for the further reaction of NO. It is possible that the NO reduction can also be favorable in addition to the NO oxidation mechanism. The formation of some intermediate organic radicals that reduced the NO_x (NO and NO₂) into N₂ and oxygen gas (O₂) because of the presence of hydrocarbons has been discussed by Higashimoto et al.³⁶ Therefore, oxidation and reduction of NO could occur in the presence of acetone because acetone can act as a reducing agent in this system. However, because of instrument limitation, the NO reduction intermediates such as nitrous oxide (N₂O) and its final product, N₂, could not be detected at the present time. The confirmation of the NO oxidation/reduction mechanisms requires further study.

On the other hand, the selectivity of NO₂ was reached finally at approximately 100% in the absence of acetone. These results clearly indicate that the NO molecules were predominately oxidized into NO₂ in the absence of acetone. The generated NO₂ may react immediately with freely available OH radical to form HNO₃ by eqs 2 and 3; hence, the acid accumulation can cause the catalyst deactivation. To further confirm this, catalyst samples for the PCO of NO in the presence and absence of acetone were analyzed by FT-IR and the results are depicted in Figure 9. It can be seen that the peaks appearing at 1385 cm⁻¹ are due to the formation of nitrate species on the surface of the catalyst.^{11,35} The FT-IR spectrum of the sample in the presence of NO and acetone clearly indicates that it has a less intense peak at 1385 cm⁻¹, which suggests less formation of HNO₃ on the surface of the catalyst. On the other hand, when only NO was presented in the gas stream, the increase in peak intensity at

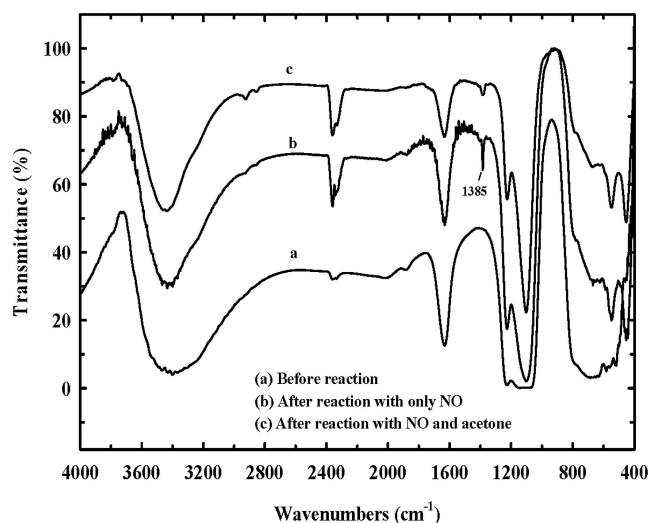


Figure 9. FT-IR spectra of 60 wt % $\text{TiO}_2/\text{H-ZSM-5}$ composite catalyst before and after photocatalytic reaction.

1385 cm^{-1} indicates the formation of more HNO_3 on the surface of the catalyst. Thus the hypothesis that the co-existence of acetone and NO in the gaseous stream could diminish the acid formation is confirmed.

CONCLUSIONS

Combined effects of TiO_2 catalyst/zeolite adsorbent composite was suggested as an effective photocatalytic system for the simultaneous removal of multiple pollutants in the ambient air under UV irradiation. The 60 wt % $\text{TiO}_2/\text{H-ZSM-5}$ composite was found to be the optimal composite ratio for better removal efficiencies ($\geq 90\%$) of NO and acetone vapors than those of commercial TiO_2 (ST-01) catalyst and zeolite (H-ZSM-5) adsorbent under humid conditions. It was found that the co-existence of acetone and NO in the gaseous stream could reduce the acid accumulation on the surface of the catalyst and enhance their removal as compared with their individual presence in the gas stream. The results on the selectivity of NO_2 also indicated that the possibility of simultaneous NO oxidation/reduction mechanisms are present with the co-existence of NO and acetone in a humid environment; however, further studies are required to confirm this hypothesis.

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REFERENCES

- Wang, S.; Ang, H.M.; Tade, M.O. Volatile Organic Compounds in Indoor Environment and Photocatalytic Oxidation: State of the Art; *Environ. Int.* **2007**, *33*, 694-705.
- Namiesnik, J.; Gorecki, T.; Kozdronzabiegala, B.; Lukasiak, J. Indoor Air-Quality (IAQ), Pollutants, Their Sources and Concentration Levels; *Build. Environ.* **1992**, *27*, 339-356.
- Ao, C.H.; Lee, S.C. Combination Effect of Activated Carbon with TiO_2 for the Photodegradation of Binary Pollutants at Typical Indoor Air Level; *J. Photochem. Photobiol. A Chem.* **2004**, *161*, 131-140.
- Guillemot, M.; Mijoin, J.; Mignard, S.; Magnoux, P. Volatile Organic Compounds (VOCs) Removal over Dual Functional Adsorbent/Catalyst System; *Appl. Catal. B Environ.* **2007**, *75*, 249-255.
- Blocki, S.W. Hydrophobic Zeolite Adsorption: a Proven Advancement in Solvent Separation Technology; *Environ. Prog.* **1993**, *12*, 226-230.
- Fujishima, A.; Rao, T.N.; Tryk, D.A. Titanium Dioxide Photocatalysis; *J. Photochem. Photobiol. C Photochem. Rev.* **2000**, *1*, 1-21.
- Kitano, M.; Matsuoka, M.; Ueshima, M.; Anpo, M. Recent Developments in Titanium Oxide-Based Photocatalysts; *Appl. Catal. A Gen.* **2007**, *325*, 1-14.
- Coronado, J.M.; Kataoka, S.; Tejedor, I.T.; Anderson, M.A. Dynamic Phenomena during the Photocatalytic Oxidation of Ethanol and Acetone over Nanocrystalline TiO_2 : Simultaneous FT-IR Analysis of Gas and Surface Species; *J. Catal.* **2003**, *219*, 219-230.
- Deng, X.; Yue, Y.; Gao, Z. Gas-Phase Photo-Oxidation of Organic Compounds over Nanosized TiO_2 Photocatalysts by Various Preparation; *Appl. Catal. B Environ.* **2002**, *39*, 135-147.
- Augugliaro, V.; Coluccia, S.; Loddo, V.; Marchese, L.; Martra, G.; Palmisano, L.; Schiavello, M. Photocatalytic Oxidation of Gaseous Toluene on Anatase TiO_2 Catalyst: Mechanistic Aspects and FT-IR Investigation; *Appl. Catal. B Environ.* **1999**, *20*, 15-27.
- Lim, T.H.; Jeong, S.M.; Kim, S.D.; Gyenis, J. Photocatalytic Decomposition of NO by TiO_2 Particles; *J. Photochem. Photobiol. A Chem.* **2000**, *134*, 209-217.
- Zhang, J.; Ayusawa, T.; Minagawa, M.; Kinugawa, K.; Yamashita, H.; Matsuoka, M.; Anpo, M. Investigations of TiO_2 Photocatalysts for the Decomposition of NO in the Flow System: the Role of Pretreatment and Reaction Conditions in the Photocatalytic Efficiency; *J. Catal.* **2001**, *198*, 1-8.
- Tseng, Y.H.; Kuo, C.-S.; Huang, C.-H.; Li, Y.-Y.; Chou, P.-W.; Cheng, C.-L.; Wong, M.-S. Visible-Light-Responsive Nano- TiO_2 with Mixed Crystal Lattice and Its Photocatalytic Activity; *Nanotechnology* **2006**, *17*, 2490-2497.
- Atkinson, R. Atmospheric Chemistry of VOCs and NO_x ; *Atmos. Environ.* **2000**, *34*, 2063-2101.
- Kwok, E.S.C.; Atkinson, R. Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: an Update; *Atmos. Environ.* **1995**, *29*, 1685-1695.
- Atkinson, R. Gas Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes; *J. Phys. Chem. Ref. Data* **1997**, *26*, 215-290.
- Ao, C.H.; Lee, S.C. Enhancement Effect of TiO_2 Immobilized on Activated Carbon Filter for the Photodegradation of Pollutants at Typical Indoor Air Level; *Appl. Catal. B Environ.* **2003**, *44*, 191-205.
- Ao, C.H.; Lee, S.C.; Yu, J.Z.; Xu, J.H. Photodegradation of Formaldehyde by Photocatalyst TiO_2 : Effects on the Presences of NO, SO_2 and VOCs; *Appl. Catal. B Environ.* **2004**, *54*, 41-50.
- Ao, C.H.; Lee, S.C.; Mak, C.L.; Chan, L.Y. Photodegradation of Volatile Organic Compounds (VOCs) and NO for Indoor Air Purification Using TiO_2 : Promotion Versus Inhibition Effect of NO; *Appl. Catal. B Environ.* **2003**, *42*, 119-129.
- Yu, H.; Lee, S.C.; Yu, J.; Ao, C.H. Photocatalytic Activity of Dispersed TiO_2 Particles Deposited on Glass Fibers; *J. Mol. Catal. A Chem.* **2006**, *246*, 206-211.
- Tao, Y.; Wu, C.-Y.; Mazzyck, D.W. Removal of Methanol from Pulp and Paper Mills Using Combined Activated Carbon Adsorption and Photocatalytic Regeneration; *Chemosphere* **2006**, *65*, 35-42.
- Tao, Y.; Schwartz, S.; Wu, C.-Y.; Mazzyck, D.W. Development of a TiO_2/AC Composite Photocatalyst by Dry Impregnation for the Treatment of Methanol in Humid Airstreams; *Ind. Eng. Chem. Res.* **2005**, *44*, 7366-7372.
- Thevenet, F.; Guaitella, O.; Herrmann, J.M.; Rousseau, A.; Guillard, C. Photocatalytic Degradation of Acetylene over Various Titanium Dioxide-Based Photocatalysts; *Appl. Catal. B Environ.* **2005**, *61*, 58-68.
- Yamashita, H.; Ichihashi, Y.; Anpo, M.; Hashimoto, M. Louis, C.M. Photocatalytic Decomposition of NO at 275 K on Titanium Oxides Included within Y-Zeolite Cavities: the Structure and Role of the Active Sites; *J. Phys. Chem.* **1996**, *100*, 16041-16044.
- Hu, Y.; Rakhmawaty, D.; Matsuoka, M.; Takeuchi, M.; Anpo, M. Synthesis, Characterization and Photocatalytic Reactivity of Ti-Containing Micro-and Mesoporous Materials; *J. Porous Mat.* **2006**, *13*, 335-340.
- Ao, C.H.; Lee, S.C.; Zou, S.C.; Mak, C.L. Inhibition Effect of SO_2 on NO_x and VOCs during the Photodegradation of Synchronous Indoor Air Pollutants at Parts per Billion (ppb) Level by TiO_2 ; *Appl. Catal. B Environ.* **2004**, *49*, 187-193.
- Chan, C.C.; Ozkaynak, H.; Spengler, J.D.; Sheldon, L. Driver Exposure to Volatile Organic Compounds, Carbon Monoxide, Ozone and Nitrogen Dioxide under Different Driving Conditions; *Environ. Sci. Technol.* **1991**, *25*, 964-972.
- American Society of Heating, Refrigerating, and Air-Conditioning Engineers; available at <http://www.ashrae.org/education/page/1481> (accessed March 13, 2009).

29. Taiwan Indoor Air Quality Association (in Chinese); available at <http://www.iaq.org.tw> (accessed March 13, 2009).
30. Bai, H.; Chen, C.; Lin, C.; Den, W.; Chang, C. Monodisperse Nanoparticle Synthesis by Atmospheric Pressure Plasma Process: an Example of a Visible Light Photocatalyst; *Ind. Eng. Chem. Res.* **2004**, *43*, 7200-7203.
31. Sang, S.; Chang, F.; Liu, Z.; He, C.; He, Y.; Xu, L. Difference of ZSM-5 Zeolites Synthesized with Various Templates; *Catal. Today* **2004**, *93*, 729-734.
32. Wang, H.Q.; Wu, Z.B.; Zhao, W.R.; Guan, B.H. Photocatalytic Oxidation of Nitrogen Oxides Using TiO₂ Loading on Woven Glass Fabric; *Chemosphere* **2007**, *66*, 185-190.
33. Komazaki, Y.; Shimizu, H.; Tanaka, S. A New Measurement Method for Nitrogen Oxides in the Air Using an Annular Diffusion Scrubber Coated with Titanium Dioxide; *Atmos. Environ.* **1999**, *33*, 4363-4371.
34. Atkinson, R. Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions; *Chem. Rev.* **1985**, *85*, 69-201.
35. Bellamy, L.J. *The Infra-Red Spectra of Complex Molecules*, 2nd ed., Wiley: London, U.K., 1975.
36. Higashimoto, S.; Matsuo, M.; Zhang, S.G.; Yamashita, H.; Kitao, O.; Hidaka, H.; Anpo, M. Characterization of the VS-1 Catalyst Using

Various Spectroscopic Techniques and Its Unique Photocatalytic Reactivity for the Decomposition of NO in the Absence and Presence of C₃H₈; *Micropor. Mesopor. Mat.* **2001**, *48*, 329-335.

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