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Preparation of composite TiO_2-zeolite sheets using a papermaking technique and their application to environmental improvement

Part II *Effect of zeolite coexisting in the composite sheet on NO_x removal*

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Sheets with a photocatalytic action were prepared using a papermaking technique. These sheets included single TiO_2-sheet (Ti) and composite TiO_2 sheets with A type zeolite (Ti-ZeA) and Y type zeolite (Ti-ZeY). A sheet (ZeA-Ti sol) containing A type zeolite treated with TiO_2 sol was also prepared. Nitrogen monoxide (NO) was photocatalytically decomposed continuously when these sheets were used under UV irradiation. The subsequent photooxidation of NO to NO_2 and of NO_2 to HNO_3 was observed. The NO_x removal efficiencies of the sheets increased in the following order; Ti-ZeY < Ti < Ti-ZeA < ZeA-Ti sol. The reaction mechanism is discussed on the basis of the combined effects of the photocatalytic ability of TiO_2 and the function of zeolites to adsorb NO and retain the products. © *2003 Kluwer Academic Publishers*

1. Introduction

Nitrogen oxides (NO_x) discharged from automobiles and factories cause atmospheric pollution leading to acid rain and photochemical smog [1–3] and also spread illnesses such as asthma [4]. The higher concentration of NO_x in urban areas has become a serious problem [5–7]. As a solution to these problems, NO_x removal using TiO_2 as a photocatalyst has recently been reported [8–12]. It is well known that NO_x is oxidized to nitric acid (HNO_3) after the formation of nitrogen dioxide (NO_2) by TiO_2 photooxidation [10–13]. However, some of the intermediate NO_2 is released from the TiO_2 surface into the atmosphere before the NO_2 is oxidized to HNO_3. At the same time, the covering of the TiO_2 surface by the HNO_3 generated decreases the photocatalytic activity.

In this study, composite sheets of inorganic materials consisting of TiO_2, zeolite and ceramic fiber were applied to the removal of NO_x. The preparation of composite TiO_2-zeolite sheets using a papermaking technique has already been described [14–16] and their usefulness as materials to remove volatile organic compounds has been reported [16]. Zeolites, which have been widely applied in various industrial fields because of their unique adsorptive activity [17–20], are believed to retain NO_2 on the sheet and to trap HNO_3 formed on the TiO_2 surface. In addition, any NO_x existing in a dilute concentration will be expected to be concentrated by zeolite. The efficiency of removal of NO_x must therefore be greatly improved by the application of a TiO_2-zeolite composite sheet.

In this report, A type and Y type zeolites were selected and composite TiO_2-zeolite sheets were prepared using a papermaking technique. Although an alumina sol was applied as a binder in a previous study [15], TiO_2 sol was used in an attempt to improve the strength of the sheets in this work. The synergistic effect of the composite TiO_2-zeolite sheets together with UV irradiation ($\lambda = 365$ nm) on the photocatalytic oxidation of NO_x was investigated in detail and the roles of adsorbent and the distribution of TiO_2 on the sheets are discussed.

2. Experimental section

2.1. Materials

The pulp used was a bleached hardwood kraft pulp beaten to a Canadian Standard Freeness (CSF) of 265 ml in a Technical Association of the Pulp and Paper Industry (TAPPI) Standard beater. A type zeolite (ZeA) was obtained from Wako Pure Chemical Industries, Ltd (A-4, powder). Y type zeolite (ZeY) and ceramic fiber were kindly provided by Mitsubishi Heavy Industry Ltd. and TiO_2 by Ishihara Techno Co. Table I

TABLE I Elemental composition of the zeolites

Component (wt%)	ZeA	ZeY
Na	16.9	1.6
Mg	0	0
Al	34.6	3.6
Si	47.8	92.4
K	0.7	2.4
Ca	0	0

shows the elemental composition of the zeolites analyzed by energy dispersive X-ray spectroscopy (EDS, JED-2140, JEOL Ltd.).

Poly(diallyldimethylammonium) chloride (PDADMAC) and anionic polyacrylamide (A-PAM) were used as retention aids. The binders used were an alumina sol and a TiO_2 sol supplied by Nissan Chemicals Inc. and Ishihara Techno Co., respectively.

2.2. Preparation of the composite sheets [14–16]

Pulp slurry was mixed with PDADMAC, followed by the addition of suspensions of TiO_2, zeolite and ceramic fiber, and A-PAM in that order. The composition of the sheet-making stock was pulp 10%, ceramic fiber 24.5%, zeolite 0–65.5% and TiO_2 0–65.5%. The levels of addition of PDADMAC and A-PAM were 0.5% and 1.0% on total solids, respectively. Handsheets with 250 g/m^2 were prepared according to TAPPI method-205. The wet sheets were pressed under 350 kPa for 5 minutes and then dried in a convection oven at 105°C for 30 minutes.

After being soaked in the alumina sol or TiO_2 sol, the composite sheets were pressed under 350 kPa for 5 minutes and then dried in an air-conditioned chamber (20°C, 65% RH) for 24 hours. The sheets were then ignited in an electric furnace at 700°C for 20 minutes to remove the wood pulp fibers used in the preparation of the sheets and to strengthen the inorganic sheets by calcination of the binder.

The sheets were designated as follows: Ti (containing only TiO_2), Ti-ZeA and Ti-ZeY (containing TiO_2 and ZeA or ZeY), and ZeA-Ti sol and ZeY-Ti sol (containing ZeA or ZeY and treated with a TiO_2 sol).

2.3. Photocatalytic oxidation

The removal of NO_x ($NO + NO_2$) was studied at room temperature and atmospheric pressure. The sample gas (50% RH) containing 0.25 ppm NO, which was produced by the air purifier (SGPA-1000, Shimadzu) and 100 ppm NO/N_2 (Sumitomo Seika Chemicals Co. Ltd.), passed through the reactor containing the sheet at a flow rate of 1.5 L/min. Sheets 25 mm × 75 mm in size were placed in a flow reactor equipped with a UV lamp (FC2V36/200T4, TOHSHIBA; 2 W, 365 nm) and were irradiated through a Pyrex glass window. The UV light intensity at the surface of sheet was about 0.3 mW/cm^2. The concentrations of NO and NO_2, which was generated by the TiO_2 photocatalysis, were continuously monitored at the gas outlet using a chemiluminescence NO_x analyzer (CLAD-1000A, Shimadzu) over a period of 5 hours. The amount of NO_x removed was calculated according to:

$$Q_{NO_x} = Q_{NO} - Q_{NO_2}$$

where Q_{NO_x} = the amount of NO_x removed (μmol), Q_{NO} = the amount of NO removed, (μmol), and Q_{NO_2} = the amount of NO_2 generated (μmol).

After 5 hours, the composite sheet was immersed in 35 ml deionized water for an hour. The concentrations of nitrate ($NO_3{}^-$) and nitrite ($NO_2{}^-$) in the solution were determined using capillary electrophoresis (CAPI-3100, Otsuka Electronics Co., Ltd.), in order to evaluate the photooxidation by the composite sheet. The separation capillary was 75 μm × 50 cm (37.5 cm to the detector) with 2 mM trimesic acid, 50 mM 2-amino-2-hydroxymethyl-1,3-propanediol and 0.15 mM hexadecyltrimethylammonium hydroxide as the buffer. Samples were introduced by gravity injection (25 mm; 60 s). The separation voltage was −10 kV and indirect UV detection was accomplished at 230 nm. The column temperature was maintained at 30°C.

2.4. Strength of the composite sheets [15]

After conditioning the sample sheets at 20°C and 65% RH for at least 24 hours, their strengths were evaluated as the maximum compressive load, according to the ring crush test (Tappi test method-T818).

2.5. Surface analysis of the composite sheets

The components on the sheet surface were analyzed by the X-ray photoelectron spectroscopy (XPS, AXIS-HSi spectrometer; Shimadzu/Kratos Co., Japan). The high-resolution XPS spectra of the sheet surfaces were obtained using a monochromatic Al K_α X-ray source (1486.6 eV) under the X-ray generation conditions at a voltage 15 kV and a current of 10 mA. The vacuum level of the analyzing chamber was maintained below 5×10^{-7} Pa during the XPS measurements. Pass energy and step width in the detection of photoelectron were set at 80 eV and 0.05 eV, respectively.

3. Results and discussion

3.1. Photooxidation of NO_x by a composite TiO_2-zeolite sheet

Fig. 1 shows the behavior of NO_x with and without the UV irradiation in the presence of the TiO_2 sheet (Ti), and the composite TiO_2-ZeA sheet (Ti-ZeA; TiO_2:ZeA = 1:1) and TiO_2-ZeY sheet (Ti-ZeY; TiO_2:ZeY = 1:1 by weight). When the sheets were not irradiated with UV light, the concentration of NO was constant (about 0.24 ppm) and that of NO_2 was zero. When the UV light was turned on, however, photocatalytic NO oxidation took place suddenly to produce NO_2 with a rapid reduction of NO concentration.

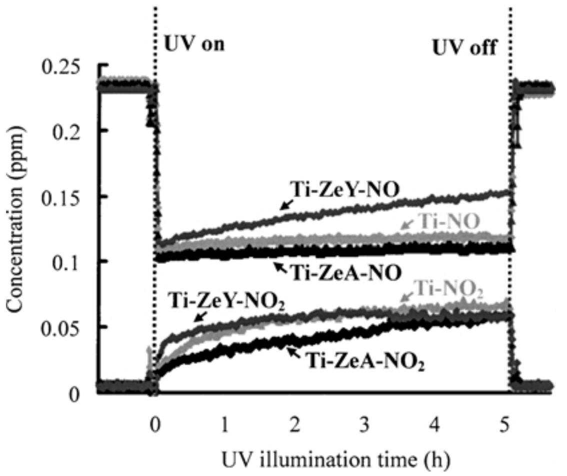

Figure 1 NO_x removal using the Ti, Ti-ZeA and Ti-ZeY sheets.

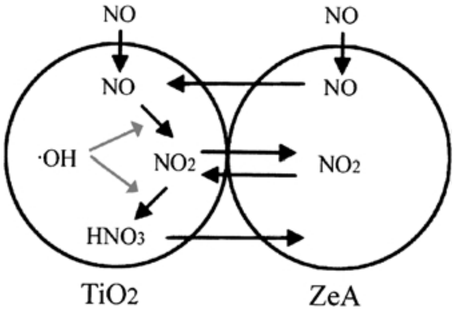

Figure 2 Proposed mechanism of NO_x removal by the Ti-ZeA sheet.

In the case of the Ti sheet, the NO concentration remained almost constant (about 0.11 ppm) throughout the experimental period during UV irradiation, and NO_3^- and NO_2^- were detected at concentrations of 0.66 μmol and 0.48 μmol respectively in the extracted solution leached from the sheet (Table II). This indicated that HNO_3 was formed on the sheet surface by the further photooxidation of NO_2. The concentration of NO_2 produced by the Ti sheet continuously increased with the passage of time and was always higher than that of the NO_2 generated by the Ti-ZeA sheet. These results suggested that the accumulation of HNO_3 on the sheet surface decreased the activity of the photocatalyst. Thus, some of the NO_2 was thought to be released into the atmosphere before NO_2 was oxidized to HNO_3.

On the other hand, in the case of the Ti-ZeA sheet, the NO was continuously removed during the UV irradiation, and the outlet concentration of NO_2 was lower than that from the Ti sheet. Table III gives the amounts of NO_x removal per a unit weight of TiO_2 on the sheet and of NO_2 generation. These values show that the combination of TiO_2 and ZeA is a useful way of promoting the efficiency of NO_x removal. NO was also oxidized to HNO_3 and NO_2 by TiO_2 photocatalysis on the Ti-ZeA sheet as shown in Table II (NO_3^-; 0.29 μmol, NO_2^-; 1.25 μmol). The concentration of NO_2^- formed on the Ti-ZeA sheet was higher than that of NO_2^- on the Ti sheet. It was thought that NO_2 formed on the Ti-ZeA sheet was effectively adsorbed by ZeA on the sheet. Similar phenomena were also observed for the mixture of TiO_2 and active carbon or hydroxyapatite [12, 13]. Fig. 2 shows the proposed mechanism of NO_x removal by the Ti-ZeA sheet. NO captured by ZeA migrates onto TiO_2 and is oxidized to NO_2, and a part of the NO_2 generated is returned to ZeA to be retained. The NO_2 adsorbed by ZeA is further oxidized to HNO_3 by diffusion to the TiO_2 photocatalyst on the sheet, since the amounts of NO_2 produced by Ti-ZeA sheet were smaller than those of NO_2 generated by the Ti sheet. The ZeA appears to play an important role in providing sufficient time for the TiO_2 photocatalyst to oxidize NO to HNO_3. The HNO_3 formed was transferred from TiO_2 surface onto the ZeA, which was able to fix HNO_3. The lowering of the activity of the TiO_2 photocatalyst on the Ti-ZeA sheet was not observed under the conditions in this experiment and the composite Ti-ZeA sheet had a high performance for the removal of NO_x.

TABLE II The amounts of NO_3^- and NO_2^- recovered by the sheets

Sheet	NO_3^- (μmol)	NO_2^- (μmol)	Total (μmol)
Ti sheet	0.66	0.48	1.14
Ti-ZeA sheet	0.29	1.25	1.54
Ti-ZeY sheet	0.41	0.73	1.14
ZeA-Ti sol sheet	1.45	0.80	2.25
ZeY-Ti sol sheet	0.35	0.57	0.92

TABLE III The amounts of NO_x removed and NO_2 generated

Sheet	NO_x (μmol/g)	NO_2 (μmol)
Ti sheet	4.52	0.97
Ti-ZeA sheet	10.7	0.78
Ti-ZeY sheet	6.44	0.98
ZeA-Ti sol sheet	16.2	0.32
ZeY-Ti sol sheet	7.21	0.59

The effect of ZeY added to the Ti sheet on NO_x removal is also shown in Fig. 1. The concentrations of NO and NO_2 generated by the Ti-ZeY sheet increased gradually with increasing irradiation time. The amounts of NO_2 generated by the Ti-ZeY sheet were larger than those produced by the Ti-ZeA sheet, as shown in Table III. Although the NO_2 produced by the photooxidation of NO was temporarily adsorbed by ZeY, it was immediately desorbed from the sheet surface because of the low adsorptivity of ZeY for NO_2. Accordingly, the amounts of NO_2 generated by the Ti-ZeY sheet had a tendency to increase compared with the amounts generated by the Ti and Ti-ZeA sheets. At the same time, the activity of the photocatalyst decreased with the accumulation of HNO_3 on the surface of the TiO_2 photocatalyst. It appeared that the adsorptivity of ZeY for HNO_3 was lower than that of ZeA for HNO_3. These results were thought to depend on the narrower pore size of ZeA (about 0.4 nm) compared with that of ZeY (about 0.7 nm). Additionally, the differences in Si/Al ratios and the sodium content between ZeA and ZeY, as shown in Table I, also may influence the adsorptivity for NO_2 and HNO_3. The removal efficiency of NO_x by the Ti-ZeY sheet was inferior to that of NO_x by the Ti-ZeA sheet, and ZeY added to the composite sheet did not contribute to the photooxidation of NO_x.

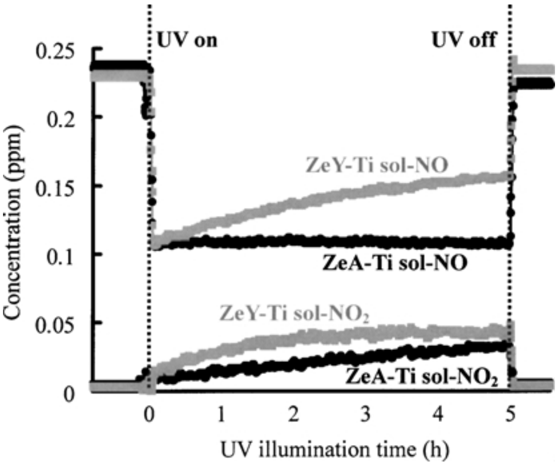

Figure 3 NO$_x$ removal using the ZeA-Ti sol and ZeY-Ti sol sheets.

3.2. Photooxidation of NO$_x$ by a zeolite sheet treated with TiO$_2$ sol solution

The strength of the ZeA and ZeY sheets after treatment with the TiO$_2$ sol solution and ignition at 700°C was about 50 N, which is similar to that of the zeolite sheets treated with an alumina sol, as reported in previous paper [15]. This means that the sheet has sufficient strength for practical use.

Fig. 3 shows the effect of the ZeA-Ti sol and the ZeY-Ti sol sheets on the NO$_x$ removal. The amounts of TiO$_2$ in the ZeA-Ti sol and ZeY-Ti sol sheets were the same as in the Ti-ZeA (TiO$_2$:ZeA = 1:1 by weight) and Ti-ZeY (TiO$_2$:ZeY = 1:1 by weight) sheets, respectively. These values were determined by subtracting the weight of the zeolite sheet without binder treatment from the weight of the treated zeolite sheet.

In the case of the ZeY-Ti sol sheet subjected to UV irradiation, the outlet concentration of NO gradually increased with time after the sudden decrease due to the irradiation. This result was similar to that of the Ti-ZeY sheet shown in Fig. 1. For the reason mentioned above, ZeY could not effectively retrieve HNO$_3$, and the accumulation of HNO$_3$ on the ZeY-Ti sol sheet surface led to a decrease in TiO$_2$ activity.

On the other hand, the ZeA-Ti sol sheet could effectively remove NO$_x$. The amounts of NO$_x$ removed and NO$_2$ generated by the ZeA-Ti sol sheet were the most reasonable in this work, as shown in Table III. The concentration of NO$_3{}^-$ detected in a solution from the ZeA-Ti sol sheet was also the largest observed. It is thought that the HNO$_3$ produced was isolated from the TiO$_2$ surface on the ZeA-Ti sol sheet by the effect of ZeA adsorption and that the activity of TiO$_2$ photocatalyst on the ZeA-Ti sol sheet was not therefore lost.

To confirm the amounts of TiO$_2$ existed on the sheet surface, XPS analysis was carried out and the peaks of Ti from TiO$_2$, and of Si from ZeA and ceramic fiber were obtained. The atomic ratio calculated from Ti$_{2p}$ and Si$_{2p}$ peak area in XPS spectra of ZeA-Ti sol was 2.8, while that of Ti-ZeA sheet was 1.2. These results suggested that the amount of TiO$_2$ on the surface of ZeA-Ti sol sheet was greater than that on the Ti-ZeA sheet and also that TiO$_2$ on the ZeA-Ti sol sheet was more uniformly distributed when the ZeA sheets were soaked in a TiO$_2$ sol. The NO, which was adsorbed by ZeA, was effectively oxidized to HNO$_3$ in a shorter time than on the Ti-ZeA sheet and the concentration of NO$_2$ generated by the ZeA-Ti sol sheet decreased according to the mechanism proposed in Fig. 4. Accordingly, the amounts of NO$_x$ removed by ZeA-Ti sol sheet were the greatest in this study.

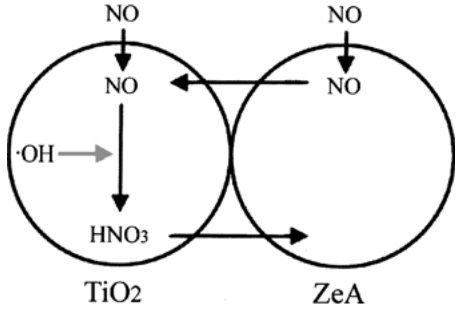

Figure 4 Proposed mechanism of NO$_x$ removal by the ZeA-Ti sol sheet.

These results indicate that soaking of the zeolite sheets in TiO$_2$ sol is an effective method of enhancing both their strength after ignition at 700°C and their performance with regard to NO$_x$ removal.

4. Conclusions

The addition of ZeA to a TiO$_2$ sheet is useful for the effective removal of NO$_x$ by a TiO$_2$ photocatalyst, and NO$_x$ could be continuously removed by the Ti-ZeA sheet. The significant roles of the adsorbent in the sheet were its effect on the concentration of NO and its retention of NO$_2$ and HNO$_3$. The ZeA-Ti sol sheet was the most effective for the continous removal of NO$_x$ under UV irradiation. The sheet strength after ignition at 700°C was also improved by treatment with TiO$_2$ sol. These results lead to the conclusion that the composite TiO$_2$-zeolite sheet is potentially applicable as a material which can effectively remove NO$_x$ from the environment.

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