Removal of NO\textsubscript{x} Using the Reductive Properties of TiO\textsubscript{x} (0 < x < 2)

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Removal of NO\textsubscript{x} is one of the most urgent environmental issues. NO decomposition has been carried out utilizing the reductive properties of TiO\textsubscript{x}, (0 < x < 2) (i.e., low valence materials of titanium oxides), as represented by Ti-coated Al\textsubscript{2}O\textsubscript{3} balls prepared by fine particle bombardment, or TiO\textsubscript{x} powders (for example, so-to-speak Ti-black powders used for liquid crystal displays as the black matrix). In the absence of oxygen, NO is found to mostly decompose into NH\textsubscript{3} by means of Ti-coated Al\textsubscript{2}O\textsubscript{3} balls or TiO\textsubscript{x} powders at approximately 150°C, accompanied by traces of N\textsubscript{2}O. A similar result is also obtained even in the presence of about 20% oxygen. The formation of NH\textsubscript{3} is further effective in reducing NO to give water and N\textsubscript{2} as shown by the urea-SCR (selective catalytic reduction) system used currently in practice in diesel engines. [doi:10.2320/matertrans.M2009282]

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1. Introduction

The emission of volatile organic compounds (VOCs) in the printing or painting industry, as well as in diesel exhaust causes serious environmental issues such as photochemical oxidants, sick house syndrome, and photochemical smog.\(^1\) We have previously shown the complete removal of volatile organic compounds (VOCs) using thermally excited holes in TiO\textsubscript{2} at high temperatures of about 350–500°C.\(^2\)–\(^6\) The present technology utilizes the powerful oxidative properties of holes for VOC decomposition. Furthermore, we have reported that the diesel exhaust can completely be decomposed by thermally excited TiO\textsubscript{2}.\(^4\),\(^5\)

In the course of our studies based upon the oxidative properties of TiO\textsubscript{2}, we came across Ti-coated Al\textsubscript{2}O\textsubscript{3} balls\(^7\) prepared by fine particle bombardment (abbreviated to FPB)\(^8\) and found their powerful reductive properties.\(^9\) The reductive properties arise from a thin TiO\textsubscript{x} layer (i.e., low valence materials of titanium oxides) that exists on the surface of Al\textsubscript{2}O\textsubscript{3} balls. That is, TiO\textsubscript{x} possesses a strong reducing power when di-valent TiO\textsubscript{x} is dissolved into water-containing media to give tetra-valent titanium hydroxides, leaving behind electrons on the Al\textsubscript{2}O\textsubscript{3} balls.\(^9\) Likewise, stoichiometric TiO powders as well as the so-called Ti-black powders\(^10\) that possess compositions of TiO\textsubscript{x}, (0 < x < 2) are also expected to behave in a similar way. The purpose of the present investigation is to apply the above TiO\textsubscript{x} compounds for the reduction of NO\textsubscript{x} in order to provide an alternative technology to the urea system used currently in practice.

The urea-SCR (i.e., selective catalytic reduction using urea as reducing agent) is a well established technique for DeNO\textsubscript{x} of stationary diesel engines.\(^11\) NO\textsubscript{x} in diesel exhaust is composed of more than 99% NO and a few percent of NO\textsubscript{2}. In the urea-SCR, NH\textsubscript{3} is first formed by reaction between urea and water, and then NH\textsubscript{3} reacts with NO to decompose into N\textsubscript{2} and water as follows: 4NH\textsubscript{3} + 4NO + O\textsubscript{2} → 4N\textsubscript{2} + 6H\textsubscript{2}O, 2NH\textsubscript{3} + NO + NO\textsubscript{2} → 2N\textsubscript{2} + 3H\textsubscript{2}O, and 8NH\textsubscript{3} + 6NO\textsubscript{2} → 7N\textsubscript{2} + 12H\textsubscript{2}O.

2. Experiment

2.1 Materials

The Ti-coated Al\textsubscript{2}O\textsubscript{3} ball (product name: PIP balls)\(^7\) of about 4 mm in diameter prepared by FPB was obtained from Fuji Kihan, CO. LTD. Details on the ball preparation were described in our previous paper.\(^9\) The coated Ti-layer had a thickness of about 1–3μm.

Commercially available TiO-particles (0.5–2 mm in diameter; product No. 7102-0013) were purchased from NICHIA and pulverized into about 100μm in diameter. The present TiO-particles bear a brownish color and appear slightly metallic. The composition of the product is nearly stoichiometric (TiO: 1 : 1) according to the manufacturer.

Ti-Black powders (product name: Tilack D) was purchased from Ako Kasei Corporate. The product is pure black and used, for example, for liquid crystal displays as the black matrix. Tilack D is prepared by reducing TiO\textsubscript{2} with NH\textsubscript{3} and the composition is about TiO\textsubscript{1.5} according to the manufacturer. The specific surface area was about 9.53 m\textsuperscript{2}/g.

Cordierite honeycomb substrates (2MgO-2Al\textsubscript{2}O\textsubscript{3}-5SiO\textsubscript{2}) with 200 cells per square inch were purchased from Kyocera Corporation. Acetone and toluene of electronic grade were obtained from Junsei Chemical. Nitrocellulose of RS-60 [C\textsubscript{6}H\textsubscript{5}O\textsubscript{2}(NO\textsubscript{2})(OH)]\textsubscript{n} (n = 360) was obtained from KCNC.

2.2 Fixation of TiO or Ti-black powders onto cordierite honeycomb substrates

Fixation of the powdered sample onto cordierite honeycomb substrates was made in order to test it in a practical way, using a non-aqueous suspension developed previously for the electrophoretic deposition of oxides.\(^12\),\(^13\) 10 g of TiO or Ti-black powders was first dried at 200°C for 1 h to eliminate water. The powder was then suspended in 100 mL of acetone solution containing 0.20 g of nitrocellulose. The suspension was conditioned in the presence of zirconia balls (0.2 mm in diameter) using a paint shaker for 30 min. After that, a cylindrical honeycomb substrate (26 mm in diameter and 50 mm in length) was dipped in the suspension for 1 min.

2.3 Experiment for NO decomposition

An autoclave of about 300 mL was used for Ti-coated Al\textsubscript{2}O\textsubscript{3} balls; whereas a pyrex glass tube (26 mm in diameter) was employed for the honeycomb unit. The autoclave included about 250 mL of Ti-coated Al\textsubscript{2}O\textsubscript{3} balls or 100 mL of powdered TiO. In the case of powdered TiO, the sample
was stirred by a stirrer at 150 rpm, while the stirrer was not used in Ti-coated Al2O3 balls.

1000 ppm NO based on Ar, or about 800 ppm NO based on a mixture of Ar and O2 (Ar/O2 = 4/1 in volume; about 20% oxygen) was used for the decomposition experiment. The former was for the experiment in the absence of oxygen; whereas the latter was for the experiment in the presence of oxygen for the study of the influence of oxygen on the NO decomposition characteristic. The NO gas was first bubbled into deionized water in order to prepare wet NO and then introduced into the reactor with a flow rate of 100 or 1000 mL/min. The decomposed gas was analyzed in the temperature-increase run by an RG-102 quadrupole mass-filter (ULVAC) as a function of temperature. The heating rate was 10°C/min and each target temperature was maintained for five minutes, when the gas analysis was carried out. Raman spectra were measured before and after NO decomposition experiment on TiO and Ti-black powders, using an NRS-3100 laser Raman spectrophotometer from JASCO Corp.

3. Results and Discussion

3.1 NO Decomposition with Ti-coated Al2O3 balls or powdered TiO in the autoclave

NO Decomposition was carried out in the autoclave with a NO flow rate of 100 mL/min in the absence of oxygen. Figure 1 shows the decomposition characteristic of NO with the Ti-coated Al2O3 balls as a function of temperature. NO starts to decompose at approximately 150°C, and the decomposition is nearly completed at approximately 250°C, accompanied by the NH3 formation. The quantity of the NH3 formation is about 0.1% (i.e., 1000 ppm), where the amount of NH3 is expressed in percent relative to Ar. This suggests that the reaction is assumed to proceed with the following equation: 2NO + 2TiO2 → 2NH3 + 2TiO2

In powdered TiO as shown in Fig. 2, NH3 is again formed in quantity of about 0.08%, but it accompanies the formation of N2O (0.02%), suggesting the following reaction: 3NO + 3TiO + H2O → NH3 + N2O + 3TiO2.

The NH3 formation as a result of NO decomposition may sound negative, but obviously this is a good result, because NO is known to react with NH3 to give water and N2 as stated in Introduction regarding the urea-SCR reaction. This means that TiO2 has a double effect in NO decomposition. The formation of TiO2 or TiO2x+1 is also borne out by the following Raman spectra measured, before and after the NO decomposition, on the powdered TiO. The color of the reaction product appears also rather whitish.

Figure 3 shows the Raman spectra of powdered TiO measured before and after the NO decomposition, together with TiO2 references of the rutile and anatase phases (ST-01 and TTO-55(N) from ISK, respectively).

3.2 NO Decomposition with TiO or Ti-black-coated honeycomb units

Figure 4 shows the NO decomposition characteristic with TiO-coated honeycomb units with a NO flow rate of 1000 mL/min in the absence of oxygen. The “onset/termination” temperatures for the NO decomposition are higher with the honeycomb system by about 150°C in comparison with those of the corresponding powdered system as shown in Fig. 2. However, the tendency of the NO decomposition is nearly the same, as accompanied by the formation of NH3 and N2O.

The Ti-black-coated honeycomb units were also tested with a NO flow rate of 1000 mL/min in the absence of oxygen and the result is shown in Fig. 5. The decomposition characteristic was quite similar to that of the TiO-coated honeycomb system, but no noticeable formation of N2O was observed either, just as in the case of Ti-coated Al2O3 powders (Fig. 1). The reason why only powdered TiO gives a small amount of N2O remains unclarified. On the other hand, some difference was recognized in the phase of the Ti-black
3.3 Influence of oxygen on the NO decomposition in the Ti-black-coated honeycomb system

Since the NO$_x$ decomposition is assumed to be carried out in air in practice, the influence of oxygen on the decomposition characteristic was studied by use of a mixed carrier of Ar and O$_2$ (i.e., Ar/O$_2$ = 4/1 in volume: about 20% oxygen). The experiment was performed with a flow rate of 100 mL/min.

Figure 7 shows the decomposition characteristic of the NO decomposition as a function of temperature. The formation of NH$_3$ starts at approximately 200°C. Except this, no significant difference is recognized in the NO decomposition process in comparison with that in the absence of oxygen as shown in Fig. 5.

4. Conclusions

NO decomposition was carried out utilizing the reductive properties of TiO$_x$, as represented by Ti-coated Al$_2$O$_3$, powdered TiO (nearly 1:1 composition), and Ti-black powders (about TiO$_1.5$) in the absence or presence of 20% oxygen.

In all samples, the NO decomposition proceeds efficiently, yielding NH$_3$ as the main reaction product, while TiO or Ti-black powders were mostly oxidized to TiO$_2$. The NH$_3$ thus formed can subsequently be used to reduce NO into water and N$_2$, as shown by the urea-SCR system used currently in practice in diesel engines. Furthermore, the presence of 20% oxygen is found to be almost harmless in NO decomposition.

REFERENCES