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Title: Visible-Light-Assisted Selective Catalytic Reduction of NO with NH₃ on Porphyrin Derivative-Modified TiO₂ Photocatalysts

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Abstract

Porphyrin-derivative modified TiO₂ photocatalysts showed high photocatalytic activity for the selective catalytic reduction of NO with NH₃ in the presence of O₂ under visible-light irradiation. Tetra(p-carboxyphenyl)porphyrin (TCPP) was the most effective photosensitizer among the five porohyrin derivatives investigated. NO conversion and N₂ selectivity of 79.0% and 100% respectively, were achieved at a gas hourly space velocity of 50,000 h⁻¹. UV-Vis and photoluminescence spectroscopies revealed the presence of two species of TCPP on the TiO₂ surface; one was a TCPP monomer and the other was a H-aggregate of the TCPP molecules. It was concluded that the TCPP monomer is an active species for the photo-assisted selective catalytic reduction (photo-SCR). Moreover, an increase in the fraction of H-aggregates with the increasing TCPP loading amount resulted in a decrease in the decrease of the photocatalytic activity of the photo-SCR.

1. Introduction

NO_x, which is present in the exhaust gas of stationary emission sources, is removed by the selective catalytic reduction with NH₃ (NH₃-SCR) over vanadium oxide-based catalysts according to the following equation: $(4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O})$ ¹⁻³.

The NH₃-SCR process is performed at temperatures above 573 K. To save the energy used for heating the catalyst bed, novel catalysts are required for performing the NH₃-SCR at low temperatures⁴⁻⁶. Photocatalysis is one of the promising candidates for the NH₃-SCR because photocatalytic reactions proceed at room temperature. We have reported the photo-assisted selective catalytic reduction (photo-SCR) of NO with NH₃ in the presence of O₂ over TiO₂ photocatalysts under UV-light irradiation⁷⁻¹⁰. In this system, the NO conversion and N₂ selectivity of 90% and 99%, respectively, were achieved at a gas hourly space velocity (GHSV) of 8,000 h⁻¹, which is sufficient for the deNO_x process in typical stationary sources such as power plants, blast furnaces, and incinerators. However, a very high GHSV was required in diesel engines owing to the limited installation space of the deNO_x process and a high flow rate of the exhaust gas. The volume of the catalyst was required to be of the order of the volume of the diesel engine cylinder (typical GHSV in a three-way catalyst is approximately 100,000 h⁻¹)¹¹. Unfortunately, the NO conversion decreased with the increasing GHSV in the photo-SCR system and it decreased to 40% at a GHSV of 100,000 h⁻¹¹⁰. Therefore, the photocatalytic activity of the photo-SCR has to be improved at a high GHSV region in order to remove the NO_x from the exhaust gas of diesel engines.

Expansion of the adsorption wavelength to the visible-light region is an effective way of improving the photocatalytic activity. TiO₂ photocatalysts do not absorb visible light because of their wide band gap (> 3.2 eV). Surprisingly, the photo-SCR proceeds to

some extent under visible–light irradiation over the TiO₂ photocatalysts. This is due to the direct electron transfer from the electron donor level of the N 2p orbital of the adsorbed NH₃ to the conduction band of the Ti 3d orbital of TiO₂ (in–situ doping)^{12, 13}. However, the photocatalytic activity under visible–light irradiation is not sufficient for the application of the photo–SCR technology to the system at a high GHSV region. Thus, the proposed study aims to increase the photocatalytic efficiency under visible–light irradiation.

Porphyrin derivatives have absorption bands in the visible region owing to the π – π^* transitions. Porphyrin derivatives are widely used as sensitizers in dye-sensitized solar cells (DSSCs)¹⁴⁻¹⁷ and dye–sensitized photocatalysts¹⁸⁻²⁰ under visible-light irradiation owing to the following properties: 1) they exhibit intense absorption bands in the visible–light region, and 2) their photochemical and electrochemical properties can be tuned by the modification of the substituents and selection of the central metal. In previous studies, the porphyrin-sensitized photocatalysts were used for performing liquid phase reactions such as the hydrogen production from water²⁰, and degradation of organic compounds^{18, 19, 21}. However, there are only a few reports on the reactions involving porphyrin–sensitized photocatalysts in the gas phase. Recently, Ismail et al. reported that the porphyrin–sensitized mesoporous TiO₂ films exhibited an improved photocatalytic activity for the photodegradation of acetaldehyde in the gas phase under visible–light irradiation²². The porphyrin derivative–modified photocatalyst works efficiently as a visible–light response photocatalyst in the gas phase. In this study, we used five types of porphyrins for the modification of the TiO₂ photocatalyst, and investigated their performances in the photo–SCR using a gas flow reactor at a high GHSV of 50,000 h⁻¹.

2. Results and Discussion

2.1 Effects of functional group in the porphyrins

Figure 1 shows the conversion of NO during the photo-SCR over the various porphyrin derivative-modified TiO₂ photocatalysts at a GHSV of 50,000 h⁻¹ after 6 h of visible-light irradiation, because the steady state reaction rate was obtained after 6 h. The conversion of NO over the unmodified TiO₂ photocatalyst was 13.4% under visible-light irradiation. Modification of the TiO₂ photocatalyst with the porphyrin derivatives greatly enhanced the photocatalytic conversion of NO under the visible-light irradiation as shown on the top of the Figure 1. Among the five porphyrin derivative-modified TiO₂ photocatalysts, the TCPP-TiO₂ photocatalyst showed the highest conversion of NO (71.4%). The conversion of NO decreased in the following order: TCPP-TiO₂ > TPP-TiO₂ > TSPP-TiO₂ > TMPP-TiO₂ > TAPP-TiO₂ > TiO₂. Hence, it can be seen that the porphyrin functional group used for the modification of TiO₂ had a significant effect on the photo-SCR activity.

Figure 2 shows the UV-Vis DR spectra of the various porphyrin modified TiO₂ photocatalysts. The unmodified TiO₂ photocatalyst did not absorb the visible-light above 400 nm. The modification of the porphyrin derivatives increased the absorption in the visible-light region. The absorption at 420 nm (Soret band) decreased in the following order: TCPP-TiO₂ > TPP-TiO₂ ≈ TSPP-TiO₂ > TMPP-TiO₂ > TAPP-TiO₂ > TiO₂. The order of the absorption is consistent with that of the NO conversion. The photocatalytic activities of NO were strongly dependent on the absorbance in the visible-light region, which suggested that the porphyrin derivatives functioned as photosensitizers under visible-light irradiation.

2.2 Effect of TCPP loading on the activity of photo-SCR

Figure 3 shows the UV/Vis DR spectra of the different loading amounts of the TCPP-TiO₂ photocatalysts. One major peak and four minor peaks were observed in the visible region in each sample. The major peak is the Soret band ($S_2 \leftarrow S_0$ transition) and the four minor peaks are the Q bands ($S_1 \leftarrow S_0$ transition). The Q bands are attributed to the 0-0 and 0-1 components of the non-degenerated Q_x and Q_y bands (etio type)²³, as expected for the D_{2h} symmetry. The increase in the TCPP loading amount enhanced the capability of visible-light absorption.

The peak positions of the Soret band and Q bands as a function of TCPP loading are shown in Table 1. The peak position of the Soret band of 1.3 μmol g⁻¹ TCPP-TiO₂-IMP (417 nm) corresponded to those of the TCPP molecules dissolved in CH₃OH (418 nm). The TCPP molecules existed as a monomer in the CH₃OH solution and the peak position of the TCPP monomer coincided with that reported previously²⁴. Thus, the TCPP molecules existed as monomers on the TiO₂ surface at the low loading amount of 1.3 μmol g⁻¹. The peak position of the Soret band was shifted from 417 nm to 407 nm (blue-shift) when the loading amount of TCPP was increased from 1.3 μmol g⁻¹ to 62.5 μmol g⁻¹. The origin of the blue-shift can be explained on the basis of a “face to face” stacking pattern of TCPP (H-aggregate) according to Kasha’s exciton theory²⁵. Thus, the blue-shifted peak observed at 407 nm can be attributed to the Soret exciton band in the H-aggregates of the TCPP. The gradual spectral shift can be explained as the result of the relative contribution of the monomers and H-aggregates. The H-aggregates were generated with the increase in the TCPP loading. The contribution of the H-aggregates became dominant for the Soret band of adsorption spectra of various loading amount of TCPP-TiO₂, which results in the gradual blue shift of the Soret band.

On the other hand, the peak positions of the Q bands of 1.3 $\mu\text{mol g}^{-1}$ TCPP-TiO₂-IMP (519, 555, 592, 649 nm) were slightly shifted to longer wavelengths compared to those of the TCPP monomer in CH₃OH (515, 549, 590, 646 nm). The slight red-shift can be ascribed to the aggregation of TCPP²⁴ and/or the interactions between the TCPP and a solid surface²⁶. The peak positions of the four Q bands of the TCPP-TiO₂-IMP were shifted to longer wavelengths with an increase in the TCPP loading amount. The peak position of the Q bands of the H-aggregates of the TCPP is larger than that of the TCPP monomers²⁴. Thus, the red-shift of the Q bands is due to the generation of the H-aggregates. Consequently, both the monomers and H-aggregates of TCPP are generated on TiO₂ and the fraction of the H-aggregates increased with the increasing TCPP loading amount.

Figure 4 shows the effect of various loading amounts of TCPP-TiO₂-IMP on the photo-SCR. The conversion of NO increased with the increasing TCPP loading amount up to 12.5 $\mu\text{mol g}^{-1}$. The surface density of TCPP molecules on 12.5 $\mu\text{mol g}^{-1}$ TCPP-TiO₂-IMP is estimated to be 2.8×10^{-2} molecule nm^{-2} . As shown in Figure 3, increasing the loading amount of TCPP enhanced the capability of the visible-light absorption, which leads to the higher conversion of NO. On the other hand, the conversion of NO decreased when the TCPP loading was higher than 12.5 $\mu\text{mol g}^{-1}$. The UV-Vis spectroscopy revealed that the H-aggregates of TCPP were generated with the increase of the TCPP loading amount. The excited state lifetime of the H-aggregates was slightly shorter than those of the monomers^{24,27}. The generation of H-aggregates with a short excited state lifetime decreased the electron transfer efficiency from the excited state of TCPP to the conduction band of TiO₂ due to non-radiative deactivation, which possibly resulted in the decrease of the photo-SCR activity.

2.3 Photo-SCR under various reaction conditions

Table 2 summarizes the concentrations of N₂ in the outlet gas for the photo-SCR under various reaction conditions. The conversion of NO in the photo-SCR over TCPP-TiO₂-IMP was 79.0% (Entry 1) and the activity was stable for at least 6 h of visible-light irradiation (the time course is shown in Figure S1 in the supporting information). N₂ was the only product observed and N₂O was not detected in any of the reactions. The utilization of visible-light was advantageous for the high selectivity to N₂, since N₂O was generated as a by-product of the photo-SCR over TiO₂ photocatalyst under UV-light irradiation. Turnover number (TON) of TCPP was calculated to be 810 after 6 h of visible-light irradiation. Thus, the total N₂ in the outlet gas was originated from the nitrogen atoms of NO and NH₃ molecules in the gas phase and not from the TCPP molecules. The reaction hardly proceeded over the TCPP-TiO₂ photocatalyst without a substrate such as NO, NH₃, and O₂ (Entry 2, 3, and 4). The O₂ concentrations did not affect the generation rate of N₂ over 2% (Entry 1, 5, and 6). The TCPP-SiO₂-IMP showed much lower activity under the same reaction conditions than that of the TCPP-TiO₂-IMP (Entry 7), although the TCPP on SiO₂ absorbed visible-light as well as that on TiO₂ as shown in Figure 5. In addition, the activity of the photo-SCR over the TCPP-TiO₂ photocatalyst prepared by a physical mixture method (TCPP-TiO₂-MIX) was similar to that of the unmodified TiO₂, although the TCPP-TiO₂-MIX absorbed in the visible region as shown in Figure 5.

Figure 6 shows the photoluminescence spectra of TCPP-TiO₂-IMP, TCPP-SiO₂-IMP, TCPP-TiO₂-MIX, and TCPP monomer in CH₃OH. Two emission bands were observed in the TCPP monomer in CH₃OH solution (650 and 714 nm), which coincided with the

previously reported values²⁴. The emission bands at 650 nm and 714 nm can be attributed to the transition from the vibrational ground state of S₁ to the vibrational ground state of S₀ (Q_{x(0,0)} transition) and to the vibrational excited state of S₀ (Q_{x(0,1)} transition) of the TCPP monomer, respectively^{24, 28}. The peak positions of the emission bands in the TCPP-TiO₂-IMP (654 and 715 nm) were almost similar to those of the TCPP monomer in CH₃OH. It is reported that the emission bands of the H-aggregates of TCPP have lower intensity and are shifted to longer wavelengths than those of the monomers²⁹, which is totally different from the emission spectrum of the TCPP-TiO₂-IMP. Accordingly, the emission bands of TCPP-TiO₂-IMP were mainly composed of the TCPP monomer emissions.

Two emission bands were observed at 658 and 713 nm, and the peak positions were similar to those of the TCPP in CH₃OH (650 and 714 nm) and TCPP-TiO₂-IMP (654 and 715 nm) (Figure 6). Thus, the TCPP species on SiO₂ possesses a monomeric state, which is similar to that on TiO₂. The low activity of TCPP-SiO₂-IMP can be explained by an electron transfer mechanism, which is the key step in the DSSCs and dye-sensitized photocatalysts. In the first step of the photo-SCR over the TCPP-TiO₂-IMP, the TCPP is excited by the visible-light irradiation. In the next step, the electron transfer occurs from the photo-excited TCPP to the conduction band of TiO₂. However, the electron transfer cannot occur from the photo-excited TCPP to the conduction band of SiO₂ because the energy level of the SiO₂ conduction band is much higher than that of the lowest unoccupied molecular orbital (LUMO) of TCPP, which results in the low activity of the TCPP-SiO₂-IMP. Hence, the photo-SCR over TCPP-TiO₂-IMP under visible-light irradiation proceeds via the electron transfer from the photo-excited TCPP to the conduction band of TiO₂.

No emission peak was observed for the TCPP-TiO₂-MIX and TCPP powder (Figure 6). The interaction between the TCPP molecules might lead to the non-radiative deactivation of the photo-excited states of TCPP, resulting in the luminescence quenching for the TCPP-TiO₂-MIX and TCPP powder. These results explain the low activity of the TCPP-TiO₂-MIX, *i.e.* though the TCPP molecules on the TCPP-TiO₂-MIX absorb visible-light, they do not function as a photosensitizer under visible-light irradiation because of the fast non-radiative quenching.

2.4 On-off response tests of visible light irradiation

Figure 7 shows the on-off response for the photo-SCR under visible-light irradiation over the TCPP-TiO₂ photocatalyst at a GHSV of 50,000 h⁻¹. The conversion of NO was about 6% without visible-light irradiation. The conversion of NO significantly increased to 86.5% under visible-light irradiation, indicating the function of the TCPP-TiO₂ photocatalyst as a visible-light-driven photocatalyst for the photo-SCR. The conversion of NO gradually decreased to 81.2% with the increasing irradiation time, although the conversion was restored to the original level (85.5%) after the on-off action. The decrease in the conversion of NO with the irradiation time was not due to the decomposition of TCPP. If the TCPP on the TiO₂ surface was decomposed under visible-light irradiation, the initial conversion of NO was expected to decrease gradually in the second, third, and fourth times. However, we did not observe a decrease in the initial conversion of NO. The recovery of the initial conversion of NO took place reversibly.

3. Experimental Section

3.1 Catalyst Preparation

A TiO₂ powder (ST-01, anatase, 273 m² g⁻¹) was purchased from Ishihara Sangyo Kaisha, Ltd. A SiO₂ powder (630 m² g⁻¹) was prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in a water-ethanol mixture at boiling point, followed by calcination in dry air at 773 K for 5 h. Tetraphenylporphyrin (TPP), Tetra(*p*-carboxyphenyl)porphyrin (TCPP), Tetra(*p*-sulfonatephenyl)porphyrin (TSPP), Tetra(*p*-methoxyphenyl)porphyrin (TMPP), and Tetra(*p*-aminophenyl)porphyrin (TAPP) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification (see Figure 1). The porphyrin derivatives were impregnated over the TiO₂ powder and the porphyrin-modified TiO₂ photocatalysts were abbreviated to porphyrin-TiO₂ (e.g. TCPP-TiO₂). Various loading amount of TCPP-TiO₂ catalysts were prepared by an impregnation method using 1 M NH₃ aqueous solution as a solvent (TCPP-TiO₂-IMP). A TCPP-modified SiO₂ catalyst was prepared by the impregnation method as shown above (TCPP-SiO₂-IMP). A physical mixture catalyst of TCPP and the TiO₂ powder was prepared as a reference (TCPP-TiO₂-MIX).

3.2 Photocatalytic reaction

The photo-SCR was carried out in a conventional fixed-bed flow system at an atmospheric pressure. The catalyst was fixed with quartz wool and filled up in a quartz reactor with flat facets (H12 mm × W10 mm × D1.0 mm). The reaction gas composition was as follows: NO 1000 ppm, NH₃ 1000 ppm, O₂ 2–10%, He balance. 300 W Xe lamp (PERKIN-ELMER PE300BF) equipped with a L-42 cut-off filter was used as a light source ($\lambda > 400$ nm) and the sample was irradiated from the one side of the flat facets of

the reactor. N₂ and N₂O were analyzed by SHIMADZU GC-8A TCD gas chromatographs equipped with MS-5A and Porapak Q.

3.3 Characterization

UV-Vis transmission adsorption and diffuse reflectance spectra were obtained with a UV-Vis spectrometer (JASCO V-650). Transmission adsorption spectra were measured using a 1 cm quartz cell at room temperature in the scan range of 300–800 nm. Photoluminescence spectra were recorded on a Hitachi F-7000 fluorospectrometer in the scan range of 550–760 nm at an excitation wavelength of 410 nm. The concentrations of TCPP in methanol solution used in the adsorption and emission spectroscopy were 3.4×10^{-6} mol L⁻¹ and 1.0×10^{-6} mol L⁻¹, respectively.

Conclusion

We found that porphyrin derivative-modified TiO₂ functions as a visible-light-driven photocatalyst for the photo-SCR. The TCPP-modified TiO₂ photocatalyst showed the highest activity of the photo-SCR among the TiO₂ photocatalysts modified with the five porphyrin derivatives investigated. We elucidated the state of TCPP on TiO₂ affect the photocatalytic conversion of NO and the active species is a TCPP monomer adsorbed on TiO₂ due to efficient electron transfer from the photo-excited TCPP monomer to the conduction band of TiO₂.

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Table 1. Peak positions of the soret band and Q bands

Sample	Loading of TCPP / $\mu\text{mol g}^{-1}$	Soret / nm	Q _{y(0, 1)} / nm	Q _{y(0, 0)} / nm	Q _{x(0, 1)} / nm	Q _{x(0, 0)} / nm
TCPP-TiO ₂ -IMP	1.3	417	519	555	592	649
TCPP-TiO ₂ -IMP	6.3	416	520	557	592	651
TCPP-TiO ₂ -IMP	12.5	411	521	559	593	652
TCPP-TiO ₂ -IMP	37.5	411	522	562	595	654
TCPP-TiO ₂ -IMP	62.5	407	522	560	594	653
TCPP-TiO ₂ -MIX	12.5	419	529	565	600	658
TCPP-SiO ₂ -IMP	12.5	422	521	556	593	649
TCPP in MeOH	–	418	515	549	590	646

Table 2. Result of photo-SCR under various reaction conditions

Entry	Catalyst	Inlet gas conc. (ppm)			N ₂ conc. ^a (ppm)
		NO (ppm)	NH ₃ (ppm)	O ₂ (%)	
1	TCPP-TiO ₂ -IMP ^b	1000	1000	2	790
2	TCPP-TiO ₂ -IMP ^b	0	1000	2	57
3	TCPP-TiO ₂ -IMP ^b	1000	0	2	24
4	TCPP-TiO ₂ -IMP ^b	1000	1000	0	42
5	TCPP-TiO ₂ -IMP ^b	1000	1000	5	780
6	TCPP-TiO ₂ -IMP ^b	1000	1000	10	771
7	TCPP-SiO ₂ -IMP ₂ ^b	1000	1000	2	63
8	TCPP-TiO ₂ -MIX ^b	1000	1000	2	140

^aConcentration of N₂ in the outlet gas. Catalyst amount: 110 mg (TiO₂, TCPP-TiO₂), 50 mg (TCPP-SiO₂), ^bTCPP loading: 12.5 μmol g⁻¹.

Figure legends

Figure 1.

Title: Structures of porphyrin derivatives and conversion of NO in the photo–SCR over the various porphyrin derivative–modified TiO₂ photocatalysts after 6 h of visible–light irradiation (loading of porphyrin derivative: 18 μmol g⁻¹, catalyst amount: 110 mg, NO: 1000 ppm, NH₃: 1000 ppm, O₂: 2 %, GHSV: 50,000 h⁻¹).

Figure 2.

Title: UV–Vis diffuse reflectance spectra of (A) TiO₂, (B) TCPP–TiO₂, (C) TSPP–TiO₂, (D) TPP–TiO₂, (E)TMPP –TiO₂, and (F)TAPP –TiO₂.

Figure 3.

Title: UV–Vis diffuse reflectance spectra of various loading of TCPP–TiO₂. (A) 0 μmol g⁻¹, (B) 1.3 μmol g⁻¹, (C) 6.3 μmol g⁻¹, (D) 12.5 μmol g⁻¹, (E) 37.5 μmol g⁻¹, and (F) 62.5 μmol g⁻¹.

Figure 4.

Title: Dependence of conversion of NO on TCPP loading on TiO₂ (catalyst amount: 110 mg, NO: 1000 ppm, NH₃: 1000 ppm, O₂: 2 %, GHSV: 50,000 h⁻¹).

Figure 5.

Title: UV–Vis diffuse reflectance spectra of (A) TCPP–TiO₂(IMP), (B) TCPP–SiO₂, and (C) TCPP–TiO₂(MIX), and adsorption spectra of 3.4×10⁻⁶ mol L⁻¹ TCPP in methanol (D).

Figure 6.

Title: Photoluminescence spectra of (A) TCPP-TiO₂-IMP, (B) TCPP in methanol, (C) TCPP-SiO₂-IMP, (D) TCPP-TiO₂-MIX, and (E) TCPP powder. The excitation wavelength was 410 nm. The spectra of (A), (C), (D), and (E) were measured at the voltage of photomultiplier tube of 700 V and spectrum (B) was of 450 V. Loading of TCPP was 12.5 μmol g⁻¹, and the concentration of TCPP in methanol was 1.0×10⁻⁶ mol L⁻¹.

Figure 7.

Title: Conversion of NO during several on/off cycles of visible-light irradiation over the TCPP/TiO₂ photocatalyst: each cycle consisted of two-hours light on and off (TCPP loading: 12.5 μmol g⁻¹, catalyst amount: 110 mg, NO: 1000 ppm, NH₃: 1000 ppm, O₂: 2 %, GHSV: 50,000 h⁻¹).