Photocatalytic decomposition of N\textsubscript{2}O in the presence of CO on Ti/USY photocatalysts

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Abstract

A highly dispersed Ti-oxide species was prepared within an ultra stable Y-zeolite (USY zeolite) by an impregnation method. Moreover, the Ti-oxide loaded USY (Ti/USY) zeolite showed higher photocatalytic activity for the decomposition of N\textsubscript{2}O in the presence of CO to produce N\textsubscript{2} and CO\textsubscript{2} than the standard TiO\textsubscript{2} (P-25) photocatalyst at 298 K. The photocatalytic reaction rate was found to strongly depend on the Ti loadings of Ti/USY. XRD, XANES, UV-vis and photoluminescence investigations revealed that this highly dispersed Ti-oxide species plays an important role as the active sites in the photocatalytic decomposition of NO in the presence of CO.

Keywords: Ti-oxide species, Ti/USY, N\textsubscript{2}O decomposition with CO

Introduction

Recently, the photocatalytic decomposition of NO\textsubscript{x} (NO, N\textsubscript{2}O and NO\textsubscript{2}) into N\textsubscript{2} has attracted much attention in the development of clean and efficient purification systems that address atmospheric pollution. NO\textsubscript{x} is discharged into the atmosphere by transportation exhaust, power plants, and electric power generators. Among such NO\textsubscript{x} pollutants, N\textsubscript{2}O is one of the most damaging greenhouse gases with a long lifetime in the atmosphere (Angelidis, T.N, 2003). The development of clean and safe photocatalytic systems that can reduce such toxic agents and address the greenhouse effect is strongly desired. And in fact, NO\textsubscript{x} derived from exhaust gases have been successfully removed photocatalytically by direct decomposition (Anpo M, 1998; Hu Y, 2003; Zhang J, 2000; Zhanpeisov, 1998) or reduction with various reducing agents such as NH\textsubscript{3}, CO or C\textsubscript{n}H\textsubscript{m} (Uner D.O, 1998). The removal of nitrogen oxides (NO\textsubscript{x}, x=1,2) from exhaust gases have also been carried out by semiconducting photocatalysts under UV or visible light irradiation (Anpo M, 1997).

The present work deals with the preparation of a highly dispersed Ti-oxide species on ultra stable Y-zeolites (USY zeolites) and a study of their photocatalytic activity for the decomposition of N\textsubscript{2}O in the presence of CO. Special attention has been focused on the relationship between the local structure of the Ti-oxide species and their photocatalytic activity.

Materials and Methods

USY (Ultra Stable Y-zeolite: Si/Al = 260) was provided by TOSOH Co. The Ti-oxide loaded USY (Ti/USY) were prepared by an impregnation method using titanium(IV) ammonium oxalate solutions with varying Ti contents of 0.5, 1 and 5 wt%. The obtained powder samples were calcined in air at 773 K for 5 h. The prepared Ti/USY catalysts were characterized by diffuse reflectance UV-vis absorption, XRD, XANES and photoluminescence measurements.

Prior to spectroscopic measurements and photocatalytic reactions, the Ti/USY catalysts were degassed at 673 K for 1 h, heated in O\textsubscript{2} at the same temperature for 1.5 h, and finally evacuated at 473 K to 10\textsuperscript{-6} Torr. Photocatalytic reactions were carried out in a quartz reactor under UV light irradiation of the catalysts in the presence of N\textsubscript{2}O (15 µmol) and CO (15 µmol) using a 100 W high-pressure Hg lamp at 298 K for 3 h. The reaction products were analyzed by on-line gas chromatography. The UV absorption spectra were recorded with a Shimadzu UV-2200A spectrometer. The XRD patterns were observed with a Shimadzu XRD-6100 using Cu K\textalpha radiation. The XANES spectra were obtained at the BL-12C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. The photoluminescence was measured at 77 K with a SPEX Fluorog-3 spectrofluorometer.
Results and Discussion

Figure 1 shows the XRD patterns of Ti/USY with various Ti loadings. These Ti/USY catalysts exhibited typical XRD patterns assigned to the FAU structure, regardless of the Ti loading while the intensity of the XRD peaks decreased with an increase in the Ti content. These results suggest that the zeolite frameworks may be partially destroyed by the incorporation of the Ti-oxide species into the USY zeolite.

![Figure 1 XRD patterns of (a) the USY zeolite and Ti/USY with different Ti contents of: (b) 0.5, (c) 1 and (d) 5 wt%.

As can be seen in Fig. 2, the UV-vis spectra of Ti/USY with low Ti loadings (0.5 – 1 wt%) showed an absorption band at around 220 nm assigned to the ligand-to-metal charge-transfer transition (LMCT) between the oxygen ligands to the Ti(IV) ions of the highly dispersed Ti-oxide species (Zhang J, 2000). It was clearly seen that the band intensity increases with an increase in the Ti content from 0.5 to 1 wt%.

![Figure 2 Diffuse reflectance UV-vis spectra of (a) the USY zeolite and Ti/USY with different Ti contents of: (b) 0.5, (c) 1, (d) 5 wt%, and (e) TiO_2 (P-25, Degussa) for reference.

As compared with P-25, the absorption edges of Ti/USY with low Ti loadings (0.5 – 1 wt%) shifted to shorter wavelength regions by 50 nm. On the other hand, Ti/USY (5 wt%) exhibits an absorption band at around 250-300 nm attributed to the aggregated crystalline TiO_2 phase (Shioya Y, 2003).

Figure 3 shows the photoluminescence spectrum of the Ti/USY catalysts at 77 K. These photocatalysts exhibit photoluminescence spectra at around 400-650 nm upon excitation with UV light of around 280 nm. The observed photoluminescence and absorption bands are in good agreement with those previously observed with the highly dispersed Ti-oxide species prepared in silica matrices (Anpo M, 2001).

![Figure 3 Photoluminescence spectra of Ti/USY with different Ti contents of: (a) 0.5, (b) 1, and (c) 5 wt%.

The photoluminescence spectrum can be attributed to the radiative decay process from the charge transfer excited state to the ground state of the highly dispersed Ti-oxide species (Anpo M(ed), 2000), as shown in the following scheme:

\[
\text{Ti}^{4+} - \text{O}^{2-} \rightleftharpoons \text{hv} \rightarrow \text{Ti}^{3+} - \text{O}^{-}
\]

The intensity of the photoluminescence decreased with an increase in the Ti content, showing that the aggregated Ti-oxide species becomes dominant at higher Ti loadings (5 wt%), in good agreement with the UV-vis results.

Figure 4 shows the XANES spectra of Ti/USY with different Ti loadings. At low Ti loadings of 0.5 and 1 wt%, a single pre-edge peak due to the highly dispersed Ti-oxide species was observed while with Ti loadings of 5 wt%, three peaks with lower intensities due to the aggregate Ti-oxide species were formed (Anpo M, 2001). These results clearly suggest that the coordination number of the Ti atoms increased with an increase in the Ti content.

The reaction time profiles of the photocatalytic decomposition of N_2O in the presence of CO on the 0.5 wt% Ti/USY at 298 K are shown in Fig. 5. UV light irradiation of Ti/USY in the presence of N_2O and CO led to the efficient formation of N_2 and CO_2 with an increase in the irradiation time. However, in dark reactions, no N_2 and CO_2 were formed. Moreover, the ratio of the number of N_2 molecules
on the number of Ti atoms exceeded 1.3 after 1 h UV irradiation, indicating that this reaction proceeds photocatalytically.

Figure 4 XANES spectra of Ti/USY with different Ti contents of: (a) 0.5, (b) 1, and (c) 5 wt%.

Figure 5 Reaction time profile of the photocatalytic decomposition of N$_2$O in the presence of CO on the 0.5 wt% Ti/USY at 298 K.

Figure 6 Effect of the Ti loading of Ti/USY on N$_2$O conversion and the yields of N$_2$ and CO in the photocatalytic decomposition of N$_2$O in the presence of CO.

From UV-vis and photoluminescence investigations, electron transfers from the photoexcited Ti-oxide species in a highly dispersed state to the anti-bonding molecular orbital (LUMO) of N$_2$O may initiate the photocatalytic decomposition of N$_2$O in the presence of CO, similarly to the reaction scheme reported for NO decomposition on the Ti/Y-zeolite or N$_2$O decomposition on Ag$^+$/zeolite catalysts (Ichihashi Y, 1997; Matsuoka M, 2003).

Conclusions

Ti/USY catalysts of varying Ti loadings were prepared by an impregnation method. The Ti/USY catalysts with low Ti loadings (0.5, 1 wt%) were found to involve a highly dispersed Ti-oxide species, while Ti/USY (5 wt%) mainly involved an aggregated Ti-oxide species. Ti/USY was, thus, found to act as efficient photocatalysts to decompose N$_2$O in the presence of CO to form N$_2$ and CO$_2$ stoichiometrically. The photocatalytic decomposition rate of N$_2$O in the presence of CO was also found to strongly depend on the Ti-oxide loadings of Ti/USY. UV-vis and photoluminescence investigations revealed that the photoexcitation of the Ti-oxide species in a highly dispersed state could initiate the decomposition of N$_2$O in the presence of CO to form N$_2$ and CO$_2$.

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References


