Photoluminescence Properties of the Vanadium Silicalite-1 Catalyst and Its Photocatalytic Reactivity for the Reduction of NO with Propane

Shinya Higashimoto, Shu Guo Zhang, Hiromi Yamashita, Yasuyuki Matsumura,† Yoshie Souma,† and Masakazu Anpo*
Department of Applied Chemistry, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 593
†*Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Osaka 563*

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The vanadium silicalite-1 catalyst (VS-1) has been found to include highly dispersed V-O moieties having a tetrahedral coordination in C_{3v} symmetry, which exhibits a photoluminescence spectrum attributed to the radiative decay from the charge transfer excited state. Also, the photocatalytic reduction of NO into N_2 was found to proceed much more efficiently in the presence of propane than with the direct photocatalytic decomposition of NO without propane. The dynamic quenching of the photoluminescence spectrum by the addition of NO and propane indicate that the excited state of the V-O moieties plays a significant role in this photocatalytic reaction.

Nitric oxide is an extremely toxic air pollutant emitted largely from the reaction with N_2 and O_2 in high temperature combustion processes. The reduction of NO is currently an urgent and challenging issue.[1] Meanwhile, zeolites incorporated with transition metal ions such as Ti, V, Fe, etc. have attracted a great deal of attention as new and effective catalysts for various processes involving the synthesis of fine chemicals.[2]

In particular, vanadium silicalite has been shown to have unique catalytic properties in many oxidation reactions of olefins in the presence of aqueous H_2O_2.[3,4] However, a clear identification and characterization of the nature and local structure of the active vanadium species in the zeolite has not been clarified yet. The present study deals with the investigation of the photoluminescence properties and the photocatalytic reduction of NO in the presence of propane on the vanadium silicalite (VS-1) catalyst.

The VS-1 catalyst (Si/V=120) was hydrothermally synthesized in accordance with previous literature[5] using tetraethylorthosilicate (TEOS) and $VOSO_4{\cdot}nH_2O$ as the starting materials and tetrapropyl ammonium hydroxide (TPAOH) as a template. Prior to in situ photoluminescence measurements and photocatalytic reactions, the catalyst (80 mg) was calcined in O_2 (>20Torr) at 725 K for 3 h and then degassed at 475 K for 2 h up to 10^{-6} Torr. Photocatalytic reactions of NO and propane were carried out at 298 K with a high pressure mercury lamp through a UV cut filter (λ>280 nm) in a quartz cell (35.0 ml) connected to a vacuum line (about 10^{-6} Torr). The products were analyzed by an online gaschromatograph.

Results of XRD and IR measurements show that the VS-1 catalyst corresponds with the topological studies of MFI zeolites as well as that the incorporated V-O moieties exist in the zeolite framework.[4] Furthermore, FT-EXAFS measurements show the V-O moieties have a tetrahedral coordination in C_{3v} symmetry.[6]

As shown in Figure 1, the VS-1 exhibits a photoluminescence spectrum having a vibrational fine structure at around 400-650 nm upon excitation at around 300 nm, which coincides with the photoluminescence spectrum of tetrahedrally coordinated V-O moieties in C_{3v} symmetry highly dispersed on Vycor glass.[7]

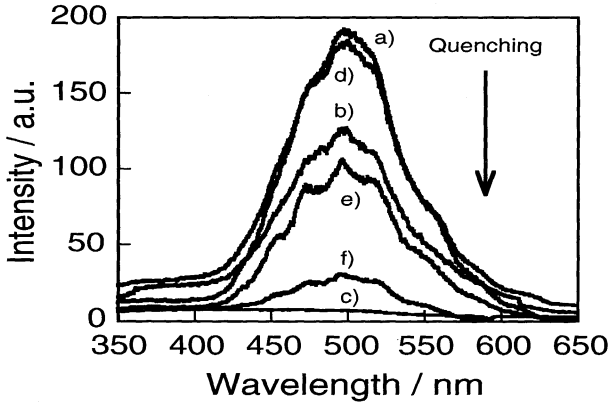

Fig. 1. The effect of the addition of NO or propane on the photoluminescence spectrum of the VS-1 catalyst. Pressure of added NO: a) 0, b) 1.8, c) 3.5 Torr, d) degassed after c); propane: e) 0.04, f) 0.4 Torr. Measured at 77 K.

The width and the maximum position of the emission band do not change upon varying the excitation wavelength, indicating that there is only one luminescent species. The excitation and emission spectra are attributed to the following charge transfer processes on the V-O moieties of the tetrahedral vanadate ions (VO_4^{3-}), involving an electron transfer from O^{2-} to V^{5+} ions and a reverse radiative decay from the charge transfer excited triplet state.[8]

$$(V^{5+}=O^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (V^{4+}-O^{-})^{*} \qquad \text{(charge transfer excited state)}$$

Being in good agreement with the observed quenching of the photoluminescence of V-oxide supported on Vycor glass with NO or methane,[1] the addition of propane or NO onto the VS-1 catalyst leads to the efficient quenching of the photoluminescence as well as a shortening of the photoluminescence lifetime. However, after evacuation, the intensity of the photoluminescence spectrum was found to recover to its original intensity. These results show that propane or NO interacts dynamically with the excited state of V-O moieties, suggesting that this catalyst can be utilized as an effective photocatalyst for the activation of NO or propane.

Figure 2 shows the reaction time profile of N_2 yields in the the photocatalytic reaction of NO with and without propane on the VS-1 catalyst. UV irradiation of the VS-1 catalyst in the presence of a mixture of NO and propane leads to the evolution of N_2 as a major product together with O_2 and N_2O as minor products, while no products could be detected under dark conditions. Furthermore, neither UV irradiation of the silicalite-1 zeolite itself nor of a mixture of NO and propane led to the formation of N_2. The photocatalytic reduction of NO on the VS-

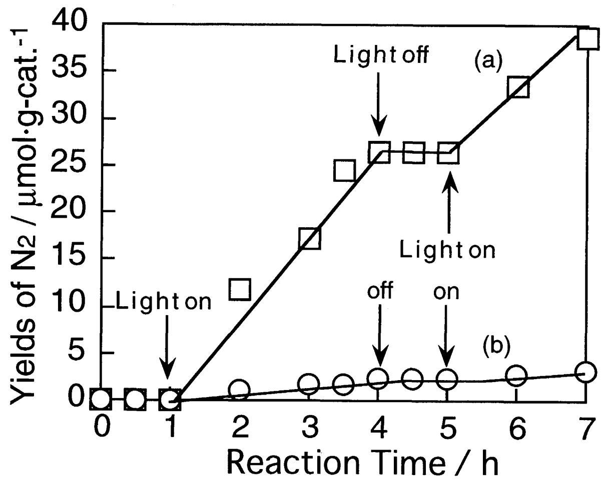

Fig. 2. The reaction time profiles of the photocatalytic decomposition of NO with (a) and without propane (b) on the VS-1 catalyst. (Added propane: 1.97×10^{-4} mol·g-cat^{-1}, NO: 1.82×10^{-4} mol·g-cat^{-1}, Reaction temperature: 295 K)

1 catalyst was found to proceed much more efficiently in the presence of propane than the direct decomposition of NO without propane while leading to the formation of propylene, ethylene and oxygen-containing compounds such as CH_3CHO and CO_2. Furthermore, the turnover frequency of the catalyst exceeded unity after prolonged UV irradiation. These results strongly indicate that this reaction proceeds photocatalytically while the photocatalytic reduction of NO was found to proceed efficiently in the presence of propane on the VS-1 catalyst.

Figure 3 shows the yields and the selectivitiy of N_2 formation in the photocatalytic reduction of NO in the presence of propane. The yields as well as the selectivity of N_2 increase in proportion to the amount of added propane. On the other hand, the yields of N_2O formation decreased and the yields of oxygen-containing products such as CH_3CHO and CO_2 increased when the amount of propane added was increased. Furthermore, the photocatalytic reduction of NO in the presence of various kinds of hydrocarbons such as methane and ethane have also been carried out and it was found that the efficiency of the photocatalytic reduction of NO strongly depends on the kind of hydrocarbons used. Among these hydrocarbons, propane was found to show the highest enhancement of the photocatalytic reduction of NO on the VS-1 catalyst. On the other hand, photocatalytic reduction of NO was not enhanced in the presence of CO molecules, while the photoadsorption of NO and propane was observed at low pressure. Only small amounts of NO were adsorbed under UV irradiation in the presence of NO alone, while greatly enhancing the adsorption in the presence of a mixture of NO and propane. Furthermore, the charge transfer excited state, $(V^{4+}-O^{-})$ abstracts a H atom from the hydrocarbons, even from methane to form the corresponding radicals, as reported in previous literature.[1,9] Taking these results into consideration, we are able to propose the importance of the intermediate species formed from NO and hydrocarbon-radical, which was subsequently followed by the further reaction with NO to produce N_2 as well as CH_3CHO and CO_2.

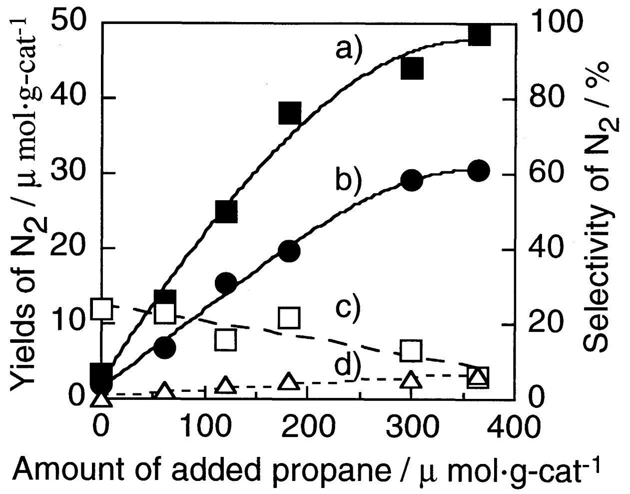

Fig. 3. The effect of the amount of added propane on the yields (a) and the selectivity of N_2 formation (b) and the yields of N_2O (c) and CO_2(d) formation . (Amount of added NO: 1.82×10^{-4} mol·g-cat^{-1}, Irradiation time: 7 h)

Thus, it can be seen that the VS-1 catalyst was found to have tetrahedrally coordinated V-O moieties in the zeolite framework present in a highly dispersed state. The charge transfer excited state of these V-O moieties, $(V^{4+}-O^{-})$ shows a high photocatalytic reactivity for the decomposition of NO into N_2 and O_2. In the presence of propane the photocatalytic reaction was dramatically enhanced, its extent depending on the pressure of propane. The intermediate complex species formed from NO and the hydrocarbon-radical play a vital role in the enhancement of the photocatalytic reduction of NO molecules.

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