Suppressed N₂O formation during NH₃ selective catalytic reduction using vanadium on zeolitic microporous TiO₂

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Emission of N₂O from mobile and off-road engine is now being currently regulated because of its high impact compared to that of CO₂, thereby implying that N₂O formation from the exhaust gas after-treatment system should be suppressed. Selective catalytic reduction using vanadium supported TiO₂ catalyst in mobile and off-road engine has been considered to be major source for N₂O emission in the system. Here we have demonstrated that vanadium catalyst supported on zeolitic microporous TiO₂ obtained from the hydrothermal reaction of bulk TiO₂ at 400 K in the presence of LiOH suppresses significantly the N₂O emission compared to conventional VOₓ/TiO₂ catalyst, while maintaining the excellent NOx reduction, which was ascribed to the location of VOₓ domain in the micropore of TiO₂, resulting in the strong metal support interaction. The use of zeolitic microporous TiO₂ provides a new way of preparing SCR catalyst with a high thermal stability and superior catalytic performance. It can be also extended further to the other catalytic system employing TiO₂-based substrate.

Ever increasing demand for the reduction of greenhouse gas results in the more stringent regulation on its emission and also the corresponding research and development to capture or convert into inert molecule¹. Compared to that of a major greenhouse, CO₂, N₂O has a high greenhouse gas effect up to 300 times². Therefore, the impact of N₂O emission can be comparable to that of CO₂ though the emission concentration of N₂O is relatively low. Most recent diesel engine emission regulation is now started to include N₂O because of its high impact and stability in stratosphere³. For diesel engine emission control under lean condition, urea SCR (selective catalytic reduction) system is the state of art technology for the reduction of NO₂ in most engine companies⁴. Under lean condition where the air to fuel ratio is far beyond the stoichiometric condition, the N₂O formation can be suppressed readily while the system has been maintained under oxidizing condition. However, the emission of N₂O from diesel engine can be increased when the reducing agent for NO₂ is introduced in the SCR system following the reactions, such as 2NH₃ + 2NO + O₂ = N₂O + N₂ + 3H₂O, 2NH₃ + 2O₂ = N₂O + 3H₂O and NH₄NO₃ = N₂O + 2H₂O³. The former two reactions were believed to be the major pathway for N₂O formation in which bimolecular reaction can occur.

For NO₂ abatement, VOₓ catalyst supported on TiO₂ has been used widely in most diesel engines⁵–⁸. There are numerous investigations on the improvement of the catalytic performance using additives such as Ce or W and also using peculiar TiO₂ synthesized using sol-gel method or organic or inorganic templating method⁹–¹⁵. However, VOₓ supported on TiO₂ of relatively low surface area is the state of
Indeed, the current VO$_x$/TiO$_2$ catalyst emits N$_2$O when the reducing agent is present in the stream. The current emission level of N$_2$O is 50 mg per mile, which also depends on the catalyst composition and the system configuration such as diesel oxidation catalyst-selective catalytic reduction-diesel particulate filter. The N$_2$O emission characteristics of the VO$_x$/TiO$_2$ catalyst should be improved under reducing condition. For this purpose, an economically viable catalyst has to be developed in the near future.

It has been demonstrated that the hydrothermal conversion of commercially available TiO$_2$ in the presence of alkaline hydroxide produces unique TiO$_2$ structures differently depending on the species of alkaline hydroxide. Recently, the addition of LiOH, NaOH and KOH to the hydrothermal medium was reported to result in the formation of zeolitic microporous TiO$_2$, nanotube and nanorod, respectively, which seems to be a cost-effective process. The obtained microporous nanocrystalline TiO$_2$ showed a large surface area of 250 m$^2$/g with a pore volume of 0.15–0.20 cc/g, which was similar to those of zeolites and also suitable for catalyst preparation.

The formation mechanism of TiO$_2$ nanotube by hydrothermal synthesis in the presence of NaOH has been studied extensively but it is not clarified yet. Initial work on the formation mechanism of TiO$_2$ nanotube suggested that the nanotube is obtained with an acid washing and subsequent Na$^+$ ion exchange after the formation of amorphous TiO$_2$ during hydrothermal reaction between NaOH and bulk TiO$_2$. The other mechanism proposed that the bond breaking of 3-dimensional TiO$_2$ structure formed layered 2-dimensional structure and finally 1-dimensional nanotubes through sheet folding mechanism. The removal of Na$^+$ cation from the nanotube also deteriorates readily the thermal stability when it is heated at high temperature.

However, the use of zeolitic microporous TiO$_2$ prepared from alkaline condition has not been explored yet. Thus, it is interesting to know whether the zeolitic microporous TiO$_2$ has a high thermal stability or not and also is suitable for catalytic application as a substrate. For the first time in the present work, the zeolitic microporous nanocrystalline TiO$_2$ has been demonstrated as a catalyst support for VO$_x$ over selective catalytic reduction of NO$_x$ using ammonia in order to decrease the N$_2$O formation.

Results
Figure 1 shows the scanning electron micrographs and transmission electron micrographs of the zeolitic microporous TiO$_2$ after the hydrothermal treatment. The morphology of the particle after the hydrothermal
conversion contained sharp edges, suggesting the formation of the well-crystallized TiO\(_2\), which was consistent with the literature\(^{19-21}\). The obtained TiO\(_2\) had the typical argon adsorption-desorption isotherm consistent with the Langmuir isotherm type containing micropore mostly where the micropore area estimated from t-plot was \(\sim 200\, \text{m}^2\text{g}^{-1}\), corresponding to 80% of the total surface area of which the pore size was estimated to be \(\sim 7\, \text{Å}\). The corresponding surface area and pore volume were controlled to be \(250 \pm 20\, \text{m}^2\text{g}^{-1}\) and \(0.20 \pm 0.05\, \text{cc}\text{g}^{-1}\), respectively, depending on the hydrothermal reaction condition.

Also, the presence of the mesopore was observed above \(P/P_0 > 0.9\) but its portion can be decreased with the increase of hydrothermal reaction time. Such mesopore formation was also shown clearly in Fig. 1(c) where the mesopore was formed with several interconnecting crystalline TiO\(_2\) frameworks of which the thickness was 3–4 nm.

Therefore, the results of the transmission electron micrograph observation supported the corresponding unique TiO\(_2\) structure containing the micropore and also the mesopore of which the size was 5–7 nm, which was consistent with the result of argon and nitrogen adsorption-desorption measurement.

The hydrothermal conversion of the bulk TiO\(_2\) into zeolitic microporous TiO\(_2\) in the presence of LiOH seems not to follow the sheet folding mechanism like TiO\(_2\) nanotube. The intercalation of Li\(^{+}\) ion into the TiO\(_2\) structure leads to the formation of the Li\(^{+}\)-O-Ti bond similar to that of Na\(^{+}\) case, resulting in the partial delamination of the TiO\(_2\) layer where the interaction between the layers is high enough to induce the combination of the corresponding layers\(^{25,26}\).

The thermal stability of the zeolitic microporous TiO\(_2\) under ambient condition either with the presence or absence of the saturated water was also investigated using the X-ray diffraction pattern (XRD) and N\(_2\) adsorption and desorption isotherms as a function of heating temperature. Nearly up to 773 K, the microporous structure was retained as evidenced from the results of the nitrogen adsorption-desorption isotherm for the sample shown in Fig. 2 even though the microporous structure was collapsed significantly with the increase of temperature in the presence of water. The XRD of the sample also showed that the crystalline anatase structure appeared to be the major phase when the samples were heated above 773 K. The combined results from XRD and nitrogen adsorption-desorption isotherm confirmed the transformation of microporous TiO\(_2\) to macroporous TiO\(_2\). The moderate thermal stability of the zeolitic
microporous TiO₂ due to the crystal growth into anatase in the presence of water may limit the catalytic application at higher temperature. However, many catalytic applications including photocatalysis or solar energy harvesting can adopt the present zeolitic microporous TiO₂.

VOₓ was supported onto the corresponding unique TiO₂ structure following the procedure reported in the literature. However, the supporting VOₓ catalyst up to 5 wt% resulted in the lower surface area of 105 m²g⁻¹ with 0.19 ccg⁻¹ because of the high calcination temperature at 773 K though the sample still contained large surface area. These textural properties were maintained before and after the catalytic reaction measurement. The TEM observation of VOₓ incorporated TiO₂ as shown in Fig. 3 suggested that most VOₓ particle are located inside the pores of the zeolitic microporous TiO₂, ~7 Å without changing the corresponding morphologies. Thereby, the VOₓ particle was observed clearly as a spot in Fig. 3(c) while there was no particle on the external surface of the TiO₂ though the elemental analysis showed the presence of V in the same region as shown in Fig. 3(d), which can be beneficial for the catalytic reaction. Further, increasing V content in the present also did not alter the location of V.

Figure 4 shows the catalytic performance of the V/TiO₂ catalyst after the calcination at different temperatures also under various reaction conditions. Increasing V content in the catalyst improved the catalytic performance of the NOₓ reduction comparable to that of conventional V/TiO₂ catalyst containing 5 wt% V over the whole reaction temperature range while the N₂O formation was much lower than that of conventional catalyst. The N₂O formation from the present V/TiO₂ was increased with the increase in the temperature where NH₃ was combined with NOₓ to produce N₂O. The effect of the calcination temperature was also pronounced to increase the N₂O formation at high temperature but the N₂O formation was still lowered than that of the conventional catalyst by more than 80%. Also, the V/TiO₂ catalyst prepared from the microporous TiO₂ resulted in the superior catalytic performance over the SCR reaction both in the presence of water in the reactant stream and after the aging in the presence of water at 773 K for 12 h, as shown in Fig. 4(c,d). In the presence of water in the stream the low temperature catalytic activity was decreased while the high temperature catalytic activity was increased slightly because of competitive adsorption of NH₃ and H₂O suppressing the NH₃ oxidation.

Under the present condition, the main reaction for N₂O formation is believed to be 2NH₃ + 2NO + O₂ = N₂O + N₂ + 3H₂O following the literature. The catalytically active VOₓ inside the pore, ~7 Å was believed to have a strong metal support interaction with TiO₂, resulting the smaller VOₓ particle size.
as referred from Fig. 3. Thus, the strong metal-support interaction between TiO$_2$ and VO$_x$ led to the formation of Bronsted acid site with high strength, which is beneficial for selective catalytic reduction of NO by NH$_3$. The N$_2$O formation can be suppressed up to ~80% because of the increased Bronsted acidity of the VO$_x$ small particle in the microporous zeolitic TiO$_2$ where the superior SCR activity can be maintained as illustrated in Fig. 4(c). This result was partly consistent with the increased N$_2$O formation on the V/TiO$_2$ catalyst when the catalyst deteriorates because of the sintering$^9$. Also, it was possible to include NH$_3$ oxidation by O$_2$ as potential pathway for the following N$_2$O formation reaction: \[ 2\text{NH}_3 + \text{O}_2 = \text{N}_2 + 3\text{H}_2\text{O} \] where the catalyst deactivation was severe like the commercial V/TiO$_2$ catalyst in the presence of water or after hydrothermal aging. One possibility to explain the superior catalytic performance V supported on zeolitic microporous TiO$_2$ over the SCR reaction was that the growth of the vanadium oxide particle size can be limited due to the pore size, implying the encapsulation of vanadium oxide particle surrounded by TiO$_2$ matrix.

We have demonstrated that the zeolitic microporous TiO$_2$ with moderate thermal stability can be prepared from the simple hydrothermal conversion from commercially available bulk TiO$_2$ of low grade, 98% or lower in the presence of LiOH at 400–440 K, which can be scaled up easily for industrial process. The obtained zeolitic microporous nanocrystalline TiO$_2$ contains the micropore up to 80% referred from the t-plot method. For the first time, it was proved that the supporting VO$_x$ into such zeolitic microporous TiO$_2$ resulted in the high NO$_x$ reduction activity with lower N$_2$O formation, which was ascribed to the location of catalytically active VO$_x$ particles in the microporous TiO$_2$, resulting the strong metal-support interaction and consequently the increased Bronsted acidity. Therefore, the zeolitic microporous TiO$_2$ has potential as a substrate for the SCR reaction below 773 K while the thermal stability of the microporous TiO$_2$ was retained.
Methods

**Synthesis of zeolitic microporous TiO₂.** TiO₂ anatase (Aldrich, 98%) of 2–8 g was added to the solution containing 10 M or more LiOH in the Teflon lined autoclave for hydrothermal heating at 400–440 K for 72 hr under rotating condition at 40 rpm. After cool down to room temperature, the slurry was neutralized with 0.1 N HCl under stirring for 6 hr. The solution was filtered and washed with deionized water thoroughly. The acidification and filtration was repeated three times to remove the residual trace metal hydroxides. The obtained product was dried at 330 K in an oven and calcined under flowing oxygen at 673 K for 4 h. The inductively coupled plasma analysis of the obtained sample showed that the residual Li was ~6 ppm level, indicating the complete removal of Li⁺ by the neutralization and subsequent thorough washing. The scale up to ~100 g per batch was also demonstrated to give the same textural properties.

**Preparation of VOₓ in zeolitic microporous TiO₂.** All catalysts were prepared by applying wet impregnation of vanadium precursor solution on titania. Ammonium metavanadate (99%, Sigma Aldrich) was dissolved in diluted oxalic acid solution (0.5 M) to produce the solution of vanadium precursor. Anatase TiO₂ powder (DT-51 Millennium Chemicals) was used as support to prepare the conventional catalyst containing 5 wt% V. The samples with 1 wt%, 3 wt% and 5 wt% V₂O₅ loading on TiO₂ were prepared. After impregnation process in a rotary evaporator, catalysts were dried and then calcined at 673 K or 773 K for 4 h in air.

**SCR activity measurement of VOₓ in zeolitic microporous TiO₂.** SCR activity was measured in a fixed-bed quartz tubular reactor. Catalysts were sieved to 300–500 μm in diameter then loaded in the reactor. 500 ppm NO, 500 ppm NH₃, 2% O₂ and balanced with N₂ were introduced as reactants. In order to examine the catalytic activity in the presence of water, the reactant containing 500 ppm NO, 500 ppm NH₃, 2% O₂, 3% H₂O balanced with N₂ was used. The catalyst was further aged in the presence of 10% O₂, 5% H₂O balanced with N₂, at 500 °C for 12 h before catalytic reaction.

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Author Contributions
S.G.L. and H.J.L. synthesized the zeolitic microporous TiO₂ and performed the samples characterization and data analysis. I.S. and S.Y. performed the catalytic experiments investigation. D.H.K. and S.J.C. designed the research. All authors co-wrote the manuscript.

Additional Information
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