Improvement of the Catalytic Performance of Pd/WO_3/ZrO_2 in the Selective NO–CH_4–O_2 Reaction by the Addition of Water Vapor

Kazu Okumura,* Tetsuji Kusakabe, Naoko Yasunobu, and Miki Niwa
Department of Materials Science, Faculty of Engineering, Tottori University, Koyama-cho, Tottori 680-8552

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The Pd/WO_3/ZrO_2 catalyst exhibited activity for the NO–CH_4–O_2 reaction in the presence of water vapor when WO_3 monolayer covered the ZrO_2 surface. The selectivity of methane consumption for NO reduction was considerably improved by the addition of 10% of water vapor.

Recently, much attention has been directed to the metal loaded catalyst for catalytic reduction of NO_x using hydrocarbons as reductants. Among various hydrocarbons, methane is the most preferable because it is the main component of natural gas. Many kinds of catalysts were found to be efficient for the catalytic reduction of NO. However, the activity is sometimes severely suppressed by water vapor. Therefore, the enhancement of tolerance to the water vapor is an important subject. Pd is promising at this point because it is relatively tolerant to water vapor.[1] On the other hand, as for the support components, zeolites such as ZSM-5 and mordenite have been used to keep the active Pd species, where the Brønsted acid sites played an important role to generate the active Pd center.[2,3] However, zeolite has a disadvantage when it is used in the presence of water vapor. This is because water vapor causes the elimination of Al from the zeolite framework, which leads to the irreversible suppression of the catalytic activity of Pd. WO_3 supported on ZrO_2 exhibits strong Brønsted acidity, when WO_3 covers the ZrO_2 surface as a monolayer form.[4,5] The monolayer-WO_3/ZrO_2 is promising to be used as a support for Pd, because it is expected to be tolerant to water vapor.[6] In the present study, catalytic NO–CH_4–O_2 reaction was carried out over Pd loaded on WO_3/ZrO_2. Especially, the attention was focused on the influence of water vapor on the catalytic performance and acid properties of Pd/WO_3/ZrO_2 catalyst.

ZrO_2 was prepared by the hydrolysis of zirconium oxynitrate solution using aqueous ammonia, followed by calcination in air at 573 K. The obtained ZrO_2 was immersed in an ammonium tungstate solution. After drying, the obtained solid was calcined at 923 K for 4 h under an atmospheric condition to obtain WO_3/ZrO_2. Pd was loaded on WO_3/ZrO_2 by an ion exchange method using $Pd(CH_3)_4Cl_2$ solution. It was then treated with N_2 at 773 K for 4 h. The loaded amount of Pd was measured by an ICP method. Before the reaction, the catalyst was treated in flowing O_2 at 773 K for 1 h. A mixture of NO, O_2 and methane (NO, 1000 ppm; CH_4, 1000 ppm; O_2, 1%; He balance; total flow rate, 150 mL min^{-1}) was fed over 2 g of the catalyst at 623 K, and the outlet gas was analyzed by a gas chromatograph and a NO_x meter. Water was fed into the reactor with a microfeeder. Water was vaporized at the inlet of the reactor and then mixed with the reactant gas mixture.

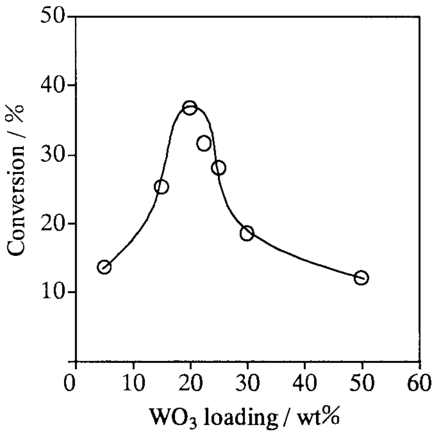

Figure 1. Dependence of the NO conversion on the WO_3 loading; Pd loading, 0.07 wt%.

Firstly, the influence of the WO_3 loading on the catalytic reaction of Pd was examined. Figure 1 shows the dependence of the conversion of NO to N_2 on the WO_3 loading. The Pd loading was fixed at 0.07 wt%. The reaction was carried out under the dry conditions. The maximum conversion of NO was obtained when the WO_3 loading reached 20 wt%. Considering the surface area of the catalyst (96 m^2 g^{-1}), the value corresponded to the formation of WO_3 monolayer over the ZrO_2 surface.[5] Therefore, it was inferred that the Brønsted acid sites generated on the WO_3 monolayer effectively anchored the active Pd species.

In the next step, the catalytic performance was studied over the Pd/WO_3/ZrO_2 with various Pd loadings. The loading of WO_3 was fixed at 20 wt%. When the reaction was carried out under the dry conditions, the NO conversion first increased with Pd content (Figure 2(a)). The maximum value was obtained when Pd loading reached 0.17 wt%. However, the further increase in the Pd loading lowered the value. Alternatively, the conversion of methane to carbon dioxide

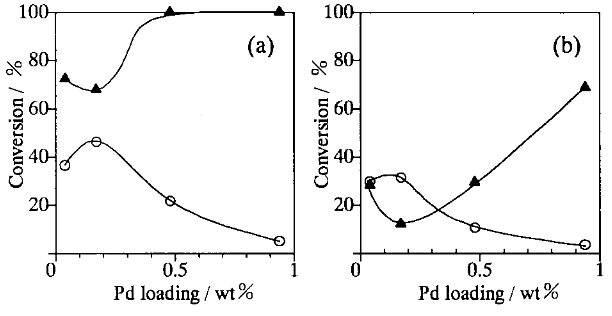

Figure 2. Dependence of the conversion of NO (○) and methane (▲) on the Pd loading; (a) dry condition, (b) in the presence of 10% of water vapor.

reached 100% when the Pd loading exceeded 0.48 wt%. Probably, this is because of the formation of agglomerated PdO, which was favorable for the simple methane combustion.[7] However, the feature changed significantly in the presence of 10% of water vapor (Figure 2(b)). The conversion of methane to carbon dioxide was considerably suppressed. On the other hand, the change in the NO conversion was small. As a result, the selectivity of CH_4 to CO_2 consumed for the NO–CH_4–O_2 reaction increased under the water vapor. Especially when the Pd loading was 0.17 wt%, the conversion of methane was half that of NO. Considering the reaction stoicheometry and the gas composition, the fact meant that the oxidation of methane was completely suppressed. In other words, the selectivity for NO reduction reached 100% in the presence of water vapor. The improvement of the selectivity is an important phenomenon, taking the fact into account that the water vapor usually hindered the NO reduction. However, a promoting effect of water vapor on the selective reduction of NO has been reported by using C_3H_6, C_3H_8, *iso*-C_4H_{10} and *n*-octane as a reductant.[8–10] In the present case, the effect of water vapor was attributed to the enhancement of Brønsted acid acidity over the WO_3/ZrO_2 as proved by IR spectra of adsorbed pyridine.

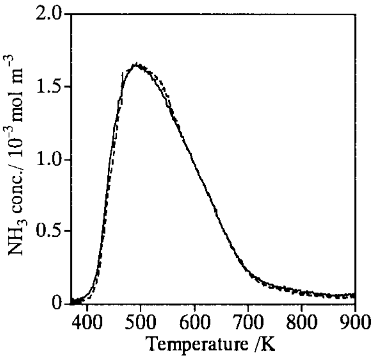

Figure 3. Temperature programmed desorption of ammonia over $Pd/WO_3/ZrO_2$. Solid line, pretreated; dotted line, after NO-CH_4-O_2 reaction under 10% of water vapor for 17 h.

Finally, in order to examine the influence of water vapor on the acid properties of $Pd/WO_3/ZrO_2$ catalyst, temperature programmed desorption (TPD) of ammonia was measured before and after the reaction. This is because it was considered that the acidity played an important role to keep the active dispersed PdO species.[11,12] TPD spectrum measured after the reaction completely agreed with that measured before the reaction (Figure 3). Therefore, the acid site of WO_3/ZrO_2 was not affected by the exposure to water vapor during the catalytic reaction. The fact was contrasted with the result obtained for the zeolite support.

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