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Catalytic activity of Pd loaded on WO_3/Al_2O_3 for $NO–CH_4–O_2$ in the presence of water vapor

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Abstract

Pd loaded on various kinds of monolayer supports was applied for selective reduction of NO by methane in the presence of O_2 and water vapor. $Pd/WO_3/Al_2O_3$ exhibited the highest conversion of NO to N_2 among Pd loaded monolayer supports. The catalyst was relatively tolerant and reversible upon the exposure of water vapor. This is due to the enhanced amount of Brønsted acid sites under the moisture as evidenced by the IR measurement of adsorbed pyridine. The Brønsted acid sites generated on WO_3/Al_2O_3 support were required to give the dispersed Pd species, similar to on the zeolite.

Keywords: Palladium; NO_x; Monolayer; EXAFS

1. Introduction

Metal loaded catalysts for catalytic reduction of NO_x using hydrocarbons as reductants have been extensively studied from the viewpoint of environmental protection, since NO_x is harmful and causes acid rain. Methane is the most preferable reductant among various hydrocarbons in the reduction of NO, because it is the main component of natural gas. Many kinds of supported metal catalysts were found to be effective for the catalytic reduction of NO by methane. However, the activity of catalysts was often severely suppressed by water vapor. Therefore, the improvement 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]. Usually, zeolites such as ZSM-5 and mordenite have been used as supports for Pd, where strong Brønsted acid sites played an important role to generate the active Pd center [2,3]. However, zeolite had disadvantageous character when it was used in the presence of water vapor at high temperature. 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. Although much effort has been directed to improve tolerance of zeolite against water vapor, the use of simple metal oxide support with acid property can be used as an alternative support for Pd. The monolayer type oxides were recognized to show Brønsted acidity [4,5]. In some combinations of oxides, the acid strength was comparable to that of zeolites [6]. Therefore, the monolayer-oxides are promising to be used as a support for Pd because of the generation of Brønsted acidity and their simple structure. The existence of strong Brønsted acid is essential for Pd to act as active species for selective reduction of NO. Indeed, Pd or Pt supported on SO_4^{2-}/ZrO_2 and WO_3/ZrO_2 have been examined as catalysts for removal of NO by methane [7–9]. In this study, in order to find active catalysts for NO reduction under the water vapor, many kinds of monolayer-oxides were employed as supports for

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Pd and the catalytic performance was tested. Furthermore, we have studied the composition, acid properties and structure of Pd loaded on WO_3/Al_2O_3 in detail, which was active in the reduction of NO.

2. Experimental

MgO (JRC-MGO-4 1000A), Al_2O_3 (JRC-ALO-4), TiO_2 (JRC-TIO-4) was supplied from the Catalysis Society of Japan. ZrO_2 was prepared by the calcination of zirconium hydroxide at 573 K for 4 h. α-Al_2O_3 was prepared by calcination of Al_2O_3 (JRC-ALO-4) at 1673 K for 5 h. SnO_2 was prepared by the hydrolysis of $SnCl_2 \cdot 2H_2O$ solution with 4 N NH_4OH. The precipitate was washed with water repeatedly until no Cl^- ion was detected by $AgNO_3$ solution. WO_3, MoO_3 and $PO_4{}^{3-}$ were supported on these oxides with impregnation method form $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and H_3PO_4, respectively. The samples were finally calcined at 923 K in air. Exceptionally, MoO_3/SnO_2 and WO_3/Al_2O_3 were calcined at 773 and 673 K, respectively. Pd was loaded on the supports through an ion exchange method using $Pd(NH_3)_4Cl_2$ solution (Pd loading: 0.2 wt.%). It was then treated with N_2 at 773 K for 4 h. Benzaldehyde ammonia titration (BAT) experiment to measure the extent of coverage by WO_3 on Al_2O_3 was carried out in the same manner reported already [10]. Benzaldehyde was repeatedly injected at 523 K in a flow of He until no further adsorption of aldehyde was observed. Finally, ammonia was injected at 673 K to desorb benzonitrile. Benzonitrile was quantitatively analyzed by the FID, and the coverage by WO_3 over Al_2O_3 was calculated.

The catalytic measurements were carried out using fixed bed flow reactor. 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 473 K, and the outlet gas was analyzed by a gas chromatograph and a chemiluminescence NO_x meter. NO conversion was calculated based on the decrease in NO concentration. 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.

The acid property was measured using temperature programmed desorption (TPD) of ammonia. The sample was evacuated at 773 K prior to the measurement. The TPD data was collected with ramping rate of 10 K min^{-1}. Mass spectrometer was used to monitor the desorbed NH_3. The water vapor treatment was conducted before measurement in order to remove the weakly adsorbed NH_3.

Pd K-edge (24.3 keV) EXAFS was measured at BL38B101 station of Japan Synchrotron Radiation Research Institute (SPring-8) in a transmission mode. The storage ring was operated at 8 GeV with a ring current of 70–93 mA. Si(3 1 1) single crystal was used to obtain monochromatic X-ray beam. Two ion chambers filled with Ar and Ar (30%)/Kr (70%) were used as detectors of I_0 and I, respectively. The measurements were carried out at room temperature. The sample was transferred to aluminum cells with two Kapton windows connected to a flow reaction system without contacting air. The data was analyzed using REX2000, Version 2.0.4 program (Rigaku Co.).

3. Results and discussion

3.1. Catalysis of Pd loaded on various kinds of monolayer supports

In the beginning, the catalytic activity of Pd loaded on various kind of monolayer support was compared in order to find out the active combination of oxide supports. The physical properties of the prepared samples were summarized in Table 1. The loading of WO_3, MoO_3 and $PO_4{}^{3-}$ corresponded to the monolayer coverage in every catalyst, considering the surface density and the size of the supported oxides. Fig. 1 shows the conversion of CH_4 and NO over these catalysts measured at 723 K. The reaction was carried out in 10% water vapor. The NO conversions of $PO_4{}^{3-}/ZrO_2$, MoO_3/SnO_2, MoO_3/ZrO_2, WO_3/α-Al_2O_3, WO_3/TiO_2, WO_3/SnO_2, WO_3/MgO were less than 6%, although these catalysts were active in the total oxidation of methane. On the other hand, Pd loaded on WO_3/Al_2O_3 and WO_3/ZrO_2 exhibited substantial activity. Namely, conversions from NO to N_2 were 26 and 22% over WO_3/Al_2O_3 and WO_3/ZrO_2, respectively. TOF of Pd loaded ZSM-5 catalyst was about five times as high as that of

Table 1
Physical properties of monolayer supports (Pd was not loaded)

Sample	Loading (wt.%)	BET surface area ($m^2 g^{-1}$)	Surface area per gram support ($m^2 g^{-1}$)	Surface density of supported oxides (nm^{-2})
WO_3/γ-Al_2O_3	20	128	161	4.0
WO_3/ZrO_2	25	118	157	5.5
WO_3/MgO	15	137	161	2.8
WO_3/SnO_2	2	16	16	3.2
WO_3/TiO_2	8	43	47	4.8
WO_3/α-Al_2O_3	1	4	4	6.6
MoO_3/ZrO_2	12	142	161	3.5
MoO_3/SnO_2	2	16	16	4.6
PO_4^{3-}/ZrO_2	8	178	193	2.9

$Pd/WO_3/Al_2O_3$ under the same reaction conditions. However, it was noticed that the WO_3/Al_2O_3 exhibited the highest conversion of NO to N_2 among the tested monolayer samples. Therefore, we have further studied the acid properties and the catalysis of $Pd/WO_3/Al_2O_3$, which showed the highest conversion of NO at 723 K.

3.2. Dependence of the acid property and catalysis of $Pd/WO_3/Al_2O_3$ on the WO_3 loading

Fig. 2 shows the dependence of CH_4 and NO conversions on the WO_3 loading of WO_3/Al_2O_3. A maximum conversion of NO was obtained when WO_3 loading reached 20 wt.%. Taking the surface area of the sample (128 $m^2 g^{-1}$) into account, the loading corresponded to the monolayer coverage of WO_3 over Al_2O_3, where the density of W was calculated to be 4.04 nm^{-1}. The conversion of CH_4 gradually decreased monotonously with increase in the WO_3 loading. Fig. 3 shows the dependence of acid amount and surface area of WO_3/Al_2O_3 on the WO_3 loading. The total acid amount of WO_3/Al_2O_3 was measured using NH_3 TPD method. The acid amount reached the maximum when the WO_3 loading was 20 wt.%. This loading of WO_3 (20 wt.%) coincided with the optimum composition of $Pd/WO_3/Al_2O_3$ for the conversion of NO. However, the surface area decreased with increase in the WO_3 loading. From the coincidence of optimum WO_3 loading for the conversion of

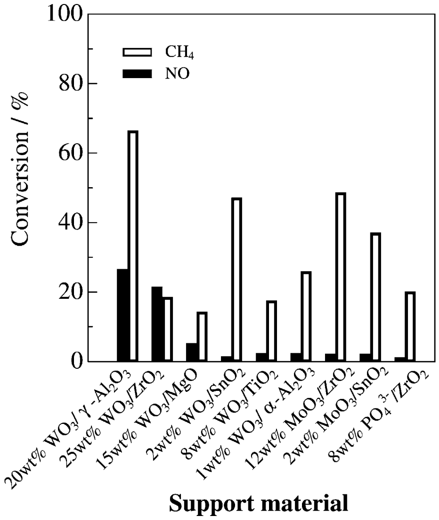

Fig. 1. Conversion of CH_4 and NO over various kinds of monolayer catalysts; Pd loading, 0.2 wt.%; NO, 1000 ppm; CH_4, 1000 ppm; O_2, 1%; H_2O, 10%; total flow rate, 150 ml min^{-1}; reaction temperature, 723 K.

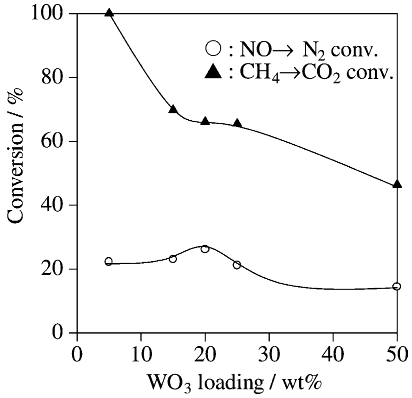

Fig. 2. Dependence of the conversion of CH_4 (▲) and NO (○) on the WO_3 loading of WO_3/Al_2O_3; Pd loading, 0.2 wt.%; reaction temperature, 723 K.

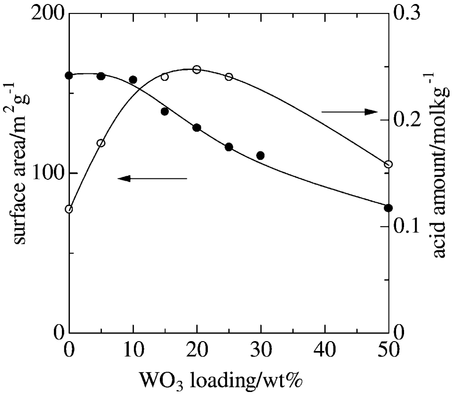

Fig. 3. Dependence of acid amount and surface area on the WO_3 loading of WO_3/Al_2O_3 supports.

NO and acid amount, it was inferred that the monolayer coverage of WO_3 over Al_2O_3 brought about the generation of active Pd species in which the highest acid amount of acid site was generated. This was consistent with the fact that the monolayer-WO_3/Al_2O_3 has been used as catalyst for the isomerization of olefins [11,12]. The WO_3 monolayer formation could be directly proven by BAT method is shown in Fig. 4. In this figure, the coverage of WO_3 increased linearly with W concentration, and the value reached 90% with $4\,nm^{-2}$. Therefore, it was confirmed that the WO_3/Al_2O_3 with the highest acid amount was obtained when WO_3 monolayer covered Al_2O_3 surface completely at $4\,nm^{-1}$.

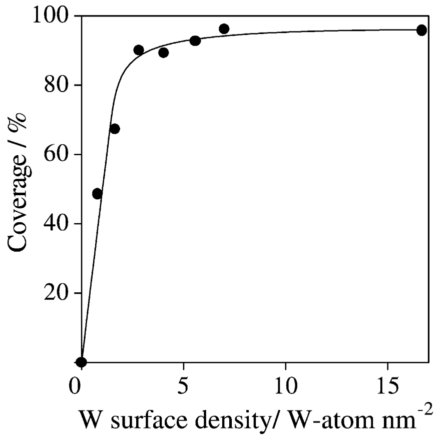

Fig. 4. Relationship between coverage of WO_3 over Al_2O_3 and surface density of WO_3 determined by means of BAT method.

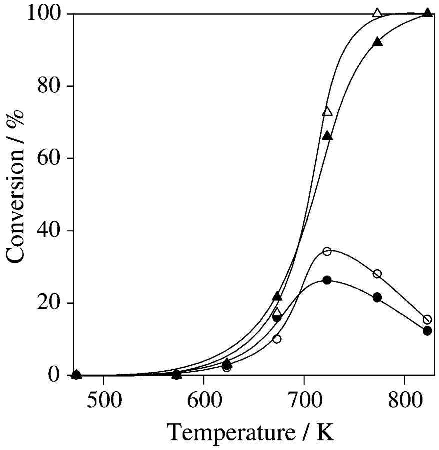

Fig. 5. Dependence of the conversion of NO (●, ○) and CH_4 (▲, △) on the reaction temperature measured in the 10% (closed symbol) or 0% (open symbol) water vapor; $Pd/WO_3/Al_2O_3$ catalyst; Pd loading, 0.2 wt.%; WO_3 loading, 20 wt.%.

3.3. Influence of the water vapor on the catalysis of Pd/monolayer-WO_3/Al_2O_3

Fig. 5 shows the catalytic performance of $Pd/WO_3/Al_2O_3$ conducted in the presence or absence of water vapor. The maximum conversion of NO decreased by 8% through the addition of 10% water vapor. However, the degree of deactivation was less than that observed on Pd/HZSM-5 sample, where the conversion of NO decreased from 73 to 34% under the same conditions [13]. Thus, it could be noticed that the $Pd/WO_3/Al_2O_3$ was relatively tolerant to the water vapor. Fig. 6 shows

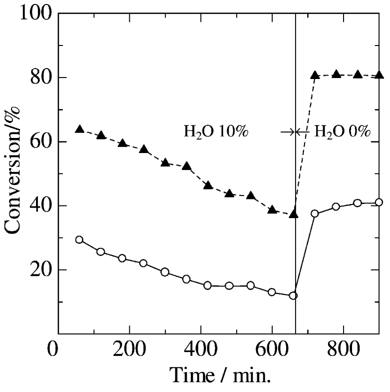

Fig. 6. Time dependence of NO (○) and methane (▲) conversion for NO–CH_4–O_2 reaction over $Pd/WO_3/Al_2O_3$ catalyst; Pd, 0.2 wt.%; WO_3, 20 wt.%.

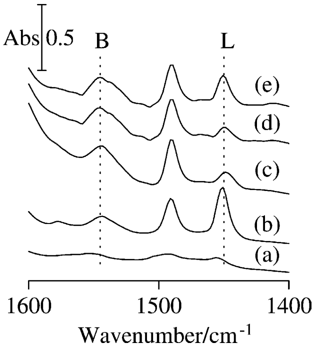

Fig. 7. IR spectra of Pd/WO_3/Al_2O_3; Pd loading, 0.2 wt.%; WO_3 loading, 20 wt.%: (a) evacuated at 723 K; (b) pyridine was adsorbed at 373 K; (c) water vapor was exposed at 373 K; (d) water vapor was exposed at 723 K; (e) evacuated at 723 K.

the dependence of NO and methane conversion on the time on stream. Although the conversion of NO gradually decreased, the activity immediately restored after switching off the water vapor at 660 min. The behavior was contrasted with that on Pd loaded zeolite catalysts, which showed irreversible suppression of the conversion of NO after exposure of water vapor due to the deterioration of Brønsted acidity.

In order to reveal the origin for the tolerance of Pd/WO_3/Al_2O_3 catalyst to the water vapor, IR spectra of adsorbed pyridine were measured. Fig. 7 shows the IR spectra of pyridine adsorbed on Pd/WO_3/Al_2O_3 measured after various treatments. The peaks appeared at 1545 and 1451 cm^{-1} could be straightforwardly assigned to the pyridine adsorbed on the Brønsted and Lewis acid sites, respectively. The intensity of pyridine adsorbed on Brønsted acid sites increased after the exposure of 2.7 Pa water vapor by a factor of two. However, the Lewis sites decreased after the treatment. The fact suggested that the Lewis sites were converted into the Brønsted ones through the exposure of water vapor. The phenomenon was similar to that obverted on WO_3/ZrO_2 in that the Brønsted acidity was enhanced in the water vapor [9]. Therefore, the effect of water vapor was attributed to the enhancement of Brønsted acid acidity over the WO_3/Al_2O_3. Probably this phenomenon was responsible for the tolerance of the catalyst against water vapor, since the presence of Brønsted acid sites was essential for the generation of highly dispersed species, which was active for NO reduction. It could be supposed that the enhanced Brønsted acid sites prevented the dispersed PdO from the sintering caused by water vapor.

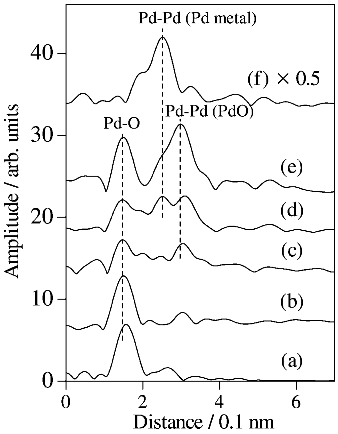

Fig. 8. Pd K-edge EXAFS Fourier transforms of (a) Pd/HZSM-5 (Si/Al_2=23.8; Pd, 0.2 wt.%) oxidized at 673 K and (b–d) Pd/WO_3/Al_2O_3; Pd loading, 0.2 wt.%; WO_3 loading, 20 wt.%; (b) oxidized at 773 K; (c) after NO–CH_4–O_2–H_2O reaction at 723 K; (d) after reaction at 823 K; (e) PdO; (f) Pd foil; Fourier transform was conducted from 30 to 105 nm^{-1}.

3.4. Characterization of Pd structure using EXAFS

In order to study the role of support oxide in the genesis of active Pd center and to characterize the structure of Pd under the reaction conditions, EXAFS of Pd/WO_3/Al_2O_3 was measured before and after reaction. Fig. 8 shows the Pd K-edge EXAFS spectra of Pd loaded on WO_3/Al_2O_3 as well as reference samples. After the pretreatment in oxygen at 773 K, the generation of highly dispersed Pd oxide was observed. The fact was confirmed from the disappearance of Pd–Pd peak at 0.30 nm characteristic of the bulky PdO as can be seen in the spectrum of authentic PdO powder. The spectrum obverted in Pd/WO_3/Al_2O_3 was quite similar to that in the oxidized Pd/HZSM-5. In Pd/HZSM-5, Brønsted acid site was considered to keep the dispersed PdO species over HZSM-5, which was active in the catalytic reduction of NO by methane. From the similarity in the structure, it was inferred that the Brønsted acid sites generated on WO_3/Al_2O_3 played the role to anchor the dispersed PdO. In order to reveal the influence of water vapor, EXAFS spectra were measured after the reaction in the presence of 10% water vapor. Fig. 8(c) and (d) show the EXAFS spectra of Pd/WO_3/Al_2O_3 measured after the reaction at 723 and 823 K, respectively. In the spectrum measured after reaction at 723 K, the growth of Pd–Pd peak characteristic of PdO was observed, indicating the generation of slightly agglomerated PdO during the reaction. Therefore, it was supposed that the gradual decrease in activity under the 10% water vapor was due to the sintering of PdO, which was caused by water vapor. The fast regeneration of activity through switching off the water vapor suggested that the redispersion of the agglomerated PdO occurred quickly through stopping the water vapor (Fig. 6). The intensity of the Pd–Pd peak (PdO) increased accompanied by raising the reaction temperature to 723 K in EXAFS spectrum. At the same time, a novel peak appeared at 0.25 nm, which could be attributed to the Pd metal from the comparison with the spectrum of Pd foil (Fig. 8(f)). At this temperature, the activity of Pd began to decrease as shown in Fig. 5. The fact indicated that the deactivation of Pd at elevated temperature was caused by the partial reduction of PdO by methane and the generation of agglomerated Pd metal.

4. Conclusions

The monolayer-WO_3/Al_2O_3 was a promising support for Pd among various kinds of monolayer type oxides when it was used for NO reduction by methane under the O_2 and water vapor conditions. The highest activity of Pd was reached when WO_3 monolayer covered over Al_2O_3 surface, where the generation of maximum amount of Brønsted acid was observed. The catalyst was relatively tolerant to the water vapor that showed quick restoration of activity by switching off the water vapor. The increase in the Brønsted acid amount was observed under the water vapor. The Brønsted acid sites were essential for keeping the highly dispersed Pd species as similar to the zeolite case.

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