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Preparation of supported Pt-M catalysts (M = Mo and W) from anion-exchanged hydrotalcites and their catalytic activity for low temperature NO-H_2-O_2 reaction

S. Hamada, S. Hibarino, K. Ikeue, M. Machida *

Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

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Abstract

The NO-H_2-O_2 reaction was studied over supported bimetallic catalysts, Pt-Mo and Pt-W, which were prepared by coexchange of hydrotalcite-like Mg-Al double layered hydroxides by $Pt(NO_2)_4^{2-}$, MoO_4^{2-}, and/or WO_4^{2-} and subsequent heating at 600 °C in H_2. The Pt–Mo interaction could obviously be seen when the catalyst after reduction treatment was exposed to a mixture of NO and H_2 in the absence of O_2. The Pt-HT catalyst showed the almost complete NO conversion at 70 °C, whereas the Pt-Mo-HT showed a negligible conversion. Upon exposure to O_2, however, Pt-Mo-HT exhibited the NO conversion at the lowest temperature of $\geq$30 °C, compared to $\geq$60 °C required for Pt-HT. EXAFS/XANES, XPS and IR results suggested that the role of Mo is very sensitive to the oxidation state, i.e., oxidized Mo species residing in Pt particles are postulated to retard the oxidative adsorption of NO as NO_3 and promote the catalytic conversion of NO to N_2O at low temperatures.

Keywords: NO-H_2-O_2 reaction; Platinum; Molybdenum; Hydrotalcite

1. Introduction

Catalytic NO-H_2 reactions in the presence of excess O_2 have been investigated using Pt catalysts supported on various oxides [1–9]. However, the higher selectivity to N_2O rather than N_2 would devalue the advantage of the lower reaction temperature ($\leq$100 °C) of these catalysts, because increasing attention is given in avoiding the formation of this effective greenhouse gas. One possible way to improve the N_2 selectivity is the modification by promoters. Yokota et al. [1] reported that the N_2 selectivity of Pt/SiO_2 in the NO-H_2-O_2 reaction was increased by the addition of Na and Mo, which would suppress the oxidation of Pt even in the presence of excess O_2. We have previously reported that oxide supports having both moderate acidic and basic sites are requested for better N_2 selectivity compared to acidic oxide supports like SiO_2 and zeolites [6–9]. Pt supported on TiO_2-ZrO_2 exhibited the higher selectivity to N_2 rather than N_2O [6,8]. The addition of Na as a Lewis base to Pt-ZSM5 improved the N_2 selectivity [8], because Na promotes the oxidative adsorption of NO as NO_2-type species, which would play a role of an intermediate to yield N_2.

On this concern, Mg-Al oxides formed from hydrotalcite-like double layered hydroxides (HT) are promising because of their acid/base sites formed in the porous structure with a large surface area [10–12]. The thermal decomposition of Pt complex-exchanged hydrotalcites (Pt-HT) yields highly dispersed Pt catalysts efficient for this reaction [13–15]. In the present study, supported bimetallic catalysts, Pt-M/Mg-Al-O (M = Mo and W), were prepared by coexchange of HT to apply for the low temperature NO-H_2-O_2 reaction. The effect of additives (Mo and W) on the catalytic activity and selectivity of Pt was studied from structural and chemical view points.

2. Experimental

2.1. Catalyst preparation

A hydrotalcite-like compound, $Mg_{0.74}Al_{0.26}(OH)_2(NO_3)_{0.26}\cdot nH_2O$, was prepared by the co-precipitation method [13].

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* Corresponding author. Tel.: +81 96 342 3651; fax: +81 96 342 3651.
E-mail address: machida@chem.kumamoto-u.ac.jp (M. Machida).

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$Mg(NO_3)_2{\cdot}6H_2O$ (14.8 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (5.2 mmol) were dissolved into a distilled water (20 mL) and resulting mixed solution was added dropwise into NH_3 aqueous solution (1 M, 100 mL) with vigorous stirring at room temperature. The precipitate was centrifuged, washed with distilled water and then dried under reduced pressure overnight. The powder thus obtained (HT) was exchanged in aqueous solutions of $K_2Pt(NO_2)_4$ at room temperature for 24 h to obtain $Pt(NO_2)_4^{2-}$-exchanged HT, which are abbreviated as Pt-HT. For the preparation of Pt-M coexchanged HTs (Pt-M-HT, M = Mo and W), mixed aqueous solutions of $K_2Pt(NO_2)_4$ and K_2MoO_4 or K_2WO_4 were used. As exchanged phases were washed with distilled water, dried under reduced pressure and heated at 600 °C in a flow of H_2 for 2 h to yield 1 wt% Pt and 0–10 wt% M-loaded catalysts.

2.2. Characterization

Unless otherwise stated, Pt-M-HTs with 1 wt% Mo and 5 wt% W loading were used for characterization. Crystal phases were determined by powder X-ray diffraction (XRD, Rigaku Multiflex) using monochromated Cu Kα radiation (30 kV, 30 mA). Chemical composition of as prepared catalysts was determined by an energy disperse X-ray fluorescence measurement (Horiba MESA-500W). Specific surface area was calculated by BET method from N_2 adsorption isotherm measured at 77 K (Belsorp-mini). The microstructure was observed by TEM (JEOL 2000FX, 200 kV). X-ray photoelectron spectroscopy (XPS) spectra were measured on a VG Sigmaprobe spectrometer using Al Kα radiation (15 kV, 7 mA). The charging effect of XPS spectra was carefully corrected with adventitious carbon at 284.5 eV as a reference.

Pt L_{III}-edge XAFS spectra were recorded at BL-10B station of Photon Factory, High Energy Accelerator Research Organization at Tsukuba (Proposal #2004G088) using a Si(3 1 1) channel-cut monochromator. Injection beam energy was 2.5 GeV and ring current was 300–450 mA. Pt L_{III}-edge spectra were recorded at room temperature in a transmission mode using the ionization chambers filled with the detector gases of Ar/N_2 (=15/85) for the incident beam and of Ar for the transmitted beam, respectively. A sample was pressed into a disk after sample volume was adjusted by polyethylene powder to give appropriate absorbance at the edge energy for the XAFS measurement. After drying under reduced pressure overnight, the disk packed into a polyethylene package under Ar atmosphere. The XAFS data were processed by a REX 2000 (Rigaku) program assembly. The EXAFS oscillation is extracted by fitting a cubic spline function through the post edge region. In order to extract the amplitude and phase shift function for Pt-N, Pt-O, and Pt-Pt, $K_2Pt(NO_2)_4$, PtO_2 and Pt foil were used as reference. XANES spectra were normalized at the absorbance of 11,575.5 eV. The integrated white line intensity in the XANES spectrum was calculated in the range of 11,513.6–11,575.5 eV and was normalized by the value obtained from the Pt foil.

2.3. Adsorption and catalytic measurement

NO adsorption was measured in a conventional flow reactor equipped with a water-cooled infrared image furnace. A granulated catalyst (10–20 mesh, 0.2 g) was fixed by quartz wool in a Pyrex glass tube (4 mm i.d.). The catalyst was pretreated at 400 °C in 5% H_2/He flow for 1h before use. Breakthrough curves of NO_x adsorption were measured in a flowing gaseous mixture of 0.16% NO, 10% O_2, balanced with He supplied at $0.24\ s\ g\ cm^{-3}$. The concentration of NO_x ($NO + NO_2$) in the effluent was measured by using a chemiluminescence NO_x analyzer (Shimadzu NOA-7000). FT-IR spectra of NO_x species adsorbed on catalysts were recorded on a Jasco FTIR-610 spectrometer equipped with a temperature-controllable diffuse reflectance reaction cell (Jasco DR600A) with a KBr window to allow in situ measurement under controlled gas environments at atmospheric pressure. The sample was treated in a stream of 5% H_2/He at 400 °C for 1 h and subsequently cooled down to 50 °C. After purging with He for 30 min, gas mixtures of 0.16% NO, 10% O_2 balanced with He was admitted to the cell for 2 h. This was followed by spectra measurement of NO_x adsorbates in a flowing He at 50 °C.

Catalytic NO-H_2-O_2 reaction was also carried out in a conventional flow reactor. Prior to catalytic reactions, all the catalyst was preheated at 400 °C in a flow of 5% H_2/He. A mixed gas consisting of 0.08% NO, 0 or 10% O_2, 0.28% H_2, balanced with He was supplied to the catalyst bed at $W/F = 0.24\ s\ g\ cm^{-3}$. Effluent gas was analyzed using a chemiluminescence NO_x analyzer (Shimadzu NOA-7000) and a TCD gas chromatograph (Shimadzu GC-8A) with molecular sieve-5A and Porapak-Q columns.

3. Results and discussion

3.1. Structure and property of Pt-M-HT (M = Mo and W)

The XRD patterns of coexchanged Pt-M-HT (M = Mo and W) before calcination were very similar to that of pristine HT with a brucite-type layered structure. The change of interlayer distance could not be observed even in the case of large amounts of exchange (ca. 3% for 1 wt% Pt and ca. 60% for 10 wt% Mo loadings). However it was confirmed that the interlayer distance was increased slightly from 0.89 to 0.93 nm by the complete exchange (100% for 16.6 wt% Mo loading). After heating at 600 °C in H_2, the layered structure was collapsed to yield an MgO-like phase with a low crystallinity. Fig. 1 shows the BET surface area of as calcined Pt-M-HT catalysts with different loadings of M (1 wt% Pt). A large surface area of Pt-HT (177 $m^2\ g^{-1}$) was due to the micropores and mesopores, which were created by the thermal decomposition of the HT phase [13–15]. With increasing addition of Mo or W, the surface area was decreased monotonically, but the shape of N_2 adsorption isotherms and TEM observation could not detect significant difference between Pt-HT and Pt-M-HT. The decreased surface area would therefore be due to the pore blockage caused by deposition of Mo and W oxides. The Pt dispersion of Pt-HT measured by the H_2-O_2 titration was 61%,