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Characteristics of $Pt/WO_3/CeO_2/ZrO_2$ catalysts for catalytic reduction of NO by CO

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ABSTRACT

Various supported Pt catalysts ($Pt/WO_3/CeO_2/ZrO_2$; Pt/ZrO_2, Pt/CeO_2, Pt/CeZrO, $Pt/WO_3/ZrO_2$, and Pt/WO_3/CeZrO) were prepared and characterized, and their characteristics of catalytic reductions of NO by CO with or without oxygen were investigated. TPR and CO-TPD showed that Pt/CeO_2 and Pt/CeZrO could be easily reduced by CO while the reduction by CO was inhibited with the introduction of WO_3 in the case of Pt/WO_3/CeZrO. According to NO-TPD, NO reduction could not proceed over the catalysts (Pt/WO_3/CeZrO, Pt/ZrO_2, $Pt/WO_3/ZrO_2$) to remain in an oxidized state even after reduction by CO, but NO reduction was possible over Pt/CeO_2 and Pt/CeZrO catalysts when reduced by CO. For NO + CO reaction without oxygen, those easily reducible catalysts (Pt/CeO_2 and Pt/CeZrO) exhibited better catalytic performances. With excess oxygen, however, Pt/WO_3/CeZrO and $Pt/WO_3/ZrO_2$ catalysts exhibited higher NO conversions to N_2 and N_2O especially at a low temperature. The acidity from ZrO_2 and WO_3 in $Pt/WO_3/CeO_2/ZrO_2$ catalysts should play an important role on their NO conversion only in the presence of excess oxygen.

1. Introduction

Nowadays the catalytic reduction of NO by CO has attracted much attention for reducing NO_x emissions from automotive gas, and many researches using noble metal catalysts (Rh, Pt and Pd) were reported recently [1–7]. Due to the scarcity and high price of Rh, Pt was considered to be a better catalytic candidate for the catalytic reduction of NO.

Since CeO_2 had a good thermal stability and could enhance the migration and exchange of oxygen species by storing and releasing oxygen, it should be a proper support for Pt catalyst [8]. In order to improve the limitation that CeO_2 was sintered at 750 °C [9], some Ce atoms in its crystal lattice were replaced by other cations (such as Zr). This replacement would lead to the microstrain which should improve thermal stability as well as oxygen exchanging ability [10–14]. A new generation of mixed oxides based on CeO_2 and ZrO_2 has been developed recently. Since these kinds of catalysts could exchange the oxygen with reactants and were somewhat important for the redox reactions, the oxygen storage capacity (OSC) would be an important factor in exploring their catalytic performance. However, Pt catalyst supported on CeO_2–ZrO_2 mixed oxide has not been widely investigated in the catalytic reduction of NO by CO so far.

As reported by Regalbuto and Wolf [15], the addition of WO_3 to Pt/SiO_2 was believed to produce a small number of Pt-WO_3 adlineation sites having very high NO dissociation activity and increased the activity toward the NO–CO reaction. Perez-Hernandez et al. [16] suggested that the acid–basic sites on Pt/ZrO_2-CeO_2 catalysts were important for NO + CO reaction; while the acid properties, generated by zirconia content in the support, seemed to be important for NO + CH_4 reaction. Also several studies have demonstrated the importance of the acidic sites in the NO + CH_4 reaction [17–19]. Other authors have reported that the role of acid sites is to promote the NO oxidation step [20–24] on NO reduction with hydrocarbon. However, WO_3 supported on ZrO_2 can produce super-acidic sites and the effect of acidity from ZrO_2 and WO_3 is worth to be investigated.

In this work, the $Pt/WO_3/CeO_2/ZrO_2$ catalysts (Pt/ZrO_2, Pt/CeO_2, Pt/CeZrO, $Pt/WO_3/ZrO_2$, and Pt/WO_3/CeZrO) were prepared and their catalytic activities for NO + CO reaction with or without oxygen were discussed in terms of redox property and acidity measured by temperature-programmed experiments.

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2. Experimental

2.1. Preparation of catalysts

CeO_2, ZrO_2, and CeZrO (CeO_2–ZrO_2 mixed oxides, mole ratio of Ce:Zr = 0.65:0.35) were prepared by a precipitation method. $ZrO(NO_3)_2$ and $Ce(NO_3)_3$ (Aldrich Chemical Company) were used as metal precursors. The ammonia water (3 wt%) was added dropwise to the solution of metal precursors at 30 °C. The obtained slurry (milk yellow) was aged at 30 °C for 24 h in the solution, keeping the pH around 10, and the hydroxide was filtered, washed, and dried in a convection oven at 110 °C for 24 h. The samples were calcined in air at 700 °C for 5 h.

WO_3/CeZrO and WO_3/ZrO_2 with WO_3 content of 15 wt% were prepared by incipient wetness impregnation method. The aqueous solution of ammonium metatungstate ($[(NH_4)_6(H_2W_{12}O_{40})$–$nH_2O]$, Aldrich Chemical Company) was added to CeZrO and ZrO_2 powder with a solution/powder ratio of 10 mL/g, followed by stirring at room temperature for 12 h, evaporating at 70 °C, and drying at 110 °C for 24 h. The samples were calcined in air at 700 °C for 5 h.

Five supported Pt catalysts with Pt content of 1 wt% (Pt/WO_3/CeO_2/ZrO_2; Pt/ZrO_2, Pt/CeO_2, Pt/CeZrO, Pt/WO_3/ZrO_2, and Pt/WO_3/CeZrO) were also prepared by incipient wetness impregnation method (the same procedure as above WO_3 supporting process), in which tetraammineplatinum ($Pt(NH_3)_4Cl_2$–H_2O, Aldrich Chemical Company) was used as Pt precursor. The samples were calcined in air at 550 °C for 3 h.

2.2. Catalyst characterization

Temperature-programmed experiments were carried out in a conventional flow apparatus (Pulsechemisorb 2705, Micromeritics Inc.), equipped with a thermal conductivity detector (TCD) and a quadruple mass spectrometer (Prisma-QMS200M3). The samples (0.1 g) were degassed in He flow at 200 °C for 2 h, then cooled and stabilized at a temperature. Detailed experimental procedures are described in Table 1.

The BET surface areas were measured by N_2 adsorption using ASAP2010 (Micromeritics Inc.). The samples were degassed at 150 °C, and N_2 adsorption was carried out at 77 K. The crystal structures of prepared samples were confirmed by powder X-ray diffraction (XRD) pattern using monochromic Cu Kα radiation (Rigaku, D/MAX III).

Also Pulsechemisorb 2705 (Micromeritics Inc.) with a thermal conductivity detector was used to determine the Pt dispersions. The amount of CO adsorbed on Pt was determined on Pulsechemisorb 2705 by an ordinary CO pulse method and an O_2–CO_2–H_2–CO pulse method newly proposed by Takeguchi et al. [25]. The details of each procedure are explained in the following:

- Ordinary CO pulse method: The catalyst (0.1 g) was degassed in O_2 flow at 300 °C for 1 h, then cooled down to 30 °C and flushed with He for 10 min. The catalyst was reduced from 30 to 400 °C in H_2(5%)/Ar flow at a heating rate of 10 °C/min, then flushed with He at 400 °C for 10 min. After the sample was cooled down to 30 °C, 0.1 mL of CO was pulsed every 3 min until the intensity of the peak was a constant value.
- O_2–CO_2–H_2–CO pulse method: The catalyst (0.1 g) was degassed in O_2 flow at 300 °C for 1 h, then cooled down to 30 °C and flushed with He for 10 min. Temperature-programmed reduction (TPR) was carried out in H_2(5%)/Ar flow at a heating rate of 10 °C/min and was stopped as soon as the first reduction peak ended. After the sample was cooled down to 30 °C, it was flushed with He for 10 min and was exposed to O_2 flow for 10 min. CO_2 was fed to the sample for 10 min, and then purged with He for 10 min. H_2(5%)/Ar gas was fed to the sample for 10 min, and then purged with He for 1 h. 0.1 mL of CO was pulsed every 3 min until the intensity of the peak was a constant value.

A chemisorption stoichiometry ratio, CO:Pt, of 1:1 was assumed for both cases.

2.3. Catalytic activity measurement

The catalytic activity was measured using a fixed-bed flow reactor at atmospheric pressure. Prior to each reaction, the catalysts (0.5 g) were pretreated in O_2(5%)/He flow at 550 °C for 2 h. A feed gas mixture of CO, NO and O_2 passed through the catalyst bed, and He was used to balance the total flow rate to 260 mL/min (GHSV = 40,000 h^{-1}). Two kinds of reaction modes were employed: (1) NO + CO reaction in the absence of oxygen (feed: CO(0.5%), NO(0.5%)/He); (2) NO + CO reaction in the presence of excess oxygen (feed: CO(0.5%), NO(0.5%), O_2(2%)/He). Catalyst bed temperature was raised at a rate of 2 °C/min from room temperature to 600 °C under continuous flow of reactant stream. The effluent gas was analyzed by on-line gas chromatographs (column: Molecular Sieve 5A & Porapak Q) equipped with TCD for the analysis of CO, O_2, N_2 and N_2O. NO_x analyzer was employed to analyze the concentration of NO and NO_2. NO conversion to $N_2 + N_2O$ was defined as follows:

$$\text{NO conversion to}\,N_2 + N_2O\,(\%) = 2(y_{N_2,\text{out}} + y_{N_2O,\text{out}})/y_{\text{NO,in}} \times 100$$

where $y_{\text{i,in}}$ and $y_{\text{i,out}}$ are the mole fraction of compound i at inlet and outlet of reactor, respectively.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 displayed the XRD patterns of the catalysts. Monoclinic and tetragonal phases of zirconia were identified in the Pt/ZrO_2

Table 1
The detailed procedures of temperature-programmed experiments

Experiments	Procedures
NH_3-TPD	Pretreatment in O_2(5%)/He flow at 550 °C for 1 h, purge in He flow at 30 °C for 1 h, then NH_3 adsorption at 80 °C for 30 min, purge in He flow at 100 °C for 1 h, then NH_3-TPD in He flow (10 °C/min)
H_2-TPR	Pretreatment in O_2(5%)/He flow at 550 °C for 1 h, purge in He flow at 30 °C for 1 h, then H_2-TPR in H_2(5%)/Ar flow (10 °C/min)
H_2-TPR after reduction by CO	Pretreatment in O_2(5%)/He flow at 550 °C for 1 h, purge in He flow at 30 °C for 1 h, then reduction by CO at 100 °C for 1 h, purge in He flow at 30 °C for 1 h, then H_2-TPR in H_2(5%)/Ar flow (10 °C/min)
CO-TPD	Pretreatment in O_2(5%)/He flow at 550 °C for 1 h, purge in He flow at 30 °C for 1 h, then CO adsorption at 30 °C for 1 h, purge in He flow at 30 °C for 1 h, then CO-TPD in He flow (10 °C/min)
NO-TPD after reduction by CO	Pretreatment in O_2(5%)/He flow at 550 °C for 1 h, purge in He flow at 30 °C for 1 h, then reduction by CO at 100 °C for 1 h, purge in He flow at 500 °C 1 h, then NO adsorption in NO(0.1%)/He flow at 30 °C for 1 h, purge in He flow at 30 °C for 1 h, then NO-TPD in He flow (10 °C/min)