Lean reduction of NO by C_3H_6 over Ag/alumina derived from Al_2O_3, AlOOH and $Al(OH)_3$

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Abstract

The effectiveness of Ag/Al_2O_3 catalyst depends greatly on the alumina source used for preparation. A series of alumina-supported catalysts derived from AlOOH, Al_2O_3, and $Al(OH)_3$ was studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet–visible (UV–vis) spectroscopy, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, O_2, $NO + O_2$-temperature programmed desorption (TPD), H_2-temperature programmed reduction (TPR), thermal gravimetric analysis (TGA) and activity test, with a focus on the correlation between their redox properties and catalytic behavior towards C_3H_6-selective catalytic reduction (SCR) of NO reaction. The best SCR activity along with a moderated C_3H_6 conversion was achieved over Ag/Al_2O_3 (I) employing AlOOH source. The high density of Ag–O–Al species in Ag/Al_2O_3 (I) is deemed to be crucial for NO selective reduction into N_2. By contrast, a high C_3H_6 conversion simultaneously with a moderate N_2 yield was observed over Ag/Al_2O_3 (II) prepared from a γ-Al_2O_3 source. The larger particles of Ag_mO ($m > 2$) crystallites were believed to facilitate the propene oxidation therefore leading to a scarcity of reductant for SCR of NO. An amorphous Ag/Al_2O_3 (III) was obtained via employing a $Al(OH)_3$ source and 500 °C calcination exhibiting a poor SCR performance similar to that for Ag-free Al_2O_3 (I). A subsequent calcination of Ag/Al_2O_3 (III) at 800 °C led to the generation of Ag/Al_2O_3 (IV) catalyst yielding a significant enhancement in both N_2 yield and C_3H_6 conversion, which was attributed to the appearance of γ-phase structure and an increase in surface area. Further thermo treatment at 950 °C for the preparation of Ag/Al_2O_3 (V) accelerated the sintering of Ag clusters resulting in a severe unselective combustion, which competes with SCR of NO reaction. In view of the transient studies, the redox properties of the prepared catalysts were investigated showing an oxidation capability of Ag/Al_2O_3 (II and V) > Ag/Al_2O_3 (IV) > Ag/Al_2O_3 (I) > Ag/Al_2O_3 (III) and Al_2O_3 (I). The formation of nitrate species is an important step for the $deNO_x$ process, which can be promoted by increasing O_2 feed concentration as evidenced by $NO + O_2$-TPD study for Ag/Al_2O_3 (I), achieving a better catalytic performance.
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1. Introduction

Facing up with the potential energy crisis, the use of lean-burn gasoline engine and diesel engine becomes a popular tendency in order to improve the fuel economy via a more complete combustion of fuel at excess oxygen [1]. NO_x abatement under such oxidizing atmosphere is a great challenge because it requires using the limited reductant to selectively react with NO rather than O_2.

Cu-ZSM-5 was the first catalyst showing promising activity for lean NO_x reduction [2], but the zeolite-based catalysts suffer

from low hydrothermal stability and easy deactivation by carbonaceous deposits and SO_2 poisoning [3,4]. Supported-precious metal (such as Pt and Pd) catalysts have an excellent low-temperature activity along with a good resistance to steam and SO_2 poisoning compared to ion-exchanged zeolites [5,6]. Nevertheless, the formation of nitrous oxide, an undesirable greenhouse gas causing global warming, and a narrow temperature range for NO reduction limit their practical application [7,8]. Silver catalysts were deemed as the most effective materials for SCR of NO in excess oxygen and were investigated intensively since 1990s [9–13]. Serving as a support for silver, γ-Al_2O_3 is superior to TiO_2, SiO_2, ZrO_2, TiO_2–ZrO_2 and Ga_2O_3 [14–16]. Moreover, most of reports have already suggested that highly isolated Ag cations, strongly bonded to alumina, are the active sites for NO-SCR process

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[17], whereas metallic silver clusters dominate in the high-silver content alumina-based catalysts, which are less selective for NO reduction and good for the direct combustion of hydrocarbons [18]. Various methods including choosing alumina with smaller pore size and narrower pore-size distribution [19], limiting the silver loading [20], mixing the transition metal precursor with the support precursor in a sol–gel state [21], and leaching out the larger Ag clusters by dilute acid [11], were therefore attempted to prepare a catalyst containing highly dispersed silver. Much attention was paid by previous researchers to correlate the nature of Ag species with their catalytic behaviors as mentioned in literature [11,17,20]. Few reports were however concerned by the relationship between SCR performance and the redox properties of the catalyst.

For the purpose to obtain the best SCR performing catalysts, a colloidal solution containing AlOOH or $Al(OH)_3$ has been employed as a precursor of alumina support in this study. It is hoped that their –OH groups might contribute to Ag species being evenly dispersed and anchored on the alumina surface. Some attractive interaction is also expected during the activation procedure converting Boehmite or aluminum hydroxide to γ-alumina. Ag/Al_2O_3 catalyst was also prepared using commercial γ-Al_2O_3 as a support for a comparative study. The physicochemical properties of prepared catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet–visible (UV–vis) spectroscopy, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, O_2 and NO + O_2-temperature programmed desorption (TPD), H_2-temperature programmed reduction (TPR), thermal gravimetric analysis (TGA) and activity test towards NO reduction by propene in the presence of oxygen. Emphasis will be placed on clarifying the relation between the redox properties of the silver catalysts with their catalytic activities for both NO reduction and C_3H_6 oxidation.

2. Experimental

2.1. Preparation method

Alumina-supported silver catalysts were prepared by impregnating the commercial AlOOH (Catapal 18N80), Al_2O_3 (Catabx SBa 150) and $Al(OH)_3$ (Pfaltz & Bauer) supports with an aqueous solution containing desired amounts of silver nitrate (99%, Aldrich) under an intense stirring at room temperature for 4 h. These mixtures were condensed under vacuum using a rotor evaporator (R110, Brinkmann), thereafter, dried at 110 °C for 4 h and calcined at 500 °C for 5 h under a 10% O_2/He gas flow to obtain the final products designated as Ag/Al_2O_3 (I), Ag/Al_2O_3 (II) and Ag/Al_2O_3 (III), respectively. Further calcination of Ag/Al_2O_3 (III) at 800 and 950 °C for 5 h results in the samples denoted as Ag/Al_2O_3 (IV) and Ag/Al_2O_3 (V). Corresponding aluminas (Al_2O_3 (I), Al_2O_3 (II) and Al_2O_3 (III)) were also prepared by the same procedure except for the addition of silver nitrate.

2.2. Physicochemical properties

BET surface areas of the materials were measured by nitrogen adsorption at −196 °C using an automated gas sorption system (NOVA 2000, Quantachrome) operating in continuous mode. The specific surface area was determined from the linear part of the BET curve ($P/P_0 = 0.01$–0.10). Pore volume and average diameter were obtained from the pore size distribution curve, which was calculated from the desorption branch of N_2 adsorption/desorption isotherms using the Barrett–Joyner–Halenda (BJH) formula.

The Ag contents of the prepared samples were analyzed by atomic absorption spectroscopy (AAS) using a Perkin-Elmer 1100B spectrometer after the samples were dissolved in a mixture of 25 ml of 10% HCl and 2 ml of concentrated HF at 60 °C for 24 h.

Powder X-ray diffraction (XRD) patterns were recorded using a Siemens D 5000 diffractometer and Cu Kα radiation ($\lambda = 1.5406$ Å) with a 0.05° step scan from 20 to 80° in 2θ angle. Crystal domain sizes (D) were evaluated by means of the Scherrer equation after Warren's correction for instrumental broadening. The identification of the crystal phases took place using the JCPDS data bank.

The morphologies of alumina-based samples were recorded at 50,000× magnification by scanning electron microscopy (SEM), using a JEOL JSM 840A at 110 kV.

Ultraviolet–visible diffuse reflectance spectra (UV–vis DRS) were collected using a spectrophotometer (Lambda 40, Perkin-Elmer) equipped with a diffuse reflectance attachment (DRA) (Harrick). The UV–vis spectra were collected at room temperature in air in the range of 215–600 nm with a resolution of 2 nm. MgO powder (99.99%, Aldrich) was used as a reference.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained using a Bio-Rad FTS 60 system fitted with a MCT detector with a resolution of 2 cm^{-1} over the spectral domain of 600–4000 cm^{-1}. A fraction of 10 mg catalyst was diluted into 190 mg KCl (99.99%, Anachemia) and then loaded in the sample holder of a Harrick diffuse reflectance cell.

2.3. Transient analyses

Transient studies were carried out with a multifunctional catalyst testing and characterization system (RXM-100, ASDI), equipped with a quadrupole mass spectrometer (MS) (UTI 100), a thermal gravimetric analyzer (TGA) (CAHN) and a thermal conductivity detector (TCD).

Prior to the TPD of O_2, and NO + O_2, 50 mg samples were treated under an atmosphere of 10% O_2, and 3000 ppm NO + 1% or 10% O_2, respectively, with a total flow rate of 20 cm^3/min at 500 °C for 1 h and then cooled down to room temperature under the same flow, subsequently, flushed with 20 cm^3/min He for 40 min to remove the physisorbed molecules. The temperature was then raised up to 800 °C for O_2-TPD and 500 °C for NO + O_2-TPD at a rate of 10 °C/min. O_2 and NO desorbed during TPD experiments were simultaneously detected and on-line recorded using MS with the mass numbers of 32 and 30, respectively.