



Ag/bauxite catalysts: Improved low-temperature activity and SO₂ tolerance for H₂-promoted NH₃-SCR of NO_x



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ABSTRACT

A series of Ag/bauxite catalysts were applied in H₂-promoted selective catalytic reduction (SCR) of NO_x. In comparison with 3Ag/Al₂O₃, 3Ag/bauxite exhibits higher catalytic activity at low temperature, stronger resistance to SO₂ poisoning and better regenerability in SCR of NO_x. NO_x conversion of 3Ag/bauxite at 100–200 °C is more than 60%, which is much higher than less than 7% in 3Ag/Al₂O₃. NH₃-TPD and *in situ* DRIFTS studies confirm the presence of Lewis and Brønsted acid sites in Ag/bauxite, and Lewis acid sites are the major acid sites. H₂-TPR, UV–vis, *in situ* DRIFTS and DFT calculation show that FeO_x and metallic Ag clusters are main active species in SCR of NO_x at low temperature.

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1. Introduction

Air pollution by nitrogen oxides (NO_x) is one of the most serious environmental problems. Catalytic reduction of NO_x in exhaust gases plays an important role in NO_x abatement [1]. Several promising techniques including NO_x storage and reduction (NSR) and selective catalytic reduction (SCR) have been adopted for removal of NO_x [2]. Among these techniques, SCR of NO_x with either hydrocarbons (HC-SCR) or ammonia/urea (NH₃-SCR) is an effective process in the treatment of industrial flue gas [3]. V₂O₅/TiO₂ with WO₃ or MoO₃ as promoters are typical and efficient commercial catalysts for SCR of NO_x [4]. Nevertheless, these catalysts usually suffer from some problems, such as toxicity of vanadium, SO₂ oxidation to SO₃, over-oxidation of NH₃ to N₂O, and employment within a high and narrow temperature window of 300–400 °C [4]. Many efforts have been devoted to development of low-temperature and SO₂-tolerant SCR catalysts [5].

Recent studies have shown that Ag/Al₂O₃ is one of promising catalysts in SCR of NO_x, and shows good catalytic activity and selectivity when H₂ is co-fed with either HC or NH₃ as reductants [6,7]. Ag-based systems also possess moderate tolerance to SO₂ and H₂O, but their lack of catalytic activity below 200 °C still remains a

huge problem [8]. One common way to improve low-temperature activity of Ag/Al₂O₃ is modification of Al₂O₃ support or replacement by more effective supports. For examples, Nb-doped Ag/Al₂O₃ has been found to exhibit higher NO_x conversion at low temperature than Ag/Al₂O₃ [9]. Mg-doped Ag/Al₂O₃ has been reported to possess better sulfur tolerance and higher catalytic activity than Ag/Al₂O₃ in HC-SCR of NO_x [10]. Ag/MgO–CeO₂–Al₂O₃ has also been reported to possess higher catalytic activity and N₂ selectivity in SCR of NO_x by ethanol than Ag/Al₂O₃ [11]. A considerable enhancement of SCR of NO_x by propene in 5 wt%Ag/Al₂O₃–TiO₂ has been shown in comparison with 5 wt%Ag/Al₂O₃. Similar results were also observed when Ag/Al₂O₃ was doped by Ti and Si [12]. The superior properties in these bi- or multi-oxide supports are mainly ascribed to synergetic interactions among the compositions as well as between supports and active species [5]. Since composite supports may greatly influence catalytic performances of SCR catalysts, the exploration of new types of supports has attracted considerable attention in SCR of NO_x. In the context, bauxite is well known to be a cheap, readily available and non-toxic oxide support in the catalytic reactions, which is composed of Al₂O₃, FeO_x, SiO₂, TiO₂, CaO and trace of platinum [13], the compositions are advantageous in NO_x removal [13,14], but the investigation of Ag/bauxite in SCR of NO_x is still unexplored. In our continuous efforts to develop low-temperature and SO₂-tolerant SCR catalysts, herein, we present a series of Ag/bauxite catalysts for SCR of NO_x, NO_x conversion in Ag/bauxite is much higher than Ag/Al₂O₃ at 100–250 °C, moreover,

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3Ag/bauxite shows better sulfur resistance and regeneration ability than 3Ag/Al₂O₃ in H₂-promoted NH₃-SCR of NO_x.

2. Experimental

2.1. Catalyst preparations

Ag/bauxite was prepared by deposition method. Thermal-treatment natural bauxite (1.0 g) in water (50 mL) was heated to 60 °C for 3 h, AgNO₃ (1, 3 and 6 wt% Ag against bauxite) in H₂O (10 mL) were dropwisely added, the resultant mixture was evaporated to dryness at 60 °C, dried at 120 °C overnight and calcined at 550 °C for 2 h. For comparison, 3 wt% Ag was also deposited on commercial γ -Al₂O₃ (Alfa-Aesar, 180 m²/g) with the same method as that of Ag/bauxite.

2.2. Catalytic activity tests

SCR activity measurement was performed in a fixed-bed stainless steel reactor (inner diameter = 8 mm). Before each test, a sample of 0.5 g was reduced by 5 vol% H₂/Ar at 500 °C for 2 h, and followed by treatment using 3 vol% O₂/Ar at 500 °C for 2 h. After cooled to test temperature, the feed gas (482 ppm NO, 500 ppm NH₃, 0.67 vol% H₂ and 3 vol% O₂ balanced with Ar) was introduced using mass-flow controllers at a total flow rate of 600 mL/min, and the corresponding GHSV is 72,000 h⁻¹. 10.0 vol% H₂O was added to feed gas stream to examine resistance of catalysts against H₂O at 350 °C. SO₂ poisoning experiment was performed by exposing samples to the feed gas containing additional 50 ppm SO₂ at 350 °C. The sulfated samples were regenerated by 3.5 vol% H₂ at 500 °C for 60 min. The selectivities of N₂ and N₂O were analyzed using a GC7820 A. Transient response method (TRM) of 3Ag/bauxite was carried out at 200 °C [14b]. 500 ppm NO, 0.05 vol% O₂, 1 vol% H₂ and 500 ppm NH₃ were fed. The outlet gas concentrations were continuously monitored by mass spectrometer and UV analyzer.

2.3. Characterizations

X-ray diffraction (XRD) patterns were recorded on a RIGAKU-Miniflex II X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). N₂ physisorption measurement was performed on an ASAP 2020 apparatus, the sample was degassed in vacuo at 180 °C at least 6 h before the measurement. Transmission Electron Microscope (TEM) was performed on a FEI TECNAI G²F20 microscope. O₂ chemisorption at 150 °C was conducted on an AutoChem 2920 equipped with a TCD detector. Before O₂ chemisorption measurement, the calcined sample was reduced *in situ* by 20 vol% H₂/Ar (50 mL/min) at 400 °C for 3 h, and then outgassed under vacuum at 350 °C for 16 h.

Diffuse reflectance UV–vis spectra were collected on a Perkin Elmer Lambda 950 spectrophotometer equipped with an integrating sphere in the range from 200 and 800 nm using BaSO₄ as the reference for baseline emendation. To keep Ag state as it was, the sample was quickly cooled to room temperature under N₂ after SCR test.

Ammonia temperature-programmed desorption (NH₃-TPD) was conducted on an AutoChem 2920 equipped with a TCD detector. A sample of 0.1 g was pretreated in Ar at 500 °C for 1 h. After cooled to 50 °C, the sample was exposed to 1 vol% NH₃/Ar for 0.5 h, followed by flushing with Ar at 100 °C to remove physisorbed ammonia, and then cooled down to 50 °C. NH₃-TPD was measured from 50 to 800 °C at 10 °C/min.

In situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) was recorded on a Nicolet Nexus FT-IR spectrometer in the range of 650–4000 cm⁻¹ with 32 scans at a resolution of 4 cm⁻¹. Prior to each experiment, the sample was pretreated at 350 °C for 0.5 h in a gas flow of N₂ to remove any adsorbed impurities, and

then cooled down to 50 °C. The background spectrum was collected under N₂ and automatically subtracted from the sample spectra. Afterward, NH₃ (500 ppm balanced with He) was introduced to the cell in a flow rate of 30 mL/min at 100 °C for 1 h to ensure complete absorption saturation. After physisorbed ammonia was removed by flushing wafer with helium at 100 °C for 3 h, DRIFTS spectra were recorded at 50–400 °C.

H₂ temperature-programmed reduction (H₂-TPR) was performed on AutoChem II 2920 equipped with a TCD detector, in which the samples were pretreated in an air flow (30 mL/min) at 500 °C for 0.5 h, and were followed by purging with Ar (30 mL/min) at the same temperature for 0.5 h, after cooled to room temperature, the temperature was increased at 5 °C/min up to 800 °C by a temperature-programmed controller in gas flow of 10 vol% H₂/Ar (30 mL/min).

Density functional theory (DFT) calculations were carried out using Gaussian 03 (Revision D.02) suite of programs. Geometric optimization of the structures and frequency analyses were carried out by using MP2 (Second order approximation of Møller-Plesset perturbation theory) method. In these calculations, the Hay-Wadt double- ζ with a Los Alamos relativistic effect basis set (Lanl2dz) consisting of the effective core potentials (ECP) was used to describe all of atoms. The analytically calculated vibrational wavenumbers were scaled by 0.963. The theoretical IR spectra were simulated by GaussSum 2.2.5 program. The spectra were convoluted with Lorentzian curves, and the full width at half maximum of each peak was 3 cm⁻¹.

3. Results and discussion

3.1. Texture and structure properties

BET surface area of bauxite is 194 m²/g, which is decreased to 158–192 m²/g after the addition of Ag (Table S1) owing to blockage or filling of partial pores by Ag species. Similarly, the addition of 3 wt% Ag to γ -Al₂O₃ results in the decrement of surface area from 180 to 137 m²/g. Pore diameters in Ag/bauxite are in the mesoporous range from 2.21 to 2.56 nm, which are much smaller than that in 3Ag/Al₂O₃. XRD patterns demonstrate that both bauxite and Ag/bauxite possess three strong characteristic peaks (Fig. S1), which are identified as Al₂O₃ (JCPDS No. 10-425), Fe₂O₃ (JCPDS No. 06-0502) and mullite phase. In addition, a weak peak at 14.4° is also observed in Ag/bauxite, which is assigned to the characteristic peak of beidellite [Al₁₃Si₁₉Al₅O₆₀(OH)₁₂Na₂] phase. No characteristic peaks of Ag species are observed in Ag/bauxite and 3Ag/Al₂O₃, suggesting that they are finely dispersed on bauxite (Al₂O₃) or they are too small to be detected by XRD analysis. TEM images show that the average size of Ag particles in 3Ag/bauxite is 4.5 nm, which is much smaller than that in 3Ag/Al₂O₃ (7.5 nm) (Fig. S2). O₂ chemisorption was further performed to investigate dispersion of Ag. As shown in Table S1, Ag dispersion in 3Ag/bauxite is 24%, which is higher than 3Ag/Al₂O₃ (16%). The mean diameters of Ag particles are also derived from dispersion values assuming the particles to be rough sphere in shape, Ag particle sizes in 3Ag/bauxite and 3Ag/Al₂O₃ are 5.8 and 7.4 nm, respectively.

3.2. UV–vis spectra

Since various types of Ag species have been proposed as the active components in reduction of NO_x and partial oxidation of NH₃, diffuse reflectance UV–vis study was used to identify the states of Ag [14]. As shown in Fig. 1, there are three absorption bands in Ag/bauxite, representing three different states of Ag. Peaks at 219 nm may be assigned to the electronic transition of highly dispersed ionic Ag⁺ from 4d¹⁰ to 4d⁹5s¹ [15], while bands at 320 and

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