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Copper-impregnated Al–Ce-pillared clay for selective catalytic reduction of NO by C_3H_6

Qichun Lin [a], Jiming Hao [a,*], Junhua Li [a], Zifeng Ma [b], Weiming Lin [c]

[a] Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, PR China
[b] Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China
[c] Department of Chemical Engineering, Guangzhou University, Guangzhou 510405, PR China

Abstract

The selective catalytic reduction (SCR) of NO by hydrocarbon is an efficient way to remove NO emission from lean-burn gasoline and diesel exhaust. In this paper, a thermally and hydrothermally stable Al–Ce-pillared clay (Al–Ce-PILC) was synthesized and then modified by SO_4^{2-}, whose surface area and average pore diameter calcined at 773 K were 161 m^2/g and 12.15 nm, respectively. Copper-impregnated Al–Ce-pillared clay catalyst (Cu/SO_4^{2-}/Al–Ce-PILC) was applied for the SCR of NO by C_3H_6 in the presence of oxygen. The catalyst 2 wt% Cu/SO_4^{2-}/Al–Ce-PILC showed good performance over a broad range of temperature, its maximum conversion of NO was 56% at 623 K and remained as high as 22% at 973 K. Furthermore, the presence of 10% water slightly decreased its activity, and this effect was reversible following the removal of water from the feed. Py-IR results showed SO_4^{2-} modification greatly enhanced the number and strength of Brönsted acidity on the surface of Cu/SO_4^{2-}/Al–Ce-PILC, which played a vital role in the improvement of NO conversion. TPR and XPS results indicated that both Cu^+ and isolated Cu^{2+} species existed on the optimal catalyst, mainly Cu^+, as Cu content increased to 5 wt%, another species CuO aggregates which facilitated the combustion of C_3H_6 were formed.

Keywords: Cu/SO_4^{2-}/Al–Ce-PILC; SCR of NO; C_3H_6; Acidity; Copper species

1. Introduction

Nitric oxides (NO_x) from combustion facilities are the main pollutants that contribute to the formation of acid-rain, smog, and ground level ozone. Therefore, stringent regulations around the world [1–3] have led to the development of efficient $DeNO_x$ technologies. To date, much research related to the SCR of NO by hydrocarbons (HCs) has been undertaken and reported in the literature due to its potential application for lean-burn gasoline and diesel engines, where the noble-metal three-way catalysts do not work well in the presence of excess oxygen [4]. Many classes of catalysts, including supported noble metals (e.g. Pt, Pd, Rh, and Au) [5–10], metal oxides (e.g. CuO, Ag_2O, SnO_2, and In_2O_3) [5,11–18], and zeolite types (e.g. Cu-ZSM-5, Cu-Al-MCM-41) [19–23], have been investigated in the HC-SCR reaction. Among them, metal-exchanged ZSM-5 has been widely examined due to higher NO removal than for other catalysts. However, the catalyst was low thermal stability and severe deactivation by H_2O. Hence, continuing efforts are made to develop new catalysts.

Pillared interlayered clays (PILCs) offer good possibilities. They are two-dimensional zeolite-like materials prepared by exchanging charge-compensating cations between clay layers with large inorganic metal hydroxycations, which are oligomeric and are formed by hydrolysis of metal oxides or salts [24]. After heating, the intercalated species undergo dehydration and dehydroxylation to form stable metal oxide clusters that act as pillars keeping the silicate layers apart and creating interlayer spaces. Since PILCs have a number of attractive features, such as a well-developed two-dimensional structure, tunable pore size, high thermal stability, and exchangeable acidity, they have attracted much attention as potential catalyst materials in many reaction systems, including SCR reactions [4,25–27]. It has been reported that metal-exchanged PILCs were more tolerant to H_2O and SO_2 than metal-exchanged zeolites [4].

In the present study, montmorillonite was pillared by multi-oligomeric hydroxyl cations to synthesize Al–Ce-PILC, and

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* Corresponding author. Tel.: +86 10 62782195; fax: +86 10 62773650.
E-mail address: hjm-den@mail.tsinghua.edu.cn (J. Hao).

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then modified by SO_4^{2-}. Cu/SO_4^{2-}/Al–Ce-PILC catalysts were prepared by impregnation and applied to the reduction of NO by C_3H_6 in excess oxygen. The influence of SO_4^{2-} modification and Cu content on the catalytic performance was investigated. The physical properties of Al–Ce-PILC were evaluated by powder XRD and BET, and Cu/SO_4^{2-}/Al–Ce-PILC was characterized by Py-IR, TPR, and XPS in order to relate the chemical properties of the catalysts to their performance. Finally, the effect of water vapor on the catalytic performance and the structure of the catalyst were studied.

2. Experimental

2.1. Synthesis of Al–Ce-PILC

The starting clay used in this study was a purified sodium-exchanged Xinyang montmorillonite, which had a particle size of 2 μm or less and a cation-exchange capacity (CEC) of 80 meq./100 g.

Pillared clays incorporated with alumina and rare earth were synthesized according to the procedure described in Ref. [28]. A suitable volume of 0.2 mol/dm^3 NaOH was added dropwise to a stirred solution of 0.2 mol/dm^3 $AlCl_3 + CeCl_3$ in order to obtain an OH/(Al + Ce) mole ratio of 2.0. The Al/Ce mole ratio was kept at 5. The resulting solution was aged for 7 days at room temperature and then heated at 333 K for 2 h before the pillaring process. In a typical pillaring procedure, the Na-montmorillonite (Na-Mont) was dispersed in deionized water to form a 1.0 wt% clay slurry. The slurry was then stirred at room temperature for 24 h to improve its dispersion. The amount of Al–Ce pillaring solution required to obtain an (Al + Ce)/Na-Mont content of 10 mmol/g was then added dropwise to the clay slurry. The mixture was stirred for 3 h at 333 K, and then washed with deionized water until free of chloride ($AgNO_3$ test). The sample was then dried in air at 333 K for 24 h and calcined at 773 K for 6 h. Subsequently, Al–Ce-PILC was impregnated in a suitable volume of 0.5 mol/dm^3 $(NH_4)_2SO_4$ at 333 K for 1 h with stirring. After filtration, the sample was first dried at 383 K in air for 12 h and then calcined at 773 K for another 6 h to obtain Al–Ce-PILC with SO_4^{2-} modification (SO_4^{2-}/Al–Ce-PILC).

2.2. Catalyst preparation

Cu-based catalysts were prepared by impregnating Al–Ce-PILC or SO_4^{2-}/Al–Ce-PILC with a cupric nitrate solution. The copper content of the catalysts was adjusted by changing the concentration of the aqueous $Cu(NO_3)_2$ solution (the minimum volume required to wet the solid). After impregnation for 6 h, the solvent was evaporated under an infrared lamp. The samples were then dried and calcined at 773 K for 6 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were measured with a Shimadzu Model XD-610 diffractometer, and Ni-filtered Cu Kα radiation (λ = 1.5415 Å) was utilized in an X-ray tube operated at 30 kV and 200 mA.

N_2 adsorption was determined at 77 K on a TriStar 3000 Micromeritics instrument. The samples were previously degassed at 523 K for 2 h. Specific surface areas were calculated by the BET method. For porosity analysis, the BJH method was used.

The FT-IR spectra of chemisorbed pyridine (Py-IR) were obtained on a Perkin-Elmer Model 2000 spectrophotometer in the 1750–1420 cm^{-1} range. The self-supported sample wafers were outgassed at 773 K for 1 h prior to pyridine adsorption. After the adsorption of pyridine at room temperature, the catalysts were outgassed at 373, 473, 573, and 673 K, and their spectra were recorded.

Temperature programmed reduction (TPR) measurements were made to identify the copper species and their reducibility on the catalyst surface. 0.05 g sample of catalyst was charged in a U-shape quartz microreactor. It was then outgassed by heating at 15 K/min in a helium flow (20 ml/min) up to 773 K, kept at this temperature for 30 min, then was cooled to room temperature and stabilized under an Ar/H_2 flow (99.9990% purity, 95/5 volumetric ratio, 20 ml/min). The temperature and detector signals were continuously recorded with heating of 10 K/min up to 973 K.

To identify the state of the copper on the catalyst surface, X-ray photoelectron spectroscopy (XPS) was examined by a Physical Electronics Company Quantum-2000 Scanning ESCA Microprobe that used an Al Kα radiation source. The charging effect of the XPS spectra was calibrated by justifying the carbon (1 s) line at 284.6 eV associated with hydrocarbon impurities on the catalyst surface.

2.4. Catalytic activity measurement

Catalytic activity was measured in a fixed-bed quartz flow reactor at a flow rate of 200 ml/min and a space velocity (GHSV) of 24,000 h^{-1}. The reaction temperature was controlled by a programmable temperature controller. The catalyst was preconditioned at each reaction temperature for 30 min before the analysis was started. The feed composition was 1200 ppm C_3H_6, 2200 ppm NO, 2% O_2, and 10% H_2O (when used), and helium was used as balance. Water vapor was generated by passing helium gas through a gas-wash bottle containing deionized water. The reactants and products were analyzed by on-line gas chromatography (Shimadzu GC 17A) and a chemiluminescence NO/NO_2/NO_x analyzer (Thermo Environmental Instruments, model 42C). The GC columns used were Porapak Q for separation of N_2O, CO_2, and C_3H_6, and molecular sieve 5 Å for separating of O_2, N_2, and CO. The N_2O concentration leaving the reactor was below a conservative estimate of the limit of detection (<10 ppm) and so will not be further discussed. The catalytic activity was evaluated in terms of NO and C_3H_6 conversion defined as follows:

$$X_{NO} = \frac{[N_2]}{2[NO]_0} \times 100\%,$$

$$X_{C_3H_6} = \frac{[C_3H_6]_0 - [C_3H_6]}{[C_3H_6]_0} \times 100\%.$$