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Ru-In/H-SSZ-13 for the selective reduction of nitric oxide by methane: Insights from temperature-programmed desorption studies

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ABSTRACT

The selective catalytic reduction of nitric oxide by methane (CH_4-SCR) represents the most desirable technique for the post-treatment of nitrogen oxide emissions from gas-fired power plants and the efficient CH_4-SCR catalysts are being explored. We herein report the construction of bimetallic Ru-In/H-SSZ-13 catalyst, which exhibited remarkable performance in CH_4-SCR under the reaction conditions of a high gas hourly space velocity (GHSV) of 75,000 h^{-1} and in the presence of 6% H_2O. In Ru-In/H-SSZ-13, the close contact between Ru and In species was confirmed by transmission electron microscopy (TEM) analysis, and their electronic interaction was verified by means of X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction by hydrogen (H_2-TPR). All these features made Ru-In/H-SSZ-13 an elegant example of zeolite-based cooperative catalytic system for CH_4-SCR. The surface species formed and their stability on Ru/H-SSZ-13, In/H-SSZ-13 and Ru-In/H-SSZ-13 were investigated by temperature-programmed desorption (TPD) experiments, from which the individual role of H-SSZ-13, Ru and In sites and their cooperation in CH_4-SCR were discussed in detail.

1. Introduction

Nitrogen oxides (NO_x, including NO and NO_2), along with sulfur oxide (SO_2), non-methane volatile organic compounds (NMVOCs) and ammonia (NH_3), are recognized as the major air pollutants that do great harm to the environment and human health [1,2]. The selective catalytic reduction (SCR) technology has been extensively investigated for the post-treatment of NO_x in excess oxygen and different types of reductants, e.g. NH_3 [3–7], H_2 [8–10], hydrocarbons [11–16] and oxygenates [17,18], have been employed. NH_3-SCR has been commercialized in NO_x abatement from coal-fired power plants and heavy-duty diesel engines for years. Under the background of replacing coal by natural gas (main component: CH_4) as clean fuel for urban power plants, CH_4-SCR has been receiving more and more attention in recent years [11,19–34]. Compared with NH_3, CH_4 appears to be a more attractive reductant in gas-fired power plants due to its noncorrosive and easily-available characteristics. On the other hand, CH_4 is chemical inert and hard to be activated, which makes CH_4-SCR more difficult than NH_3-SCR. To our knowledge, the efficient CH_4-SCR catalysts working under simulated conditions of gas-fired power plant exhaust, i.e. at high gas-hourly space velocities (GHSVs) and in the presence of excess steam, are still being explored.

Zeolites can provide ideal scaffolds for redox active components and additional acid sites, e.g. Brønsted acid sites, for SCR reaction, making them the most promising support materials for deNO_x applications [4,6,12,35–37]. Currently, the small-pore zeolites (e.g. CHA [5,7,38], KFI [39] and LTA [40]) are attracting more attention than the medium-pore (e.g. MFI and FER) or large-pore (e.g. FAU and BEA) zeolites for NH_3-SCR. A major advantage of small-pore zeolites lies in their good stability against framework dealumination, which should be more important for CH_4-SCR at high reaction temperatures (~500 °C). However, to our knowledge, the small-pore zeolites are rarely employed as support materials for CH_4-SCR catalysts. For the CH_4-SCR reaction, In-containing zeolites have been extensively investigated during the past decades [23–29]. To improve the catalytic performance of In-containing zeolites, modifications by a second transition metal, e.g. Ce [30], Fe [31], Pd [32], Co [33] and La [34], have been reported to be a feasible strategy. The major role of the second transition metal is proposed to promote the oxidative activation of NO for CH_4-SCR.

Inspired by the above-mentioned research progresses, we herein report the design of a robust Ru-In/H-SSZ-13 catalyst for CH_4-SCR, which exhibits remarkable catalytic performance under harsh reaction conditions, i.e. at a high GHSV of 75,000 h^{-1} and in the presence of 6% steam. H-SSZ-13 is employed as zeolite support to ensure the stability of catalyst as well as to create the close interaction between In and Ru species. For an insight into the individual role of Ru, In and H-SSZ-13

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during CH_4-SCR, the stability of surface species formed on Ru-In/H-SSZ-13 (dominating N_xO_y species) is investigated by means of temperature-programmed desorption technique, which has been widely employed in studying lean NO_x traps [41–44].

2. Experimental

2.1. Catalyst preparation

The chemical reagents were purchased from Alfa Aesar (analytical grade) and used directly as received. All catalysts were prepared by wet impregnation in which various commercial zeolites in their H-forms (from Sinopec), i.e. H-SSZ-13 (Si/Al = 12), H-ZSM-5 (Si/Al = 12), H-beta (Si/Al = 12), H-mordenite (Si/Al = 11) and SAPO-34 (P/Si = 4), were used as supports. In a typical process, desired amounts of metal precursors (see Supporting Information for details) were dissolved in excess water to form solution, to which zeolite support was added. After stirring at room temperature for 24 h, slurry was obtained and the water was removed in a rotary evaporator at 80 °C at reduced pressure. The solid residue was dried, heated in Ar at 550 °C for 2 h, reduced in 10% H_2/Ar at 450 °C for 1 h and re-oxidized in 10% O_2/Ar at 450 °C for 1 h. The final product was denoted as x%Me-y%In/Z, where x% and y% indicated the weight loadings of the second metal and In, respectively, and Z represented the type of zeolite support.

2.2. Catalyst characterization

The chemical compositions of samples were analyzed on an IRIS Advantage inductively coupled plasma atomic emission spectrometer (ICP-AES).

The X-ray diffraction (XRD) patterns of selected zeolite samples were recorded on a Bruker D8 ADVANCE powder diffractometer with a Cu-Kα radiation ($\lambda = 0.1542$ nm) at a scanning rate of 4°/min in the region of 5-50°.

The transmission electron microscopy (TEM) images of selected zeolite samples were acquired on a FEI Tecnai G^2 F20 electron microscope. The high angle annular dark filed scanning transmission electron microscopy (HAADF-STEM) images were acquired on a FEI Talos electron microscope. Element mapping analysis was performed under HAADF-STEM mode using a FEI built-in energy dispersive spectrum.

The X-ray photoelectron spectra (XPS) of samples were conducted on a Thermo Scientific ESCALAB 250Xi spectrometer with monochromatic AlKα X-ray source ($h\nu = 1486.6$ eV). The accurate binding energies (± 0.1 eV) were determined with reference to the C 1 s line of adventitious carbon at 284.8 eV.

The experiments of temperature-programmed reduction by hydrogen (H_2-TPR) were performed on a Quantachrome ChemBET 3000 chemisorption analyzer. Typically, the sample of ca. 0.1 g was pretreated in flowing Ar at 300 °C, cooled to 50 °C in the same atmosphere and purged with 5%H_2/Ar for 30 min. H_2-TPR was then performed in flowing 5%H_2/Ar (30 mL/min) at a heating rate of 10 °C/min.

The Ar adsorption-desorption isotherms of samples before and after CH_4-SCR reaction were measured at −186 °C on a Quantachrome iQ-MP gas adsorption analyzer. Before Ar adsorption, the samples were dehydrated at 200 °C for 2 h. The total surface area was calculated via the Brunauer Emmett Teller (BET) equation.

The water uptake experiments at 27 °C were also performed on the Quantachrome iQ-MP gas adsorption analyzer. Before the adsorption measurements, the calcined samples were degassed at 200 °C overnight.

The ^{27}Al solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were performed with hydrated samples on a Bruker Avance III 400WB spectrometer at the resonance frequency of 104.3 MHz. The spectra were recorded upon $\pi/6$ single pulse excitation, with the repetition time of 0.5 s, and the sample spinning rate of 8 kHz.

The acid strength of zeolite supports was determined by the ^1H MAS NMR with deuterated acetonitrile (CD_3CN) as a probe molecule. The spectra were recorded on a Bruker Avance III 400WB spectrometer at the resonance frequency of 400.1 MHz, with $\pi/2$ single pulse excitation and the repetition time of 10 s. The samples for characterization were fully dehydrated, loaded with acetonitrile-d_3 (99.9% deuterated) and evacuated at 25 °C for 1 h to eliminate physisorbed acetonitrile.

2.3. Catalytic study

The CH_4-SCR reaction was performed in a fixed-bed micro-reactor at atmospheric pressure. Typically, 0.12 mL catalyst sample (20–40 mesh) was placed in a quartz reactor and pretreated in 10% O_2/Ar at 450 °C for 1 h. After cooling to designated temperature in He, the reactant gas mixture (typically 2500 ppm NO, 4000 ppm CH_4, 4% O_2, 6% H_2O, He balance) was fed to the catalyst sample to start the reaction. The outlet gas was analyzed on-line with a NO_x analyzer (Ecotech EC9841) and a gas chromatograph (Techcomp GC7900, equipped with a Plot TDX-1 packed column, a nickel conversion furnace and a FID detector for the analysis of CH_4 and CO_x, as well as a Porapak Q packed column and a TCD detector for the analysis of N_2O and N_2). During the reaction, the outlet gas was also analyzed with a Pfeiffer Omnistar GSD 320 mass spectrometer, and the following mass fragments sensible to the system perturbation were monitored: CH_4 (m/e = 16), NO (m/e = 30), NO_2 (m/e = 46), O_2 (m/e = 32), N_2 (m/e = 28), N_2O/CO_2 (m/e = 44), HCHO (m/e = 29). The NO and CH_4 conversions are defined as follows:

$$\text{NO conversion}(\%) = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\%$$

$$\text{NO conv. to N}_2(\%) = \frac{2 \times [\text{N}_2]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\%$$

$$\text{NO conv. to NO}_2(\%) = \frac{[\text{NO}_2]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\%$$

$$\text{CH}_4\text{ conversion}(\%) = \frac{[\text{CH}_4]_{\text{inlet}} - [\text{CH}_4]_{\text{outlet}}}{[\text{CH}_4]_{\text{inlet}}} \times 100\%$$

$$\text{CH}_4\text{ conv. to CO}_2(\%) = \frac{[\text{CO}_2]_{\text{outlet}}}{[\text{CH}_4]_{\text{inlet}}} \times 100\%$$

2.4. Temperature-programmed desorption analysis

The temperature-programmed desorption (TPD) experiments were performed on the fixed-bed micro-reactor at atmospheric pressure. In a typical process, 0.12 mL catalyst sample was placed in a quartz reactor, pretreated in 10% O_2/Ar at 450 °C for 1 h, and then cooled down to 50 °C in flowing He. The gas mixture, i.e. 1%CH_4-99%He, 1%NO-99% He, 1%NO-10%O_2-89%He or 1%NO_2-99%He, was fed to the catalyst sample for saturated adsorption at 50 °C. After purging with He for 1 h to remove the weakly adsorbed species, the TPD profiles were recorded in flowing He (20 mL/min) at a heating rate of 10 °C/min. The desorption products were on-line analyzed with the Pfeiffer Omnistar GSD 320 mass spectrometer.

3. Results

3.1. Catalyst characterization

The XRD patterns of H-SSZ-13 and supported catalysts are shown in Fig. S1. All samples exhibited typical diffraction lines corresponding to CHA zeolite topology. Besides, no characteristic diffraction lines of Ru and/or In species could be observed, probably due to the low loadings of metal species and their good dispersion. In the SEM image of 0.5% Ru-2%In/H-SSZ-13, the homogeneous dispersion of Ru and In species on zeolite support was clearly observed in the micrometer scale (Fig. S2). EDS analysis revealed the weight loadings of 0.5 and 2.0% for Ru and In, respectively, which matched perfectly well with the target