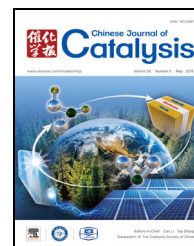


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Article

Bimetallic Cr-In/H-SSZ-13 for selective catalytic reduction of nitric oxide by methane

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ABSTRACT

Bimetallic Cr-In/H-SSZ-13 zeolites were prepared by wet impregnation and investigated for selective catalytic reduction of nitric oxide by methane (CH₄-SCR). Reduction-oxidation treatments led to close contact and interaction between Cr and In species in these zeolites, as revealed by transmission electron microscopy and X-ray photoelectron spectroscopy. Compared to monometallic Cr/H-SSZ-13 and In/H-SSZ-13, the bimetallic catalyst system exhibited dramatically enhanced CH₄-SCR performance, i.e., NO conversion greater than 90% and N₂ selectivity greater than 99% at 550 °C in the presence of 6% H₂O under a high gas hourly space velocity of 75 000 /h. The bimetallic Cr-In/H-SSZ-13 showed very good stability in CH₄-SCR with no significant activity loss for over 160 h. Catalytic data revealed that CH₄ and NO were activated on the In and Cr sites of Cr-In/H-SSZ-13, respectively, both in the presence of O₂ during CH₄-SCR.

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1. Introduction

Nitrogen oxides derived from boilers, engines, and power plants contribute to the formation of photochemical smog and acid rain and are harmful to human health [1]. The selective catalytic reduction of nitrogen oxides (NO and NO₂) by hydrocarbons (HC-SCR) is a promising strategy for the post-treatment of nitrogen oxides in excess oxygen, and CH₄ is an attractive reductant because of its low cost and easy availability in natural gas power plants. In China, CH₄-SCR is now attracting particular interest in the move to replace coal with natural gas as a raw material for urban power plants. However, because of its chemical inertness, methane is difficult to activate, which remains a key problem in the CH₄-SCR [2–5]. However, NO oxidation, the role of which is still unclear and seems depend-

ent on the catalysts employed [6], is an important step in the CH₄-SCR.

Zeolites, known as microporous crystalline aluminosilicates, can be directly used as catalysts [7,8] and are more frequently used as catalyst supports [9] in SCR. Transition-metal-modified zeolites have been extensively investigated for CH₄-SCR in past decades [10–33]. Among them, In-modified zeolites appear to be most active monometallic catalysts for CH₄-SCR because of the effective activation of CH₄ by In species [22–29,32]. It was claimed that methane can be activated on In₂O₃ sites to generate oxygenates, which then react with nitrate to generate N₂ [22]. Alternatively, the H₂NCO intermediate formed by the reaction between NO₂ and partially oxidized methane on intrazeolite InO⁺ sites was proposed to be the actual NO reductant in the CH₄-SCR [23]. To improve the CH₄-SCR activity, second

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transition metals, e.g., Pd [13,14], Co [3,19], and Ce [20], were introduced to In-zeolites, and the major role of the second transition metals was proposed to promote the oxidative activation of NO [3,14,16,20]. For example, the cobalt oxide clusters in Co-In/HZSM-5 showed a positive effect on the oxidation of NO to NO₂, which promoted the CH₄-SCR [3]. Similarly, palladium in Pd-In/H-ZSM-5 promoted the oxidation of NO and increased the formation of the activated nitrate species, while In⁺/InO⁺ sites suppressed the formation of less reactive isocyanate and nitrile species [14].

In this work, we aimed to develop an efficient catalyst for the CH₄-SCR, i.e., achieving good activity and stability in the presence of excess H₂O and under high space velocity conditions. H-SSZ-13, a high-silica zeolite with a CHA topology, was first used as a catalytic support for CH₄-SCR because of its high stability against framework dealumination. Bimetallic Cr-In/H-SSZ-13 was optimized and its structure-activity relationship in the CH₄-SCR was analyzed.

2. Experimental

2.1. Catalyst preparation

All the chemical reagents employed in this study were of analytical grade from Alfa Aesar and used as received without further purification. Commercial zeolites in their H form with similar Si/Al ratios of 24, i.e., H-SSZ-13, H-ZSM-5, and H-beta, as well as amorphous SiO₂ (surface area of 210 m²/g) were used as supports, and metal modifiers were introduced via wet impregnation. In a typical process, the zeolite support was immersed in a solution containing the desired amount of indium nitrate and chromium nitrate and stirred at room temperature for 24 h. Subsequently, the solvent of the slurry was removed in a rotary evaporator at 80 °C, and the residue was dried in an oven at 80 °C for 12 h. The obtained solid sample was calcined in Ar at 550 °C for 2 h, reduced in 10% H₂/Ar at 450 °C for 1 h, and oxidized in 10% O₂/Ar at 450 °C for 1 h. The final product was denoted as x%Cr-y%In/Z, where x% and y% indicate the weight loadings of Cr and In, respectively, and Z indicated the type of zeolite support. Bimetallic In-containing samples, i.e., Me-In/H-SSZ-13 (Me = Ti, V, Mn, Fe, Co, Ce, Zr, and Mo), were prepared via similar procedures.

2.2. Catalyst characterization

The chemical compositions of samples were analyzed on an IRIS Advantage inductively coupled plasma atomic emission spectrometer.

Transmission electron microscopy (TEM) images of selected samples were acquired on an FEI Tecnai G² F20 electron microscope. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired on an FEI Talos electron microscope. Element mapping analysis was conducted under HAADF-STEM mode using an FEI built-in energy dispersive spectrum.

X-ray photoelectron spectra (XPS) of samples were acquired on a Thermo Scientific ESCALAB 250Xi spectrometer with a

monochromatic Al K_α X-ray source (*hν* = 1486.6 eV). Accurate binding energies (±0.1 eV) were determined with reference to the C 1s line of adventitious carbon at 284.8 eV.

The temperature-programmed desorption of ammonia (NH₃-TPD) was performed on a Quantachrome ChemBET 3000 chemisorption analyzer. In a typical experiment, the sample was saturated with 5% NH₃/He at 50 °C and then purged with He at the same temperature for 1 h to eliminate the physical absorbed ammonia. The NH₃-TPD profile was recorded in flowing He at a heating rate of 10 °C/min from 50 to 600 °C.

The experiments of temperature-programmed reduction by hydrogen (H₂-TPR) were also performed on the Quantachrome ChemBET 3000 chemisorption analyzer. In a typical experiment, a sample of 0.1 g was pretreated in 10% O₂/He at 450 °C for 1 h, cooled to 50 °C, and purged for 1 h in flowing He. The H₂-TPR profile was recorded in 5% H₂/Ar (30 mL/min) at a heating rate of 10 °C/min. The outlet gas was passed through a dry-ice trap, and the hydrogen consumption was calculated using CuO as a reference.

2.3. Catalytic study

The CH₄-SCR reaction was performed in a fixed-bed micro-reactor at atmospheric pressure. Typically, a 0.12 mL catalyst sample (20–40 mesh) was placed in a quartz reactor and pretreated in 10% O₂/Ar at 450 °C for 1 h. After cooling to the designated temperature in He, the reactant gas mixture (NO = 2500 ppm; CH₄ = 4000 ppm; O₂ = 4%, H₂O = 6%, He balance) was fed to the catalyst to start the reaction. The total flow rate was set at 150 mL/min resulting in a gas hourly space velocity (GHSV) of 75 000 /h. The outlet gas (H₂O removed by cold trap) was analyzed on-line by a NO_x analyzer (Ecotech EC9841) and a gas chromatograph (Techcomp GC7900, equipped with a Plot TDX-1 packed column and an FID detector for the analysis of CH₄ and CO_x, as well as Porapak Q packed column and TCD detector for the analysis of N₂O and N₂). During the reaction, the outlet gas stream was analyzed by a mass spectrometer (Pfeiffer Omnistar GSD 320), and the following mass fragments sensible to the system perturbation were monitored: CH₄ (*m/e* = 15), NO/NO₂ (*m/e* = 30), NO₂ (*m/e* = 46), O₂ (*m/e* = 32), N₂ (*m/e* = 28), CO₂ (*m/e* = 44), NH₃ (*m/e* = 17), H₂O (*m/e* = 18), and HCHO (*m/e* = 29). The NO and CH₄ conversions are defined as follows:

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

$$\text{NO conversion to N}_2 = 2[\text{N}_2]_{\text{outlet}} / [\text{NO}]_{\text{inlet}} \times 100\%$$

$$\text{NO conversion to NO}_2 = [\text{NO}_2]_{\text{outlet}} / [\text{NO}]_{\text{inlet}} \times 100\%$$

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

$$\text{CH}_4 \text{ conversion to CO}_2 = [\text{CO}_2]_{\text{outlet}} / [\text{CH}_4]_{\text{inlet}} \times 100\%$$

$$\text{CH}_4 \text{ conversion to CO} = [\text{CO}]_{\text{outlet}} / [\text{CH}_4]_{\text{inlet}} \times 100\%$$

The temperature-programmed surface reaction (TPSR) of CH₄-SCR was performed on a quartz tube reactor, and the products were analyzed on-line by a Pfeiffer Omnistar GSD 320 mass spectrometer.

3. Results and discussion

3.1. Catalyst characterization

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