



The ordered mesoporous transition metal oxides for selective catalytic reduction of NO_x at low temperature



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ABSTRACT

The ordered mesoporous Co₃O₄, NiO and NiCo₂O₄ were synthesized by nanocasting method using mesoporous KIT-6 as a hard template. Their structural and textural properties were well characterized by powder X-ray diffraction, transmission electron microscopy and nitrogen physisorption. The surface areas of these catalysts are 380–426 m²/g. Selective catalytic reduction (SCR) of NO_x with hydrogen demonstrates that NiCo₂O₄ possesses the highest catalytic activity at 50–400 °C, whose NO_x conversion is more than 70% at 150 °C, and N₂ selectivity is more than 90% at 100–400 °C. In addition, NiCo₂O₄ exhibits better stability in the presence of 100 ppm SO₂ and 10 vol% H₂O in SCR of NO_x at 250 °C. XPS analyses show that surface adsorption oxygen concentration in NiCo₂O₄ is higher than that in Co₃O₄ and NiO. The synergistic effect between Ni and Co is responsible for the enhancement of low-temperature SCR activity and the improvement of regeneration performance in NiCo₂O₄. In comparison with NiCo₂O₄-CP synthesized by co-precipitation method, the ordered mesoporous structure in NiCo₂O₄ provides larger surface area, more activated oxygen species and more reductive species, resulting in higher SCR performance at low temperature.

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1. Introduction

Nitrogen oxides (NO_x) are mainly derived from stationary pollution sources and the combustion of gasoline and diesel in transportation vehicles, which are hazardous to the environment and human health [1]. A number of techniques have been developed to reduce the emission of NO_x. Among them, selective catalytic reduction (SCR) of NO_x with either hydrocarbon (HC-SCR) or ammonia/urea (NH₃-SCR) is an efficient technique to remove NO_x from diesel vehicles and stationary sources [2]. For decades, V₂O₅-WO₃ (MO₃)/TiO₂ are widely used as commercial NH₃-SCR catalysts [3]. However, many problems, such as ammonium sulfate deposition, ammonia slip, air heater fouling and high running cost, are encountered in the practical use of NH₃-SCR. In comparison with NH₃-SCR, H₂-SCR is a promising alternative in NO_x removal because of high activity toward NO_x reduction and zero emission of greenhouse gases [4], especially for industrial sites where H₂ is readily available. Therefore, it is highly desirable to replace NH₃ with non-toxic and less expensive H₂.

Pt-based and Pd-based catalysts have been revealed to possess good catalytic activity in H₂-SCR of NO_x at low temperatures [5–7]. For examples, 0.3 wt%Pt/11wt%WO₃/ZrO₂ was reported to show high NO_x conversion below 200 °C, superior N₂ selectivity of about 90%, outstanding hydrothermal stability and strong resistance against SO₂ in H₂-SCR [5a]. 100% conversion of NO and 85% N₂ selectivity were obtained in 0.1 wt%Pt/MgO-CeO₂ when 1.5 vol% H₂ was used as a reductive agent [5b,c]. NO_x conversion of 89% and N₂ selectivity of 79% at 140 °C were found in 1 wt%Pt/Ti-MCM-41 [6]. NO_x conversion of more than 80% at 140–180 °C was presented in 1 wt%Pd/TiO₂/Al₂O₃ [7a]. However, high cost of precious metals and their sensitivity to sulfur poisoning have inhibited their large-scale applications. Many efforts have been devoted to searching for the alternatives of Pt-based catalysts in H₂-SCR of NO_x.

Transition metal oxides have been widely used as catalysts in various reactions because of their low price, ready synthesis and good redox property [8]. Among them, highly ordered mesoporous materials are of particular advantages, such as regular texture, narrow pore size distribution and adjustable porous structure, which can result in promising applications in catalysis [9,10]. The nanocasting route using silica materials as hard templates is an effective method for the synthesis of ordered mesoporous transition metal oxides, the resultant oxides usually show high

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surface area and good stability under harsh reaction conditions [11]. Recently, highly ordered mesoporous Co_3O_4 was synthesized using mesoporous silica as a hard template, and displayed excellent catalytic activity for CO preferential oxidation in H_2 -rich gases [12]. Compared with single metal oxides, bi- or multi-metal oxides usually show superior general properties owing to synergistic interactions of their compositions [13,14]. It is known that Ni^{2+} and Co^{2+} can form a homogeneous solid solution owing to the similarity of their unit cell structures, the replacement of Co at octahedral sites with Ni can affect the bonding strength of metal-oxygen, resulting in different adsorption energies for $-\text{OH}$ species at catalytic sites [9,13]. The adsorbed OH can interact with NO at the interface of metal oxides, forming an intermediate NO_2 and a hydrogen atom. Therefore, a combinational use of Ni and Co oxides may result in higher catalytic activities in SCR than single metallic counterparts. However, to our knowledge, the preparation and applications of ordered mesoporous bimetal oxides in SCR of NO_x have seldom been reported. In our continuous efforts to develop low-temperature and SO_2 -tolerant catalysts for NO_x removal [15], herein, we report a series of transition metal oxides with highly ordered mesopores, Co_3O_4 , NiO and NiCo_2O_4 . The catalysts show superior NO_x conversion, high N_2 selectivity, strong resistance against SO_2 and H_2O in H_2 -SCR of NO_x .

2. Experimental

2.1. Catalyst preparations

Mesoporous KIT-6 was synthesized according to the literature methods [11]. Mesoporous NiCo_2O_4 was prepared using as-synthesized KIT-6 as a hard template. Briefly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (total mass: 1.0 g) with the molar ratio of 1:2 were dissolved in ethanol (20 mL). After stirring at room temperature for 1 h, 0.5 g of KIT-6 was added. The suspension was stirred at room temperature for 12 h, and followed by calcination at 400°C for 3 h, then treated with NaOH, washed and dried. The resultant sample was denoted as NiCo_2O_4 . Mesoporous Co_3O_4 and NiO were prepared using the same procedures.

As a comparison, NiCo_2O_4 -CP was also synthesized by co-precipitation method. A solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (total mass: 1.0 g) with the molar ratio of 1:2 in H_2O (20 mL) was stirred at room temperature for 1 h, NaOH (0.24 mol/L) was dropwise added until pH to 10. After the mixture was stirred at room temperature for 12 h, the precipitate was collected by centrifugation, washed with distilled water and then calcined at 400°C for 3 h.

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 0.4 g of 20–30 mesh sample was reduced by 3.5 vol% H_2/Ar at 500°C for 2 h. After cooled to test temperature, the feed gas (342 ppm NO, 1.5 vol% H_2 and 3 vol% O_2 balanced by Ar with H_2/NO ratio at 43.9) was introduced using mass-flow controllers at a total flow rate of 600 mL/min, the corresponding GHSV is $90,000 \text{ h}^{-1}$. H_2/NO feed ratios at 5, 7.5, 10 and 20 were also measured under the same conditions. SO_2 poisoning experiment was performed by exposing samples to feed gas containing additional 100 ppm SO_2 at 250°C . Resistance against H_2O was examined through introducing 10 vol% H_2O into feed gas at 250°C . The outlet NO_x concentration was monitored by an on-line chemiluminescence $\text{NO}-\text{NO}_2-\text{NO}_x$ analyzer (Model 42i-HL, Thermo Scientific). N_2 selectivity was analyzed using a GC 7820A. The outlet N_2O and NH_3 were analyzed using an FTIR spectrometer (Nicolet Nexus 6700) with a heated,

multiple-path gas cell. NO_x conversion was calculated according to the following equation after a steady state was achieved at the given temperature for 1 h.

$$\text{NO}_x \text{ Conversion (\%)} = \frac{(\text{NO}_{\text{xinlet}} - \text{NO}_{\text{xoutlet}})}{\text{NO}_{\text{xinlet}}} \times 100\%.$$

Transient response method (TRM) of mesoporous NiCo_2O_4 was carried out at 150°C , a feed gas of 350 ppm NO, 3 vol% O_2 and 1.5 vol% H_2 balanced by Ar was introduced. The outlet gas concentrations were continuously monitored by mass spectrometer and UV analyzer.

2.3. Characterizations

Powder X-ray diffraction (XRD) was performed on a Rigaku-DMAX2500PC diffractometer using a $\text{Cu}-\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). N_2 physisorption measurement was performed on an ASAP 2020 apparatus, the sample was degassed in vacuo at 180°C at least 6 h before each measurement. H_2 temperature-programmed reduction (H_2 -TPR) was performed on AutoChem II 2920 equipped with a TCD detector, in which the sample was pretreated under air flow (30 mL/min) at 500°C for 0.5 h, followed by purging with Ar (30 mL/min) at the same temperature for 0.5 h. After cooling to room temperature, the temperature was increased to 800°C at $5^\circ\text{C}/\text{min}$ by a temperature-programmed controller in a gas flow of 10 vol% H_2/Ar (30 mL/min). For the repeated H_2 -TPR, the sample was reduced from room temperature to 500°C and hold at 500°C for 0.5 h. Then, the sample was re-oxidized in 5 vol% O_2/Ar flow at 500°C for 1 h to ensure complete oxidation of sulfides to sulfates. After cooling to room temperature, the test of the repeated H_2 -TPR was performed. X-ray photoelectron spectroscopy (XPS) analysis was performed on Physical Electronics Quantum 2000, equipped with a monochromatic Al-K α source ($\text{K}\alpha = 1,486.6 \text{ eV}$) and a charge neutralizer. Transmission electron microscope (TEM) measurements were carried out on a JEM-2010 microscope operating at 200 kV in the mode of bright field.

3. Results and discussion

3.1. TEM and HR-TEM

TEM images of KIT-6 indicate that it possesses the expected cubic mesoporous structure [9], the corresponding distance between two lattice fringes is 10 nm (Fig. S1). As expected, Co_3O_4 , NiO and NiCo_2O_4 show highly ordered mesoporous structures with particles size about 6–8 nm (Fig. 1), and the lattice fringes can be clearly observed in their HR-TEM, suggesting highly crystalline nature of mesoporous frameworks [9c]. The spacing distances between two fringes in Co_3O_4 are 0.46 and 0.24 nm, corresponding to (1 1 1) and (2 2 0) planes, respectively. The mesoporous structure of Co_3O_4 is comparable with analogues synthesized by nanocasting method [9c]. It was reported that (1 1 1) plane in Co_3O_4 mainly contains Co^{2+} , while (2 2 0) plane only consists of Co^{3+} and provides favorable sites for oxygen adsorption in catalytic reactions [11]. In NiO, the lattice spacing of 0.21 and 0.25 nm corresponds to (2 0 0) and (1 1 1) planes of cubic Fm3m crystal lattices, respectively [10b]. The distances between the adjacent fringes in NiCo_2O_4 are 0.47, 0.28 and 0.23 nm, which are in conformity with (1 1 1), (2 2 0) and (2 2 2) planes, respectively [10a]. Selected-area electron diffraction (SAED) patterns (insets of Fig. 1) of the catalysts indicate that NiO and NiCo_2O_4 are polycrystalline [10c].

3.2. Structural and textural properties

The ordered mesoporous structures of the catalysts were further demonstrated by low-angle XRD patterns. As shown in Fig. 2a,

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