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Supercritical water syntheses of transition metal-doped CeO_2 nano-catalysts for selective catalytic reduction of NO by CO: An *in situ* diffuse reflectance Fourier transform infrared spectroscopy study

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ABSTRACT

In the present study, we synthesized CeO_2 catalysts doped with various transition metals (M = Co, Fe, or Cu) using a supercritical water hydrothermal route, which led to the incorporation of the metal ions in the CeO_2 lattice, forming solid solutions. The catalysts were then used for the selective catalytic reduction (SCR) of NO by CO. The Cu-doped catalyst exhibited the highest SCR activity; it had a T_{50} (i.e., 50% NO conversion) of only 83 °C and a T_{90} (i.e., 90% NO conversion) of 126 °C. Such an activity was also higher than in many state-of-the-art catalysts. *In situ* diffuse reflectance Fourier transform infrared spectroscopy suggested that the MO_x-CeO_2 catalysts (M = Co and Fe) mainly followed an Eley-Rideal reaction mechanism for CO-SCR. In contrast, a Langmuir-Hinshelwood SCR reaction mechanism occurred in CuO-CeO_2 owing to the presence of Cu^+ species, which ensured effective adsorption of CO. This explains why CuO-CeO_2 exhibited the highest activity with regard to the SCR of NO by CO.

1. Introduction

Nitrogen oxides (NO_x)—which are generated by many combustion processes, both stationary and mobile—are considered primary atmospheric pollutants [1,2]. The emission of NO_x into the atmosphere can cause series environmental issues, including photochemical smog, acid rain, and ozone depletion [3,4]. Currently, the selective catalytic reduction (SCR) of NO_x is considered one of the most efficient techniques for the removal of stationary-source NO_x [5–7]. The SCR of NO using CO as a reducing agent has been studied extensively in recent decades because NO and CO coexist in many industrial exhaust gases [8–10]. However, this approach presents several challenges such as ensuring low-temperature activation, resistance to O_2 and SO_2, and durable operation.

Noble metals have been used extensively as efficient catalysts for the CO-SCR reaction. However, owing to the high cost and poor resistance to sulfur/phosphate of noble metals [11], much effort has been devoted to developing transition metal oxide catalysts, and cerium-based catalysts have attracted the

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greatest interest. CeO_2 is an essential rare earth oxide with excellent oxygen storage capacity and redox behavior [12,13], which may be attributed to the flexible transformation between valence states ($Ce^{4+}\leftrightarrow Ce^{3+}$) [14−16]. Many transition metals have been introduced into the CeO_2 lattice to modify its physical and chemical properties for various catalytic applications [17]. The synergistic effect arising from such modifications has become a primary focus in the catalysis research community [18–22]. Yao *et al*. [23] reported that a doped CeO_2 ($Ce_xSn_{1-x}O_2$) exhibited superior catalytic performance compared with undoped CeO_2 owing to the greater number of catalytic domains; Ma *et al*. [24]obtained a highly active $Ce_xCu_{1-x}O_2$ catalyst characterized by the presence of an intergrowth system comprising imperfect monoclinic CuO and cubic crystal CeO_2.

In the present study, we prepared a series of MO_x-CeO_2 catalysts (M = Co, Fe, or Cu) using a supercritical water (sc-H_2O) hydrothermal route [25]. The catalysts were subsequently characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area measurement, and hydrogen temperature-programmed reduction (H_2-TPR). The CO-SCR reaction activity of the catalysts was evaluated using *in situ* diffuse reflectance Fourier transform infrared spectroscopy (DRFTIR). We expect that this work will provide an in-depth understanding of the effectiveness of transition metal-doped CeO_2 catalysts in the CO-SCR reaction for NO removal.

2. Experimental

2.1. Catalyst preparation

The transition metal-doped catalysts were prepared in our laboratory using a three-pump hydrothermal flow system (CHFS). The reactor, tubing, and components were made from grade 316 stainless steel (Swagelok™). The apparatus (Fig. S1) consisted of a metal salt solution high-performance liquid chromatography (HPLC) pump (P2), a base solution HPLC pump (P3), and a water HPLC pump (P1). Deionized water was pre-heated to the appropriate temperature (500 °C) by pumping it through an electric coil (2.5 kW). The deionized water was then brought into contact with a metal salt solution containing $Ce(NO_3)_3{\cdot}6H_2O$ (0.1 mol·L^{-1}) and $M(NO_3)_x{\cdot}yH_2O$ (0.02 mol·L^{-1}), and a flow of NaOH solution (1 mol·L^{-1}) at a mixing point (a 1/4″ counter-current mixer that was assisted by a 500 °C band heater), whereupon there was rapid co-precipitation of the crystalline products. The aqueous suspension was cooled using a water jacket, passed through a 7-μm in-line filter, and collected from the exit of a back-pressure regulator (BPR). Flow rates of 7.5, 7.5, and 30 mL·min^{-1} were used for the metal salt solution, the base solution, and the water stream, respectively. The system pressure was maintained at approximately 23.0 MPa. Solids were recovered by centrifuging the suspension and freeze-drying to yield the final products.

2.2. Measurement of catalytic activity

The SCR of NO by CO was conducted in a fixed-bed quartz tubular reactor with a thermocouple at its center. The catalysts were pre-treated in a N_2 flow at 500 °C for 1 h before each test. The catalytic activity of each 40–60 mesh catalyst (2.2 mL) was examined and the experiments were performed at 60 to 300 °C. The inlet gas comprised NO (600 ppm), CO (1200 ppm), and N_2 (the balance), and had a gas hourly space velocity (GHSV) of 40,000 h^{-1}. NO, NO_2, and O_2 concentrations were monitored using a Testo 350 flue gas analyzer. NO conversion and selectivity were evaluated as follows:

NO conversion (%) = $([NO]_{in} - [NO]_{out})/[NO]_{in} \times 100\%$

N_2 selectivity (%) = $(1 - 2[N_2O]_{out}/([NO]_{in} - [NO]_{out}) \times 100\%$

where the "in" and "out" subscripts indicate the inlet and outlet concentrations of NO/N_2O in the steady state, respectively.

2.3. Characterization of the catalysts

2.3.1. XRD and BET

XRD patterns were recorded using a Rigaku D/Max RA diffractometer with Cu-K_α radiation (λ = 0.15418 nm) at 40 kV and 150 mA. All XRD patterns were obtained with scattering angles (2θ) ranging from 10° to 80° at a step size of 0.026°. The crystal phases of the catalysts were identified according to the Joint Committee on Powder Diffraction Standards (JCPDS) database.

The BET surface areas (BETs) were determined using N_2 physisorption at −196 °C using Micrometrics ASSP 2020 equipment. Prior to N_2 adsorption, each catalyst was degassed for 2 h under vacuum at 200 °C.

2.3.2. H_2-TPR

H_2-TPR was conducted in TP-5089 equipment (Tianjin Xianquan Industry and Trade Development Co., Ltd.); before each test, the catalysts (0.05 g) were maintained at 400 °C for 1 h and purged with 3% O_2/He gas at a flow rate of 50 mL·min^{-1}, then cooled to 100 °C. Subsequently, they were preheated at 100 °C for 40 min, then further heated to 900 °C at a rate of 10 °C·min^{-1} while purging with 5% H_2/N_2 gas at a flow rate of 35 mL·min^{-1}. The variation in H_2 concentration was recorded using a thermal conduction detector (TCD).

2.3.3. In situ DRFTIR study

Fourier-transform infrared spectroscopy (FTIR) spectra were acquired using an *in situ* DRFTIR cell equipped with a gas flow apparatus. The DRFTIR measurements were obtained using ZnSe windows coupled to Bruker tensor 27 FTIR spectrometers. Inside the DRFTIR cell, the catalysts were pretreated in a He atmosphere at 300 °C for 2 h, then cooled to 100 °C. The background spectrum was obtained using flowing He, and was subtracted from the spectrum of each catalyst.

3. Results and discussion

3.1. XRD and BET measurements

The phase identities and purities of the M-doped CeO_2 catalysts (M = Co, Fe, or Cu) were evaluated by XRD. As shown in Fig. 1, all the catalysts displayed distinct XRD reflections at approximately 28.6°, 33.2°, 47.5°, 56.4°, and 76.9° for cubic