



Structure sensitivity of selective catalytic reduction of NO with propylene over Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ catalysts



Jie Liu^a, Qidong Zhao^a, Xinyong Li^{a,b,c,*}, Junhong Chen^{b,**}, Dongke Zhang^{c,**}

^a Key Laboratory of Industrial Ecology and Environmental Engineering and Key Laboratory of Fine Chemicals, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

^b Department of Mechanical Engineering, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

^c Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

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ABSTRACT

The structure sensitivity of selective catalytic reduction (SCR) of NO with propylene over Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ catalysts was investigated systematically in a series of characterizations and *in situ* DRIFT spectroscopy. A Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ catalyst with a hierarchical structure was fabricated successfully using a hydrothermal method (Hy-Sample), and shown to exhibit excellent SCR performance with high reaction rate and turnover frequency (TOF). The physico-chemical properties, mass transfer, and SCR activity of the catalyst depended on the preparation method. Another sample of Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ catalyst prepared using a co-precipitation method (Co-Sample) exhibited a disordered, irregular morphology, whose SCR activity, as determined in a fixed bed reactor, was significantly lower than that of Hy-Sample. In comparison, Hy-Sample possessed an enhanced redox property, and its highly ordered morphology greatly promoted the generation of active sites, including the fine-dispersed CuO species and surface adsorbed oxygen. Consequently, NO and C_3H_6 were readily adsorbed and activated over Hy-Sample and induced the formation of important intermediates with high reactivity, such as isocyanate ($-\text{NCO}$) and cyanide ($-\text{CN}$) species. However, the activation capacity of Co-Sample toward reactants was very weak, and the sequential deficiency of N-containing organics could be the primary reason for the poor SCR activity of Co-Sample.

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1. Introduction

Ever-increasing environmental concerns in the last decades have spurred both academic and industrial research, and development effort to devise new methods for elimination of NO_x originating from stationary and mobile sources. For the removal of NO_x from vehicles, selective catalytic reduction of NO_x with hydrocarbons (HC-SCR) is considered as a potential technology from the view of economy, energy-saving and safety as it can eliminate the NO_x and un-burnt hydrocarbons in the exhaust simultaneously [1–3]. However, the current HC-SCR technology is still insufficient

for commercial application, and further fine-tuning of catalytic materials is essential to gain satisfactory SCR performance.

As a second generation catalyst support after SiO_2 , TiO_2 has been employed commercially in the SCR reactions, such as the well-known catalysts $\text{V}_2\text{O}_5\text{-TiO}_2$ and V_2O_5 (WO_x or MoO_x)/ TiO_2 [4,5]. However, some crystal transformation of TiO_2 occurs at high temperatures, resulting in catalyst deactivation [6]. To enhance the thermal stability of TiO_2 , many studies have been carried out. Recently, due to the excellent stability against thermal treatments, ZrO_2 as a doping component has been shown to improve the performance of TiO_2 [7–9]. On the other hand, owing to the ionic radius difference between Zr^{4+} (0.87 Å) and Ti^{4+} (0.64 Å), the partial substitution of Ti by Zr could lead to lattice distortion of TiO_2 and then induce the generation of abundant surface defects. Consequently, the gas-phase NO_x can be more readily adsorbed on the Zr-doped TiO_2 catalysts during the SCR reaction [10–13]. Furthermore, the weak acidic and basic sites on the surface of ZrO_2 also improve the tolerance of catalysts against SO_2 poisoning [6,14,15].

Among the alternatives of active components examined for the low-temperature SCR reaction, copper has been widely explored

* Corresponding author at: Key Laboratory of Industrial Ecology and Environmental Engineering and Key Laboratory of Fine Chemicals, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China. Tel.: +86 41184707733; fax: +86 41184707733.

** Corresponding authors.

E-mail addresses: xinyongli@hotmail.com (X. Li), jhchen@uwm.edu (J. Chen), dongke.zhang@uwa.edu.au (D. Zhang).

due to its efficacy and relatively low cost [16–19]. It is well known that the SCR performance of catalysts depends on the dispersion, nuclearity and oxidation state of the active components, which could be controlled by tailoring catalyst preparation method efficiently [6,12].

In the present study, we designed a new type Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ mixed oxide catalyst using a facile hydrothermal method. The as-prepared catalyst was shown to possess a special hierarchical morphology assembled by hollow spheres. Meanwhile, another sample of Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ mixed oxide was prepared by a co-precipitation method and used as a contrast to investigate the relationship between the properties of catalyst and the synthesis method. A series of physical-chemical characterizations were performed to help reveal the structure sensitivity of the SCR reaction over the Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ catalysts. Moreover, the *in situ* DRIFT spectroscopy was also used to investigate the structure sensitivity of the SCR reaction by examining the reactant adsorption as well as the formation and transformation of intermediates during the SCR process. The findings in this work would contribute to the rational design of SCR catalysts by fine-tuning the surface fabrication.

2. Experimental

2.1. Catalyst preparation

Two Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ catalysts were synthesized using the hydrothermal and co-precipitation methods, respectively. In the hydrothermal process, certain amounts of titanium tetrachloride (TiCl_4) and zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) were dissolved in deionized water in ice-water bath, and then cupric acetate ($\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and urea ($\text{CO}(\text{NH}_2)_2$) were added. After stirring for 2 h, an equal amount of ethanol (EtOH) was added dropwise into the above solution. The molar composition of $\text{TiCl}_4:\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}:\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}:\text{H}_2\text{O}:(\text{NH}_4)_2\text{SO}_4:\text{CO}(\text{NH}_2)_2:\text{EtOH}$ was controlled to be 1:1:0.16:146:2:36:46. The final mixed solution was then transferred into an autoclave, sealed, heated to and maintained at 95 °C for 24 h. In the co-precipitation process, this same final mixed solution was reflux condensed in a thermostatic oil bath at 95 °C for 24 h. Both slurries obtained in the two methods were filtered after cooling to the room temperature, washed with deionized water and ethanol, and dried at 80 °C for 12 h. The resultant powders were calcinated at 400 °C for 4 h with a heating rate of 2 °C min^{-1} . The Cu-doped $\text{Ti}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}$ samples prepared using the hydrothermal and co-precipitation methods were labeled as Hy-Sample and Co-Sample, respectively. Moreover, to investigate the high-temperature treatment effect on Hy-Sample, another two samples were prepared by hydrothermal method also, and these samples were calcinated at 600 and 800 °C for 4 h, respectively, by the same heating rate of 2 °C min^{-1} .

2.2. Characterization

The exact copper content in the samples was determined with an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin-Elmer Optima 3300 DV apparatus). The specific surface area, pore volume and average pore diameter of catalyst were measured using physical adsorption of N_2 at -196 °C with NOVA 1200 (Quanta Chrome). The catalyst morphology was characterized by scanning electron microscope (SEM, FEI-Quanta 450), transmission electron microscope (TEM, FEI-TECNAI G20), and high-resolution transmission electron microscopy (HR-TEM, FEI-TECNAI G20). Electron paramagnetic resonance (EPR) analysis was performed at room temperature using a Bruker (A200-9.5/12) operating at the X

band (~9.8 GHz). The magnetic field was modulated at 100 kHz and the g value was determined from the precise frequency and magnetic field values. Hydrogen-temperature programmed reduction (H_2 -TPR) analysis was carried out on a Chembet PULSAR TPR/TPD (p/n 02139-1), and the H_2 consumption in the effluent was monitored with a TCD detector. X-ray photoelectron spectra (XPS) were recorded using a Thermo ESCALAB 250XI electron spectrometer. Binding energies of Cu 2p, O 1s and Zr 3d were calibrated using C 1s ($\text{BE} = 284.8 \text{ eV}$) as a standard.

2.3. Catalytic test

The SCR activity measurement was carried out in a fixed-bed quartz tube reactor (6 mm internal diameter) containing 200 mg catalyst (40–60 mesh). Prior to an experiment, the catalyst was pretreated at 250 °C for 1 h in an Ar stream, and the activity test was performed from 150 °C to 450 °C at a heating rate of 10 °C min^{-1} . The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm C_3H_6 , 10 vol.% O_2 , 10 vol.% H_2O (when used) and 100 ppm SO_2 (when used), with He as balance. The total flow rate was 100 ml min^{-1} , which corresponded to an hourly space velocity (GHSV) of approximately 30,000 h^{-1} . The concentrations of NO, NO_2 and CO in the inlet and outlet gases were measured using a chemiluminescence gas analyzer (Testo 350). The concentrations of N_2 , N_2O and C_3H_6 were analyzed using a gas chromatograph (Agilent 7890 A), and the corresponding columns were 5A molecular sieve and Paropak Q columns with a thermal conductivity detector (TCD) and a 6X-104D column with a flame ionization detector (FID), respectively.

The NO conversion, C_3H_6 conversion, NO_2 yield, N_2 yield, N_2O yield and CO yield were calculated as follows:

$$\text{NO conversion} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{C}_3\text{H}_6 \text{ conversion} = \frac{[\text{C}_3\text{H}_6]_{\text{in}} - [\text{C}_3\text{H}_6]_{\text{out}}}{[\text{C}_3\text{H}_6]_{\text{in}}} \times 100\% \quad (2)$$

$$\text{NO}_2 \text{ yield} = \frac{[\text{NO}_2]}{[\text{NO}]_{\text{in}}} \times 100\% \quad (3)$$

$$\text{N}_2 \text{ yield} = \frac{[\text{N}_2] \times 2}{[\text{NO}]_{\text{in}}} \times 100\% \quad (4)$$

$$\text{N}_2\text{O yield} = \frac{[\text{N}_2\text{O}] \times 2}{[\text{NO}]_{\text{in}}} \times 100\% \quad (5)$$

$$\text{CO yield} = \frac{[\text{CO}]/3}{[\text{C}_3\text{H}_6]_{\text{in}}} \times 100\% \quad (6)$$

The reaction rate and turnover frequency (TOF) for NO conversion were calculated according to the following equations:

$$R_{\text{NO}} = X_{\text{NO}} \nu / m_{\text{cat}} / S_{\text{BET}} \quad (\text{mol s}^{-1} \text{ m}^{-2}) \quad (7)$$

$$\text{TOF} = \frac{(P_{\text{v}}/R_{\text{T}})X_{\text{NO}}}{m_{\text{cat}}\beta_{\text{Cu}}/M_{\text{Cu}}} \cdot (\text{s}^{-1}) \quad (8)$$

where X_{NO} (%) is the NO conversion, ν (mol s^{-1}) the flow rate of NO, m_{cat} (g) the mass of the catalyst, S_{BET} ($\text{m}^2 \text{ g}^{-1}$) the BET specific surface area, P the standard atmospheric pressure ($1.01 \times 10^5 \text{ Pa}$), R the proportional constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T (K) the reaction temperature, β_{Cu} (%) the Cu loading calculated from the XPS spectra, and, finally, M_{Cu} the molar mass of Cu (63.54 g mol^{-1}).

2.4. In situ DRIFT study

In situ DRIFT spectra were recorded using an FTIR spectrometer (Bruker VERTEX 70-FTIR) equipped with a liquid- N_2 -cooling high-sensitivity MCT detector and DRIFT cell. Prior to each experiment, the sample (~50 mg) was pretreated in He stream (50 ml min^{-1})

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