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Solvent effects during the synthesis of $Cr/Ce_{0.2}Zr_{0.8}O_2$ catalysts and their activities in NO oxidation

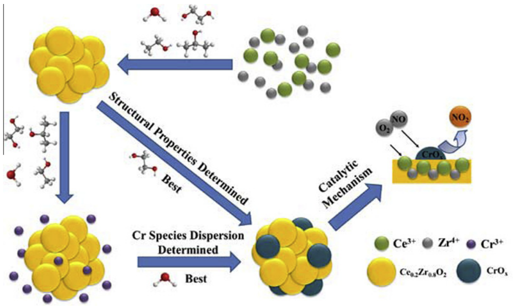
Wei Cai, Qin Zhong *, Jie Ding, Yunfei Bu

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

HIGHLIGHTS

- We prepared $Cr/Ce_{0.2}Zr_{0.8}O_2$ in four solvents via the common but simple method.
- The structural properties of $Cr/Ce_{0.2}Zr_{0.8}O_2$ are determined by that of $Ce_{0.2}Zr_{0.8}O_2$.
- H_2O impregnation benefits for the well dispersion of Cr species.
- The amount of surface Ce^{3+} and Cr^{6+} ratios are the key factors in NO oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

The solvent effects during the synthesis of a NO oxidation catalyst, $Cr/Ce_{0.2}Zr_{0.8}O_2$ were evaluated with four solvents of the precursor solution (H_2O, ethanol, ethylene glycol and isopropanol). The physicochemical characteristics were investigated by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, high-resolution transmission electron microscope (HR-TEM), X-ray photoelectron spectroscopy (XPS) and $NO(O_2)$ temperature-programmed desorption ($NO(O_2)$-TPD). The results indicate that the structural properties of $Cr/Ce_{0.2}Zr_{0.8}O_2$ are determined by the $Ce_{0.2}Zr_{0.8}O_2$ support, and the solvents have impact on the surface properties. The adoption of ethylene glycol in the preparation of $Ce_{0.2}Zr_{0.8}O_2$ support leads to the reduce of particles sizes, the increase of surface area and the generation of surface Ce^{3+}, which is due to the appropriate polarity and the slow drying condition. Moreover, the present of H_2O in the impregnation process could increase the dispersion of Cr species. The activity test confirms that the surface Ce^{3+} and Cr^{6+} ratios are the key factors in NO oxidation.

1. Introduction

The emission of nitrogen oxides (NO_x) produced from stationary and mobile combustion sources is one of the major contributors in the atmospheric contamination [1], and this will lead to undesirable severe damage to the human health [2,3]. Catalytic oxidation of NO plays a decisive role in NO_x storage and reduction (NSR) [4–6], continuously regenerating trap (CRT) [7] and selective catalytic reduction (SCR) [8–10], which are the main technologies for NO_x removing. The key of the oxidation is NO to NO_2, and if the ratio of NO/NO_x equals to about 60%, the removal effect will be the optimum [11]. Ceria–zirconia solid solutions ($Ce_xZr_{1-x}O_2$) were prepared for oxidation due to their excellent abilities of releasing/storing oxygen [12,13], and for Cr-contained catalysts, which were also applied for oxidation, was due to their strong oxidizing property [14]. In our previous work [15], we found that effects of Cr and $Ce_xZr_{1-x}O_2$ in the oxidation were separated, in which NO was adsorbed on the sites of Cr, and O_2 was adsorbed and activated on the surface of $Ce_xZr_{1-x}O_2$.

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* Corresponding author. Tel./fax: +86 25 84315517.
E-mail address: zq304@mail.njust.edu.cn (Q. Zhong).

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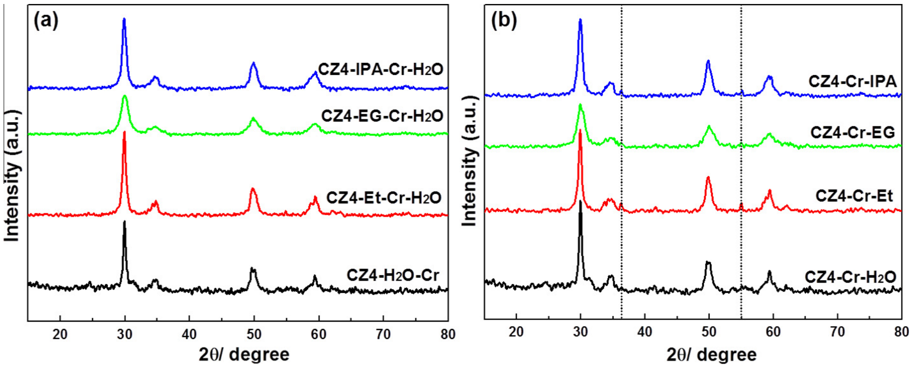

Fig. 1. XRD patterns of $Cr/Ce_{0.2}Zr_{0.8}O_2$ catalysts. (a) H_2O impregnation; (b) corresponding solvent impregnation.

Some studies found that the changes of solvents in the preparation of the catalysts could improve the surface properties and the electronic structure, hence enhanced the catalytic activity [16–18]. Kavitha et al. reported the effects of solvent on the electronic structures of nano zinc oxide [19]. Yang et al. found that the morphology of nanostructured Co_3O_4 could be controlled in different solvents, such as ethanol, ethylene glycol and glycerol, and in glycerol, nanonet-like Co_3O_4 exhibited the highest capacitance [20]. The luminescence intensity over LaF_3:Ln^{3+} was investigated by Phaomei et al. in different solvents, (e.g. water, ethylene glycol, dimethyl sulfoxide), and samples prepared in ethylene glycol exhibited the highest luminescence intensity [21]. Rico-Pérez et al. studied N_2O decomposition over $RhO_x/Ce_yPr_{1-y}O_2$ in different solvents, and the positive effects of water impregnated were found [22]. However, so far there are few reports on the solvent effects on the different synthetic stages of $Cr/Ce_xZr_{1-x}O_2$, to the best of our knowledge.

Hence, in our current work, four different solvents (H_2O, ethanol, ethylene glycol and isopropanol) were adopted in the two synthetic stages of $Cr/Ce_xZr_{1-x}O_2$ to evaluate the effects of these solvents. Our previous study indicated $Cr/Ce_xZr_{1-x}O_2$ with Ce/Zr = 1:4 exhibited the highest NO conversion [23]. In this work, the crystalline and surface structures were investigated by XRD, HR-TEM, BET, XPS and $NO(O_2)$-TPD. This work illustrates the composition–structure–property relationships, shedding light on the design and rationalization of the practical catalysts.

2. Experimental

2.1. Catalysts preparation

All the chemicals were purchased from Alfa Aesar and used as received without further purification. The water used throughout all experiments was purified through a Millipore system. The $Ce_{0.2}Zr_{0.8}O_2$ supports were prepared via the simple dissolution–desiccation–calcination process in different solvents, and Cr species were loaded on the support by the impregnation method. The solvents adopted in the impregnation processes were divided into two cases: (1) solvent was the same as that used in the preparation of the support; (2) H_2O in all cases. Typical synthetic processes were shown as below. The $Ce(NO_3)_3$ and $ZrOCl_2$ were dissolved in different solvents (deionized water, ethanol, ethylene glycol and isopropanol) according to the molar ratio of Ce:Zr = 1:4. The resulting solution was kept in stirring for 1 h, then refluxed in the water-bath at 60 °C for 4 h and dried at 120 °C (T = 160 °C, when ethylene glycol used) for 12 h. After calcination at 500 °C for 6 h, $Ce_{0.2}Zr_{0.8}O_2$ was obtained. The as-prepared $Ce_{0.2}Zr_{0.8}O_2$ was dispersed in 0.1282 mol L^{-1} (10% in mass) $Cr(NO_3)_3$ solution, then the solution was refluxed in the water-bath at 60 °C for 4 h. The $Cr/Ce_{0.2}Zr_{0.8}O_2$ catalyst was obtained after dried at 120 °C for 12 h and then calcined at 500 °C for 6 h. For simplification, while the corresponding solvent was adopted in the impregnation process, these catalysts were denoted as CZ4-Cr-H_2O, CZ4-Cr-Et, CZ4-Cr-EG and CZ4-Cr-IPA, referring to deionized water, ethanol, ethylene glycol and isopropanol as solvent, respectively. While H_2O was used as the solvent, these catalysts were denoted as CZ4-Cr-H_2O, CZ4-Et-Cr-H_2O, CZ4-EG-Cr-H_2O, and CZ4-IPA-Cr-H_2O, respectively. For comparison, the catalyst adopted ethanol as solvent in the synthesis of $Ce_{0.2}Zr_{0.8}O_2$ and H_2O as solvent in the impregnation process was also prepared. The drying temperature in the synthesis of $Ce_{0.2}Zr_{0.8}O_2$ was 40 °C, which was about 37 °C lower than the boiling point, similar to the synthesis of CZ4-EG. The catalyst was named as CZ4-Et-40-Cr-H_2O.

Table 1
The grain size, surface area, average pore size and TPD peak area of $Cr/Ce_{0.2}Zr_{0.8}O_2$ catalysts.

Samples	Grain size[a] (nm)	BET ($m^2\ g^{-1}$)	Average pore size (nm)	Peak area (NO)	Peak area (O_2)
CZ4-Cr-H_2O	16	64	10	3082	46,929
CZ4-Et-Cr-H_2O	16	25	6	1530	27,313
CZ4-EG-Cr-H_2O	7	75	4	2833	51,275
CZ4-IPA-Cr-H_2O	14	35	7	3117	49,038
CZ4-Cr-Et	15	31	5	1199	26,203
CZ4-Cr-EG	8	79	4	1880	42,478
CZ4-Cr-IPA	13	37	8	1496	39,727

[a] Grain size of the catalysts determined from the XRD diffraction peak by Scherrer equation.

2.2. Characterizations

Powder X-ray diffraction patterns of the samples prepared in different solvents were recorded in the 10–80° 2θ range (scan speed = 8° min^{-1}, step value is 0.04°) using a Beijing Purkinje general instrument XD-3 (Cu Kα radiation, λ = 1.5418 Å).

BET surface area and pore size distribution (calculated by Barrett–Joyner–Halenda (BJH) method) of these samples were determined by N_2 adsorption–desorption isotherms at −196 °C using a Gold App V-sorb 2008 Analyzer. Prior to N_2 measurements, the samples were outgassed at 200 °C for 12 h in the vacuum.

The TEM–HRTEM studies were made on a JEM-2100 (JEOL) instrument equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV. Samples for TEM analysis were prepared by crushing the materials in an agate mortar and dispersing ultrasonically in isopropanol. After well dispersion, a droplet was deposited on a copper grid supporting a perforated carbon film and allowed to dry. The specimen was examined under vacuum at room temperature.

XPS analyses were performed on a Thermo ESCALAB 250 spectrometer. The X-ray source utilized was Al Kα X-rays