



Morphology-dependent properties of $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts for low temperature dibromomethane (CH_2Br_2) oxidation

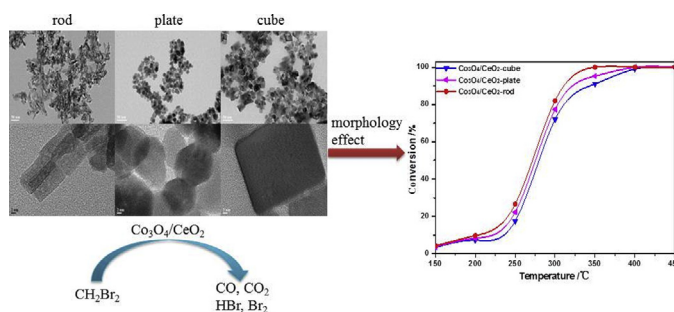
Jian Mei, Yu Ke, Zhongjue Yu, Xiaofang Hu, Zan Qu, Naiqiang Yan*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, PR China

HIGHLIGHTS

- $\text{Co}_3\text{O}_4/\text{CeO}_2$ -rod exhibited the high catalytic activity of CH_2Br_2 oxidation.
- CeO_2 morphology strongly affected Co_3O_4 - CeO_2 interactions and structures of $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts.
- Co^{3+} species, surface-adsorbed oxygen and oxygen vacancies were most abundant on $\text{Co}_3\text{O}_4/\text{CeO}_2$ -rod.
- The reaction mechanism for CH_2Br_2 oxidation over $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

Brominated hydrocarbons are a typical pollutant in purified terephthalic acid (PTA) exhaust gas, which is harmful for human health and the environment once released to the atmosphere. In this study, three $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts with different CeO_2 morphologies (rod, plate, and cube) were prepared and were used for low temperature dibromomethane (CH_2Br_2) oxidation, which was used as the model compound for brominated hydrocarbons. The experimental results showed that $\text{Co}_3\text{O}_4/\text{CeO}_2$ -rod achieved significantly higher catalytic activity, with a T-90 of approximately 312 °C for CH_2Br_2 oxidation and higher selectivity to CO_2 than $\text{Co}_3\text{O}_4/\text{CeO}_2$ -plate and $\text{Co}_3\text{O}_4/\text{CeO}_2$ -cube. All of the $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts investigated were stable for at least 30 h at 500 ppm CH_2Br_2 and 10% O_2 at a GHSV of 75,000 $\text{mL}/(\text{g}\cdot\text{h})^{-1}$, and the final products were CO_x , Br_2 , and HBr , without the formation of other Br-containing organic byproducts. The higher catalytic activity of $\text{Co}_3\text{O}_4/\text{CeO}_2$ -rod was attributed to the high content of Co^{3+} , more surface-adsorbed oxygen, and more oxygen vacancies in their exposed {100} and {110} planes. In addition, Co_3O_4 had a stronger interaction with CeO_2 -rod, making it superior for CH_2Br_2 oxidation. Moreover, on the basis of the analysis of products and *in situ* DRIFTS studies, a credible reaction mechanism for CH_2Br_2 oxidation over $\text{Co}_3\text{O}_4/\text{CeO}_2$ catalysts was proposed.

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1. Introduction

Volatile organic compounds (VOCs) not only are recognized as one of potent and important contributors to air pollution [1], but also put human health and the environment at risk [2]. Particu-

larly, increasing attention is being paid to purified terephthalic acid (PTA) exhaust gas because of its high toxicity and difficulty of treatment [3], and the staging of massive protests against such projects in China in recent years. The PTA exhaust gas contains various organic compounds, such as p-xylene (PX), brominated hydrocarbons, and acetic acid methyl ester [4]. Among all of the treatment methods, catalytic oxidation is one of the most popular methods to treat PTA exhaust gas, by reason of its low energy

* Corresponding author.

E-mail address: nqyan@sjtu.edu.cn (N. Yan).

consumption and lower contents of secondary pollutants [5]. Nevertheless, the existence of brominated hydrocarbons in PTA exhaust gas demands that the catalyst must have the ability to resist bromine-poisoning. Therefore, the key issue in this method is to develop a high-performance catalyst to remove brominated hydrocarbons.

Currently, researchers are mainly focusing on two types of catalysts for brominated hydrocarbons oxidation, including noble metals [6] and transition metal oxides [3]. In spite of noble metal catalysts display prominent catalytic activity, the low resistance to bromine-poisoning and high cost limits their industrial applications. In contrast, transition metal oxide catalysts have gained increasing attention on account of their low cost, high catalytic activity, and high stability to brominated hydrocarbons oxidation. Thus, it is of great interest to develop transition metal oxide catalysts for brominated hydrocarbons oxidation.

Among many transition metal oxides, the Co-based catalyst has been proven to have a good catalytic performance for brominated hydrocarbons oxidation [7]. However, the catalytic activity, product-selectivity, and stability of the Co-based catalyst need to be further improved. CeO₂ is often used as a support in the catalytic reaction, such as CuO/CeO₂ [8], Au/CeO₂ [9], and FeOOH/CeO₂ [10], by reason of its prominent oxygen mobility [11], high oxygen storage capacity [12], and some acidic properties [13]. In addition, CeO₂ as a support can promote the dispersion of metal oxides and increase the metal-support interaction [14]. In the past few years, it has been found that the catalytic performance of CeO₂ is affected by exposed lattice planes [15]. Generally, different lattice planes are exposed in different CeO₂ morphologies. For instance, CeO₂ nanorods are prone to expose two {100} planes and four {110} planes [16], while CeO₂ nanocubes expose six {100} planes [17]. On the basis of density functional theory, the chemical activities of the different CeO₂ planes follow the order: {111} < {100} < {110} [18], which reveals that it is easier to produce oxygen vacancies on the CeO₂ {110} plane. Until now, there have been many reports about morphology effects of the CeO₂ support on dry-reforming of methane [18] and oxidation of CO [19]. It is reported that Co₃O₄/CeO₂ catalysts have been studied in the field of catalysis due to their unique physicochemical properties. For example, Guo et al. reported that Co₃O₄/meso-CeO₂ had a good catalytic performance for CO preferential oxidation in H₂-rich gases because of the high dispersion of cobalt oxides on meso-CeO₂ supports [20]. Tian et al. found that (Co₃O₄)_{50%}/CeO₂ had a better reducibility and activity oxygen species, which coincided with its high catalytic activity for CO oxidation [21]. However, research about Co₃O₄/CeO₂ catalysts, relating the effect of CeO₂ morphology on the catalytic performance for brominated hydrocarbons oxidation, is rare.

In this study, Co₃O₄/CeO₂ catalysts with different CeO₂ morphologies (rod, plate, and cube) were prepared and were used for dibromomethane (CH₂Br₂) oxidation, which was chosen as the model compound for brominated hydrocarbons. The physicochemical properties of Co₃O₄/CeO₂ catalysts with different CeO₂ morphologies were studied. The CH₂Br₂ conversion, analysis of products, and catalyst stability were also investigated. On the basis of the analysis of products and *in situ* DRIFTS studies, a credible reaction mechanism for CH₂Br₂ oxidation over Co₃O₄/CeO₂ catalysts was proposed.

2. Experimental section

2.1. Catalyst preparation

CeO₂ nanorods and nanocubes were prepared by the hydrothermal method. Typically, 3.48 g Ce(NO₃)₃·6H₂O and 19.2 g NaOH

were dissolved in 40 mL ultrapure water, respectively. Next, the NaOH solution was dripped into the Ce(NO₃)₃ solution, and the mixed solution was magnetic stirred for 60 min. Then, the mixed solution was transferred into a stainless steel reaction kettle with Teflon lining and maintained at constant temperatures (rods: 100 °C; and cubes: 180 °C) for 24 h.

CeO₂ nanoplates were prepared by the CTAB (Cetyltrimethyl Ammonium Bromide)-assisted hydrothermal method. Typically, 0.73 g CTAB and 2.61 g Ce(NO₃)₃·6H₂O were dissolved in 80 mL ultrapure water and magnetic stirred for 30 min. Subsequently, 8 mL NH₃·H₂O was dripped into the mixed solution and magnetic stirred for 30 min, and then the mixed solution was transferred into a stainless steel reaction kettle with Teflon lining and maintained at 100 °C for 24 h.

After filtering and washing with ultrapure water, the obtained precipitates were dried at 60 °C for 12 h, and then calcined at 500 °C for 3 h in air.

Co₃O₄/CeO₂ catalysts with different CeO₂ morphologies (rod, plate, and cube) were prepared by the impregnation method. CeO₂ powders were mixed with Co(NO₃)₂·6H₂O solution under magnetic stirring at 60 °C to gain Co₃O₄/CeO₂ (5 wt% Co/CeO₂). The samples were dried at 60 °C for 12 h, and then calcined at 500 °C for 3 h in air. The samples were flagged as CeO₂-rod, CeO₂-plate, CeO₂-cube, Co₃O₄/CeO₂-rod, Co₃O₄/CeO₂-plate, and Co₃O₄/CeO₂-cube.

2.2. Catalyst characterization

X-ray diffraction (XRD) were performed on the Shimadzu XRD-6100, and the diffractograms were obtained in the 2θ range of 10°–80°, with a scanning velocity of 10°/min. The N₂ adsorption-desorption isotherms were collected using a physical adsorption instrument (Nova 2200e) at –196 °C. Before each experiment, the samples were pretreated under the condition of vacuum at 200 °C for 3 h. The specific surface area was obtained by the multipoint BET model. Raman spectra were recorded on a SENTERRA R200 microscope. The excitation source was the 532 nm line of Ar ion laser. The morphology of the samples was observed using transmission electron microscopy (TEM) (JEOL-2100F) and scanning electron microscope (SEM) (JSM-7800F). Before each experiment, the samples were evenly dispersed in ethanol solution under the condition of ultrasound. Chemical analysis of the samples was performed on the inductively coupled plasma (ICP) spectrometer with iCAP 6000 Radial. The H₂-TPR experiments were performed on an automatic chemical adsorption instrument (AutoChem II, 2920). Before each experiment, the 100 mg samples were degassed in Ar flow at 300 °C for 2 h. Subsequently, after cooling to 100 °C, the samples were heated up to 1000 °C in 10% H₂/Ar flow, with a heating rate of 10 °C/min. The NH₃-TPD experiments were also performed on an automatic chemical adsorption instrument (AutoChem II, 2920). Before each experiment, the 500 mg samples were degassed in He flow at 300 °C for 2 h. Then, after cooling to 50 °C, NH₃ adsorption was performed in 10% NH₃/He flow at 50 °C for 1 h. Subsequently, the samples were treated in He flow for 30 min to remove gaseous NH₃, and then heated up to 800 °C in He flow, with a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI-5300 (PE) spectrometer using Mg Kα radiation as the excitation source, the binding energy was calibrated using the C 1 s line at 284.8 eV as an internal standard.

2.3. Catalytic performance evaluation

The catalytic performance for CH₂Br₂ oxidation was investigated by a fixed-bed flow reactor (i.d. 6 mm). 120 mg catalyst was placed in the middle of the reactor using silica wool. The gas

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