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Catalytic destruction of chlorobenzene over mesoporous $ACeO_x$ (A = Co, Cu, Fe, Mn, or Zr) composites prepared by inorganic metal precursor spontaneous precipitation

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ABSTRACT

Mesostructured $ACeO_x$ (A = Co, Cu, Fe, Mn, or Zr) composites with large specific surface area and developed mesoporosity were prepared by inorganic metal precursor spontaneous precipitation (IMSP) method. Influences of catalyst surface area, pore structure, reducibility, and active oxygen concentration on catalytic performance were studied. Both preparation route and metal precursor type affect metal active site dispersion, and the IMSP is a desirable approach for synthesis of metal composites with homogeneous active phase distribution. The original crystalline structure of CeO_2 is well maintained although parts of transition metal cations are incorporated into its framework. The forming of $A^{n+}–O^{2-}–Ce^{4+}$ connections in $ACeO_x$ catalysts could reduce the redox potential of metal species, allowing effective redox cycles during oxidation reactions. $CuCeO_x$ demonstrates powerful catalytic efficiency with 99% of chlorobenzene (CB) destructed at 328 °C, which is much lower than the other $ACeO_x$ oxides and Cu-doped catalysts synthesized via the incipient impregnation and coprecipitation methods ($T_{99} > 405$ °C). The active site reducibility is the foremost activity determining factor for CB destruction.

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1. Introduction

Volatile organic compounds (VOCs) emitted from industrial manufacturing and municipal burning are an important class of air pollutants [1,2]. Among them, chlorinated volatile organic compounds (CVOCs) are considered as the most harmful organic contaminants due to their acute toxicity and strong bioaccumulation potential [3]. Catalytic oxidation is an effective, energy-saving, and environment-friendly approach for CVOC elimination [4]. Supported noble metal catalysts and transition metal oxides are usually employed for arene elimination. The high cost, inferior thermal stability and low resistance to poisoning of noble metals limit their practical large-scale application, especially in the case of CVOC destruction [5,6]. Transition metal oxides are a proper alternative owing to their excellent thermal stability, superior durability against deactivation, and lower price [7]. Nonporous zirconia-based catalysts, manganese and copper oxides, have been claimed for their effectiveness in CVOC destruction or dechlorination reactions [8–10]. Besides, the superior catalytic performances of nanocrystalline cobalt and iron metal oxides in CO and/or VOC oxidation have also been reported [11,12].

Ceria has recently attracted much attention as an efficient catalyst due to its abundant oxygen vacancy defects, high oxygen storage capacity, and relatively easy shuttles between Ce^{3+} and Ce^{4+} oxidation states [13,14]. However, CeO_2 deactivated quickly due to the strong adsorption of HCl or Cl_2 produced from CVOC decomposition [15]. Doping ceria with transition metals could modify the redox property of mixed oxides, enhancing the oxygen mobility and $^{\bullet}Cl$ species removal or transfer velocity, and thus, improving their catalytic activity and reaction stability during CVOC destruction. Wang et al. [16] have proposed that the $MnO_x–CeO_2$ catalysts with high Mn/(Ce + Mn) ratios presented a stable chlorobenzene (CB) oxidation performance due to the strong ability of Mn to remove $^{\bullet}Cl$ species. However, single or mixed metal oxides synthesized via the traditional methods possess nonporous structure and low active surface area, which greatly limit their low-temperature catalytic efficiency. Mesoporous transition metal oxides (MTMO) with d-shell electrons confined to nanosized walls and redox active internal surfaces show extreme fascinating prospects in VOC decomposition [17]. The synthesis of MTMO usually requires "soft" (e.g., surfactants or block copolymers) or "hard" (e.g., porous silica or carbon) structural templates [18–23]. For example, ordered mesoporous Co_3O_4 with high surface area (173 m^2/g) has been obtained by Garcia and coworkers

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through a nanocasting route using KIT-6 silica as the hard template, over which 100% propane could be totally oxidized at around 225 °C [22]. Nonetheless, the synthesis of mesostructured silica or carbon template is rather complex and time-consuming. Previously, we synthesized mesoporous CuO_x–CeO_2 catalysts with large surface area (up to 162.8 m^2/g) via a facile self-assembly method, and found that these materials possessed powerful catalytic activity for the oxidation of toluene and propanal [23]. However, the catalytic performances of mesoporous transition metal/ceria composites in CVOC oxidation were seldom considered.

Herein, mesoporous $ACeO_x$ (A = Co, Cu, Fe, Mn, or Zr) composites were synthesized using cetyltrimethylammonium bromide (CTAB) as the soft template and urea as the precipitation inducer with the aim to explore the feasibility of mesostructured composite oxides in CVOC destruction. CB was adopted as the probe molecule as it's a typical aryl chloride and usually employed as the model reagent to predict the destruction behaviors of chlorinated aromatics and dioxins [9]. Physicochemical properties of all synthesized catalysts were characterized by XRD, N_2 sorption, FE-SEM, TEM, H_2-TPR and O_2-TPD. Furthermore, the influence factors such as surface area, mesoporosity, reducibility, and active oxygen concentration were discussed in detail with the catalytic activity.

2. Experimental

2.1. Catalyst preparation

Chemicals (without further purification) used in this work are cheap and easily available inorganic metal salts, cationic surfactant (CTAB), and urea. For a typical synthesis, 5 g $Ce(NO_3)_3 \cdot 6H_2O$, 5.6 g CTAB, 7.7 g urea, and different amounts of inorganic metal precursors (metal loading = 30 wt.%) were dissolved in 190 mL deionized water. After stirring for 2 h, the metal ions, urea molecules, and CTAB micelles are homogeneous dispersed in the mixed solution. Then, the obtained mixed solutions were firstly aged in autoclaves at 80 °C for 24 h to make the inorganic metal precursors homogeneously precipitated around the CTAB/water micelles due to the persistent decomposition of urea, and the mixtures were further heated in autoclaves for 12 h at 120 °C for polycondensation and rearrangement of surfactant micelles. After that, the products were washed with distilled water and recovered by centrifugation. Finally, the recovered products were dried at 80 °C and calcined at 550 °C for 4 h to remove organic residues and gain the mesostructured metal oxides.

For comparison, the $CuCeO_x$ oxides with Cu loading of 30 wt.% were prepared by incipient impregnation (IM, named im-$CuCeO_x$) and coprecipitation (CO, named co-$CuCeO_x$) methods, and the preparation procedures can be found elsewhere [24,25]. Bulk CeO_2 was also synthesized through thermal calcination $Ce(NO_3)_3 \cdot 6H_2O$ at 550 °C for 4 h.

2.2. Catalyst characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert powder diffraction system using Cu Kα radiation (λ = 0.15418 nm) in the 2θ range of 10–80° with a scanning rate of 4°/min. N_2 sorption was collected on a Quantachrome NOVA 1200e gas sorption analyzer at 77 K. All samples were degassed under vacuum at 300 °C for 3 h before the measurement. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of *ca.* 0.99. The specific surface area was calculated at $P/P_0 = 0.05$–0.25 using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution and average pore diameter were derived from the desorption branch of the N_2 isotherm using the Barrett–Joyner–Halenda (BJH) method. Field emission scanning electron microscopy (FE-SEM) images were recorded on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were collected on a Hitachi H-7650 microscope operating at an acceleration voltage of 80 kV. Temperature programmed reduction (H_2-TPR) experiments were performed on a Micromeritics 2720 analyzer. Prior to reduction, 50 mg of the catalyst was heated in a 5% O_2/He flow (50 mL/min) from room temperature to 500 °C and held for 30 min, and then treated in a He stream at room temperature for 30 min to remove any residual oxygen. The sample was finally reduced under a 5% H_2/He (50 mL/min) from 50 to 600 °C with a heating rate of 10 °C/min. The temperature programmed desorption of O_2 (O_2-TPD) was carried out using the same apparatus as that for H_2-TPR. 50 mg of the catalyst was preheated in a 5% O_2/He flow (50 mL/min) at 500 °C for 30 min, then the sample was heated from 50 to 700 °C at a heating rate of 10 °C/min under a stream of pure He.

2.3. Catalytic activity evaluation

The catalytic performances of all prepared catalysts for CB oxidation were performed in a continuous-flow fixed-bed reactor at atmospheric pressure, consisting of a stainless steel tube with an inner diameter of 6 mm. 300 mg of the catalyst (40–60 mesh) was used in each run. The reagent gas consisted of 500 ppm of CB, 21 vol.% of O_2 and balance N_2 at a flow rate of 200 mL/min, i.e., gas hourly space velocity (GHSV) of *ca.* 30,000 h^{-1}. The effluent gas composition was analyzed online by a gas chromatograph (GC9890A, Shanghai Linghua Co., China) equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD).

The CB conversion (X_{CB}) is calculated by Eq. (1),

$$X_{CB} = \left(C_{CB,in} - C_{CB,out}\right)/C_{CB,in} \tag{1}$$

where $C_{CB,in}$ and $C_{CB,out}$ are the CB concentration (vol.%) in the inlet and outlet stream, respectively.

The CO_2 selectivity (S_{CO_2}) is calculated according to Eq. (2),

$$S_{CO_2} = n_{CO_2}/(6 \cdot n_{CB}) \tag{2}$$

where n_{CO_2} and n_{CB} are mole of CO_2 produced in the outlet gas and mole of CB feed in the inlet gas, respectively.

The reaction rate (r_{AO_x}) is calculated with X_{CB}, as follows,

$$r_{AO_x} = F_{CB} \cdot X_{CB}/\left(W_{cat} \cdot W_{AO_x}\right) \tag{3}$$

where F_{CB} is the CB feeding rate (mol/s), W_{cat} is the catalyst weight used in the reaction (g), and W_{AO_x} is the metal oxide loading (wt.%) in the $ACeO_x$ catalyst.

The effects of reaction products on the reaction rate may be ignored under differential conditions ($X_{CB} < 15\%$) [26], and the r_{AO_x} for CB destruction could be described as Eq. (4),

$$r_{AO_x} = A' \exp\left(-E_a/(R \cdot T)\right) \cdot {P_{CB}}^{\alpha} \cdot {P_{O_2}}^{\beta} \tag{4}$$

where A′ is the pre-exponential factor, E_a is the apparent activation energy, R is the molar gas constant, T is the thermodynamic temperature, and P_{CB} and P_{O_2} are the partial pressures of CB and O_2, respectively. The variations of the reactant component are negligible under differential reaction conditions, that is, A′, P_{CB}^{α}, and ${P_{O_2}}^{\beta}$ are nearly constant. Therefore, E_a can be obtained from the slope of the resulting linear plot of $\ln r_{AO_x}$ versus 1/T after taking the logarithm of Eq. (4).

3. Results and discussion

3.1. Structural and textural properties

As displayed in Fig. 1, both the preparation route and inorganic metal precursor type have evident effects on metal oxide dispersion.

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