CVD synthesis of cobalt spinel for bio-butanol combustion

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ABSTRACT

As potential substitutes for precious metals, cobalt spinel has been considered as a promising alternative catalyst for the low-temperature catalytic oxidation of biofuels. This work reports the one-step synthesis of cobalt spinel by a more elaborated approach named pulsed-spray evaporation chemical vapor deposition with a new feedstock of $Co(acac)_3$ and toluene. The obtained samples were comprehensively characterized in terms of structure and morphology (XRD, FTIR, Raman and SEM), chemical composition (XPS and EDS) and the redox properties (TPR/TPO). The structural and morphological analysis indicates that the synthesized thin films are pure cubic Co_3O_4 with homogeneous matrix with well-defined facets and straight edges. Compared to the commonly used feedstock of $Co(acac)_2$/ethanol, $Co(acac)_3$/toluene could result in a much higher growth rate, more lattice oxygen on the surface and better re-oxidation property. The Co_3O_4 film exhibits attractive performance towards the deep oxidation of *n*-butanol by preventing the formation of CO and acetaldehyde. The relationship between the peculiar structure and properties of Co_3O_4 is highlighted. The surface basic sites, specific morphology and the redox properties are proposed to play synergistic roles in the reaction sequence.

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1. Introduction

Seeking clean and sustainable energy sources has caught more and more wide attention. Biofuels are reported as one of the clean energy sources due to their high energy efficiency and low pollutant emissions [1]. Several potential biofuel candidates have been proposed in the past decades. Among them, *n*-butanol attains increasing interest owning to its advantageous physical properties compared to other alcohol biofuels [2]. Burning alcohols always emits aldehydes such as formaldehyde, acetaldehyde and other potentially hazardous aromatic compounds which are strictly regulated in emissions standards [3]. Therefore, it is urgent to intensify research of bio-butanol with clean combustion approaches. As a promising and viable technique, catalytic combustion exhibits to be an effective method to control the hydrocarbons, CO and NO_X emissions [4–6].

Catalysts used for volatile organic compounds (VOCs) oxidation include mainly noble metals and transitional metal oxides (TMOs). Numerous works evaluate the total oxidation of *n*-butanol over catalysts based in noble metals (Pt, Pd and Ru) and TMOs, particularly binary (Co-Mg) [7], ternary mixed oxides (Ce-Zr-Mn) [8,9]. However, *n*-butanol conversion over these noble metals generally produces many by-products especially aldehydes and alkenes (ethanal, propanal, butanal and butene) [10–12]. In addition, noble metals are expensive and present high poisoning tendency compared to the TMOs [13]. Although it has been established as one of the most active TMOs, quite limited studies covering the total oxidation of *n*-butanol over Co_3O_4 are available. Recently, an attempt was made in our group to study *n*-butanol conversion over natural clays as well as Co_3O_4 sample prepared via the same synthesis method [14], but a systematic study with respect to the relationship between the structure and properties still remains unclear.

Among TMOs, cobalt spinel (Co_3O_4) stands for an important functional material with applications in heterogeneous catalysis [15–19]. However, to achieve excellent performance of such materials, suitable synthesis approach capable of producing thin film of high crystallinity and purity is required. For the synthesis of Co_3O_4 thin films, many chemical vapor deposition (CVD) methods such as metal-organic CVD (MO-CVD) [20–22], plasma-enhanced CVD (PE-CVD) [23,24] were used. Among the techniques employed for the synthesis of Co_3O_4 thin films, pulsed spray evaporation chemical vapor deposition (PSE-CVD) owns the benefit of being a reliable one-pot method for the growth of complex oxides in a controlled way [25–27]. PSE-CVD deposited Co-based catalysts were intensively investigated for the deep oxidation of CO, methane, ethanol, and several saturated/unsaturated hydrocarbons [28–31]. Co^{3+}/Co^{2+} couple was found to be the active site towards the oxidation reactions via a redox mechanism [32]. Despite of the ability of cobalt spinel to participate in the oxidation of different

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compounds, up to date, none comprehensive and systematic study has been reported in the literature regarding the use of Co_3O_4 as catalyst for the total oxidation of n-butanol.

In this work, tailored synthesis of Co_3O_4 thin films were achieved using the PSE-CVD route with a new feedstock. Systematic and comprehensive characterization was performed to obtain the structural, morphological, composition and ionic states as well as the redox properties. The catalytic performance of Co_3O_4 was tested against the complete oxidation of n-butanol in a quartz flow reactor. The goal of this ongoing work is to reveal the effectiveness of PSE-CVD as suitable synthesis approach for functional transition metal oxides and apply such materials to practical combustion systems to reduce high emission of by-products in biofuels combustion, such as CO and aldehydes.

2. Experimental

2.1. Catalyst preparation

The deposition of Co_3O_4 thin films was carried out in a cold-wall stagnation point-flow CVD reactor. The setup is equipped with a PSE unit for the delivery of liquid precursor feedstock. A detailed description of the experimental setup can be found elsewhere [33]. $Co(acac)_3$ dissolved in toluene was used in a concentration of 2.5 mM as a new feedstock. The PSE delivery was programmed to use a valve opening time of 2.5 ms and a frequency of 4 Hz. The evaporation of the injected feedstock took place at 200 °C. The resulting vapor was transported in a vertical 30 cm-long chamber with N_2/O_2 flow rates of 0.16/0.50 standard liter per minute (SLM). Deposition of the thin films occurred on heated substrates including stainless steel, silicon wafer, bare glass and mesh of stainless steel (Single Plain dutch Weave (SPW) 40, 80 × 400) for variable characterization purposes. The deposition temperature was optimized to be 450 °C, and the total pressure in the reactor was kept constant at 2.0 kPa. It should be mentioned that the newly used feedstock of $Co(acac)_3$ and toluene, combined with the optimized deposition conditions, leads to a much higher growth rate (~2.50 nm/min) than those prepared with $Co(acac)_2$/ethanol (~0.42 nm/min) [21]. Such phenomenon can be explained by the fact that, toluene owns much higher electron mobility than the OH group in ethanol, which facilitates the dissolution processes of the precursor and therefore enhances the film deposition. Compared to toluene, the electronic activity in case of alcohol is in a defined small range. The active part in the alcohol is the OH^- group only, while in case of the toluene, the whole structure is active. Thus, toluene can be considered as a better solvent than alcohol.

2.2. Characterization

The identification of the crystalline phase of the grown films was performed using X-ray diffraction (XRD, Bruker D8 Focus with Cu Kα radiation), emission FTIR (Bruker VERTEX 70) and Raman spectroscopy under ambient conditions. The crystalline phases were identified by referring to the powder XRD database (JCPDS-ICDD). Home-built emission FTIR and Raman spectrometers were used to confirm the structure of cobalt oxide spinel. The microstructure was examined using Scanning electron microscopy (SEM, with a Hitachi S-450 instrument). The chemical compositions in the bulk of the prepared films were determined using Energy dispersive X-ray spectroscopy (EDS, with a Hitachi S-450 instrument) while both surface and bulk composition was evaluated by the X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi) operating with pass energy of 20 eV and energy step sited of 0.05 eV. The surface and bulk composition analysis of the films by XPS was carried out respectfully in the following situations: (a) after 1 min of 4 keV Ar^+ sputter cleaning of the film surface, to eliminate adsorbed carbon and other species, and (b) after 2 min sputtering, i.e. during the depth profile. In the fact, Ar^+ gun is used to etch the material for a 2 min before being turned off while XPS spectra are acquired. The redox behavior of the as-prepared material was investigated with an in-situ emission FTIR spectrometer via the temperature-programmed reduction and re-oxidation (TPR/TPO) mode at ramp of 3 °C/min.

2.3. Catalytic activity

The catalytic combustion of n-butanol was investigated at atmospheric pressure over Co_3O_4-coated mesh of stainless steel in a quartz tubular glass reactor. The experimental setup is shown in Fig. 1. The total flow rate was kept at 15 ml min^{-1} with 1% of fuel and 10% O_2 diluted in Ar, corresponding to the weight hourly space velocity (WHSV) of 75,000 ml g$^{-1}_{cat}$ h^{-1}. The gas flow rates were regulated by mass-flow controllers (MKS). The temperature of the reactor was raised with a ramp of 3 °C/min using a HT60 controller (Horst). The temperature of the mesh inside of the reactor was recorded using a K-thermocouple and a digital thermometer (Greisinger GMH3250). An FTIR spectrometer (Bruker VERTEX 70) with spectral resolution of 4 cm^{-1} was used to analyze the outlet gases. Details of the data treatment were described elsewhere [26]. To exclude the effect of the mesh grid, blank experiments were performed using a reactor filled with non-coated mesh (NCM) of stainless steel.

3. Results and discussion

3.1. Phase identification

The phase of the deposited cobalt oxide thin films with a thickness of ~300 nm was analyzed by using XRD, FTIR and Raman scattering spectroscopy, as displayed in Fig. 2. Fig. 2a shows the XRD patterns of the deposited oxide thin films. Six prominent peaks at 31.28°, 36.82°, 38.41°, 56.62°, 59.21° and 65.23° are observed. These diffraction peaks can be readily indexed to the (220), (311), (222), (422), (511) and (440) plane of a pure cubic structure of Co_3O_4 with the lattice constant a ≈ 8.10 Å, well consistent with the standard PDF database of cobalt spinel (JCPDS No. 74-1656). The crystallite size (D) and the microstrain (ε) were estimated to be 42 ± 5 nm and 0.06% from the XRD patterns by using the Scherrer relation $D = 0.9\lambda/\beta \cos\theta$ and $\varepsilon = \beta/2\cot\theta$ on the (311) plane with the strongest intensity, where λ represents the wavelength of the X-ray radiation and β is the diffraction broadening of the peak at half-height for Bragg's angle θ. The diffraction peaks of the samples are sharp and narrow, indicative of a relatively good crystallinity. Compared to sizes of 50 and 100 nm for Co_3O_4 prepared by water-controlled precipitation process [34], CVD made Co_3O_4 shows relatively smaller size. Assuming that samples with smaller particle size possess bigger specific area, PSE-CVD made Co_3O_4 is expected to expose a large contact area to the reactants and display excellent catalytic performance in the present work.

FTIR spectrum of Co_3O_4 spinel (Fig. 2b) presents two distinctive and significant absorption bands peaking at 544 and 649 cm^{-1}. The first absorption band ν_1 at 544 cm^{-1} was assigned to the stretching vibration mode of Co—O bond [35]. The second bands ν_2 at 649 cm^{-1} was attributed to the bridging vibration mode of O—Co—O bond [36]. The stretching and bridging vibrations are associated with the Co^{3+}-O-Co^{3+} and Co^{2+}-O-Co^{3+} distributions in the spinel lattice, respectively. Raman spectroscopy was performed to further confirm the phase of the prepared Co_3O_4 films. As depicted in Fig. 2c, the Raman spectrum shows four bands at 485, 521, 623 and 686 cm^{-1}, which correspond respectively to E_g, F^1_{2g}, F^2_{2g} and A_{1g} modes of crystalline Co_3O_4, in excellent agreement with previously reported values in the literature [37]. In all, the XRD, FTIR and Raman results show that the prepared samples are pure Co_3O_4.

3.2. Morphology

To study the morphology and microstructure of the as-synthesized spinel Co_3O_4 thin film, SEM was performed. Fig. 3 represents typical