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Porous Ni–Co bimetal oxides nanosheets and catalytic properties for CO oxidation

Ye Gou, Xin Liang [*], Biaohua Chen

Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

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ABSTRACT

Series of Ni–Co bimetal hydroxides nanosheets have been obtained by tuning the molar ratio of cobalt and nickel in an oleylamine assisted synthetic system. Porous Ni–Co bimetal oxide nanosheets with tunable compositions have been obtained by directly thermal decomposition of corresponding hydroxides at 400 °C. The physicochemical properties of these Ni–Co bimetal oxides have been fully characterized and analyzed. Compared with pure NiO and Co_3O_4, the bimetal oxides show better catalytic performance for CO oxidation. By increasing Co content in the reaction system, the as-prepared Ni–Co bimetal oxides system can be classified into three different crystal structure types. When Co percentage is less than 20%, the samples display identical cubic crystal structure with pure NiO and possess higher surface area and better catalytic performance than others. As Co percentage in the system is between 40% and 60%, the samples tend to form a stable lamellar structure of $NiCo_2O_4$. Co_3O_4 based crystal structure type of Ni–Co bimetal oxides is observed when Co percentage is more than 80%.

1. Introduction

Low-temperature oxidation of CO, perhaps the most extensively studied reaction in the history of heterogeneous catalysis, is becoming increasingly important in the context of cleaning air and lowering automotive emissions, as well as a model catalysis reaction [1,2]. Noble metal catalysts, such as supported Pd and Pt catalysts, exhibit excellent performances at low temperature for CO catalytic oxidation and have been studied for many years. However, given the restricted amount of noble metals on the earth, the development of non-noble metal catalysts as the low cost alternatives would be of great interest [3].

Transition metal oxides catalysts, such as NiO, CuO, Co_3O_4, Fe_2O_3 and Mn_2O_3, have attracted a lot of researches as the most potentially low cost alternatives to Pd and Pt catalysts for CO catalytic oxidation. Among these non-noble metal oxides, Co_3O_4 has shown good catalytic activity for CO oxidation. Sheng has reported that Co_3O_4 nanorods with predominantly exposed {1 1 0} faces can catalyze CO oxidation at −77 °C [4]. NiO is another important inorganic material which has been widely applied in the field of industrial catalysis. There have been a variety of reports about the synthesis of different NiO nanostructures including porous nano/microspheres [5], nanoflowers [6], nanosheets [7], and nanofibers. In our previous work, a facile synthetic approach for NiO nanosheets have been reported and their catalytic activities for CO oxidation have been analyzed [8,9].

Compared with single phase of metal oxides, mixed metal oxides can provide a more effective way in the exploration of catalysts with enhanced performance. Ni–Co bimetal oxides have formed a large family of inorganic materials which have potential applications in the fields of supercapacitors, electrocatalysis and environmental catalysis. It has been reported that nickel cobaltite possesses an at least two orders of magnitude higher electronic conductivity and a better electrochemical activity than NiO and Co_3O_4 [10,11]. Ni–Co bimetal oxides have also been applied as catalysts for various chemical reactions such as dehydrogenation of hydrocarbons [12], decomposition of alcohols and hydrogen peroxide [13], oxidation of various compounds such as CO [14], selective oxidation of styrene etc. [15]. It is well known that Ni^{2+} and Co^{2+} can form homogeneous solid solutions at all proportions in the crystal structure because they have very similar unit cell structures. At appropriate composition, Ni–Co bimetal oxides can form spinel nickel cobaltite ($NiCo_2O_4$). There are several synthetic methods for Ni–Co bimetal oxides, such as coprecipitation of oxalates, hydroxide carbonates, spray pyrolysis and metal hydroxides [16–20]. Among these methods, metal hydroxides prepared from solvothermal approach offer a convenient and easy way for the preparation of mixed metal oxides with different crystal structures by tuning the molar percent of $Ni^{2+}$and Co^{2+}.

In this paper, we fully investigate the influence of Co content in the Ni–Co bimetal oxide catalysts on their physicochemical properties, such as the catalytic activity, the morphology, the textural

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[*] Corresponding author. Tel.: +86 10 64412054.
E-mail address: liangxin@mail.buct.edu.cn (X. Liang).

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structure and the surface state. A strong synergistic catalysis effect has been demonstrated in the Ni–Co bimetal oxides catalysts for CO oxidation. A brief explanation has been proposed to understand the reaction by considering the Ni–Co bimetal oxides catalysts as three different types. These results can be supportive for developing bimetal oxides catalysts.

2. Materials and methods

2.1. Materials

All the chemicals were of analytical grade and used as received without further purification. $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, oleylamine and absolute ethanol were supplied by Beijing Chemical Reagent Company.

2.2. Synthesis of Ni–Co bimetal oxides

In a typical synthesis, 0.291 g mixture of $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 10 mL ethanol and 10 mL H_2O to form solution A. 2 mL oleylamine was added to 10 mL ethanol to form solution B. Solution A was mixed with solution B under strong agitation. Then, the mixture was transfered to a 50 mL autoclave. The autoclave was sealed and heated at 180 °C for 12 h. As the autoclave cooled to room temperature naturally, the supernatant solution was poured out, and the samples could be directly collected from the bottom of the autoclave. The samples were washed by dispersing in 10 mL of cyclohexane and precipitating by the addition of 10 mL of ethanol. The precipitate was dried at 80 °C to get Ni–Co bimetal hydroxides. Then, the above hydroxides were calcined in a muffle furnace at 400 °C for 2 h to obtain the final Ni–Co bimetal oxides. The temperature ramping rate was 2 °C min^{-1}.

2.3. Characterization

Powder X-ray powder diffraction (XRD) was performed on a Bruker D8-Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15{,}406$ nm). The morphology and size of the samples were characterized on a scanning electron microscope (SEM, SUPRA 55/55VP). Nitrogen adsorption and desorption isotherms were obtained at −200 °C using a Quantachrome QUADRASORB SI apparatus. The chemical composition was confirmed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 Xi). TPR-H_2 (temperature-programmed reduction with H_2) was carried out in a quartz tube reactor, and a 50 mg sample was used for each measurement. Prior to the reduction, the sample was pretreated in an O_2–He (9.98% O_2 by volume) stream at 500 °C for 30 min and in N_2 stream at 500 °C for another 30 min and then cooled to room temperature. After that, a H_2–He mixture (5.25% H_2 by volume) was switched on, and the temperature ramp was 10 °C min^{-1} from 60 to 800 °C. The catalytic activities of Ni–Co bimetal oxides for a $CO + O_2$ reaction were performed under a steady-state condition, involving a feed stream with a fixed composition of CO 2%, O_2 20% and Ar 78% by volume, where Ar was used as diluent. A quartz tube was used as a reactor, and 200 mg sample was used for each test. The reaction was carried out with the same space velocity of 10 mL g^{-1} min^{-1}. Varian GC3800 was used for analyzing the products.

3. Results and discussion

Ni–Co bimetal hydroxides nanosheets could be obtained by using $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ as starting materials in the presence of oleylamine through solvethermal treatment. Annealed at 400 °C for 2 h, the precursors were converted to Ni–Co bimetal oxides. The phase and morphology transformation of Ni–Co–O bimetal oxides were in-depth investigated at the whole range from pure NiO to pure Co_3O_4. XRD analysis of as-prepared powder samples demonstrated that the Ni–Co–O bi-metal oxides system could be classified into three different crystal structure types along with the increasing of Co content: NiO based type, $NiCo_2O_4$ based type, and Co_3O_4 based type.

As shown in Fig. 1a, XRD pattern of as-prepared NiO sample can be well indexed to the pure phase of face-centered cubic NiO (JCPDS No. 78-0429) [21]. The X-ray diffractive peaks of Ni–Co bimetal oxides with the percent of Co^{2+} at 5%, 10% and 20% are almost identical to those of pure NiO, implying that the Co atoms are doped into the crystal structure of NiO. The $NiCo_2O_4$ based crystal structure type can be observed from Ni–Co–O samples with the increasing of Co content. Fig. 1b shows the corresponding XRD patterns for Ni–Co–O bi-metal oxides with Co content 40%, 50% and 60%. The typical X-ray diffractive peaks located at 31.14° and 36.64° can be well attributed to the cubic lattice of Fd3m space group of $NiCo_2O_4$ spinel structure (JCPDS No. 20-0781) [22]. Co_3O_4 based crystal structure type is observed as Co percentage reaches 80%. XRD patterns of the samples with Co percent 80%

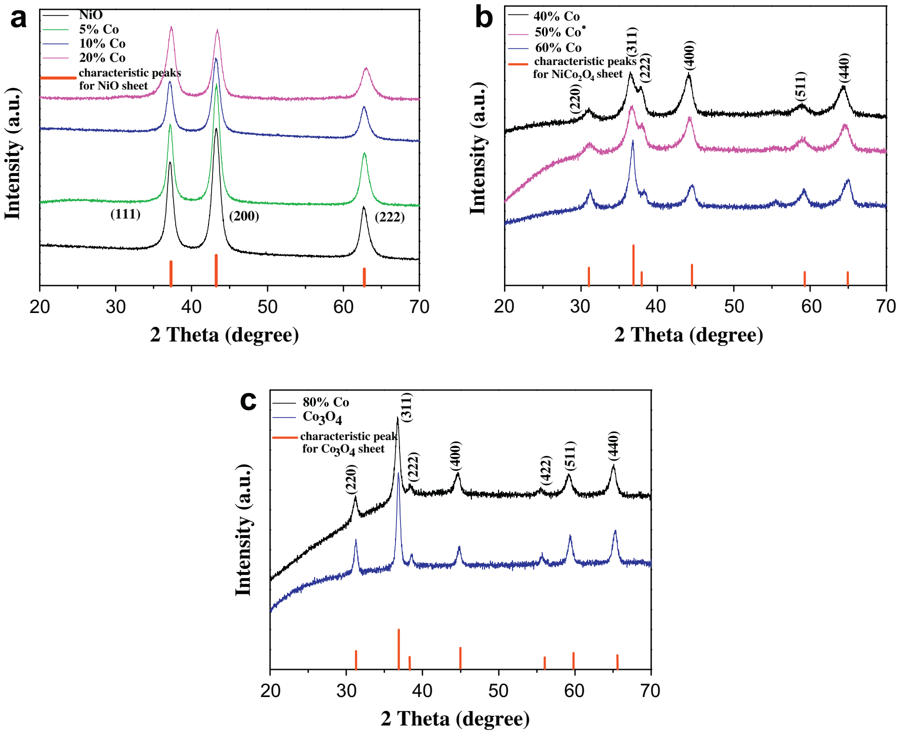

Fig. 1. XRD patterns of (a) pure NiO and samples with percentage of Co^{2+} at 5%, 10% and 20%; (b) 40%, 50% and 60%; (c) 80% and pure Co_3O_4.