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Pure and Ni-substituted Co₃O₄ spinel catalysts for direct N₂O decomposition

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A B S T R A C T

A series of $Ni_xCo_{1-x}Co_2O_4$ ($0 \le x \le 1$) spinel catalysts were prepared by the co-precipitation method and used for direct N₂O decomposition. The decomposition pathway of the parent precipitates was characterized by thermal analysis. The catalysts were calcined at 500 °C for 3 h and characterized by powder X-ray diffraction, Fourier transform infrared, and N₂ adsorption-desorption. Nickel cobaltite spinel was formed in the solid state reaction between NiO and Co₃O₄. The N₂O decomposition measurement revealed significant increase in the activity of Co₃O₄ spinel oxide catalyst with the partial replacement of Co^{2+} by Ni^{2+}. The activity of this series of catalysts was controlled by the degree of Co^{2+} substitution by Ni^{2+}, spinel crystallite size, catalyst surface area, presence of residual K^+, and calcination temperature.

1. Introduction

Nitrous oxide (N₂O) is a contributor to the destruction of ozone in the stratosphere and a strong greenhouse gas [1,2]. It is emitted from both natural and anthropogenic sources. Anthropogenic N₂O emissions come mainly from chemical industries, e.g., the production of nitric acid [2,3] and organic synthesis that use the nitric acid oxidation process, such as the production of adipic acid from the oxidation of cyclohexanol-cyclohexanone mixture [4]. The catalytic removal of N₂O from anthropogenic sources is one possible solution to protect our global environment. A wide variety of catalysts have been reported for the catalytic decomposition of N₂O to N₂ and O₂. These catalysts include noble metals [5,6], metal oxides [7,8], supported oxides [9,10], ion exchanged zeolites [11–13], hexaferrites [14], perovskites [15,16], hydrotalcites [17,18], and spinels [19–22].

Spinel oxides are a class of complex oxides with the general chemical formulas of AB₂O₄ (A ions are divalent cations occu-pying tetrahedral sites and B ions are trivalent cations that occupy octahedral sites). Cobalt oxide spinel (Co₃O₄) is receiving considerable interest [23,24]. The A component of the Co₃O₄ spinel is often partially substituted with another divalent metal such as Mg, Ni, or Zn [19,20,22] to create special properties for applications [25–27]. It was reported that the catalytic activity of Co₃O₄ spinel is affected by the preparation method, degree of Co^{2+} (A component) substitution, degree of spinel inversion and the presence of alkali dopants [19,20,22,28]. Generally, Co₃O₄-based spinels can decompose N₂O completely at low temperatures (below 500 °C) [19,20]. Their activity decrease slightly with O₂ and/or H₂O in the reactor feed [19,20]. The presence of many dopants like Zr^{4+}, Ce^{4+}, Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, or Ba^{2+} enhances the Co₃O₄-based spinel catalysts for the decomposition of N₂O [22,29–31]. There has been only one paper on the N₂O decomposition activity over Ni substituted Co₃O₄ [19], but this lacked information regarding the influence of calcination temperature and the role of the different parameters on the N₂O decomposition activity. In this pa-

per, a series of nickel cobaltite with the general formula $Ni_xCo_{1-x}Co_2O_4$ were prepared by the co-precipitation method and characterized by various techniques. The performance of the catalysts for N_2O decomposition was discussed using the degree of Co^{2+} substitution by Ni^{2+}, spinel crystallite size, catalyst surface area, presence of residual K^+, and calcination temperature.

2. Experimental

2.1. Catalysts preparation

A catalyst series with the general formula $Ni_xCo_{1-x}Co_2O_4$ (x = 0.00, 0.25, 0.50, 0.75, and 1.00) were prepared by a co-precipitation method similar to that reported by Xue et al. [29]. Briefly, an aqueous solution of K_2CO_3 (2 mol/L) was added dropwise into an aqueous solution containing stoichiometric amounts of cobalt and nickel acetate at room temperature under mechanical stirring until pH = 9.1–9.4 was reached. The slurry was stirred for 30 min and aged for 3 h. The precipitate was filtered and washed with distilled water several times. Evaporation of excess water in the precipitate cake was done by drying in an oven at 100 °C overnight. Based on thermal analysis results (vide infra), all the dried precipitates were calcined at 500 °C for 3 h. In addition, based on the N_2O decomposition activity measurement, the precipitate with x = 0.75 was calcined at 750 and 1000 °C for 3 h.

2.2. Catalysts characterization

Thermogravimetry (TGA) and differential thermal analysis (DTA) curves were recorded using a Shimadzu DTG-60 instrument. 10 mg of the dried precipitate was placed in a platinum crucible and heated at a heating rate of 10 °C/min in flowing air (40 ml/min). X-ray diffraction (XRD) patterns were recorded using a Philips X-ray diffractometer (Type PW 2103/00) employing Cu K_α radiation (λ = 0.15418 nm). Fourier transform infrared (FT-IR) spectra were obtained using the KBr disk technique on a Thermo-Nicolet-6700 FT-IR spectrophotometer. N_2 adsorption-desorption isotherms were measured on a NOVA 3200 automated gas adsorption system (Quantachrome) at liquid nitrogen temperature. The K^+ concentration in the dried samples was measured by atomic absorption using a 210 VGP atomic absorption spectrophotometer.

2.3. Catalytic activity measurements

Catalytic performance was evaluated with an isothermal plug flow reactor. The procedure was similar to that reported previously [6,22,30]. Each catalytic run was conducted using 500 mg of the catalyst and a gas mixture of N_2O (500 ppm) and N_2 as a balance gas at a flow rate of 200 ml/min. Before each run, the catalyst sample was heated at 500 °C for 1 h in a flow of N_2, and then cooled to 150 °C and the reactant was introduced. The exit concentrations were monitored by a magnetic oxygen analyzer (ABB, AO2020-Magnos 106) and a non-dispersive infrared analyzer (ABB, AO2020-Uras 14) for N_2O and NO. The

steady state was reached after about 1 h. Preliminary experiments for the decomposition of N_2O over all the catalysts showed the absence of NO in the exit gas.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Thermal analysis

The TGA thermogram, shown in Fig. 1(a), has two regions. The first region from ambient temperature to 400 °C was accompanied by two weight-loss steps. The first step has a maximum at 61 °C which was attributed to the dehydration of the carbonates. The second step was not a simple one. It was a composite step with maxima at 247 and 296 °C (DTG curve). The TGA-DTA thermogram of the cobalt carbonate parent (not shown) revealed that cobalt carbonate decomposed in three steps, with peaks at 73 (endothermic), 263 (exothermic), and 930 °C (endothermic). These steps were attributed to dehydration of the parent, decomposition of the anhydrous cobalt carbonate to Co_3O_4 spinel and the thermal reduction of Co_3O_4 spinel to CoO, respectively. Mansour reported on the thermal decomposition of nickel carbonate that it decomposed by two endothermic steps at 115 and 310 °C, which were attributed to the dehydration of the salt and decomposition of the anhydrous salt leading to the formation of NiO, respectively [32]. Accordingly, the second composite step with maxima at 247 and 296 °C (Fig. 1(a)) was assigned to the consecutive decomposition of cobalt and nickel carbonate. As shown in Fig. 1(b), one can observe three thermal events from ambient temperature to 400 °C. The first is endothermic with the maximum at 73 °C, and can be related to the dehydration process. The second peak (exothermic) with the maximum at 224 °C was attributed to the oxidation of $Co^{2+} \rightarrow Co^{3+}$ that accompanied the thermal decomposition of cobalt carbonate. The third peak at 309 °C was assigned to: (1) the solid state interaction between NiO and Co_3O_4 leading to the formation of nickel cobaltite spinel and (2) crys-
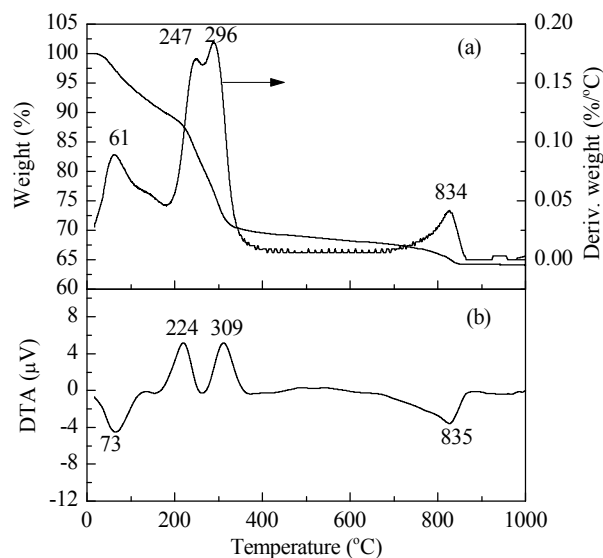
Fig. 1. TGA-DTG (a) and DTA (b) curves obtained on heating the Ni/Co precipitate mixture with x = 0.75.