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Article

Pure and Ni-substituted Co_3O_4 spinel catalysts for direct N_2O decomposition

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ABSTRACT

A series of $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ ($0 \leq x \leq 1$) spinel catalysts were prepared by the co-precipitation method and used for direct N_2O 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 N_2 adsorption-desorption. Nickel cobaltite spinel was formed in the solid state reaction between NiO and Co_3O_4 . The N_2O decomposition measurement revealed significant increase in the activity of Co_3O_4 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.

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1. Introduction

Nitrous oxide (N_2O) 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 N_2O 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 N_2O 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 N_2O to N_2 and O_2 . 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 AB_2O_4 (A ions are divalent cations occu-

pying tetrahedral sites and B ions are trivalent cations that occupy octahedral sites). Cobalt oxide spinel (Co_3O_4) is receiving considerable interest [23,24]. The A component of the Co_3O_4 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 Co_3O_4 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, Co_3O_4 -based spinels can decompose N_2O completely at low temperatures (below 500 °C) [19,20]. Their activity decrease slightly with O_2 and/or H_2O 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 Co_3O_4 -based spinel catalysts for the decomposition of N_2O [22,29–31]. There has been only one paper on the N_2O decomposition activity over Ni substituted Co_3O_4 [19], but this lacked information regarding the influence of calcination temperature and the role of the different parameters on the N_2O decomposition activity. In this pa-

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per, a series of nickel cobaltite with the general formula $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ 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 $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ ($x = 0.00, 0.25, 0.50, 0.75$, 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 $\text{pH} = 9.1\text{--}9.4$ 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 $10^\circ\text{C}/\text{min}$ in flowing air (40 ml/min). X-ray diffraction (XRD) patterns were recorded using a Philips X-ray diffractometer (Type PW 2103/00) employing $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). 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 $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ 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 $x = 0.75$.

tallization of the spinel obtained. In the second temperature range from 400 to 1000 °C, it displays one decomposition step with a maximum at 834 °C (Fig. 1(a)), which was endothermic (Fig. 1(b)). Since Co_3O_4 spinel oxide undergoes thermal reduction at temperatures as high as 930 °C [30], this step can be assigned to the thermal decomposition of nickel cobaltite. This suggestion is in good agreement with the results of Chi et al. [33] who reported that the thermal decomposition of NiCo_2O_4 spinel was at 800 °C.

3.1.2. XRD result

XRD patterns of the nickel/cobalt precipitate mixtures calcined at 500 °C are shown in Fig. 2. The pure cobalt (oxide) calcined at 500 °C showed peaks at $2\theta = 18.88^\circ, 31.07^\circ, 36.72^\circ, 38.47^\circ, 44.07^\circ, 55.58^\circ, 59.35^\circ, 65.16^\circ, 74.01^\circ, 77.19^\circ$, and 78.36° . These peaks matched well those of Co_3O_4 (JCPDS 78-1969). $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Co}_2\text{O}_4$ and $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Co}_2\text{O}_4$ samples showed the same peaks and no other phase was detected. These diffractograms matched the standard card of NiCo_2O_4 (JCPDS 73-1702) reported by other research groups [33–35]. From the absence of peaks due to NiO, one can state that Ni preferentially formed the nickel cobaltite spinel for the samples with $x = 0.25$ and 0.50 . For the samples with $x = 0.75$ and 1.0 , a further increase in the Ni content in the spinel mixture was accompanied by new peaks at $2\theta = 43.25^\circ$ and 62.84° , which were due to NiO (JCPDS 78-0643). Accordingly, one can conclude that in the utilized procedure, the formation of NiCo_2O_4 was accompanied by the formation of a trace amount of NiO as impurity. This was in good agreement with other research groups [33–35]. Lapham et al. [34] prepared NiCo_2O_4 by thermal decomposition of the metal nitrates and pointed out that the NiO phase initially appeared in the sample fired at 400 °C and it co-existed with NiCo_2O_4 in larger quantities up to the firing temperature of 600 °C. They concluded that Ni preferentially formed the spinel NiCo_2O_4 below 350 °C but gave a separate NiO phase above 400 °C. Chi et al. [33] have detected NiCo_2O_4 as a pure phase in the samples prepared by the co-precipitation method using metal nitrate and NaOH and a pretreatment temperature range of 200–350 °C. They also observed the peaks due to the NiO impurity in their XRD diffractograms for the sample calcined at 400 °C. Cabo et al. [35] have also detected the NiO impurity in

Fig. 2. XRD patterns of the $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts calcined at 500 °C.

Table 1

K^+ concentration in co-precipitated samples and crystallites size of the $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ mixtures calcined at 500 °C.

x value	K^+ concentration (mg/g)	Crystallite size (nm)
0.00	0.18	28.2
0.25	18.0	23.0
0.50	8.3	14.7
0.75	6.6	11.5
1.00	4.2	13.4

their NiCo_2O_4 spinel calcined at 550 °C. The broadening of the diffraction lines with increasing x value (Fig. 2) may signify the nano-scale characteristic of the component crystallites. The crystallite size of the spinel phase for the 500 °C calcined catalyst was calculated using the Scherrer equation [6]. The values are listed in Table 1. It is evident that increasing the Ni content in the samples led to a crystallite size decrease until $x = 0.75$, and then there was a slight increase in the NiCo_2O_4 catalyst.

The XRD patterns of the Ni/Co mixture with $x = 0.75$ calcined at different temperatures are depicted in Fig. 3. Raising the calcination temperature to 750 °C was accompanied by an intensity increase of the peaks due to the spinel phase as well as those due to NiO. Increasing the calcination temperature to 1000 °C gave a marked decrease of the peaks due to the spinel phase. Meanwhile, the intensity of the peaks attributable to NiO at $2\theta = 43.25^\circ, 62.6^\circ$, and 75.1° disappeared. In addition, new peaks emerged at $2\theta = 42.6^\circ, 61.9^\circ, 74.2^\circ$, and 78.1° . These peaks match those of CoO (JCPDS 75-0418). The diffractogram obtained for the sample calcined at 1000 °C matched that reported by Fujishiro et al. [36] for NiCo_2O_4 calcined at 900 °C, which suggested the formation of the rock salt $(\text{Ni},\text{Co})\text{O}$ as a result of the decomposition of NiCo_2O_4 .

3.1.3. FT-IR results

Figure 4 shows the FT-IR spectra of $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts calcined at 500 °C for 3 h. All the spectra have two strong absorption at 564 and 655 cm^{-1} , which were assigned to the ν_1 and ν_2 stretching vibrations of the metal-oxygen bond in cobalt spinel oxide [30,31]. Moreover, a weak absorption was observed at 450 cm^{-1} for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ and NiCo_2O_4 catalysts. This absorption is characteristic of NiO [32]. This obser-

Fig. 3. XRD patterns of $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ catalysts prepared by co-precipitation and calcined at 500 (1), 750 (2), and 1000 °C (3).

Fig. 4. FT-IR spectra of $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ calcined at 500 °C.

vation is in good agreement with the XRD results (Fig. 2). Figure 4 revealed the presence of another set of absorption at 835, 1008, and 1384–1462 cm^{-1} , which can be assigned to the different vibration modes of the carbonate anion [30,31]. It is worth mentioning that the intensity of the carbonate absorption bands was higher for the Ni-containing catalysts compared to Co_3O_4 . This finding agreed with the measured residual K^+ concentrations, showing the presence of K_2CO_3 in the samples with higher Ni content (Table 1). For the same series of catalysts, the observed absorption spectra at 1630 and 3000–3600 cm^{-1} were assigned to the H–O–H bending and O–H stretching mode of adsorbed water, respectively [31,37].

The FT-IR spectra of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ catalyst calcined at different temperatures (Fig. 5) showed that the catalyst calcined at 750 °C had a spectrum similar to that at 500 °C. This suggested that they had the same composition. Raising the calcination temperature to 1000 °C, the ν_1 stretching mode appeared only as a shoulder at 561 cm^{-1} while the ν_2 mode existed as a weak absorption at 657 cm^{-1} . Moreover, strong absorption was observed below 600 cm^{-1} . This absorption was in the IR spectral region expected of CoO [38]. Furthermore, two ab-

Fig. 5. FT-IR spectra of $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ catalysts prepared by co-precipitation and calcined at 500 (1), 750 (2), and 1000 °C (3).

sorption peaks appeared at 785 and 1047 cm^{-1} , which were attributed to the newly formed $(\text{Ni},\text{Co})\text{O}$ phase suggested by the XRD results.

3.1.4. Textural analysis

N_2 adsorption-desorption isotherms of $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts calcined at 500 °C are shown in Fig. 6(a). Adsorption occurred at very low relative pressure suggesting a strong interaction between the pore wall and adsorbate. In this case, pore filling took place without capillary condensation at $p/p_0 < 0.3$. The isotherms were Type I [39] at low pressure and Type II at higher p/p_0 values, especially for the samples having high Ni content. This feature indicated the presence of micropores with some mesopores [13]. It showed that the desorption branch approximately overlapped the adsorption branch. The specific surface areas were obtained by BET equation and are tabulated in Table 2. The introduction of Ni with $x = 0.25$ to Co_3O_4 led to a noticeable S_{BET} decrease. A further increase in x to 0.50 was accompanied by a sharp S_{BET} increase, and then approximately constant values were obtained for the catalysts with $x = 0.75$ and 1.00. An additional set of surface areas (S_t) were deter-

Fig. 6. N_2 adsorption-desorption isotherms (a) and V_a - t plots (b) of the $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts calcined at 500 °C.

mined from the volume-thickness curves (V_a - t plots). These curves were constructed using the appropriate standard t -curves [39], and the results are shown in Fig. 6(b) and Table 2. It is seen that Co_3O_4 has mainly narrow pores as indicated by the downward deviation of its V_a - t plot. This downward deviation with a little upward deviation indicated the presence of larger pores. The introduction of Ni into Co_3O_4 spinel gave V_a - t plots characterized by the presence of a positive trend (upward) followed by a negative one (downward), which indicated the coexistence of both micro- and mesopores for this series of catalysts. Meanwhile, the S_t values showed a slight decrease for the catalyst with $x = 0.25$ as compared to the one without Ni. The further addition of Ni to $x = 1.00$ gave higher S_t values compared to that of Co_3O_4 .

N_2 adsorption-desorption isotherms for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ catalyst (calcined at 750 and 1000 °C not shown) indicated that the Type I isotherm became more pronounced with a calcination temperature increase and the desorption branch basically overlapped the adsorption one. The textural data are listed in Table 3. The S_{BET} values for the 750 and 1000 °C calcined catalysts were 7.9 and 0.4 m^2/g , respectively. These values were much lower than that of the sample calcined at 500 °C (40.72 m^2/g). Clearly, the external surface area, micropore surface area, and micropore volume obtained from the t -method for this series of catalysts decreased as the calcination temperature increased. Moreover, the total pore volume decreased while the average pore diameter increased. These trends in the textural parameters can be attributed to sintering and densification, which increased with the calcination temperature.

3.2. Catalytic activity

3.2.1. Effect of $\text{Ni}^{2+}/\text{Co}^{2+}$ ratio

Figure 7 depicts the conversion of N_2O versus the x value in $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts calcined at 500 °C under different reaction temperatures. The reaction started at 250 and 200 °C for Co_3O_4 and $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Co}_2\text{O}_4$ samples, respectively, and at 150 °C for the other catalysts. The activity increased with increasing reaction temperature over all the catalysts, and reached 100% conversion at 475–500 °C over the catalysts with $x = 0.50$, 0.75, and 1.00. Preliminary experiments of N_2O conversion over pure

Fig. 7. N_2O conversion versus x value in $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts calcined at 500 °C under different reaction temperatures. (1) 125 °C; (2) 150 °C; (3) 175 °C; (4) 200 °C; (5) 225 °C; (6) 250 °C; (7) 275 °C; (8) 300 °C; (9) 325 °C; (10) 350 °C; (11) 375 °C; (12) 400 °C; (13) 425 °C; (14) 450 °C; (15) 475 °C; (16) 500 °C. Reaction conditions: 500 ppm N_2O in N_2 , 200 cm^3/min , 0.5 g.

NiO ($S_{\text{BET}} = 19 \text{ m}^2/\text{g}$) prepared by co-precipitation and calcined at 500 °C gave 42% conversion at 500 °C. Thus, the results indicated that N_2O conversion was much enhanced by the addition of Ni to Co_3O_4 spinel catalysts. In other words, the mixed NiO - Co_3O_4 catalysts calcined at 500 °C were significantly more active than the pure NiO and Co_3O_4 catalysts. This enhancement is usually referred to as a synergistic effect. Yan et al. [19] have investigated N_2O decomposition over a series of $\text{M}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ ($\text{M} = \text{Mg}$ and Ni ; $x = 0.00$ – 0.99) spinel catalysts prepared by co-precipitation, and the results showed that the catalytic activity depended on the degree of Co^{2+} substitution by Mg^{2+} or Ni^{2+} . The highest activity was observed over the $\text{Mg}_{0.54}\text{Co}_{0.46}\text{Co}_2\text{O}_4$ and $\text{Ni}_{0.74}\text{Co}_{0.26}\text{Co}_2\text{O}_4$ catalysts. The characterization results showed that pure Co_3O_4 underwent thermal reduction at a high temperature, which was indicated by the endothermic peak at 930 °C [30]. The addition of Ni ($x = 0.75$) led to a marked decrease of this peak temperature to 835 °C

Table 2

Textural data from the N_2 adsorption-desorption isotherms of the $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts calcined at 500 °C.

x value	S_{BET} (m^2/g)	S_t (m^2/g)	Micropore surface area (m^2/g)	Total pore volume (10^{-2} ml/g)	Micropore volume (10^{-2} ml/g)	Average pore diameter (nm)
0.00	16.42	14.19	2.24	1.999	1.09	4.9
0.25	11.5	9.44	2.01	1.611	1.047	5.6
0.50	39.9	26.89	12.96	3.971	6.100	4.0
0.75	40.72	28.53	12.19	3.995	5.844	3.9
1.00	40.32	31.63	8.68	4.148	4.253	4.1

Table 3

Textural properties of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ catalysts calcined at different temperatures.

Calcination temperature (°C)	S_{BET} (m^2/g)	S_t (m^2/g)	Micropore surface area (m^2/g)	Total pore volume (10^{-2} ml/g)	Micropore volume (10^{-2} ml/g)	Average pore diameter (nm)
500	40.72	28.53	12.19	3.995	5.844	3.9
750	7.92	6.18	1.77	1.099	0.906	5.5
1000	0.43	0.668	0.00	0.103	0.000	9.7

(Fig. 1(b)). In other words, the presence of Ni^{2+} enhanced the thermal reduction of the Co^{3+} . Recently, it was reported that the role of Mg^{2+} in the increase of N_2O decomposition activity over a series of $\text{Mg}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts was to enhance the $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ reduction, i.e., regeneration of the Co^{2+} ions that are required for initiating N_2O adsorption and its subsequent decomposition [22]. Based on this idea, it is plausible to suggest that the role of the added Ni^{2+} ions was also to enhance the $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ reduction and thus increase the catalytic activity. Also, it is worth mentioning that the presence of the residual K^+ would also enhance the cobalt redox process. On comparing our results with those of Sundararajan et al. [40] for N_2O decomposition over NiCo_2O_4 prepared by the thermal decomposition of the corresponding nitrates, our catalysts showed better performance. This could be attributed to the additional factor of the presence of residual K^+ . In this context, it should be mentioned that the $\text{Ni}_{0.50}\text{Co}_{0.50}\text{Co}_2\text{O}_4$, $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$, and NiCo_2O_4 catalysts contained lower K^+ concentrations compared to the $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Co}_2\text{O}_4$ sample (Table 1). This, in turn, suggested that the samples having x values in the range 0.50 to 1.00 possessed the optimal balance between the K^+ concentration and Ni content required for the highest activity. Yan et al. [19] have investigated N_2O decomposition over $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ spinel oxide catalysts and the results indicated that the activity depended on the degree of Co^{2+} substitution, and the highest activity was exhibited by the catalysts having $x = 0.36, 0.55$, and 0.75 . Using O_2 -TPD, they observed that O_2 desorption, i.e., catalyst reducibility was facilitated by the presence of Ni^{2+} in the spinel [19]. In this work, it was also shown that the addition of Ni^{2+} with $x = 0.50, 0.75$, and 1.00 to Co_3O_4 increased the specific surface area from 16.4 to $40 \text{ m}^2/\text{g}$ (Table 2). Therefore, we can also attribute the positive effect of adding NiO in promoting Co_3O_4 activity as due to its role in increasing the catalyst surface area. Xue et al. [29] have demonstrated that the addition of CeO_2 to Co_3O_4 led to an improvement in the activity for N_2O decomposition. The catalyst was the most active when the molar ratio of Ce/Co was 0.05 . Complete N_2O conversion was obtained with the $\text{Co}/\text{Ce} = 0.05$ catalyst below 400°C even in the presence of O_2 , H_2O , or NO . Based on various physico-chemical characterization, these authors proposed that the addition of CeO_2 increased the surface area of Co_3O_4 , and then facilitated the reduction of Co^{3+} to Co^{2+} by facilitating the desorption of adsorbed oxygen species, which is the rate determining step in N_2O decomposition over the cobalt spinel catalyst.

In the literature, many authors have correlated the N_2O decomposition activity with the crystallite size of the catalyst. Recently, we reported an inverse relationship between N_2O decomposition activity and the Co_3O_4 crystallite size of SrCO_3 - and BaCO_3 - Co_3O_4 catalysts [30]. Over $\text{Ag}/\text{Fe}_x\text{Al}_{2-x}\text{O}_3$ catalysts, it was demonstrated that N_2O decomposition reactivity increased with decreasing Ag crystallite size [6]. Accordingly, the higher N_2O decomposition reactivity over the catalysts with $x = 0.50, 0.75$, and 1.00 can be related to their smaller spinel crystallite size as shown in Table 1. Accordingly, we conclude that the enhancement of N_2O decomposition reactivity over $\text{Ni}_x\text{Co}_{1-x}\text{Co}_2\text{O}_4$ catalysts having $x \geq 0.25$ was due to the following factors: (1) increasing amounts of Ni^{2+} , which enhanced the

thermal reduction of Co^{3+} ions, (2) presence of residual K^+ , (3) higher surface area of the nickel-containing spinels, and (4) decrease in crystallite size.

3.2.2. Effect of calcination temperature

In the previous section, it was discussed that the highest N_2O decomposition reactivity was exhibited over the $\text{Ni}_{0.50}\text{Co}_{0.50}\text{Co}_2\text{O}_4$, $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$, and NiCo_2O_4 catalysts. Accordingly, we decided to check the influence of calcination temperature on the activity of $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$. Figure 8 shows the dependence of N_2O conversion on reaction temperature over the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ catalyst calcined at different temperatures. It is obvious that raising the calcination temperature from 500 to 750°C led to a noticeable decrease in the catalytic activity while increasing the calcination temperature to 1000°C resulted in the quenching of the catalytic activity. For example, the N_2O decomposition conversion (reaction at 500°C) was decreased from 100% to 96.5% and 2.2% on raising the calcination temperature from 500 to 750 and 1000°C , respectively. The T_{50} (temperature of 50% conversion) showed a 125°C increase on increasing the calcination temperature from 500 to 750°C . The characterization results showed that increasing the calcination temperature to 750°C was accompanied by the persistence of the composition of the 500°C calcination, i.e., the spinel phase was the major phase together with traces of NiO . On the other hand, it was found that a further calcination temperature rise to 1000°C led to the disappearance of the composition of the 750°C calcination, and the formation of a mixture of CoO and rock salt ($\text{Ni}, \text{Co})\text{O}$. Thus, one can state that the observed dramatic activity decrease from the calcination temperature increase from 750 to 1000°C was due to the decomposition of the spinel structure. In other words, it was due to the disappearance of the Co^{3+} - Co^{2+} redox couple necessary for N_2O decomposition. It was shown that increasing the calcination temperature from 500 to 1000°C led to a sharp surface area decrease. This effect is directly due to sintering which dominated at high temperatures. Thus, it is plausible to relate the observed activity decrease from the pre-treatment temperature increase to the surface area decrease.

Fig. 8. N_2O conversion versus reaction temperature over the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Co}_2\text{O}_4$ catalyst calcined at different temperatures. Reaction conditions are the same as in Fig. 7.

4. Conclusions

Structural analysis of the Ni/Co oxide system revealed the following points: (1) a solid state reaction between NiO and Co₃O₄ led to the formation of nickel cobaltite; (2) increasing Ni content led to crystallite size decrease until the catalyst with $x = 0.75$ which exhibited the smallest crystallite size in the 500 °C calcined series; (3) increasing the calcination temperature for this catalyst to 1000 °C led to changes in the phase composition accompanied by the formation of CoO as a product; in other words, a high temperature treatment facilitated Co³⁺ → Co²⁺ reduction; (4) residual amounts of K⁺ still remained in the samples, which improved the N₂O decomposition activity of this catalysts series. Catalytic activity measurements for N₂O decomposition demonstrated the following: (1) addition of nickel oxide significantly enhanced the catalytic activity of Co₃O₄ spinel oxide; (2) the high N₂O decomposition reactivity over Ni/Co mixtures compared to their individual oxides was due to several parameters which operate simultaneously, viz., role of nickel cations in enhancing the Co³⁺ → Co²⁺ reduction, smaller crystallite size, larger S_{BET} value, and the presence of residual K⁺; (3) increasing the calcination temperature from 500 to 750 °C led to a decrease in catalytic activity but resulted in a dramatic activity decrease at 1000 °C, which was attributed to the decomposition of the spinel structure.

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Graphical Abstract

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

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Ni substituted Co₃O₄ spinel oxide catalysts calcined at 500 °C gave good N₂O decomposition reactivity. The catalytic activity decreased with increasing calcination temperature up to 1000 °C.

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