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Effects of doping with CeO_2 and calcination temperature on physicochemical properties of the NiO/Al_2O_3 system

Research Article

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Abstract: The effects of doping with CeO_2 and calcination temperature on the physicochemical properties of the NiO/Al_2O_3 system have been investigated using DTA, XRD, nitrogen adsorption measurements at -196°C and decomposition of H_2O_2 at 30-50°C. The pure and variously doped solids were subjected to heat treatment at 300, 400, 700, 900 and 1000°C. The results revealed that the specific surface areas increased with increasing calcination temperature from 300 to 400°C and with doping of the system with CeO_2. The pure and variously doped solids calcined at 300 and 400°C consisted of poorly crystalline NiO dispersed on γ-Al_2O_3. Heating at 700°C resulted in formation of well crystalline NiO and γ-Al_2O_3 phases beside CeO_2 for the doped solids. Crystalline $NiAl_2O_4$ phase was formed starting from 900°C. The degree of crystallinity of $NiAl_2O_4$ increased with increasing the calcination temperature from 900 to 1000°C. An opposite effect was observed upon doping with CeO_2. The NiO/Al_2O_3 system calcined at 300 and 400°C has catalytic activity higher than individual NiO obtained at the same calcination temperatures. The catalytic activity of NiO/Al_2O_3 system increased, progressively, with increasing the amount of CeO_2 dopant and decreased with increasing the calcination temperature.

Keywords: *NiO/Al_2O • Doping • Characterization • Catalytic properties*

1. Introduction

Metal nitrates (hydrates) are the most popular precursor components for the preparation of oxides and metallic materials with wide spread properties, such as high surface catalysts, ceramics, semiconductors, gas sensors and high temperature superconductors [1-3]. Widely used procedures in the production of oxides and other materials include the thermal degradation/decomposition of metal nitrates as well as chemical vapor deposition (CVD) methods [4].

The activity and selectivity of those solids could be modified by various methods such as loading on finely divided support [5,6], subjection to ionizing radiation [7] and doping with certain foreign oxides [8,9]. Furthermore, transition metals or metal oxides on support are commonly employed to catalyze several reactions including oxidation–reduction, dehydration, dehydrogenation, cracking, alkylation, *etc.* [10-12].

The physicochemical, surface and catalytic properties of the NiO/Al_2O_3 system have been the object of several investigations by many authors [13-15]. This system has been applied in numerous fields, such as oxidative dehydrogenation of ethane to ethylene [16], NO reduction by CO and CH_4-CO_2 reforming [17,18].

In recent years, cerium-based catalysts with the presence of transition metals have attracted increasing attention due to their high oxygen storage capability (OSC). Various CeO_2-based catalysts, such as CeO_2–Al_2O_3, CeO_2–SiO_2, CeO_2–La_2O_3, CeO_2-NiO and

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CeO_2–ZrO_2 have been investigated with the aim of increasing the thermal stability and the OSC of CeO_2 [19,20].

The present work reports the study of the effects of doping with CeO_2 and calcination temperature on surface and physicochemical properties of the NiO/Al_2O_3 system. The pure and variously doped solids were treated at 300, 400, 700, 900 and 1000°C. In addition, the solid-solid interaction between NiO and Al_2O_3 was investigated. The techniques employed are differential thermal analysis (DTA), X-ray diffraction (XRD), and nitrogen adsorption measurements at -196°C. The catalytic activity of all solids was measured by using hydrogen peroxide decomposition reaction at 30, 40 and 50°C.

2. Experimental Procedures

2.1. Materials

The starting materials were solids of nickel nitrate hydrate; $Ni(NO_3)_2{\bullet}6H_2O$, ammonium cerium nitrate; $(NH_4)_2Ce(NO_3)_6$; and aluminum hydroxide; $Al(OH)_3$. The chemicals employed were of analytical grade and were supplied by Prolabo Company.

NiO/Al_2O_3 samples having the molar composition $0.2NiO/Al_2O_3$ were prepared by wet impregnation method using finely powdered aluminum hydroxide with solutions containing known amounts of $Ni(NO_3)_2{\bullet}6H_2O$ dissolved in the least amounts of distilled water making a paste. The pastes were dried at 100°C then calcined at 300, 400, 700, 900 and 1000°C for 4 h.

Three doped solid samples were prepared by treating a known amount of aluminum hydroxide with solutions containing different amounts of cerium nitrate then dried at 100°C. The obtained doped alumina samples were treated with solutions containing fixed amounts of $Ni(NO_3)_2{\bullet}6H_2O$. The obtained pastes were dried at 100°C, and then calcined at 300, 400, 700, 900 and 1000°C for 4 h. The dopant concentrations were 0.75, 1.5 and 3 mol% CeO_2, and the amount of nickel was fixed at 16.66 mol% NiO.

2.2. Techniques

DTA analysis of various uncalcined materials was carried out using Shimadzu DTA-50H systems. The rate of heating was kept at 10°C min^{-1}. The analysis was followed up at temperatures between room temperature and 1000°C with α-Al_2O_3 as a reference material. A 40 mg sample of each solid specimen was employed in each case. The measurements were carried out in a current of nitrogen flowing at a rate of 50 cm^3 min^{-1}.

An X-ray investigation of the thermal products of the different mixed solids was performed using a Bruker diffractometer (Bruker D8 advance target). The patterns were run with copper $K\alpha_1$ with secondly monochromator (λ =0.15405 nm) at 40 kV and 40 mA.

The crystallite size of phases detected at different temperatures (300, 400, 700, 900 and 1000°C) was calculated from Scherrer equation [21]: $d = B\lambda/\beta \cos \theta$, where d is the average particle size, B is the Scherrer constant (0.89), λ is the wave length of X-ray beam, θ is the diffraction angle and β is (FWHM) „full width half maximum” of the diffraction peak.

The specific surface areas of the pure and variously doped solids, calcined at 300 and 400°C, were determined from nitrogen adsorption isotherms measured at -196°C, using conventional volumetric apparatus. Before carrying out such measurements, each sample was degassed under a reduced pressure of 10^{-5} Torr for 2 h at 200°C.

The catalytic activity of individual and mixed solids obtained at different calcination temperatures was determined using H_2O_2 decomposition in aqueous solution at 30, 40 and 50°C, using 0.5 mL volume of H_2O_2 of known concentration diluted to be 20 mL with distilled water. The mass of catalyst sample taken in each kinetic experiment was fixed at 10 mg for all samples. The reaction was followed up through a gasometric measurement of oxygen liberated at different time intervals till no further O_2 was librated. Details of experimental method have been given elsewhere [22].

3. Results and discussion

3.1. The thermal behaviour of pure and doped mixed solids

DTA curves of pure and variously doped solids were determined and illustrated in Fig. 1. The DTA curve of pure nickel nitrate supported aluminum hydroxide exhibits four endothermic peaks, their minima located at 60, 150, 190 and 325°C. On the other hand, DTA curves of the doped solids showed, at lower temperature, the same number of endothermic peaks of those detected for the pure mixed solids. This means that addition of CeO_2 dopant to the reacting mixed solids enhanced the thermal decomposition of both pure nickel nitrate and aluminum hydroxide to NiO [4] and Al_2O_3 [22]. In addition, a very broad endothermic peak with a minimum located at about 750°C was detected for all pure and variously doped solids.

It can be seen from Fig. 1 that the thermograms obtained from pure and doped mixed solids were similar

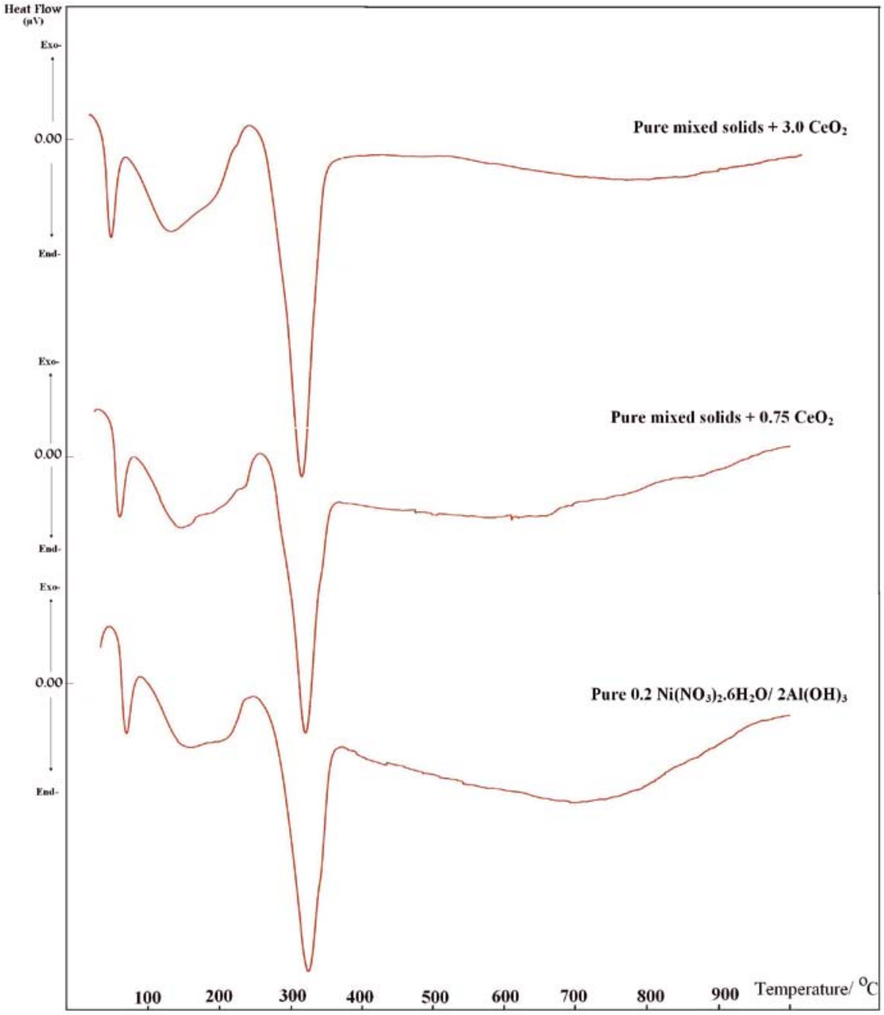

Figure 1. Differential thermal analysis (DTA) of pure solids and those doped with different amounts of cerium nitrate.

to each other. The first step in each sample represents the departure of physisorbed water as well as loss of water of crystallization from nitrate compounds. The peak located at about 190°C corresponds to the thermal decomposition of aluminum hydroxide [22] in pure and variously doped samples into Al(OOH). Furthermore, the peak located at 325°C corresponds to formation of nickel and aluminum oxides. A broad endothermic peak with its minimum located at 750°C may be the result of a possible solid–solid interaction between NiO and Al_2O_3 that may led to the formation of a nickel aluminate compound [23,24]. The identification of this compound will be discussed in the next section of the present work in the context of XRD investigations of different solids.

3.2. XRD investigation of pure and variously doped solids calcined at 300-1000°C

The X-ray diffractograms of pure and variously doped mixed solids calcined at 300, 400, 700, 900 and 1000°C were determined. The results obtained are summarized in Tables 1 and 2.

It can be seen from Tables 1 and 2 that:

(i) the diffractograms of pure and variously doped solids calcined at 300°C (not given) show the amorphous nature of the different investigated solids;

(ii) the pure and doped solids calcined at 400°C show poorly crystalline NiO and γ-Al_2O_3 phases. It should also be noted that that the doping of the system under investigation with CeO_2 resulted in a significant decrease in the degree of crystallinity and thus the crystallite size of NiO, γ-Al_2O_3;

(iii) the pure and doped mixed solids calcined at 700°C exhibit an increase the degree of crystallinity of both NiO and γ-Al_2O_3 phases associated with detection of crystalline CeO_2 phase for the doped solids;

(iv) the pure and doped solids calcined at 900°C resulted in formation of nickel aluminate as a result of solid-solid interactions between the reacting oxides [14,22,23] as follows:

$$NiO + Al_2O_3 \longrightarrow NiAl_2O_4$$

The peak height, and thus the degree of crystallinity of the detected nickel aluminate phase, increased with increasing calcination temperature up to 1000°C;

(v) doping treatment of the system under investigation with CeO_2 resulted in a significant decrease in the degree of crystallinity and crystallite size of $NiAl_2O_4$ phases that are detected at different calcination temperatures of 900 and 1000°C.

Table 1. Effect of calcination temperature and doping with CeO_2 of NiO/Al_2O_3 system on the peak height of main diffraction lines of NiO (d = 2.08 Å, 100%), Al_2O_3 (d = 1.42 Å, 100%) and $NiAl_2O_4$ (d = 2.01 Å, 100%) phases.

Pure and variously doped solids	Calcination temperature, (°C)	NiO (a.u) (d=2.08) (100%)	Al_2O_3 (a.u) (d=1.42) (100%)	CeO_2 (a.u) (d= 3.12) (100%)	$NiAl_2O_4$ (a.u) (d= 2.01) (100%)
NiO/Al_2O_3	400°C	76.5	62.2	------	------
+ 0.75 mol% CeO_2		67.1	60.7	-----	-----
+ 1.5 mol% CeO_2		58.3	60.1	------	------
+ 3.0 mol% CeO_2		55.1	57.4	------	------
NiO/Al_2O_3	700°C	86.1	82.9	------	------
+ 0.75 mol% CeO_2		77.8	69.6	16.8	-----
+ 1.5 mol% CeO_2		66.9	66.9	33.1	------
+ 3.0 mol% CeO_2		63.6	60.2	46.4	------
NiO/Al_2O_3	900°C	------	------	------	108
+ 0.75 mol% CeO_2		-----	-----	58.1	92.3
+ 1.5 mol% CeO_2		------	------	104	85.6
+ 3.0 mol% CeO_2		------	------	145	77.7
NiO/Al_2O_3	1000°C	------	------	------	110
+ 0.75 mol% CeO_2		-----	-----	66.3	95.3
+ 1.5 mol% CeO_2		------	------	148	90.6
+ 3.0 mol% CeO_2		------	------	222	86.7

Table 2. Effect of CeO_2 doping of the NiO/Al_2O_3 system on crystallite size of phases detected at different calcination temperatures.

Pure and variously doped solids	Calcination temperature, (°C)	Crystallite size of NiO, (nm)	Crystallite size of Al_2O_3, (nm)	Crystallite size of CeO_2, (nm)	Crystallite size of $NiAl_2O_4$, (nm)
NiO/Al_2O_3	400°C	12.8	11	------	------
+ 0.75 mol% CeO_2		8.3	9.7	-----	-----
+ 1.5 mol% CeO_2		7.8	8.4	------	------
+ 3.0 mol% CeO_2		7.6	8.2	------	------
NiO/Al_2O_3	700°C	12.5	9.6	------	------
+ 0.75 mol% CeO_2		11.5	9.3	9	-----
+ 1.5 mol% CeO_2		9.6	9.2	11	------
+ 3.0 mol% CeO_2		9.5	8.2	13	------
NiO/Al_2O_3	900°C	------	------	----	16
+ 0.75 mol% CeO_2		-----	-----	36.3	14.8
+ 1.5 mol% CeO_2		------	------	42.5	13.1
+ 3.0 mol% CeO_2		------	------	52.8	13
NiO/Al_2O_3	1000°C	------	------	------	17.1
+ 0.75 mol% CeO_2		-----	-----	55.1	16.9
+ 1.5 mol% CeO_2		------	------	59	15.7
+ 3.0 mol% CeO_2		------	------	70.2	14.5

Table 3. Specific surface areas of pure and doped solids calcined at 300 and 400°C.

Pure and variously doped solids	Calcination temperature, (°C)	S_{BET} (m^2 g^{-1})
NiO		86
NiO/Al_2O_3		145
+ 0.75 mol% CeO_2	300°C	150
+ 1.5 mol% CeO_2		156
+ 3.0 mol% CeO_2		161
NiO		92
NiO/Al_2O_3		150
+ 0.75 mol% CeO_2	400°C	154
+ 1.5 mol% CeO_2		160
+ 3.0 mol% CeO_2		166

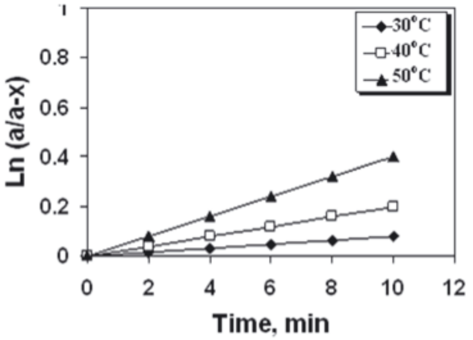

Figure 2. Dependence of ln (a/a-x) vs. time for pure NiO/Al_2O_3 calcined at 300°C

3.3. Specific surface area of pure and variously doped solids

The BET surface areas of pure the NiO/Al_2O_3 system and that of the doped one, with different amounts of CeO_2 and calcined at 300 and 400°C were determined. The computed values of S_{BET}; which represent the specific surface areas of both NiO and Al_2O_3 support material are given in Table 3. Examination of this table showed that CeO_2 doping of NiO/Al_2O_3 resulted in a measurable increase in its S_{BET} surface to an extent proportional to the amount of dopant added. It is also noticed that the S_{BET} of these solids increased with increasing the calcination temperature from 300 to 400°C which can be ascribed to creation of new pores through thermal treatment process, as well as the effective decrease in the crystallite size of particles of the doped solids [7,8,14].

3.4. Catalytic activity measurements of pure NiO/Al_2O_3 system and that doped with CeO_2

The obtained results revealed that the decomposition of H_2O_2 over pure and variously doped solids calcined at different temperatures followed first order-kinetics. Fig. 2 depicts representative first-order plots [22-24] of the catalytic reaction carried out over the NiO/Al_2O_3 system heated at 300°C. In order to account for the induced changes in the specific surface area due to CeO_2-doping, the values of the reaction rate constant per unit surface area (k_s) were calculated for each catalyst and the data obtained are given in Table 4.

It can be seen from Table 4 that:

(i) individual nickel oxide obtained by thermal treatment of pure salt at 300 and 400°C exhibits very low catalytic activity in the H_2O_2 decomposition reaction;

(ii) the catalytic activities of NiO/Al_2O_3 system obtained at 300 and 400°C are higher than that of pure nickel oxide obtained by treating the pure salt at the same calcination temperature. In this case, alumina plays a role as a catalyst support [22] and prevents the aggregation of nickel oxide to form crystalline NiO. In other words, the presence of Al_2O_3 increased the degree of dispersion of NiO grains, thus leading to a significant increase in both surface area and catalytic activity;

(iii) The catalytic activity of the system under investigation increased, progressively, with increasing the amount of CeO_2 doping. The observed increase in the catalytic activity of the NiO/Al_2O_3 system due to treatment with cerium oxide dopant reflected an effective increase in the concentration of the catalytically active constituents [6-8] of nickel species besides an increase in the surface areas of the system upon doping with CeO_2. Furthermore, the X-ray patterns of the treated mixed solids calcined at 300 and 400°C showed a progressive decrease in the degree of crystallinity and crystallite size of catalytically active species of the system under investigation, as well as increasing of surface areas of the system upon doping with CeO_2, and consequently increased the catalytic activity of the system under investigation. In other words, CeO_2 addition to NiO/Al_2O_3 system enhanced the nickel dispersion leading to a significant increase in the concentration of active sites *via* creation of new ion pairs which may improve catalytic activity [7,8,22-26].

Moreover, no measurable catalytic activity was observed for various solids thermally treated at 700, 900 and 1000°C (not given). This might be attributed to the increase of degree of crystallinity of NiO phase and/ or restriction of catalytically active constituents through the formation of a $NiAl_2O_4$ phase.

On the other hand, determination of the apparent activation energy (E_a) for the catalytic decomposition of H_2O_2 in the presence of pure and doped NiO/Al_2O_3 system has shed some light on the possible changes in the mechanism of the catalyzed reaction. Therefore, the values of k measured at 30, 40, and 50°C over the

Table 4. Effect of CeO_2-doping of NiO/Al_2O_3 system calcined at 300 and 400°C on the reaction rate constant per unit surface area (K_s) for H_2O_2 decomposition reaction conducted at 30, 40 and 50°C.

Catalyst composition	Calcenation Temperature, (°C)	K_s (30°C $min^{-1}m^{-2}$)	K_s (40°C $min^{-1}m^{-2}$)	K_s (50°C $min^{-1}m^{-2}$)
Pure Ni-salt	300°C	0.35×10^{-4}	0.81×10^{-4}	1.86×10^{-4}
NiO/Al_2O_3		0.55×10^{-4}	1.38×10^{-4}	2.76×10^{-4}
0.75 mol% CeO_2 +		1.13×10^{-4}	2.20×10^{-4}	3.33×10^{-4}
+ 1.5 mol% CeO_2		1.67×10^{-4}	2.63×10^{-4}	3.97×10^{-4}
+ 3.0 mol% CeO_2		2.48×10^{-4}	3.60×10^{-4}	5.22×10^{-4}
Pure Ni-salt	400°C	0.54×10^{-4}	1.20×10^{-4}	2.50×10^{-4}
NiO/Al_2O_3		1.33×10^{-4}	2.33×10^{-4}	4.07×10^{-4}
0.75 mol% CeO_2 +		3.38×10^{-4}	4.87×10^{-4}	6.49×10^{-4}
+ 1.5 mol% CeO_2		4.31×10^{-4}	6.06×10^{-4}	7.69×10^{-4}
+ 3.0 mol% CeO_2		5.78×10^{-4}	7.35×10^{-4}	9.52×10^{-4}

variously treated solids have allowed (E_a) to be obtained *via* direct application of the Arrhenius equation [6-8]. The values of activation energy, ΔE, are clustered in the range of 31-45 kJ mol^{-1} for the doped solids calcined at 300°C and are clustered in the range of 21-27 kJ mol^{-1} for the doped solids calcined at 400°C. The constancy of the values of activation energy for these solids points to similar nature of active centers of doped solids being different from those of pure mixed solids (67, 47 kJ mol^{-1}) calcined at the same temperatures (300 and 400°C), respectively.

Moreover, a measurable decrease in the value of (E_a) was observed as a consequence to the addition of increasing amounts of CeO_2 *via* CeO_2-doping. This finding ran parallel with the observed increase in the catalytic activity due to this treatment. The sharp decrease in apparent activation energies, with increasing content of dopant from 67 to 31 kJ mol^{-1} and from 47 to 21 kJ mol^{-1} for the samples treated at 300 and 400°C respectively, gives evidence that the nature of the catalytic active sites may be changed with increase the content of the dopant.

4. Conclusion

It can be concluded from this study that alumina acts act as a support for nickel oxides at 300 and 400°C. Crystalline nickel aluminate phase is formed at high calcination temperatures (900 and 1000°C). The specific surface areas of pure and variously doped solids increased with increasing calcination temperature, and with doping with CeO_2. The catalytic activity of the NiO/Al_2O_3 system progressively increased with increasing calcination temperature from 300 to 400°C and with increasing CeO_2 dopant. Furthermore, no measurable catalytic activity was observed for all solids calcined at 700, 900 and 1000°C.

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