

THERMAL DECOMPOSITION OF NICKEL ALUMINIUM MIXED HYDROXIDES AND FORMATION OF NICKEL ALUMINATE SPINEL

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ABSTRACT

Various nickel aluminium mixed hydroxide samples of different compositions were prepared by co-precipitation from their nitrate solutions using dilute NH_4OH . Additional samples were prepared by impregnation of hydrated Al_2O_3 , preheated at 600 and 900°C, with nickel nitrate solution in an equimolar ratio. The thermal decomposition of different mixed solids was studied using DTA. The X-ray investigation of thermal products of the mixed solids was also studied.

The results obtained revealed that the presence of NiO up to 33.3 mole % with aluminium oxide much enhanced the degree of crystallinity of the $\gamma\text{-Al}_2\text{O}_3$ phase. In contrast, the presence of Al_2O_3 much retarded the crystallization process of the NiO phase. With the exception of samples containing 20 mole% NiO, all the mixed hydroxide samples, when heated in air at 900°C, led to the formation of well-crystalline $\text{Ni Al}_2\text{O}_4$ spinel, alone, or together with either NiO or $\gamma\text{-Al}_2\text{O}_3$, depending on the composition of the mixed oxide samples. The solid containing 20% NiO and heated at 900°C was constituted of amorphous NiO dispersed in $\gamma\text{-Al}_2\text{O}_3$. Heating the nickel nitrate-impregnated Al_2O_3 in air at 800–1000°C led to the formation of $\text{Ni Al}_2\text{O}_4$ together with non-reacted NiO and $\gamma\text{-Al}_2\text{O}_3$. The degree of crystallinity of the spinel was found to increase by increasing the calcination temperature of the impregnated solids from 800 to 1000°C and by increasing the preheating temperature of the hydrated Al_2O_3 employed from 600 to 900°C.

INTRODUCTION

Binary oxide systems may have several applications as catalysts, adsorbents and semiconductors [1–5]. Their catalytic, surface and electrical properties depend mainly on the prehistory of the solids, calcination conditions and chemical composition of the mixed oxides [1,6–8].

The NiO– Al_2O_3 system may be considered as one of the most interesting binary systems. Pure NiO belongs to the *p*-type semiconductors group, and is commonly used in the catalysis of oxidation–reduction reactions [9–12]. Al_2O_3 , which behaves as an electrical insulator and acquires *n*-semiconduct-

ing character at temperatures around 700°C catalyzes dehydration reactions [13–15] (dehydration of alcohols). Therefore, the co-existence of NiO and Al₂O₃ in a binary system increases the field of application of the mixed oxide solid. Each oxide may mutually affect some of the physical properties of the other oxide such as degree of dispersion, grain size, crystallization and sintering of the solid [6].

The thermal treatment of a binary oxide system, whose cations are di- and trivalent, leads to a solid–solid interaction to give a spinel [16]. Heating NiO–Al₂O₃ mixed oxides produces Ni Al₂O₄ spinel [17]. The temperature of the spinel formation may depend on the prehistory of the solids, mode of preparation and calcination conditions [18–20].

The present investigation reports a study on thermal decomposition of nickel aluminium mixed hydroxides of varying composition using DTA, X-ray and surface area measurement techniques. The mutual effect of each oxide in the crystallization, degree of dispersion and sintering of the other oxide was studied. The effects of mode of preparation, prehistory of solids and calcination conditions on the formation of Ni Al₂O₄ were also studied.

EXPERIMENTAL

Materials

Different nickel aluminium mixed hydroxide samples having various compositions were prepared from dilute solutions of nickel and aluminium nitrate using 0.5 M NH₄OH at room temperature. The concentration of nickel and aluminium nitrate solutions was 21.2 g Ni l⁻¹ and 10.7 g Al l⁻¹, respectively. Depending on the desired composition of the mixed hydroxide, appropriate, calculated volumes of nitrate solutions were taken, and NH₄OH solution was added dropwise with continuous stirring to obtain a pH of about 8. The precipitate formed was washed thoroughly with distilled water till free from nitrate and ammonium ions and dried at 100°C for 72 h.

The mixed oxide samples were obtained by heating the corresponding mixed hydroxide in air at temperatures between 450 and 900°C for 4 h. The compositions of the prepared mixed oxides were 0.25 NiO 1 Al₂O₃, 0.50 NiO 1 Al₂O₃, 1.0 NiO 1 Al₂O₃, 2.0 NiO 1 Al₂O₃, 3 NiO 1 Al₂O₃ and 4.0 NiO 1 Al₂O₃.

Additional samples of mixed oxides were obtained by impregnation of aluminium oxide with nickel nitrate in an equimolar ratio, followed by calcination in air at temperatures between 700 and 1000°C for 1/2h. The aluminium oxide sample was prepared according to the method described and subjected to heating at 600 and 900°C for 4 h.

Techniques

Differential thermal analysis (DTA) of different mixed hydroxides and impregnated solids was carried out using a DuPont 990 thermal analyzer with differential scanning calorimeter cell. The rate of heating was $10^{\circ}\text{C min}^{-1}$ and the sensitivity was 1 mV in^{-1} .

An X-ray investigation of the thermal products of mixed hydroxides and impregnated solid samples was carried out using a Philips diffractometer type PW 1050. The patterns were run with nickel-filtered copper radiation, with $\lambda = 1.5405 \text{ \AA}$, at 36 kV and 16 mA and with a scanning speed of 2° in 2θ per min.

The surface area of some mixed oxide samples was determined from data on nitrogen adsorption at 77 K. These data were obtained using a conventional volumetric apparatus. Before each adsorption run, the solid was outgassed at 200°C for 3 h under a reduced pressure of 10^{-5} Torr.

RESULTS AND DISCUSSION

Differential thermal analysis of various nickel aluminium mixed hydroxides

Figure 1 represents the DTA curves of different mixed hydroxide specimens having various compositions. The nickel hydroxide content was 80, 75,

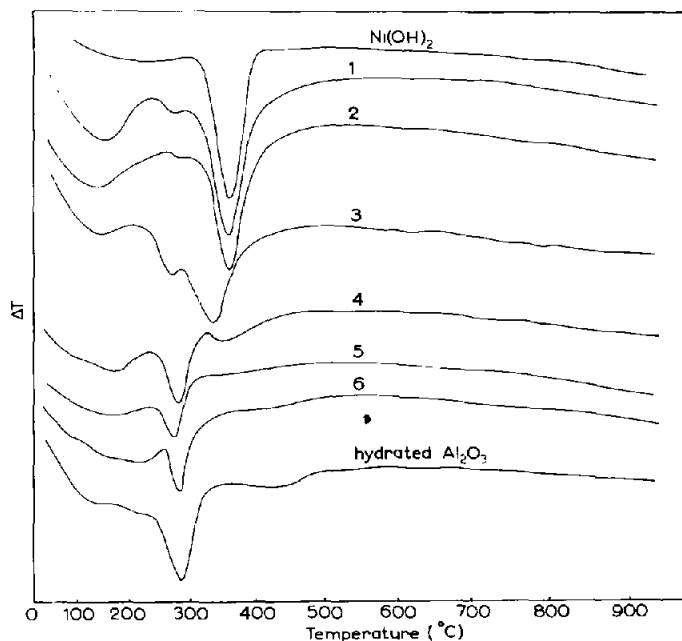


Fig. 1. DTA curves of pure $\text{Ni}(\text{OH})_2$, hydrated Al_2O_3 and different co-precipitated mixtures of both. The ratios between $\text{Ni}(\text{OH})_2$ and hydrated Al_2O_3 are 1, 4:1; 2, 3:1; 3, 2:1; 4, 1:1; 5, 0.5:1 and 6, 0.25:1.

66.6, 50, 33.3 and 20 mole %, corresponding to compositions of 4 NiO 1 Al₂O₃, 3 NiO 1 Al₂O₃, 2 NiO 1 Al₂O₃, 1 NiO 1 Al₂O₃, 0.5 NiO 1 Al₂O₃ and 0.25 NiO 1 Al₂O₃, respectively. The DTA curves of pure nickel hydroxide and hydrated alumina are also included in Fig. 1. Three endothermic peaks are observed in the DTA curves of mixed hydroxide samples. The first peak, which is extended between 100 and 200°C and has its maximum at 160°C, corresponds to the departure of physisorbed water. The area of this peak is extremely small in the case of pure Ni(OH)₂ and hydrated alumina samples, thus indicating that the mixed hydroxide samples retain much more physisorbed water than the pure hydroxide solids. The maximum of the second peak is located at 280°C in all mixed hydroxide samples and its area increases by increasing the amount of hydrated alumina. This peak may correspond to the dehydroxylation of hydrated alumina [21]. In fact, as shown in Fig. 1, a strong endothermic peak having its maximum at 280°C was observed in the DTA curve of pure hydrated alumina. The maximum of the third peak is located at about 360°C in all mixed hydroxide samples and its area, which decreases by decreasing the Ni(OH)₂ content, disappears when the Ni(OH)₂ content reaches 20 mole %. Thus, this peak indicates the decomposition of nickel hydroxide to nickel oxide.

Differential thermal analysis of nickel nitrate-impregnated alumina

Two samples of pure hydrated alumina were heated at 600 and 900°C for 4 h and then impregnated with Ni(NO₃)₂ · 6 H₂O solution in an equimolar ratio. Figure 2 represents the DTA curves of the impregnated solids. The impregnated alumina calcined at 900°C exhibits five distinct endothermic peaks which are sharp and strong. However, the last peak exhibited the

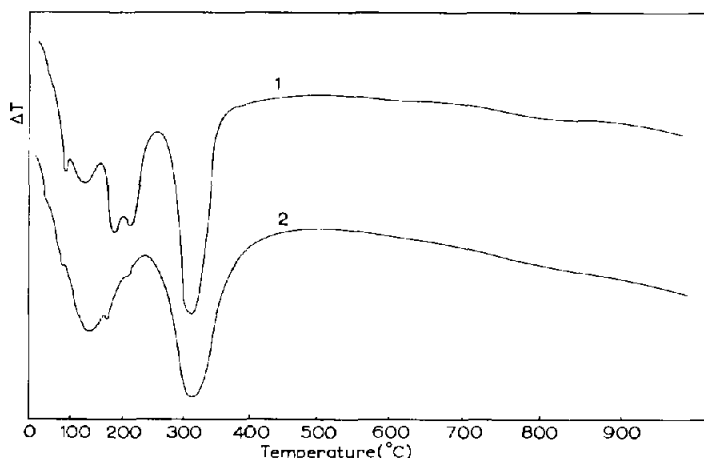


Fig. 2. DTA curves of Ni(NO₃)₂-impregnated γ -Al₂O₃. 1, γ -Al₂O₃ preheated at 900°C; 2, γ -Al₂O₃ preheated at 600°C.

highest area. The maxima of these peaks are located at 90, 130, 185, 215 and 315°C. The other impregnated alumina, calcined at 600°C, shows almost the same thermal behaviour, however, its endothermic peaks are broader. The first four peaks may correspond to the departure of water of crystallization from $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, forming $\text{Ni}(\text{NO}_3)_2$. These results indicate clearly that the six water molecules are bound to the $\text{Ni}(\text{NO}_3)_2$ molecule with different bond energies. The last peak characterizes the thermal decomposition of $\text{Ni}(\text{NO}_3)_2$ to NiO. These results will be confirmed by X-ray investigation in the next part of this study.

X-Ray investigation of the thermal products of different mixed hydroxides and impregnated solids calcined at different temperatures

Effect of Al_2O_3 on the crystallization of the NiO phase

The X-ray diffraction patterns of different mixed oxides, having various compositions and calcined in air at 450°C for 4 h, were determined. The characteristic lines of the NiO phase were only detected in the specimens containing 80, 75 and 66.6 mole % nickel oxide. It has been shown from the DTA study, previously presented, that all the mixed hydroxide samples underwent thermal decomposition at temperatures between 280 and 400°C and exhibited a state of thermal stability extending between 450 and 900°C. It seems that the process of dehydroxylation of hydrated alumina at 450°C led to the formation of amorphous $\gamma\text{-Al}_2\text{O}_3$. In fact, as seen by the X-ray investigation, the solids containing 66.6 and 80 mole % Al_2O_3 and calcined at 450°C were amorphous, and the solid containing 50% Al_2O_3 and calcined also at 450°C was constituted of poorly crystalline NiO and $\gamma\text{-Al}_2\text{O}_3$ phases. The disappearance of the well crystalline NiO phase in the mixed oxide samples containing 50 to 80 mole % aluminium oxide indicates the role of this oxide in retarding the crystallization process of NiO phase.

Effect of calcination temperature on the degree of crystallinity of NiO

Figure 3 represents the X-ray diffraction patterns of the solids having the composition 2 NiO 1 Al_2O_3 and calcined at 450, 550, 650 and 750°C. Figure 3 shows that the intensity of the characteristic lines corresponding to the NiO phase increases by increasing the calcination temperature in the range between 450 and 750°C. Therefore, the increase in temperature favours the crystallization process of NiO phase. The effect of Al_2O_3 in opposing the process of crystallization of NiO could be counteracted by raising the calcination temperature of the solid above 450°C.

Effect of NiO on the crystallization of $\gamma\text{-Al}_2\text{O}_3$

The X-ray investigation of pure hydrated alumina calcined at temperatures between 450 and 750°C revealed an amorphous nature in the solids produced. A well crystalline $\gamma\text{-Al}_2\text{O}_3$ phase was obtained by increasing the

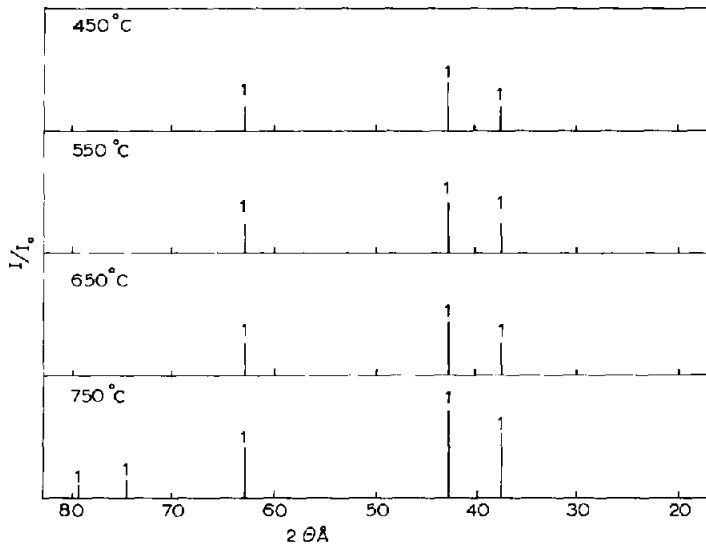


Fig. 3. X-Ray diffraction patterns of 2 NiO 1 Al₂O₃ calcined at 450, 550, 650 and 750°C. Lines 1, NiO phase.

calcination temperature of pure hydrated alumina to 900°C. In contrast, all the characteristic lines of γ -Al₂O₃ were detected in the X-ray diffraction patterns of the mixed oxide having the composition 0.5 NiO 1 Al₂O₃ and calcined at 750°C, thus indicating the formation of the well crystalline γ -phase. However, the degree of crystallinity of γ -Al₂O₃ was drastically decreased in the case of 0.25 NiO 1 Al₂O₃ calcined at 750°C. It is to be concluded that NiO much enhanced the crystallization process of γ -Al₂O₃ to an extent proportional to its concentration. It seems that the NiO crystals acted as nuclei for the crystallization of the γ -phase.

Formation of nickel aluminate spinel from nickel aluminium mixed oxides

It has been shown previously, from the X-ray investigation, that the heating of different mixed oxide samples at 450–750°C led to the formation of NiO and γ -Al₂O₃ phases having various degrees of crystallinity depending on the composition and calcination temperature. Increasing the calcination temperature to 900°C may initiate a solid–solid interaction between the two oxides producing a new compound.

Figure 4 represents the X-ray diffraction patterns of the different mixed oxides calcined at 900°C for 4 h. It is seen that, in the case of the solid having the composition 1 NiO 1 Al₂O₃ and calcined at 900°C, all the characteristic lines of Ni Al₂O₄ spinel alone were detected. This indicates the complete disappearance of both oxides through a solid–solid interaction producing a well crystalline spinel. All the characteristic lines of both NiO and Ni Al₂O₄ were detected in the case of the mixed oxide samples having

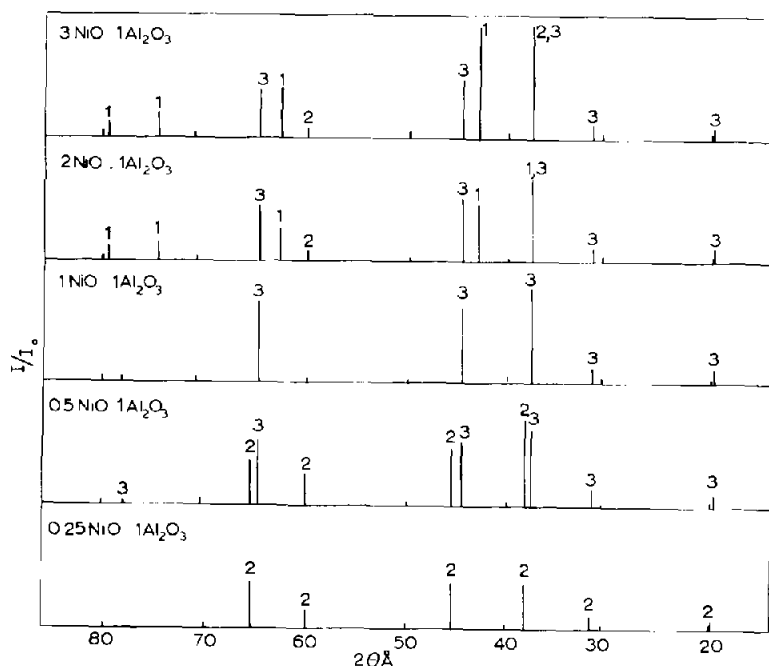
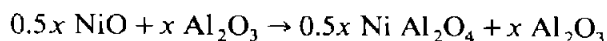
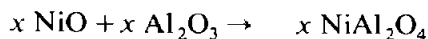


Fig. 4. X-Ray diffraction patterns of the thermal products of nickel aluminum mixed oxides calcined at 900°C . Lines 1, NiO phase; lines 2, $\gamma\text{-Al}_2\text{O}_3$ phase; lines 3, NiAl_2O_4 phase.

the compositions: 4 NiO 1 Al_2O_3 (diffraction lines not given here), 3 NiO 1 Al_2O_3 and 2 NiO 1 Al_2O_3 , while the lines of both $\gamma\text{-Al}_2\text{O}_3$ and NiAl_2O_4 were observed only in the sample 0.5 NiO 1 Al_2O_3 . The intensity of the diffraction lines of the spinel formed increases at the expense of the intensity of the diffraction lines of the non-reacted NiO. A maximum intensity for the NiAl_2O_4 lines was attained when NiO disappeared completely through the interaction with Al_2O_3 , yielding NiAl_2O_4 .

Figure 4 shows also that the solid having the composition 0.25 NiO 1 Al_2O_3 and calcined at 900°C is constituted entirely of well crystalline $\gamma\text{-Al}_2\text{O}_3$. The absence of crystalline NiO and NiAl_2O_4 phases in such a sample may indicate the enhanced effect of $\gamma\text{-Al}_2\text{O}_3$ in preventing the crystallization of NiO, which seems necessary for the formation of crystalline nickel aluminate.

The results, previously presented, conform to the stoichiometry of the chemical interaction between NiO and $\gamma\text{-Al}_2\text{O}_3$ giving NiAl_2O_4 according to



Formation of Ni Al₂O₄ from nickel nitrate-impregnated γ -Al₂O₃

Figure 5 represents the X-ray diffraction patterns of Ni(NO₃)₂-impregnated Al₂O₃ (equimolar ratio), preheated at 600°C then calcined at 700, 800, 900 and 1000°C for 1/2 h. The solids heated at 700 and 800°C are constituted of well crystalline NiO with amorphous γ -Al₂O₃, together with a minute amount of Ni Al₂O₄, as indicated by the presence of some of its diffraction lines of very weak intensity. The intensity of the characteristic lines of nickel aluminate increases by increasing the calcination temperature from 800 to 1000°C indicating an enhanced crystallization of the Ni Al₂O₄ formed.

Other Ni(NO₃)₂-impregnated Al₂O₃ samples were obtained by subjecting the alumina specimen to thermal treatment at 900°C for 4 h before impregnation. The impregnated solids were heated at 700, 800, 900 and 1000°C for 1/2 h. The X-ray investigation of these solids was carried out and the results obtained are given in Fig. 6. Figure 6 shows the absence of Ni Al₂O₄ in the solid heated at 700°C and the minimum temperature for the interaction between NiO and γ -Al₂O₃ yielding Ni Al₂O₄ is 800°C. The degree of crystallinity of the formed spinel increases by increasing the calcination temperature from 800 to 1000°C. These results are in good agreement with a majority to workers [6,18,20,22,23] who have observed the formation of Ni Al₂O₄ at temperatures not below 800°C. Furthermore, as shown in the preceding section, the spinel phase was not detected in the case of the different mixed hydroxides of various compositions heated in air for 4 h at 750°C.

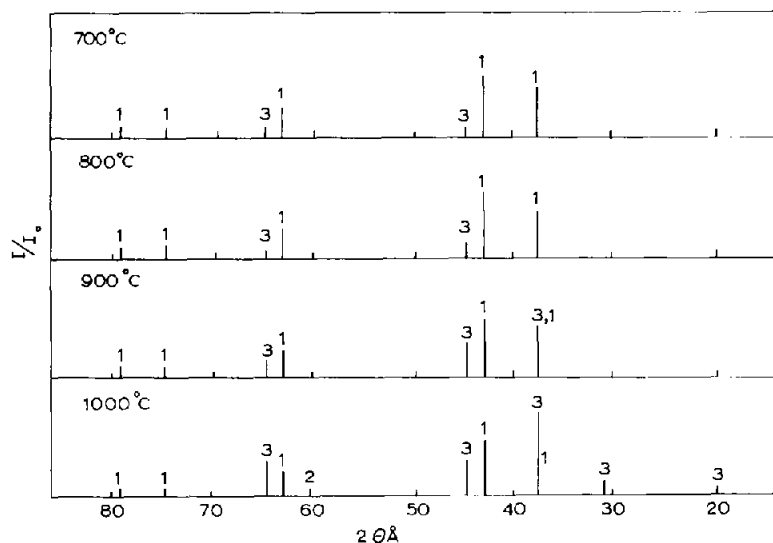


Fig. 5. X-Ray diffraction patterns of thermal products of γ -Al₂O₃ preheated at 600°C, then impregnated with Ni(NO₃)₂ solution (equimolar ratio) and calcined at different temperatures. Lines 1, NiO phase; lines 2, γ -Al₂O₃ phase; lines 3, Ni Al₂O₄ phase.

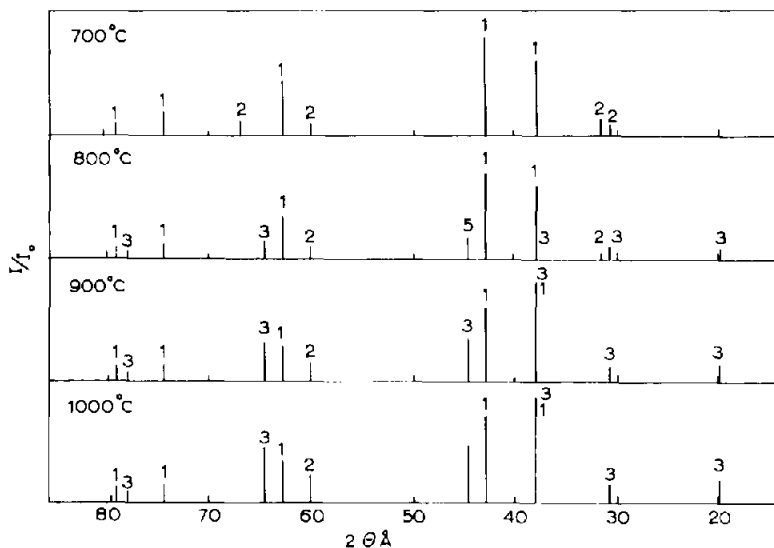
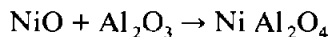


Fig. 6. X-Ray diffraction patterns of thermal products of $\gamma\text{-Al}_2\text{O}_3$ preheated at 900°C , then impregnated with $\text{Ni}(\text{NO}_3)_2$ solution (equimolar ratio) and calcined at different temperatures. Lines 1, NiO phase; lines 2, $\gamma\text{-Al}_2\text{O}_3$ phase; lines 3, $\text{Ni Al}_2\text{O}_4$ phase.

Comparison of Figs. 5 and 6 revealed that the degree of crystallinity of $\text{Ni Al}_2\text{O}_4$, which increases by increasing the calcination temperatures from 800 to 1000°C , increases also by increasing the preheating temperature of impregnated Al_2O_3 from 600 to 900°C . The product from $\gamma\text{-Al}_2\text{O}_3$ heated at 600°C , being amorphous and well crystalline at 900°C , may indicate that the interaction between NiO and $\gamma\text{-Al}_2\text{O}_3$ yielding $\text{Ni Al}_2\text{O}_4$ is more favourable in the case of crystalline oxides.

The presence of non-reacted NiO and $\gamma\text{-Al}_2\text{O}_3$ together with the spinel phase, in all specimens heated at $700\text{--}1000^\circ\text{C}$ for 1/2 h (cf. Figs. 5 and 6), revealed that the interaction between nickel and aluminium oxides yielding $\text{Ni Al}_2\text{O}_4$ is a slow diffusion reaction. Therefore, the complete conversion of the two oxides into nickel aluminate requires a thermal treatment at $800\text{--}1000^\circ\text{C}$ for a longer time. However, it has been shown by Erofeev et al. [23] that a prolonged heating of nickel aluminium mixed oxides at 800°C for 72 h gave a mixture of spinel with both oxides and the spinel was formed only in the regions where the oxides were in very close contact. The absence of any thermal effect in the DTA curves of the mixed hydroxides and $\text{Ni}(\text{NO}_3)_2$ treated $\gamma\text{-Al}_2\text{O}_3$ in the temperature range $450\text{--}900^\circ\text{C}$ (cf. Figs. 1 and 2), stands as other evidence indicating that the interaction, in the solid state, between NiO and $\gamma\text{-Al}_2\text{O}_3$ is a slow diffusion reaction even at 900°C . The increase in the degree of crystallinity of $\text{Ni Al}_2\text{O}_4$, obtained by increasing the calcination temperature from 800 to 1000°C , could be attributed to an enhanced counter-diffusion between the reacting species. The mecha-

nisms of solid-state reaction involved in spinel formation have been studied by several authors. Two mechanisms have been proposed in the case of the reaction [16]



According to the first mechanism, the solid-state reaction proceeds via counter-diffusion of Ni^{2+} and Al^{3+} ions in the anion lattice of the spinel. NiO reacts with Al_2O_3 , according to the second mechanism, by diffusion of NiO through the $\text{Ni Al}_2\text{O}_4$ - Al_2O_3 interface. The O-Ni bonds in NiO and O-Al bonds in Al_2O_3 being ionic and covalent respectively, the mobility of Ni^{2+} ions might be considerably higher than that of Al^{3+} . It seems more plausible that the solid-state reaction between the two oxides yielding nickel aluminate might occur via an energetic counter-diffusion of divalent nickel ions through the $\text{Ni Al}_2\text{O}_4$ - Al_2O_3 interface.

Specific surface area of pure NiO and that mixed with Al_2O_3

Pure NiO samples were prepared by thermal decomposition of pure $\text{Ni}(\text{OH})_2$ in air at temperatures between 350 and 750°C. The $\text{Ni}(\text{OH})_2$ sample was prepared according to the method given in the experimental section. The data of the specific surface area, measured by N_2 adsorption applying the BET method, were 140, 65, 45, 30 and 20 $\text{m}^2 \text{g}^{-1}$ for NiO prepared at 350, 450, 550, 650 and 750°C, respectively. These results indicate that the process of sintering starts to operate as soon as the oxide is formed.

The sample having the composition 3 NiO 1 Al_2O_3 was selected for the surface area measurements. The data obtained were 297, 305, 194 and 183 $\text{m}^2 \text{g}^{-1}$ for the solid calcined in air at 450, 550, 650 and 750°C, respectively. These results indicate clearly the effect of Al_2O_3 in increasing considerably the surface area of NiO. Moreover, the mixed oxide solids which showed high surface area resisted the process of sintering through a wide range of temperature between 450 and 750°C. The role played by Al_2O_3 in increasing the surface area of NiO could be attributed to a dispersion effect inducted by γ - Al_2O_3 which is commonly employed as a catalyst support. The effect of γ - Al_2O_3 in retarding the crystallization process of NiO, as previously shown, could thus be understood.

SUMMARY AND CONCLUSIONS

NiO and γ - Al_2O_3 prepared by thermal decomposition of co-precipitated mixed hydroxides at temperatures between 450 and 750°C exerted a mutual effect on the crystallization of each other. NiO enhanced the crystallization of γ - Al_2O_3 to an extent proportional to its concentration. In contrast, the γ - Al_2O_3 , even in low content (25 mole %), which much increased the degree

of dispersion of NiO leading to a considerable increase in its specific surface area, retarded the crystallization process of the NiO phase. Increasing the γ -Al₂O₃ content to 80 mole % completely prevented the crystallization of NiO, even at 900°C.

The thermal treatment at 900°C of different nickel aluminium mixed oxide samples having a γ -Al₂O₃ content not exceeding 66.6 mole %. led to the formation of well crystalline Ni Al₂O₄ which was either pure or mixed with NiO or Al₂O₃, depending on the mole ratio of the two mixed oxides.

Ni Al₂O₄ spinel was also obtained by heating the 600 and 900°C preheated γ -Al₂O₃ impregnated with Ni(NO₃)₂, at temperatures between 800 and 1000°C. The degree of crystallinity of the spinel phase formed increased by increasing the calcination temperature and by increasing the preheating temperature of γ -Al₂O₃ from 600 to 900°C.

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