

# Synthesis of nickel–aluminum oxide powders by coprecipitation

G. L. Cordeiro\*, W. K. Yoshito, V. Ussui, N. B. de Lima, D. R. R. Lazar

Energy and Nuclear Research Institute (IPEN) – Materials Science and Technology Center.  
Av. Lineu Prestes, 2242 – Cidade Universitária – ZIP Code: 05508-000 – São Paulo, Brazil

(\*) gcordeiro@usp.br

*Keywords: synthesis; coprecipitation; ceramic powders; nickel-aluminum based oxides*

## 1 Introduction

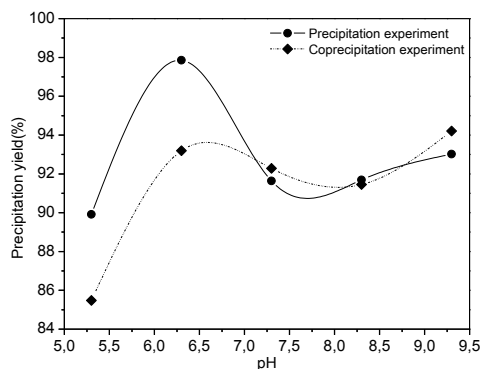
Hydrogen has a high potential in fuel cell applications since it is a clean fuel that has an important role in reducing environmental emissions. Furthermore, hydrogen can be supplied from the steam reforming of ethanol that is a renewable, less toxic and biodegradable source which can be easily stored and safely transported<sup>[1]</sup>. Nickel-based catalysts are currently used in the reforming process due to their high activity and low cost<sup>[2]</sup>. Gamma alumina is often used as a support for metallic particles because of its high surface area and high mechanical and thermal stability<sup>[3]</sup>. Ni<sup>2+</sup> interacts with alumina to form nickel-aluminum based compounds that have shown to be active to bio-oil reforming, wherein nickel oxide reduction occurs during “in situ” operation<sup>[4]</sup>. In this study, nickel-aluminum mixed oxides were prepared using ammonium hydroxide as precipitant agent. Coprecipitation yield as a function of the pH of metals solution was determined for powders with nickel content fixed at 15wt%. It was observed that metals coprecipitation yield is in the range of 85-94%. The present report also examines the effect of nickel content (15-75wt%) on phase formation of synthesized nickel-aluminum oxide powders.

## 2 Experimental

Aluminum chloride (obtained by aqueous dissolution of 99% aluminum chloride hexahydrate – Synth, Brazil) and nickel chloride (obtained by aqueous dissolution of 98% nickel chloride hexahydrate – Aldrich, USA) were the precursors used in this investigation. In order to determine the precipitation yield, appropriate amounts of nickel and aluminum solutions were mixed to produce a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with mass ratio of 15:85. A potentiometric titration procedure was used to establish the volume of 7.4 molar NH<sub>4</sub>OH aqueous solution required to precipitate the mixed salt solutions. pH values of solutions (heated at 95°C) were adjusted to 5.3, 6.3, 7.3, 8.3 and 9.3. Ni<sup>2+</sup> concentration was fixed at 0.02 molar in order to enhance Ni<sup>2+</sup> precipitation<sup>[5]</sup>. After the fractional precipitation reactions, deionized water was added twofold the suspension volume and the systems were reheated at 95°C. Precipitates were filtered, washed twice with deionized water, dried at room temperature overnight and calcined in air at 750°C for one hour. Coprecipitation reactions were performed by slowly adding the solutions of metal chlorides (heated at 95°C) into known amounts of 7.4 molar NH<sub>4</sub>OH aqueous solution with continuous stirring. After precipitation reaction, the steps described above for the titration procedure were repeated. Ni<sup>2+</sup> concentration in filtrates was determined by ICP-AES analysis (Spectro Flame M 120E – Spectro Analytical, USA) for determination of nickel precipitation and coprecipitation yield. Specific surface area was determined by applying the multipoint Brunauer-Emmett-Teller (B.E.T.) method, with adsorption/desorption of nitrogen at 77K (Quantachrome, Nova 1200, USA). For studying the effect of nickel content on preparing nickel-aluminum oxide powders, the coprecipitation route was used and the pH at the end of reactions was fixed at a value that gave the highest fractional precipitation yield. The crystalline structures of all calcined powders were investigated by XRD (Rigaku, Multiflex, USA) with Cu-K $\alpha$  radiation in 2 $\theta$  range of 10-90°, step size 0.02° and counting time of 6s. Calcined powders were denoted as Al<sub>x</sub>Ni-750 (Al= alumina, xNi= wt% nickel content, and 750 is the calcination temperature). Nickel contents were determined by energy-dispersive X-ray spectroscopy (EDX-720 – Shimadzu, USA).

## 3 Results and discussion

Fig. 1 shows nickel precipitation yield for nickel-aluminum oxide synthesis process by adding NH<sub>4</sub>OH aqueous solution to mixed nickel-aluminum chlorides solution. In ammonia medium, mixed nickel-aluminum hydroxide precipitates as a light blue gel with a yield of 90-98%.



**Fig. 1.** Nickel precipitation yield on synthesis process of Ni/Al<sub>2</sub>O<sub>3</sub> powders with mass ratio of 15:85

As pH rises from 6.3 to 9.3, precipitation yield decreases from 98 to 93% by possibly two phenomena: (a) formation of soluble nickel-amine complexes,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , which give a blue color to mother liquor, due to ammonia excess addition<sup>[5]</sup> and, (b) re-resolution of the precipitate<sup>[6]</sup>. At pH values below 6.0, precipitation yield drops to around 90% probably because of lack of  $\text{NH}_4\text{OH}$  aqueous solution for cations precipitation. Fig. 1 also shows the effect of pH on coprecipitation experiment. A similar yield is observed at pH 7.3-9.3, though it drastically diminishes to 85% at pH 5.3. The latter behaviour may be explained by the fact that ammonia rapidly evaporates when the salt solution (heated at 95°C) is added.

Nickel-aluminum oxide powder prepared at pH 6.3 exhibited high surface area ( $232.6 \text{ m}^2 \cdot \text{g}^{-1}$ ) even after the high temperature calcination treatment (750°C). XRD pattern of calcined samples coprecipitated at pH 5.3, 6.3, 7.3, 8.3, and 9.3 are given in Fig. 2a. The NiO phase was not observed for powders with 15wt% Ni loading. A close examination of XRD analysis revealed two phases, in accordance with Achouri et al.<sup>[7]</sup>:  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{NiAl}_{10}\text{O}_{16}$ , in agreement with ICDD card numbers 10-0425 and 37-1292, respectively. Broadening of X-ray diffraction lines indicates a low degree of crystallinity at high pH medium. This behaviour can be explained by ammonia molecules penetration between the layer structure, as discussed by Ramsis et al.<sup>[8]</sup>. Fig. 2b shows XRD pattern of catalysts with high Ni content. NiO crystallization starts for sample with 35wt% Ni. NiO (ICDD Card No. 65-6920) diffraction line was detected at  $2\theta = 62.95^\circ$  and its intensity increases for samples with higher Ni loading. At 55wt% Ni, formation of  $\text{NiAl}_2\text{O}_4$  (ICDD Card No. 01-1229) is quite feasible. In the presence of nickel excess, coprecipitation of precursors also allows a very intense mixing of nickel and aluminum ions, resulting in the formation of a mixed nickel-aluminum hydroxide besides nickel hydroxide, that decompose to nickel aluminate and nickel oxide, respectively, during calcination treatment. At 75wt% Ni, only NiO and  $\text{NiAl}_2\text{O}_4$  are detected.  $\gamma\text{-Al}_2\text{O}_3$  is not observed for powders with Ni content higher than 55wt%. Table 1 reports nickel contents, crystalline phases and color of powders with high Ni loading.

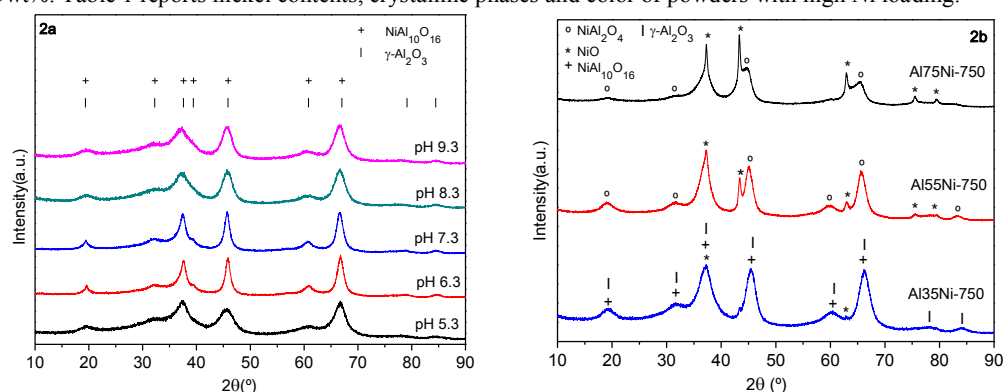


Fig. 2. XRD patterns of (a) Ni/Al<sub>2</sub>O<sub>3</sub> with mass ratio of 15:85 and (b) Ni/Al<sub>2</sub>O<sub>3</sub> as a function of Ni content.

Table 1. Properties of nickel–aluminum based oxide powders calcined at 750°C, as a function of Ni content

Sample code	Nominal Ni content (wt%)	Measured Ni content (wt%) <sup>a</sup>	Crystalline phases	Sample color
Al15Ni-750	15	13.9	$\gamma\text{-Al}_2\text{O}_3/\text{NiAl}_{10}\text{O}_{16}$	Blue
Al35Ni-750	35	22.3	$\gamma\text{-Al}_2\text{O}_3/\text{NiAl}_{10}\text{O}_{16}/\text{NiO}$	Blue
Al55Ni-750	55	41.5	$\text{NiO}/\text{NiAl}_2\text{O}_4$	Blue
Al75Ni-750	75	59.2	$\text{NiO}/\text{NiAl}_2\text{O}_4$	Green

<sup>a</sup> Determined by EDX

#### 4 Conclusions

Coprecipitation route has proven to be a suitable method for preparing nickel-aluminum mixed oxide powders. pH control must be carefully performed when using  $\text{NH}_4\text{OH}$  so as to enhance  $\text{Ni}^{2+}$  precipitation. Preparing mixed oxides at pH values around 6.3-7.3 promotes the formation of materials with a higher degree of crystallinity, that is ascribed by narrowing of X-ray diffraction lines. Results of this study also show that, according to nickel content, various crystalline phases may be formed: with 15wt% Ni loading, the sample is a mixture of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{NiAl}_{10}\text{O}_{16}$ , for 25wt% Ni content,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{NiAl}_{10}\text{O}_{16}$  and NiO are observed, and for Ni contents higher than 40wt% the systems include  $\text{NiAl}_2\text{O}_4$  and NiO phases. NiO formation might involve a nucleation of  $\text{NiAl}_2\text{O}_4$  phase wherein NiO rapidly grows. Support for this statement may be given by the fact that addition of Ni above solubility limit, at coprecipitation step, probably results in the formation of a mixed Ni-Al compound, besides  $\text{Ni}(\text{OH})_2$ .

#### Acknowledgements

Authors would like to thank National Nuclear Energy Commission (CNEN, Brazil) for the student scholarship, National Council for Scientific and Technological Development (CNPq, Brazil) for financial support and the members from XRD/CCTM, EDX/CCTM and LAQA/CQMA laboratories for technical support.

#### References

- [1] A. Bshish, Z. Yaakob, B. Narayanan, R. Ramakrishnan, A. Ebshish, Chem. Pap. **65** (2011) 251-266
- [2] M. C. Sánchez-Sánchez, R. M. Navarro, J. L. G. Fierro, Int. J. Hydrogen Energ. **32** (2007) 1462-1471
- [3] N. Bion, D. Duprez, F. Epron, Chem. Sus. Chem. **5** (2012) 76-84
- [4] F. Seyedejn-Azad, E. Salehi, J. Abedi, T. Harding, Fuel Process Technol. **92** (2011) 563-569
- [5] W. K. Yoshito, V. Ussui, D. R. R. Lazar, J. O. A. Paschoal, Mater. Sci. Forum **498-499** (2005) 612-617
- [6] S. P. S. Andrew, Chem. Eng. Sci. **36** (1981) 1431-1445
- [7] I. E. Achouri, N. Abatzoglou, C. Fauteux-Lefebvre, N. Braidry, Catal. Today **207** (2013) 13-20
- [8] M. N. Ramsis, E. R. Souaya, M. Abd-El-Khalik, S. A. Selim, J. Mater. Sci. **25** (1990) 6-14