

Nickel distribution in (Ni,Mg)/Al-layered double hydroxides

J.A. Rivera^a, G. Fetter^{a,*}, Y. Jiménez^a, M.M. Xochipa^a, P. Bosch^b

^a Universidad Autónoma de Puebla, Facultad de Ciencias Químicas, Blvd. 14 Sur y Av. San Claudio, C. P. 72570, Puebla, PUE, México

^b Universidad Nacional Autónoma de México, Instituto de Investigaciones en Materiales, Ciudad Universitaria, C. P. 04510, México, D. F., México

Received 7 June 2006; received in revised form 7 September 2006; accepted 22 September 2006

Available online 13 November 2006

Abstract

Hydrotalcites are anionic clays whose structure is lamellar. They are constituted by pairs of octahedral divalent and trivalent cations. The substitution of the divalent by the trivalent cations generates a charge excess which has to be compensated by anions such as carbonates, nitrates or iodine among others. The location of the trivalent cations is uncertain as it may depend on the synthesis method. Although hydrotalcites may be synthesized through conventional precipitation from the corresponding salts the obtained cation distribution may be altered in presence of microwave irradiation.

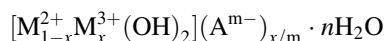
In hydrotalcites synthesized in presence of microwave irradiation, magnesium and aluminum are not homogeneously distributed: Aluminum is selectively retained in the particle core. If zinc or nickel are included in the synthesis mixture, zinc, which is a large cation, remains in the pore mouths generating lattice strain. Most of it, then, forms zinc oxide crystallites. Instead, nickel is able to reach the inner part of the hydrotalcite particle. With calcinations, 450 °C/4 h, hydrotalcite is never fully destroyed.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydrotalcite; Microwave irradiation; Microporous materials; Zinc; Aluminum; Magnesium; Nickel; Nanometrical NiO

1. Introduction

Layered double hydroxides are anionic clay-like compounds or more specifically hydrotalcite-like compounds. They are usually synthesized and their symmetry is rhombohedral or hexagonal, the corresponding chemical formula is:



where M^{2+} and M^{3+} are di- and tri-valent metals, respectively, M^{3+} ions produce positively charged layers. This charge is neutralized by A, a compensating anion with charge $m-$, as CO_3^{2-} , SO_4^{2-} , Cl^- or NO_3^- among others. The most frequent divalent metals are those whose ionic radii vary from 65 pm (Mg) to 80 pm (Mn) whereas the radii of the trivalent metal has to be comprised between 50 pm (Al) and 69 pm (Cr) [1,2].

It is currently accepted that the main properties of hydrotalcite-like compounds are determined by the concentration of the reactants in the synthesis solution, by the synthesis procedure (hydrothermal, sol-gel, microwaves, ultrasound, pH

value, among others) or by the metal ratio M^{2+}/M^{3+} [3–6]. The nature of the couple divalent–trivalent metal is most relevant.

Hydrotalcite synthesis method has been significantly improved substituting the conventional hydrothermal step by a microwave irradiation exposure [5,7]. The autoclave high-temperature treatment is, in this way, avoided and the long crystallization time is substantially reduced. In the microwave-irradiated synthesis, correlations between the features of the obtained hydrotalcite-like compound and the anion and cation nature has not been established or carefully studied. The understanding of those parameter effects should provide a control on the structural and morphological characteristics of the materials, and therefore, on the corresponding catalytic properties. These solids may be used, for example, to hydrogenate acetonitrile [8]. The acid sites are partly responsible for the formation of secondary products. The occurrence of the optimal Mg content is due to a compromise between the reducibility of nickel and the acido-basicity of the material. Hence, the metal distribution in the catalyst is crucial.

In a previous work [9] we determined that the irradiation power conditions the homogeneity of the obtained materials as at 600 W the Mg/Al-hydrotalcite is more homogeneous than the 200 W synthesis.

* Corresponding author. Fax: +52 2222443106.

E-mail address: geolarfetter@yahoo.com.mx (G. Fetter).

Microwave irradiation can be used not only to reduce preparation time as a fast heating method but to prepare original materials. In Mg/Al-hydrotalcite synthesis the irradiated materials present a concentration gradient where the core is aluminum enriched [9]. This result may be interpreted in terms of the competitive diffusion determined by charge, weight and ion size. The reaction occurs at the contact surface between the solid and the solution without involving the crystallized bulk. We have found that in Zn,Mg/Al hydrotalcites, an aluminium-enriched core is first formed and, then, magnesium is driven into the structure. Finally, zinc remains on the hydrotalcite surface in agreement with the weight and size of the considered elements.

In this work, to favour the formation of metallic catalytically active sites, Mg is partially substituted by Ni or Zn. These cations have ionic radii, 72 and 74 pm, respectively, while magnesium has 65 pm. The influence of zinc and nickel in the synthesis of Mg/Al-hydrotalcite-like compounds in presence of microwave irradiation is discussed. Two groups of hydrotalcite-like compounds were studied: on the one hand, those with the usual composition Mg/Al and, on the other, those with Zn,Mg/Al or Ni,Mg/Al where Zn^{2+} or Ni^{2+} ions compete with Mg^{2+} to form the brucite-like layers of the hydrotalcite.

2. Experimental

2.1. Hydrotalcite samples

2.1.1. Mg/Al-hydrotalcite synthesis

Mg/Al-hydrotalcite samples were synthesized from a $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich 99% and 98%, respectively) water solution, 3.2 M. A second aqueous solution, 1.86 M, was prepared with NaOH. The precipitation was carried out dropping the solutions and maintaining a constant pH of 13. The solution amounts were adjusted to correspond to Mg/Al molar ratios of 2, 3 and 4. The resulting gels were treated in a microwave autoclave (MIC-I, Sistemas y Equipos de Vidrio S.A. de C.V.) for 10 min operating at 2.45 GHz, Fig. 1, whose maximum power is 600 W. Note that the autoclave is coupled to a mechanical stirring system and that temperature and pressure can

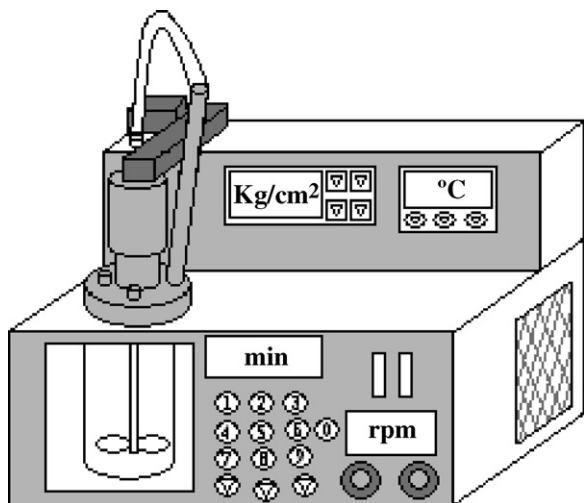


Fig. 1. Illustration of the microwave autoclave apparatus.

be programmed as they are automatically controlled through an infrared device. The autoclave volume capacity is 500 mL but our solution was always *ca.* 350 mL. The microwave irradiation power was 200 W and the temperature was fixed at 80 °C. The solids were recovered by decantation and washed several times with distilled water until the residual solution reached a pH value of 10. The solids were, then, dried in an oven at 70 °C for 14 h. To obtain the mixed oxides, a fraction of each sample was calcined in air at 450 °C for 4 h. Being aware that calcined hydrotalcites can partially reassemble with time in presence of air or humidity, the samples were stored in hermetical flasks.

2.1.2. Zn,Mg/Al-hydrotalcite synthesis

The Zn,Mg/Al-hydrotalcite samples were prepared in the same way, from $Zn(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (Merck, 99%, Aldrich 99% and 98%, respectively) using solution amounts which correspond to (Zn + Mg)/Al molar ratios of 2, 3 and 4 where the Zn:Mg molar proportion was 1:1. The samples were microwave treated at 200 W, washed, dried and calcined as described in the previous section. Zn/Al compounds were prepared and treated in the same way for comparison purposes.

2.1.3. Ni,Mg/Al-hydrotalcite synthesis

These samples were prepared in the same way as the previous ones from $Ni(NO_3)_2 \cdot 6H_2O$ (Baker, 98%) with the same molar ratios. Again, Ni/Al samples were synthesized.

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

A Bruker-axs D8-advance diffractometer coupled to a copper anode X-ray tube was used to identify the compounds. A diffracted beam monochromator selected the $K\alpha$ radiation.

2.2.2. FTIR spectroscopy

FTIR spectra in the region 4000–400 cm^{-1} were obtained with a Magna-IR Spectrometer 550 Nicolet, using KBr pellet technique.

2.2.3. Nitrogen adsorption

The BET surface areas were determined by the multipoint technique with a Micromeritics ASAP 2020 after a thermal treatment of 200 °C for 10 h in vacuum.

2.2.4. Scanning electron microscopy (SEM)

A scanning electron microscope LEICA, Stereoscan 440, was used. An energy dispersive X-ray detector coupled to the microscope provided the elemental local composition (EDX) for a depth of, approximately, 2 μm .

3. Results and discussion

3.1. Cation effect on the structure

The X-ray diffraction patterns of the Mg/Al samples, show that well crystallized hydrotalcite-like compounds are obtained,

no other crystalline compounds are identified, as reported in our previous work [9]. Only in the sample with Mg/Al molar ratio of 2, a small amount of NaNO_3 (nitratine) is observed (small and sharp peaks at $2\theta = 29.5$ and 32.0°). As the interlayer distance 003 is *ca.* 7.76 Å, the interlayered anions should be nitrates [1,2]. With calcination (450 °C for 4 h) the diffraction patterns turned out to be different, the samples are mainly MgO and show a very small percentage of hydroxalcite-like compound. The synthesis with a Mg/Al molar ratio of 2 still presents some amount of nitratine. The incorporation of zinc, independently of the molar ratio, provides similar materials composed by hydroxalcite and ZnO whose presence is not reported by Klopogge et al. [10,11] in the corresponding coprecipitation synthesis. With calcination, the sample Mg/Al = 2, is constituted only by ZnO and MgO.

When nickel was included in the synthesis mixture instead of zinc, the X-ray diffraction patterns, Fig. 2, show that more crystalline hydroxalcite is formed as the ratio Ni,Mg/Al is increased from 2 up to 4. In the 3 and 4 M ratios, no NiO is formed, all nickel is, indeed, incorporated into the hydroxalcite lattice. Still, a very small NiO peak may be observed in the Ni,Mg/Al = 2 samples. With calcination, a small amount of hydroxalcite remains in the sample Ni,Mg/Al = 4. The main compounds are, in all samples, NiO and MgO, note that MgO X-ray diffraction peaks fall at almost the same positions as NiO peaks.

The X-ray diffraction peaks observed in the Ni/Al patterns are all due to hydroxalcite, no other crystalline compounds were clearly identified, Fig. 3. With calcinations, only NiO and some amorphous compound were formed.

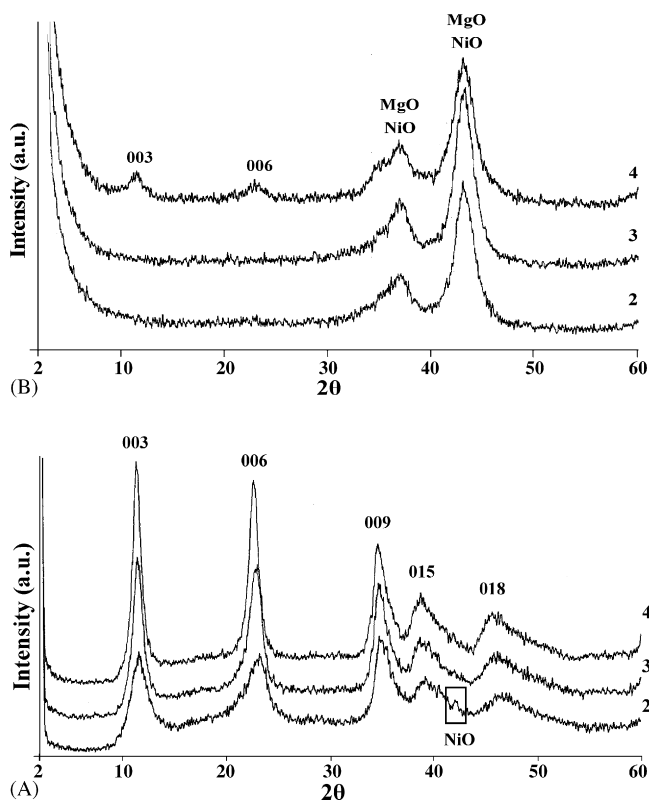


Fig. 2. X-ray diffraction patterns of the Ni,Mg/Al samples whose molar ratios are: 2, 3 and 4, all irradiated at 200 W (A) and the corresponding calcined materials (B).

3.2. Nitrates and carbonates

By infrared spectroscopy, in the non-calcined samples, the obtained spectra reproduce the general features often reported for hydroxalcite-like compounds [2,12]. Fig. 4 shows only some representative spectra. The presence of both, nitrates and carbonates, band at $1361\text{--}1381\text{ cm}^{-1}$, is shown. With calcination usually this absorption band diminishes as hydroxalcite decomposes [13] but, in our conditions, it is always present showing that hydroxalcite is not fully destroyed. Only in the calcined Ni/Al = 3 samples, the band at 1381 cm^{-1} diminished significantly. These results seem to be in disagreement with those of X-ray diffraction. However, note that to observe a compound by X-ray diffraction it has to be present in more than 3%, it has to be crystalline and the crystallite size has to be larger than *ca.* 25 Å. In infrared spectroscopy a band appears below those constraints.

3.3. Morphology

The particle morphology is compared in Fig. 5 for samples with molar ratio = 3. When nickel is incorporated (Ni,Mg/Al sample) the effect is opposite to the one reported in our previous work [9] for Zn as large homogeneous chunks (300 μm) are formed, still 70–100 μm particles are present. Note how on the edge of the particle located in the upper left corner of the image the lamellar structure can be inferred. In the Ni/Al compound this effect is confirmed as large agglomerates (80–100 μm) are

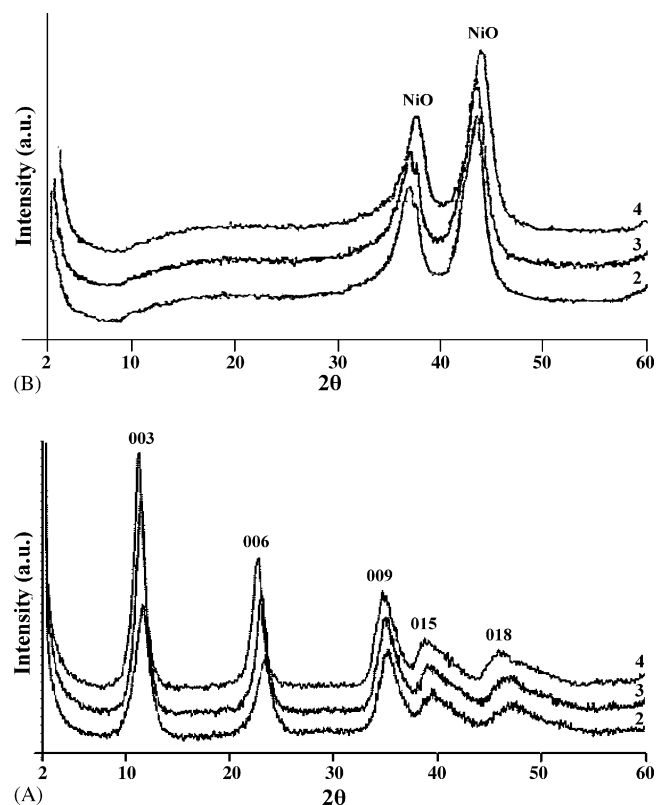


Fig. 3. X-ray diffraction patterns of the Ni/Al samples whose molar ratios are: 2, 3 and 4, all irradiated at 200 W (A) and the corresponding calcined materials (B).

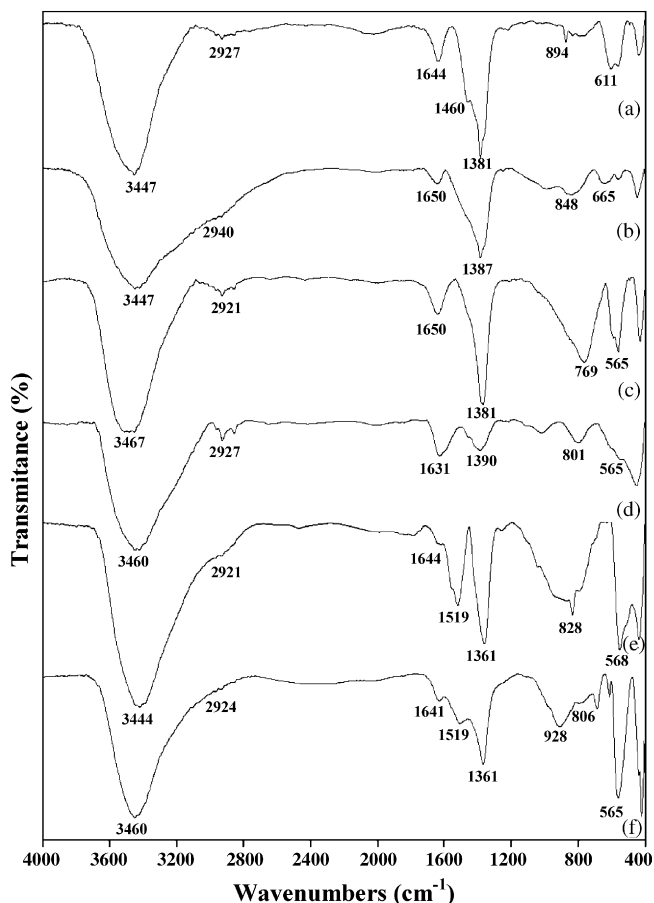


Fig. 4. Infrared spectra of the samples: (a) Ni,Mg/Al = 3, (b) calcined Ni,Mg/Al = 3, (c) Ni/Al = 3 and (d) calcined Ni/Al = 3, (e) Zn/Al = 3 and (f) calcined Zn/Al = 3.

present, they are constituted by smaller faceted planar particles whose dimensions are $1 \mu\text{m} \times 10 \mu\text{m} \times 15 \mu\text{m}$. These blocks are hydrotalcite, the only compound observed by X-ray diffraction.

3.4. Surface elemental composition

To determine the composition of the large and small particles observed in the micrographs, the local elemental

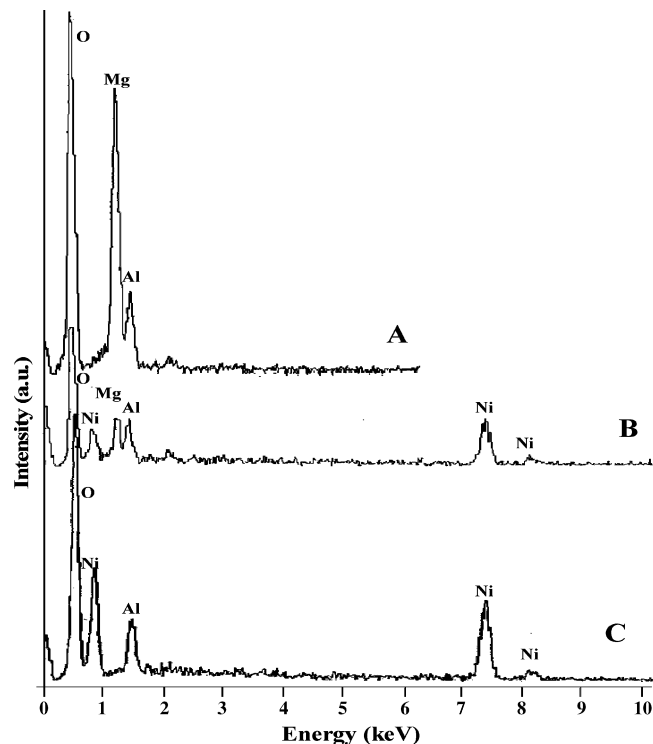


Fig. 6. EDX elemental analysis of samples Mg/Al = 3 (A), Ni,Mg/Al = 3 (B) and Ni/Al = 3 (C).

analysis was determined by EDX, Fig. 6. If the spectra of Mg/Al, Ni,Mg/Al and Ni/Al are compared the relative intensities of the peaks are not in a linear relationship. In the Ni,Mg/Al sample, the amount of Mg (relative to Al) is very small compared to the corresponding amount of Mg in the Mg/Al sample. Therefore, this material is magnesium enriched in the core. Then, the following model emerges for the Ni,Mg/Al sample: a magnesium enriched core surrounded by a nickel rich shell.

In a previous work [9], we found that magnesium was peripherally distributed in the hydrotalcite particles depending on the microwave irradiation power. If Zn is added, magnesium inhibits its diffusion [9]. The lattice strain is such that, subsequently, zinc forms zinc oxide. As nickel and zinc sizes are close (72 and 74 pm, respectively [1,2]), a similar behavior

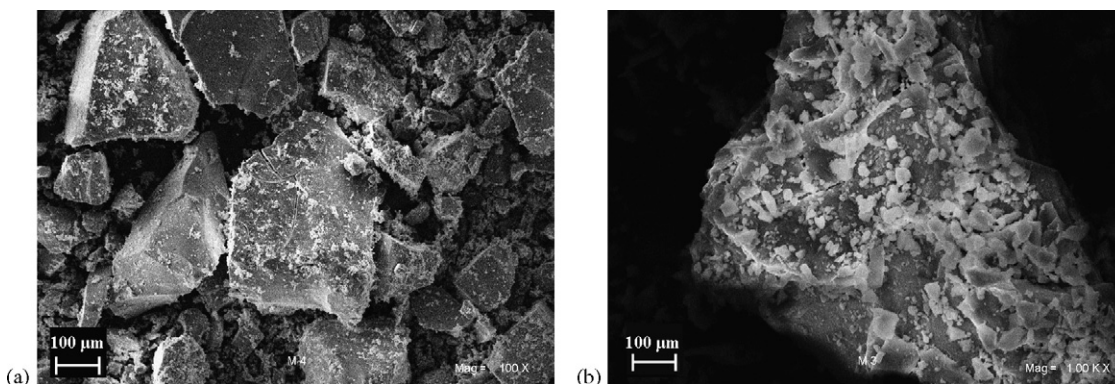


Fig. 5. Scanning electron micrographs of the samples: (a) Ni,Mg/Al = 3 and (b) Ni/Al = 3.

Table 1

Comparison of the specific surface areas (m^2/g) of the hydrotalcite-like compounds as a function of their elemental composition

Sample	$\text{M}^{2+}/\text{M}^{3+} = 2$	$\text{M}^{2+}/\text{M}^{3+} = 3$	$\text{M}^{2+}/\text{M}^{3+} = 4$
Mg/Al	68	86	110
Zn,Mg/Al	76	92	63
Zn/Al	36	60	54
Ni,Mg/Al	9	47	119
Ni/Al	97	112	100

is expected. The previously discussed results are in agreement with this proposition. Furthermore, some NiO is observed in the sample Ni,Mg/Al = 2, Fig. 2A.

3.5. Texture

Table 1 compares the specific surface areas of the various samples including the Zn/Al and Zn,Mg/Al samples for comparison purposes. In the Mg/Al sample, the specific surface area increases as a function of the $\text{M}^{2+}/\text{M}^{3+}$ ratio from 68 to $110 \text{ m}^2/\text{g}$. In the Zn/Al and the Ni/Al samples the initially lower surface area values, 36 and $97 \text{ m}^2/\text{g}$, tend to a limit of 60 and $100 \text{ m}^2/\text{g}$, respectively. If a second metal M^{2+} is incorporated the values do not follow the same pattern. If the compound is homogeneous and is only constituted by hydrotalcite, as in Ni,Mg/Al, this effect is enhanced as the values vary from 9 to $119 \text{ m}^2/\text{g}$.

When nickel is added it does not diffuse through this shell and does not reach the particle core. Most probably, nickel in excess constitutes nanometrical particles (Fig. 2), which block nitrogen access in this region of the hydrotalcite. As nickel amount is reduced, less particles are formed and the pores are freed. Indeed, by X-ray diffraction a small difference among patterns seems to agree with this proposition. In Fig. 2, as molar ratio Ni,Mg/Al increases, the X-ray diffraction peak definition improves, showing that the material is more crystalline. Furthermore, only in the X-ray diffraction pattern of the sample with a molar ratio Ni,Mg/Al of 2 a very small peak of NiO is observed ($2\theta = 42.5^\circ$). Comparison with Zn,Mg/Al materials is most interesting as in the Zn,Mg/Al composition, ZnO is formed outside the particles as large crystallites, given the similarity of size between zinc and nickel the same behavior has to be expected. Probably the differences in morphology observed in Fig. 5 can be attributed to the same mechanism.

4. Conclusion

In hydrotalcites synthesized in presence of microwave irradiation, magnesium and aluminum are not homogeneously distributed. Aluminum is selectively retained in the particle core. If zinc or nickel is included in the synthesis mixture they distribute into the particle as follows. Zinc or nickel which are large cations, if compared with aluminum or magnesium, remain in the pore mouths generating such a lattice strain that most of it forms zinc or nickel oxide crystallites detected by X-ray diffraction [9]. With calcination the corresponding metal oxides are formed. However, infrared spectroscopy, in our conditions ($450^\circ\text{C}/4 \text{ h}$), shows that hydrotalcite is never fully destroyed [14].

Acknowledgements

The technical work in X-ray diffraction and electron microscopy of Leticia Baños and José Guzmán is gratefully recognized. This work would not have been possible without the financial support of CONACYT (project 44253-Q).

References

- [1] V. Rives, M.A. Ulibarri, *Coord. Chem. Rev.* 181 (1999) 61–120.
- [2] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* 11 (1991) 173–301.
- [3] F. Prinetto, G. Guiotti, P. Graffin, D. Tichit, *Microp. Mesop. Mater.* 39 (2000) 229–247.
- [4] G. Fetter, F. Hernández, M. Maubert, V.H. Lara, P. Bosch, *J. Porous Mater.* 4 (1997) 27–30.
- [5] D. Tichit, A. Rolland, F. Prinetto, G. Fetter, M.J. Martínez-Ortiz, M.A. Valenzuela, P. Bosch, *J. Mater. Chem.* 12 (2002) 3832–3838.
- [6] A.C.C. Rodrigues, C.A. Enríques, J.L.F. Monteiro, *Mater. Res.* 6 (2003) 563–568.
- [7] B. Zapata, P. Bosch, G. Fetter, M.A. Valenzuela, J. Navarrete, V.H. Lara, *J. Inorg. Mater.* 3 (2001) 23–29.
- [8] F.M. Cabello, D. Tichit, B. Coq, A. Vaccari, N.T. Dung, *J. Catal.* 167 (1997) 142–152.
- [9] J.A. Rivera, G. Fetter, P. Bosch, *Microp. Mesop. Mater.* 89 (2006) 306–314.
- [10] J.T. Klopogge, L. Hickey, R.L. Frost, *J. Raman Spectrosc.* 35 (2004) 967–974.
- [11] J.T. Klopogge, L. Hickey, R.L. Frost, *J. Solid State Chem.* 177 (2004) 4047–4057.
- [12] T.S. Stanimirova, I. Vergilov, G. Kirov, N. Petrova, *J. Mater. Sci.* 34 (1999) 4153–4161.
- [13] F. Millange, R.I. Walton, D. O'Hare, *J. Mater. Chem.* 10 (2000) 1713–1720.
- [14] A.J. Marchi, C.R. Apesteguía, *Appl. Clay Sci.* 13 (1998) 35–48.