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Sol-Gel Synthesis of Nickel-Doped Aluminium Oxide

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Almost single-phase 8% Ni-doped alumina compositions were derived, by the sol-gel method, from both organic and aqueous media. Thermal analysis, XRD, and FT-IR showed that the use of metal organic precursors, and working in an almost fully organic medium, is more advantageous. In these conditions, Ni-doped gamma-alumina could be obtained at a relatively lower temperature, 500°C, than in case of working in an aqueous medium where a delta-alumina phase was formed at temperatures not lower than 600°C. The method of preparation did not alter the desired metal ratio as checked by atomic absorption spectroscopy.

INTRODUCTION

M-Doped aluminium oxides (where M refers to a transition metal), represent one of the most industrially potential group of aluminium compounds[1, 2]. Composites of ceramic matrix prepared in the form of oxide mixtures are important materials for their uses as catalysts and catalyst supports[3]. They are also important corrosion prevention, oxidation resistant coatings and structural ceramics[4].

The ceramic method of synthesis was the basic route to prepare doped aluminum oxides. It is based on sintering a mixture of aluminium dopant metal oxides (or a mixture of compounds that yield the respective oxides on decomposition). A solid state reaction takes place to yield the desired product. The main drawbacks of this method are the need of high temperatures, the high dependence of the product's properties and yield on the extent of mixing the oxide grains and pollution.

The sol-gel method is a good alternative where pure and homogeneous products can be obtained[5–7]. The many advantages of the sol-gel method over the conventional methods of preparation are now well known. The relatively low temperatures of sintering, the less pollution, the good command of stoichiometry, and the pronounced ease of controlling the final form and shape of the product are examples. The method can be used to prepare multi-component systems as well[8–10]. This has proved to be simpler and more reliable, than soil-state method, in synthesizing manganese doped aluminium oxide ceramics[1].

The present work is aimed to prepare nickel-doped aluminium oxide compositions by pyrolysis of gels derived both from aqueous and from non-aqueous media.

EXPERIMENTAL

Starting solutions: The double gels of nickel and aluminium were prepared from analytical-grade aluminium isopropoxide, $Al(OC_3H_7)_3$, $Al(NO_3)_3 \cdot 9H_2O$ and nickel acetylacetonate, $Ni(acac)_2$. Two solutions of aluminium, (organic and aqueous), namely A1 and A2 respectively, were prepared. A1 was a 10 mM solution of $Al(OC_3H_7)_3$ in dry benzene and kept in a closed bottle. A2 was a 10 mM solution of aluminium nitrate in distilled water. $Ni(acac)_2$ powder was dissolved in an excess of benzene. After it was adjusted to 0.40 mM, the clear solution was kept in a tightly closed bottle and named (N1), while N2 was a 0.40 mM solution of $Ni(acac)_2$ in water.

Preparation of gels: A 150 mL portion of solution A1 was stirred for 1 h at 40°C in a 500 mL flat-bottom round flask aided with a refluxing condenser. The free terminal of the condenser was covered with a plastic sheet (Para-film). Through a side-branch tube, 300 mL of solution N1 were steadily added and constant stirring was continued for 2 h. Complexation was enhanced by adding 15 mM of ethylene glycol, then the plastic cover was removed and the clear mixture was refluxed overnight. There was no sign of precipitates or clouds. The resulting sol was concentrated at 50°C where a transparent greenish yellow gel, (named G1), was formed. It was then dried in a furnace at 80°C for 6 h.

Another gel, namely G2, was formed in a 500 mL beaker by mixing the exact volumes and repeating the same procedure as for G1 except that solutions A2 and N2 were used instead of solutions A1 and N1.

Both gels were checked for their Ni/Al ratio, powdered, and heated slowly up to 400°C at a rate of 2°C min^{-1} (to avoid fast or violent combustion). The temperature was then raised to sinter the gels at 500°C for 2 h in air atmosphere. A pink to violet ceramic product was obtained from G1 and a light yellow from G2.

Characterization techniques: Atomic absorption spectroscopy method was used to check the samples for their metal contents[11, 12].

The gels were thermally characterized by TG and DTA runs using a Perkin-Elmer Instrument Model DTA 7 series (Norwalk, Connecticut, USA) in a dynamic oxygen gas flow (50 cm^3/min at 10°C/min).

FT-IR spectra of the gels, as formed and dried at 80°C, were charted using Bomem-FTIR (Michelson, Canada) between 400 and 4000 cm^{-1}. The pellets were made of 1.2% powdered gels in dry KBr for the IR runs.

Crystalline products of the heat-treated samples were followed by a Philips 1390 X-ray powder diffractometer.

RESULTS AND DISCUSSION

The lower part of Figure. 1 shows the TG curves of the two gels dried at 80°C for 6 h. In both cases, the solvents were completely removed below 200°C, after which decomposition of the organic constituents of the gel took place. For G1, decomposition was full at about 380°C (about 90°C before the full decomposition of G2). In addition, the total weight loss ratio for G1 is some lesser than that of G2 which seems to have retained much ratio of water besides nitrate at the conditions of drying.

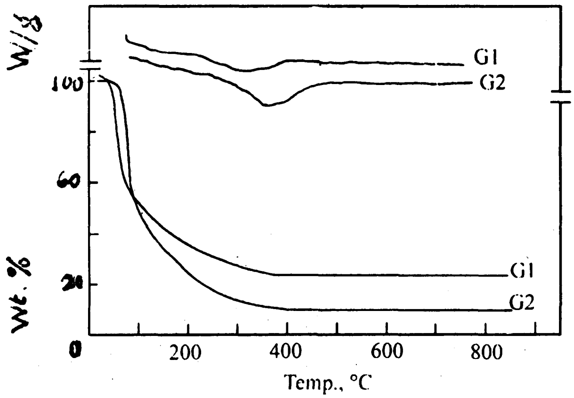

Fig. 1. TGA (lower two) and DTA (upper two) curves of gels dried at 80° and 220°C respectively.

The upper part of the same figure shows the DTA curves of the respective gels after getting rid of solvents by drying at 220°C for 1 h. No thermal events could be seen after 500°C. The endotherms below this temperature for both gels match with the weight losses shown by the respective TG curves.

Regardless of the unknown structure of either of the gel complexes, and hence the details of their decomposition mechanisms, the final products of sintering are homogeneous distributions of aluminium and nickel oxides in case of well-prepared gels.

As analyzed for their metal contents, the Ni/Al ratio was found to be nearly the same; (1/12.5 in the gels and 1/12.47 in the powders sintered at 500°C for 2 h). This indicates that the preparation conditions did not alter the desired metal composition ratio of the products.

Figure 2 shows the FT-IR spectra of both gels[14, 15]. The metal-oxygen vibrations can be seen in the region 730–450 cm^{-1}. The M—OH is the nucleophile in this kind of gelation where complexation proceeds basically via hydroxo and/or aquo hydroxo complexes and water molecule is the leaving group[1, 13]. The =CH— of the acetyl acetonate shows its bands between 800 and 930 cm^{-1} for both gels.

The strong stretching band at 1110–1000 cm^{-1} may be displayed by CH_2—OH where another strong band characteristic of this stretching is at the region 3450–3300 cm^{-1} overlapping with the strong broad one of the hydroxyl group and water at 3650–3100 cm^{-1}.

Only for G2, the nitrate group shows up, as strong bands, in the 1390–1285 cm^{-1} region and around 1650 cm^{-1}. Other significant features are CH_3 stretching at 2900 cm^{-1}, CH_n (n = 2, 3) deformation at 1400 cm^{-1}, CH_n (n = 2, 3) rocking in the region 1200–1100 cm^{-1}, and the strong bands characteristic of ketones at 1700–1600 cm^{-1}.

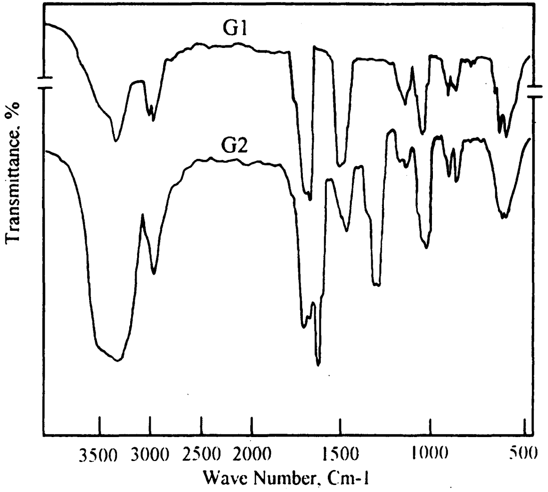

Fig. 2. FT-IR spectra of the two gels dried at 80°C.

It is clear that the metals coordination spheres in these two gels contain acetyl acetone, ethylene glycol and some water in case of G1 while for G2 the nitrate group coordinated to this gel.

The drying conditions seem to have eliminated all excess low-boiling organic solvents.

The XRD patterns of final heat-treated samples, Figure 3, show that the product is almost a single-phase solid solution (Ni-doped alumina) for both gels. This indicates a good transformation of the reaction mixture from a sol (composed of weakly interacting individual particles) into a gel composed of a continuous uniform molecule. On condensation, densification and pyrolysis, macro-particles of uniformly Ni-doped alumina are formed.

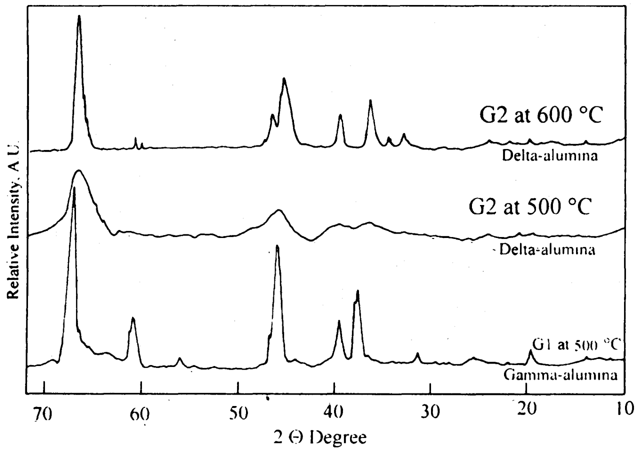

Fig. 3. XRD of the two gels at different temperatures.

There seems an advantage of deriving the Ni-doped alumina from a fully organic medium over doing so from an aqueous one. When sintered at 500°C for 2 h, the gel G1 produced a ceramic that displayed a gamma-alumina pattern. On the other hand, G2, treated at the same temperature, lead to a poorly defined pattern and needed further heating, up to about 600°C, to improve its crystallinity and display a clear delta-alumina pattern.

Conclusions

As followed by thermal analysis, FT-IR, XRD and atomic absorption spectroscopy, preparation of almost single-phase 8% Ni-doped alumina compositions, by the sol-gel method, from both organic and aqueous media was completed.

Working in a fully organic medium, and starting with organic precursors, seems to be of some advantage, as gamma-alumina composition could be obtained at a relatively lower temperature (500°C). In an aqueous medium, delta-alumina was the slowly forming composition that needed a temperature of about 600°C to be obtained.

Both methods of preparation did not alter the desired metal ratio as checked by elemental analysis.

REFERENCES

1. A. Kareiva, *Chemija (Vilnius)*, **1**, 50 (1997).
2. K. Wefers and C, Misra, Oxides and Hydroxides of Aluminium, Alcoa Laboratories (1987).
3. Ch. C. Landry, N. Pappe, M. Mason, A.W. Apblett, A.N. Tyler, A.N. MacInnes and A.R. Barron, *J. Mater. Chem.*, **5**, 331 (1995).
4. A.W. Apblett, A.C. Warren and A.R. Barron, *Chem. Mater.*, **4**, 167 (1992).
5. S. Sakka, *J. Sol-gel Sci. Technol.*, **3**, 69 (1994).
6. C.J. Brinker and G.W. Scherer, Sol-Gel Science, Academic Press, New York (1990).
7. A.F. Ali, P. Mustarelli and A. Magistris, *Mater. Res. Bull.*, **33**, 697 (1998).
8. A.F. Ali, P. Mustarelli, E. Quartarone, C. Tomasi, P. Baldini and A. Magistris, *J. Mater. Res.*, **14** (1999) (in press).
9. J. Livage, M. Henry and C. Sanchez, *Progr. Solid State Chem.*, **18**, 259 (1988).
10. B. Dunn, G.C. Farrington and B. Katz, *Solid State Ionics*, **70/71**, 3 (1994).
11. A. Kareiva and J. Barkauskas, *Chemija*, **3**, 81 (1993).
12. A.F. Ali, Ph.D. Thesis, Cairo University, Faculty of Science (1996).
13. J. Livage, *J. Sol-Gel Sci. Tech.*, **1**, 21 (1990).
14. H.M. Randall, H.G. Fowler, N. Fuson and J.R. Dangl, in: Infrared Determination of Organic Structures, Van Nostrand, New York (1949).
15. I. Bryntse and A. Kareiva, *Physica C.*, **251**, 115 (1995).

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