

Synthesis and Characterization of Si–Al, Si–Ti, Si–Zr, Al–Zr, Al–Ti, and Al–Ti–Zr Nanocomposites of Lamellar or Hexagonal Structure

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By using tetraethylortosilicate, titanium and zirconium tetrabutoxide, and aluminum sec-butoxide, as well as neutral 1,10 and 1,12 alkyldiamines or dodecyltrimethylammonium bromide as precursors, a series of six oxides, Si–Al, Si–Ti, Si–Zr, Al–Zr, Al–Ti, and Al–Ti–Zr, were obtained. These materials were characterized by infrared spectroscopy, thermogravimetry, X-ray diffraction patterns, and scanning electron microscopy. Si–Ti, Si–Zr, and Al–Ti matrices exhibit a lamellar structure, whereas the others have a hexagonal nature. With the exception of the Al–Ti matrix for which grains with spheric morphology are observed, all the other matrices exhibited grains with amorphous nature, as observed by SEM micrographs. © 2001

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INTRODUCTION

Sol–gel process provides the possibility of performing the synthesis of materials of very high homogeneity at room temperature (1). The hydrolysis and polycondensation of metal alkoxydes of the general formula $M(OR)_n$ takes a prominent part in the chemistry involved in the sol–gel process. The structure and morphology of the synthesized compounds depends strongly of the hydrolysis and polycondensation stages. For example, by using tetraethylorthosilicate, as well as neutral alkyldiamines as precursor, lamellar samples of silica can be obtained (2). The structure, as well as the thermal stability, of those matrices can be remarkably affected by the addition of transition metal chlorides (3,4), by using solid state reactions, where the copper samples are doped with potassium bromide (5), or by an increase of the external pressure (6). Furthermore, such nanocomposite materials constitute a very important class of compounds due to their potential use in a variety of fields such as catalysis, optics, magnetism, and electronics (7).

Layered and hexagonal aluminosilicates were obtained previously (8) through the specific reaction involving tetraethylorthosilicate (TEOS) and $Al(NO_3)_3 \cdot 9H_2O$ as

precursors and hexadecylamine as template molecule. For such hybrids, $LiNO_3$ was added through the reaction as an inorganic ingredient, playing a crucial role in the selective formation of the lamellar or hexagonal structure of the mesoporous aluminosilicate.

Taking into account the use of the sol–gel process, other hybrids such as silica–zirconia (9,10), zirconium titanates (11,12), and zinc–silicon nanocomposites (13) were obtained. In addition, zirconia–titania oxides with a hexagonal nanostructure exhibit particles with spherical morphology (14).

The aim of this publication is to report the synthesis and characterization of a series of six nanocomposite oxides, Si–Al, Si–Ti, Si–Zr, Al–Zr, Al–Ti, and Al–Ti–Zr. The main purpose is to illustrate that, like the observed zirconia–titania (14), double- or triple-oxide nanocomposites with hexagonal or lamellar nature can be also synthesized through the sol–gel process.

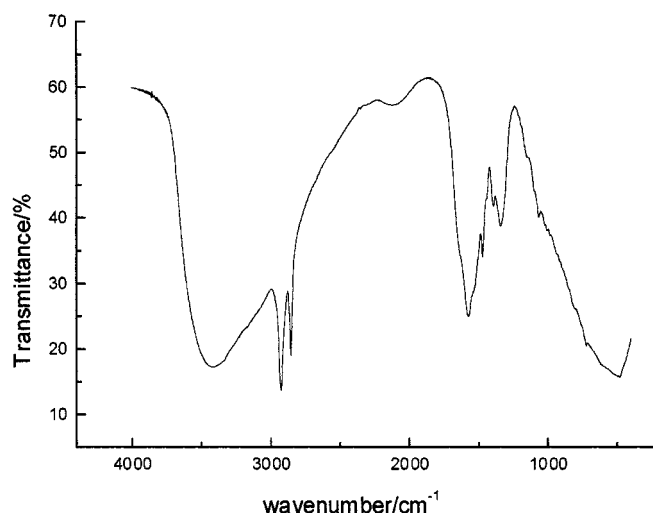


FIG. 1. Infrared spectra in the range $400\text{--}4000\text{ cm}^{-1}$, obtained in KBr discs for the Al–Zr hybrid matrix.

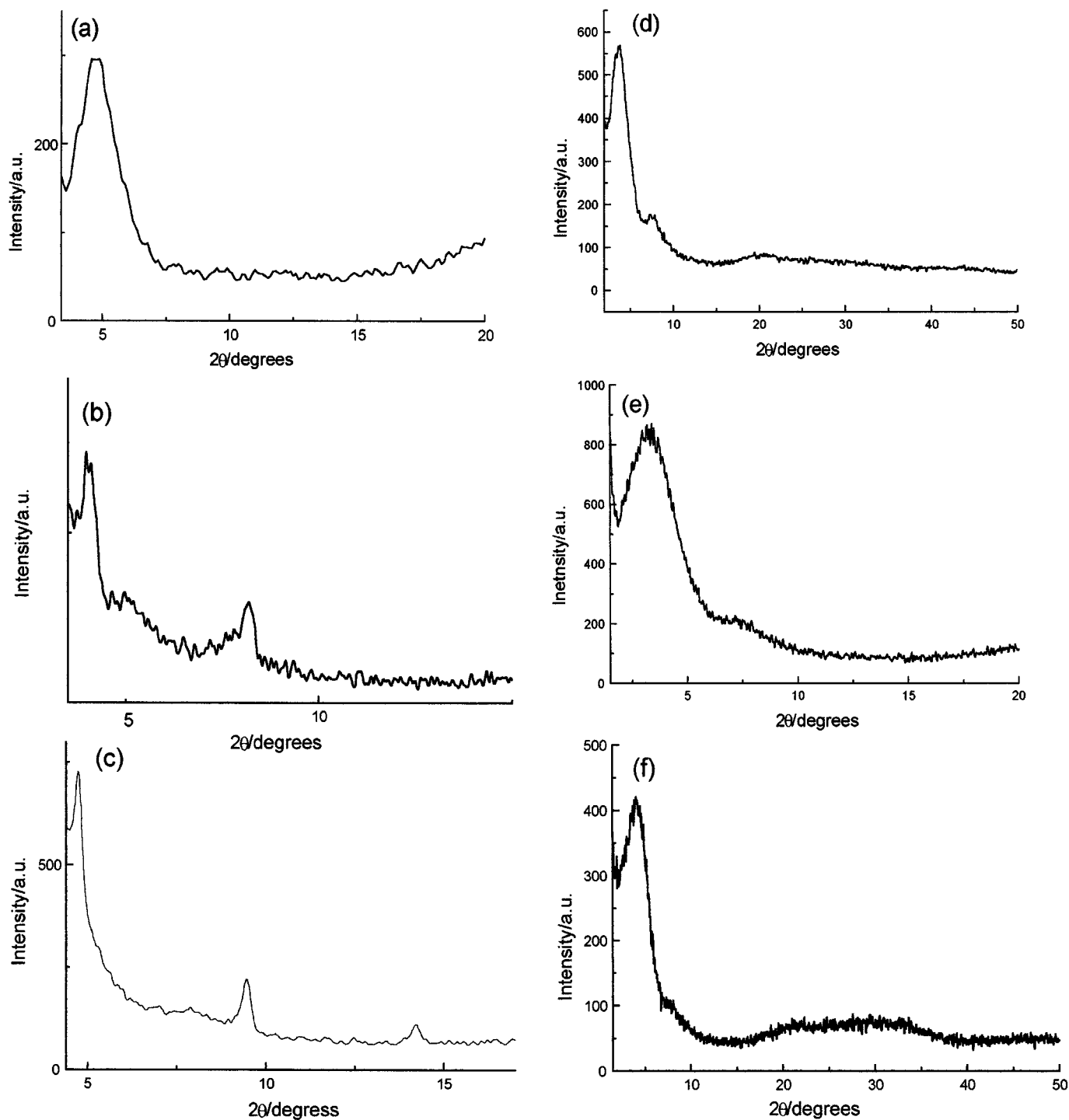


FIG. 2. X-ray diffraction patterns for the lamellar and hexagonal hybrid matrices: Si-Al (a), Si-Ti (b), Si-Zr (c), Al-Ti (d), Al-Zr (e) and Al-Ti-Zr (f).

EXPERIMENTAL

All reagents were used of analytical grade from Aldrich, and were employed without further purification. Tetraethylortosilicate, TEOS, titanium tetrabutoxyde,

TiBut, zirconium tetrabutoxyde, ZrBut, aluminum sec-butoxyde, AlBut, 1,12-diaminododecane, 1,10-diaminododecane, and dodecyltrimethylammonium bromide were employed as precursors and propanol was employed as solvent.

TABLE 1
X-ray Data for Hybrid Matrices Involving Silicon, Aluminum, Titanium and Zirconium

Matrix	2θ (°)	d (nm)	Diffraction planes	Structure
Si-Al	4.7	2.02	100	hexagonal
Si-Ti	4.1; 8.2	2.20; 1.10	001; 002	lamellar
Si-Zr	4.7; 9.4; 14.1	2.02; 1.01; 0.67	001; 002; 003	lamellar
Al-Ti	3.8; 7.6	2.32; 1.16	001; 002	lamellar
Al-Zr	3.3	2.88	100	hexagonal
Al-Ti-Zr	4.1	2.32	100	hexagonal

In a typical synthesis, the alkoxydes were mixed under stirring in a nitrogen atmosphere and the mixture was aged for 72 h. The resulting solution was added to a propanol solution of alkyldiamine or surfactant prepared previously and was aged for 72 h, when 1.0 mol of H₂O was added. The formed gel was aged for another 48 h and dried under vacuum for 24 h at 30°C. The composition of the various reaction systems used to obtain the hybrid matrices can be summarized as follows:

(a) Si-Al: 5.0 cm³ of TEOS + 5.0 cm³ of AlBut + 2.0 g of 1,12-diaminododecane + 60.0 cm³ of propanol;

(b) Si-Ti: 2.5 cm³ of TEOS + 2.5 cm³ of TiBut + 3.0 g of dodecyltrimethylammonium bromide + 30.0 cm³ of propanol;

(c) Si-Zr: 5.0 cm³ of TEOS + 5.0 cm³ of ZrBut + 2.0 g of 1,12-diaminododecane + 30.0 cm³ of propanol;

(d) Al-Ti: 4.0 cm³ of AlBut + 4.0 cm³ of TiBut + 2.0 g of 1,12-diaminododecane + 60.0 cm³ of propanol;

(e) Al-Zr: 5.0 cm³ of AlBut + 5.0 cm³ of ZrBut + 2.0 g of 1,12-diaminododecane + 60.0 cm³ of propanol; and

(f) Al-Ti-Zr: 5.0 cm³ of AlBut + 5.0 cm³ of TiBut + 5.0 cm³ of ZrBut + 2.0 g of 1,10-diaminododecane + 60.0 cm³ of propanol.

The presence of water must be avoided in the first stage of the synthetic procedure, since it is of fundamental importance to control the rate of reaction. In contrast, the lowest electronegativity of these transition metals caused a faster rate of hydrolysis and polycondensation reactions than silicon (15).

X-ray diffraction patterns were recorded on a Shimadzu apparatus using CuK α radiation (35 kV, 25 mA). Thermogravimetric data were obtained on a Shimadzu TGA-50 under argon atmosphere and with a heating rate of 5°C min⁻¹. Scanning electron micrographies were obtained by using a Jeol equipment Model JSM T-300 apparatus in an accelerating voltage of 20 kV. Infrared spectra were obtained on a Bomem equipment in the range 4000–400 cm⁻¹ with 4 cm⁻¹ of resolution, by dispersing the samples in KBr discs.

RESULTS AND DISCUSSION

The infrared spectra of the matrices obtained exhibit bands in the ranges 3000–2700 cm⁻¹ and 1100–1700 cm⁻¹. The bands at 2920 and 2847 cm⁻¹ are located in a range characteristic of the vibration modes of N–H and C–H bonds (3). As an example, the infrared spectrum of the Al–Zr matrix is shown in Fig. 1. For this sample, the peaks at 1575 and 500 cm⁻¹ are assigned to the inorganic oxide backbone.

The X-ray diffraction patterns of the synthesized matrices are shown in Figs. 2a–2f. The X-ray diffraction data are summarized in Table 1. Considering the X-ray diffraction patterns, a lamellar structure can be verified for the Si–Ti, Si–Zr, and Al–Ti matrices, whereas the others have a hexagonal nature.

The SEM micrographs obtained show that all synthesized hybrids exhibit grains with an irregular morphology, except the Al–Ti matrix, whose particles are of spheric morphology, as shown in Fig. 3. The same morphology was observed for a Ti–Zr hexagonal matrix (14), synthesized through the same route. The mapping images obtained for Si, Al, Ti, and Zr shows that, in the respective oxides, these elements are homogeneously distributed. Furthermore, the EDS elemental analyses are in agreement with the stoichiometric ratios employed in the reaction systems for each alkoxyde.

For the double-oxide matrices, the following sequence of reactions can be proposed,

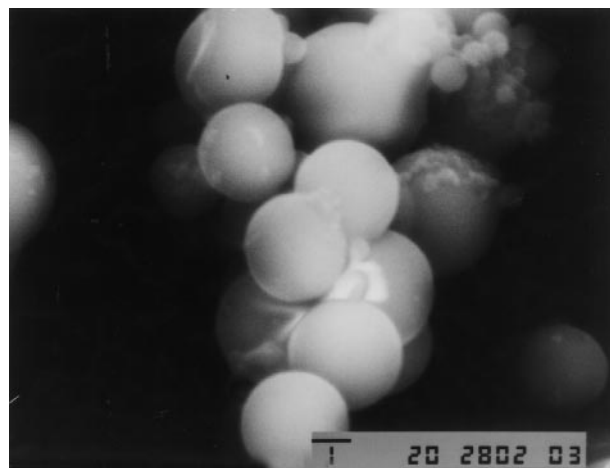
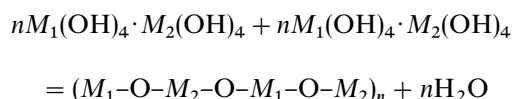
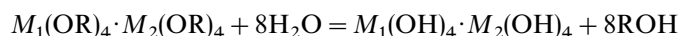


FIG. 3. Scanning electron micrograph (7500 X) of the Al–Ti matrix, showing grains with a spherical morphology. Scale bar is in micrometers.

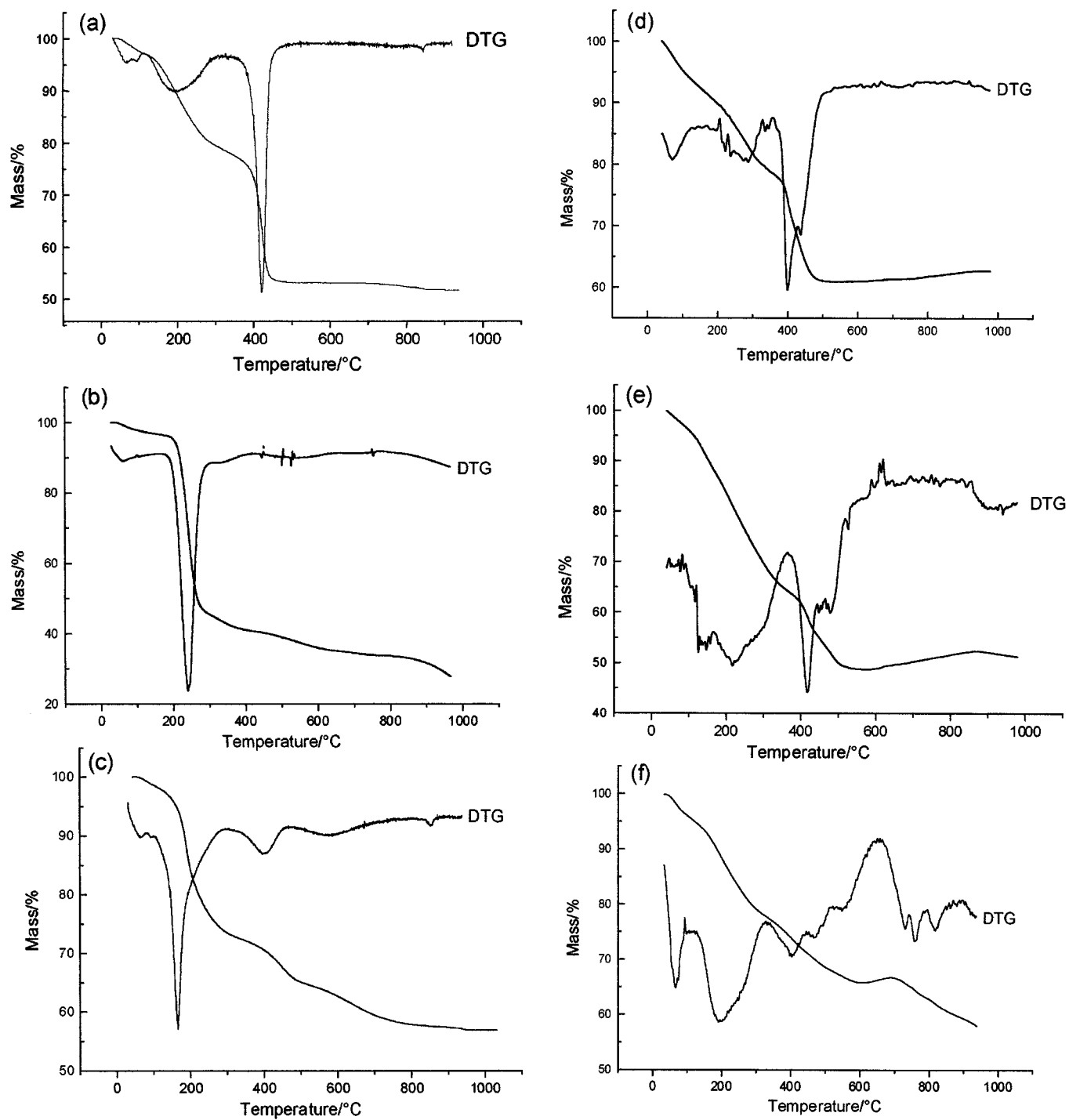


FIG. 4. Thermogravimetric and derivative curves for the lamellar and hexagonal hybrid matrices: Si-Al (a), Si-Ti (b), Si-Zr (c), Al-Ti (d), Al-Zr (e), and Al-Ti-Zr (f).

where M_1 = silicon and aluminum and M_2 = aluminum, titanium, and zirconium for M_1 = silicon and M_2 = titanium and zirconium for M_1 = aluminum. For the aluminum-titanium-zirconium hybrid matrix, a similar sequence

can be proposed with the inclusion of a M_3 alkoxyde. Despite the fact that the mechanism of the performed reactions are not well defined, the present composition resembles that established for the formation of hexagonally

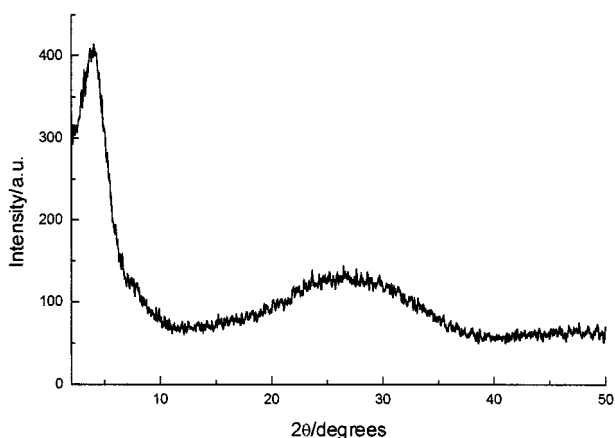


FIG. 5. X-ray diffraction pattern of the Si-Zr matrix calcinated at 300°C for 30 min.

packed niobium oxide (16) and so, a similar mechanism for the formation of the tridimensional network of the oxides can be inferred for the systems studied here.

The thermogravimetric and derivative curves for the hexagonal and lamellar hybrid matrices are shown in Figs. 4(a)–4(f). The aluminum-containing samples exhibited a first mass loss step due to the release of some water, alcohol, and nonreacted alkoxyde molecules, followed by the release of the template molecules. On the other hand, it is observed that for the synthesized hybrids the major part of the organic moiety is retained by those matrices that are thermally stable at temperatures up to 250°C. For the silicon-containing samples, it can be theorized that interactions between the NH₂ group of the template molecule and the silanol groups of the inorganic substrate (3–5) affect the thermal stability of the hybrid matrices.

To investigate the possible structural modifications suffered by the samples undergoing heating, that is, with the release of the template molecules, all samples were calcinated at 300°C for 30 min. Based on the X-ray diffraction patterns of the calcinated samples, it can be verified that Si–Al, Al–Zr and Al–Ti–Zr retain their original structures. On the other hand, Al–Ti and Si–Ti exhibits an amorphous structure after heating, whereas the Si–Zr matrix suffers

a lamellar-to-hexagonal transformation, which can be proved by comparing Figs. 1c and 5.

CONCLUSION

Based on the experimental results obtained, the oxides with double or triple composition, displaying a lamellar or hexagonal nanostructure, can be easily synthesized though the sol-gel process by using the so-called neutral amine route.

Taking into account the sequestrating capacity toward transition metals of the diamine-containing hybrids (3–5) and the possibility of production, by calcination of the metal-doped samples, of mixed oxides for catalytic purposes (17), it is possible to suppose that the synthesized hybrids could be employed for several kinds of applications.

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