Journal of Thermal Analysis and Calorimetry, Vol. 67 (2002) 229–238

THERMAL BEHAVIOUR OF A TiO_2–ZrO_2 MICROCOMPOSITE PREPARED BY CHEMICAL COATING

G. Colón[*], *M. A. Avilés, J. A. Navío and P. J. Sánchez-Soto*

Instituto de Ciencia de Materiales de Sevilla (ICMSE), Centro Mixto Consejo Superior de
Investigaciones Científicas (C.S.I.C.), Universidad de Sevilla, c/Américo Vespucio s/n,
Isla de la Cartuja, 41092 Sevilla, Spain

Abstract

A microcomposite powder in the system TiO_2–ZrO_2 as a precursor of zirconium titanate (ZT) materials has been studied by thermal methods (DTA-TG) and X-ray diffraction (XRD). The microcomposite powder has been prepared by chemical processing of crystalline TiO_2 (rutile, 10 mass% anatase), as inner core, coated with *in situ* precipitated amorphous hydrated zirconia gel, as outer core. The morphology and chemical composition of the resultant powders has been examined by SEM-EDX (Scanning electron microscopy-energy dispersive X-ray spectroscopy). Thermal behaviour of the microcomposite powder was reported, showing the dehydration and dehydroxylation of the zirconia gel, the crystallization into metastable cubic/tetragonal zirconia at temperatures 400–470°C, and the feasibility of preparing ZT powder materials by progressive reaction of TiO_2 and ZrO_2 at higher temperatures (1400°C).

Keywords: coating, microcomposite, rutile, titania, zirconia, zirconium titanate

Introduction

Compositions of the binary oxide system TiO_2–ZrO_2 have been reported to be effective acid-base bifunctional catalysts [1–5]. For instance, their application in the non-oxidative dehydrogenation of ethylbenzene to styrene [5]. Their catalytic activity has been explained by a converted two-center mechanism based on the existence of Zr–O–Ti bonds, where Zr ions act as acid sites, and Ti as basic sites [5]. The use of this binary oxide system as support for hydrodesulfuration catalysts has been also investigated [3, 4]. Wang *et al.* [3] have reported that the composition of TiO_2–ZrO_2 affects the resultant surface area and activity. It should be noted that in a previous research, Daly and coworkers [4] concluded that the preparation methodology for TiO_2–ZrO_2 not only affects its physical properties, such as surface area and porosity, but also its surface chemistry. This influences the strength of the metal-support inter-

---

[*] Author for correspondence: E-mail: colon@cica.es;
Phone: 34-5-448-9527; Fax: 34-5-446 0665

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

action, which can affect the concentration and reactivity of coordinatively unsaturated metal sites active for hydrodesulfuration catalysis.

Compositions of this binary oxide system, such as oxide mixtures, yield zirconium titanate $ZrTiO_4$ (ZT) materials after calcination at 1200–1600°C during long times, as described extensively in several reported investigations [6–10]. These methods of preparation are considered conventional methods. ZT materials have been used in a wide range of applications, such as electronic industry (useful dielectric properties in the microwave frequency regime), high-temperature pigments, technical and structural ceramics and, already mentioned, catalysis [1–15]. However, chemical processing methods, including co-precipitation and sol-gel synthesis, are more feasible processing routes to obtain reactive precursors, which will yield ZT synthesized powders but at lower temperatures than those used in conventional processing [11–16]. A previous literature review has been provided concerning conventional and chemical processing methods for the synthesis of ZT materials [17].

The present authors are involved in a research program on the synthesis of crystalline zirconium titanate (ZT) powder materials from reactive precursors. We have already reported the formation of ZT powders from a sol-gel reactive precursor [18] and the thermal evolution of $(Zr,Ti)O_2$ gels synthesized at different basic pH [19]. In a previous research [20], we have also studied an alternative chemical processing route of ZT powders. It was based on chemical coating processing as a useful method to fabricate different composites by enhanced densification, with advantages over other processing methods [21]. Thus, we have studied the coating of crystalline TiO_2 particles (*anatase*) with amorphous zirconia prepared by controlled hydrolysis of zirconyl chloride. The resultant composite was heated to produce ZT powders by reaction of both oxides, but it was observed at lower temperature than those used in conventional methods [20]. Thus, concerning the formation of ZT powder materials from alternative precursors, the aim of the present paper was to study the thermal behaviour of a new microcomposite powder prepared by chemical processing of crystalline TiO_2 (rutile), as inner core, coated with in situ precipitated amorphous hydrated zirconia gel, as outer core.

Experimental

Materials

The starting materials were crystalline TiO_2 (90 mass% rutile, 10 mass% anatase, powder supplied by Degussa), with particle size ranging between ca. 10–25 nm, and zirconyl chloride (Fluka AG, 43–44 mass% ZrO_2). $x$$ZrO_2(100–x)TiO_2$ precursor powder (x=50 mol%) was prepared by the following method. After mixing and stirring well-dispersed titania powder and the zirconyl chloride in solution using deionized water, amorphous zirconium hydroxide gel was precipitated onto TiO_2 particles by slow addition of 28 mass% aqueous ammonia solution at pH=9–10. The resultant suspension was continuously stirred during the precipitation of a white and gelatinous mass. After complete precipitation and ageing for 2 h, the suspension of coated particles was repeteadly washed with deionized water and the powder was filtered off until the filtrate showed no reaction for chloride ions ($AgNO_3$ solution test). Finally, the product was dried at 110°C using an oven, obtaining an agglomerate of white powder considered the final microcomposite.

Methods

Differential thermal analysis (DTA) and thermogravimetric (TG) curves were obtained in static air using a thermal analyzer Setaram TG-DTA 92 (model 16,18) with graphite furnace protected with argon gas. The heating rate was 10°C min^{-1} and calcined alumina was used as reference material and Pt–Pt/Rh 13% thermocouples. Samples of 40 mg exactly weighed were gently packed into cylindric Pt crucibles. X-ray powder diffraction diagrams (XRD) were obtained at room temperature and after heating several samples under DTA-TG conditions. The equipment was a Siemens (now Bruker) diffractometer, model D-501. The patterns were obtained with Ni-filtered CuK_α radiation at 36 kV and 26 mA with a scanning speed of 1° in 2θ°C min^{-1}. Specific surface area (S_{BET}) was determined with an automatic system (Micromeritics 2200 A) using nitrogen gas as the adsorbate at liquid nitrogen temperature (–195°C).

The morphology of the original (as-prepared) microcomposite was studied by Scanning Electron Microscopy (SEM) using a JEOL equipment (Model JSM-5400) at 20 kV. Chemical analysis by Energy Dispersive X-ray Spectroscopy (EDX) was performed in the SEM equipment using an Oxford Link system with Si–Li detector. The quantitative method ZAF (corrections for atomic number, absorption and X-ray fluorescence) was applied to selected EDX results and calculated chemical composition of TiO_2 and ZrO_2 were obtained.

Results and discussion

Characterization of the microcomposite

The microcomposite powder of the binary system TiO_2–ZrO_2 has been prepared by chemical processing of crystalline TiO_2 (rutile), as inner core, coated with in situ precipitated amorphous hydrated zirconia gel, as outer core, according to the processing method described above. The amorphous zirconia, as a gel, has been obtained from controlled hydrolysis of zirconyl chloride using ammonia, at pH=9–10. The amorphous nature of the zirconia coating can be seen by XRD as shown in Fig. 1, as well as the crystalline nature of inner core (TiO_2). The value of specific surface area of this composite was found of 174 m^2 g^{-1}, a value higher than that found for pure zirconia gels precipitated under the same conditions, but at pH value sligthly higher (pH=11) [22]. However, we have found a specific surface area value of 341 m^2 g^{-1} for zirconia amorphous gels prepared using the same processing conditions as described in this paper. These results suggest the strong influence of the variable ‘pH of hydrolysis’ for the zirconyl solution to yield the zirconia amorphous gel, in accordance with pre-

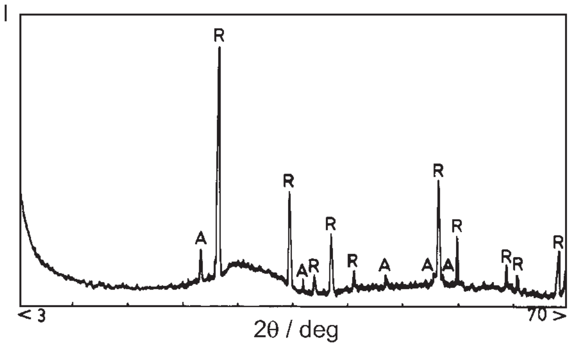

Fig. 1 X-ray diffraction diagram of the original microcomposite obtained by the chemical coating processing method (I=Intensity of X-ray peaks in arbitrary units). The surface area is $S_{BET}=174\ m^2\ g^{-1}$. R – rutile, A – anatase

vious reports [3, 4]. This will be discussed later concerning the thermal evolution. It should be noted that the value of surface area of this microcomposite can be strictly compared with that value obtained for the other one prepared previously [20], but using TiO_2 (anatase). We have found a value of specific surface area of 218 $m^2\ g^{-1}$ for this microcomposite, higher than that obtained in the present case using TiO_2 (90 mass% rutile, 10 mass% anatase) as a raw powder material for the preparation of the microcomposite. It could be associated to a previous thermal sintering pretreatment of the rutile powder used here, because rutile is the high-temperature phase as compared with anatase.

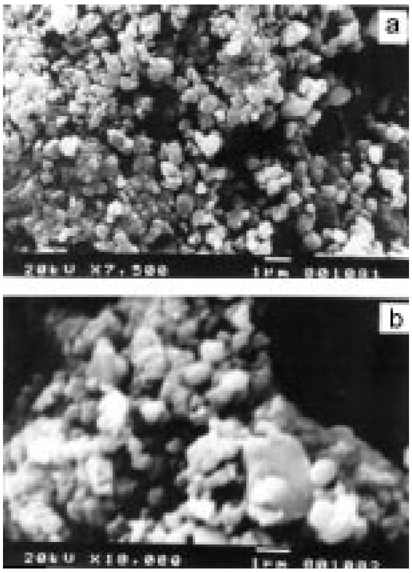

Fig. 2 SEM micrographs of the original microcomposite observed at different magnifications: a – ×7 500; b – ×10 000

Figure 2 shows two selected SEM micrographs to illustrate the morphology of this microcomposite, with observation of small regular particles of sizes less than 1 μm and wide distribution (Fig. 2a). Some agglomerates or particles larger than 1 μm were detected, for instance the observations at higher magnifications (Fig. 2b). EDX analysis (1–2 μm deep) confirmed the distribution of Zr around Ti particles, although there was also found some accumulation of Ti and/or Zr when agglomerates are observed. According to several quantitative EDX analysis, the average calculated composition was 50.65% TiO_2 and 49.35% ZrO_2. This result is in accordance with the nominal composition used in the preparation as described in Experimental section.

Thermal analysis

Figure 3 shows DTA-TG curves for the microcomposite studied. The DTG curve is also shown. Mass losses in TG are mainly associated to evolved water coming from the amorphous zirconia gel coating, which are almost finished at ca. 500°C, as confirmed by DTG analysis. It should be noted that traces of ammonia, and other evolved gases in very low proportion, were also detected by mass-spectrometry after dynamic heating under the same conditions. A total mass loss of 6.5 mass% was calculated for this microcomposite after heating at 1000°C. The DTA curve of Fig. 3 showed two broad endothermic effects centered at 112 and 202°C and an exothermic peak, al-

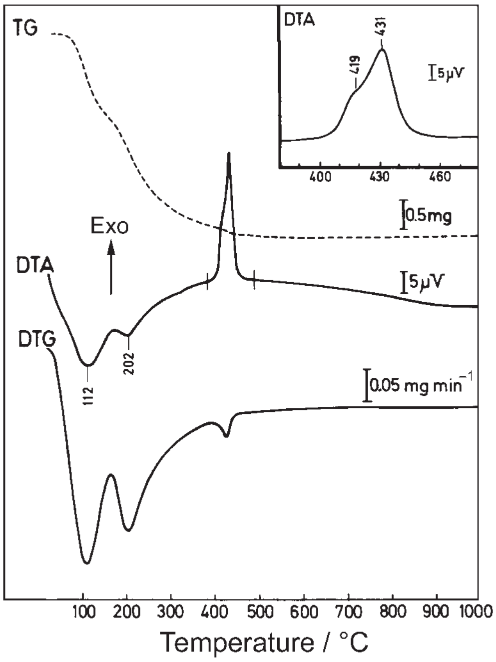

Fig. 3 DTA-TG-DTG curves of the microcomposite powder after drying previously at 110°C (initial mass=40 mg). Insert is an enlarged zone of the DTA curve to show the exothermic thermal events of crystallization

though non-symmetric, centered at ca. 430°C. The enlarged zone of the DTA curve showed that this exothermic peak has a shoulder effect at 419°C and a more intense at 431°C. The DTA exothermic effect is produced at the same time that small mass losses are detected by TG and, especially, by DTG. This thermal evolution is associated to the total and fast elimination of remained coordinated water to Zr ions, as well as strongly bound water into the pores of the amorphous coating in the microcomposite (outer zone is amorphous zirconia). The more intense DTG peaks were observed centered at 108 and 212°C, practically at the same temperatures as those of DTA endothermic broad peaks. These thermal events were associated to a faster and progressive elimination of coordinated water, as proposed studying the surface of zirconia gels [23–25]. One explanation, based on pore volumes and pore sizes, suggests that the zirconia gels, precipitated at high values of pH arise from a looser packing of the particles in the gel resulting from their coagulation prior to sedimentation [25]. Other explanation is that the surface of zirconia amorphous gels, considered a hydrous zirconium oxide, heated at low temperatures and after the elimination of weakly adsorbed water (dehydration), is covered by OH groups. This OH groups are eliminated as water by thermal reaction (dehydroxylation). The OH groups must come from $Zr(OH)_4$ polycondensation forming Zr–O–Zr bonds and evolved water. Finally, the stronger bound water is eliminated (weak DTG effect observed at 425°C in Fig. 3) prior to an exothermic reaction.

However, it is remarkable that a clear exothermic DTA effect with onset temperature at 490°C has been reported after zirconia gel precipitation at pH=10.35, whereas for pH=8.37 no apparent DTA effect was visible [26]. This suggests that the preparative and processing conditions used for the formation of zirconia amorphous gels have a strong influence on the thermal behaviour. Thus, other authors [27] studied a zirconia gel prepared by precipitation with ammonia at pH=10 from a solution of zirconyl chloride, similarly to the present investigation. They observed thermal behaviour typical of a gel product, with a fast initial loss of water at 150°C (17 mass% mass loss), ending at ca. 900°C (20 mass%) and a sharp exothermic DTA effect at 412°C using a heating rate of 10°C min^{-1}. This thermal effect in zirconia gels (and other metal oxides and hydrous oxide systems), processed *via* wet chemical routes, has been also called ‘glow exotherm’ (as studied by DSC and/or DTA) in literature [26–32]. The exact temperature of this effect depends on the preparation conditions and on the environment used during the thermal analysis experiments. It has been shown that the peak position and the magnitude of the glow exotherm is sensitive to the extent of hydration/dehydration of the zirconia precursor [33]. Consequently, it could explain the variability in peak temperatures and the influence of starting zirconia gel on the thermal behaviour. In general, the glow exotherm is detected in the range 420–470°C [26–31]. Fernández *et al.* [32] reported the glow exotherm at 480°C studying zirconia gels obtained from the hydrolysis of zirconium tetrapropoxide. They examined the effect of carbonation (adsorption of atmospheric CO_2) and the thermal evolution of their zirconia gels.

Returning to the thermal curves of Fig. 3, no other thermal effects after the glow exotherm can be detected. This is in accordance with the thermal features observed in a previous paper concerning the formation of zirconium titanate from TiO_2–ZrO_2 composites prepared by coating [20]. However, the present authors have shown the formation of a single (640°C) or two (670 and 700°C) DTA exothermic effects, after the glow exotherm, associated to the crystallization of ZT [18, 19]. This was observed studying the thermal evolution of $(Zr,Ti)O_2$ gels synthesized at different basic pH in the presence or absence of hydrogen peroxide [18, 19]. The above results are an indication of the effect of chemical processing conditions in controlling the crystallization temperature of zirconium titanate from reactive gel precursors.

X-ray diffraction

The thermal evolution of the microcomposite powder was investigated by XRD after heating at several temperatures. Figure 4 shows the XRD diagrams. After heating at 400 and 430°C (Fig. 3 insert), crystallization of metastable cubic/tetragonal zirconia (Cubic zirconia JCPDS file 27-997 and Tetragonal zirconia JCPDS file 17-923, both very coincident) takes place, which is associated to the DTA exothermic effect previously observed in Fig. 3. Monoclinic zirconia (JCPDS file 36-420) is detected after heating at higher temperatures than 470°C from metastable cubic/tetragonal zirconia transformation and can be perfectly observed next to rutile at 1000°C. In other words, the elimination of OH groups and polycondensation in the zirconia gel produces the formation of Zr–O–Zr bonds, as deduced from the oxide crystallization after heating.

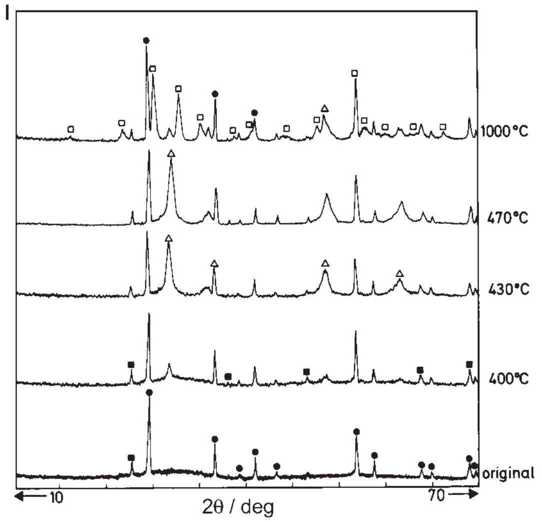

Fig. 4 X-ray diffraction diagrams of the original microcomposite powder dried at 110°C and after heating at the indicated temperatures. The different identified crystalline phases are indicated. JCPDS (Joint Committee for Powder Diffraction Standards) files are as follows: ● – rutile (TiO_2) JCPDS 21-1276; ■ – anatase (TiO_2) JCPDS 21-1272; Δ – metastable cubic/tetragonal zirconia (ZrO_2) shows coincidence of JCPDS files 27-997 (cubic) and 17-923 (tetragonal); □ – monoclinic zirconia JCPDS 36-420

Several authors reported the crystallization of zirconia phases after heating zirconia gels [25–33]. It has been also claimed the crystallization of a pseudotetragonal zirconia phase after heating at 412°C under DTA conditions [27], which must correspond to the metastable cubic/tetragonal zirconia detected in the present investigation.

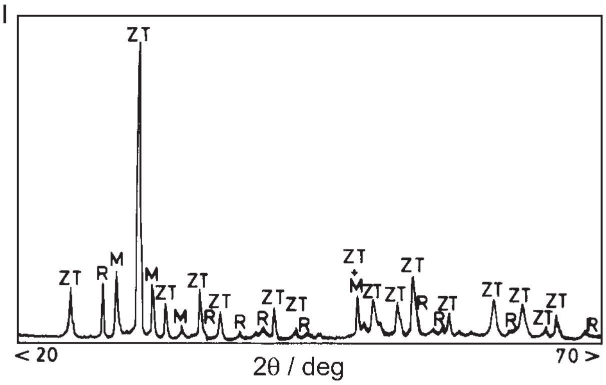

Fig. 5 X-ray diffraction diagram of the microcomposite heated at 1400°C. Symbols denoted the crystalline phases ZT – zirconium titanate; M – monoclinic zirconia; R – rutile. JCPDS files are 34-415 for ZT, 36-420 for M, and 21-1276 for T

Anatase (JCPDS file 21-1272) is detected from the original sample up to 1000°C and no conversion to rutile (JCPDS file 21-1276) was observed (Fig. 4). This is an important difference with other composite previously prepared by chemical coating processing and studied by the present authors [20]. Finally, the XRD diagram of Fig. 5 shows that the composite powder, after heating at 1400°C, yielded crystalline zirconium titanate (JCPDS file 34-415) powder materials in high proportion, besides rutile and monoclinic zirconia (JCPDS file 36-420) as residual phases. Anatase has disappeared. It should be noted that no important exothermic DTA thermal event was detected before this temperature. However, the formation of zirconium titanate in this microcomposite is produced at higher temperatures than previously reported by us in a study on $(Zr,Ti)O_2$ gels [19]. Consequently, the thermal behaviour of this microcomposite prepared by chemical coating processing is different from pure sol-gel precursors and/or co-precipitated gel powders, as it was also suggested [20]. Thus, the coating of crystalline TiO_2 particles with zirconia gel favours diffusion processes, which are involved in the formation of zirconium titanate particles emphasizing that a) the formation of ZT powder materials occurs at lower temperatures than those used in conventional processing methods [11–16] and b) there is not a release of energy associated to fast crystallization of ZT from amorphous gel precursors [18, 19].

Conclusions

In this investigation, a microcomposite powder in the binary system TiO_2–ZrO_2 as a precursor of ZT materials has been studied by thermal methods (DTA-TG) and XRD. SEM-EDX was applied to study the morphology and chemical composition of the powders. The microcomposite powder has been prepared by chemical processing of crystalline TiO_2 (rutile), as inner core, coated with *in situ* precipitated amorphous hydrated zirconia gel, as outer core. The amorphous zirconia has been obtained from controlled hydrolysis of an aqueous zirconyl chloride solution using ammonia, at pH=9–10. The thermal processes in the microcomposite powder were the following: a) dehydration and dehydroxylation of the zirconia gel; b) crystallization of metastable cubic/tetragonal zirconia at temperatures lower than 431°C, and c) the feasibility of preparing ZT powder materials by reaction of TiO_2 and ZrO_2 at higher temperatures. TiO_2 phase anatase was detected from the original sample up to 1000°C and no conversion to rutile was observed.

The formation of ZT starting from $(Zr,Ti)O_2$ gels [18, 19] and binary systems with TiO_2 (anatase) and amorphous zirconia [20], previously studied by the present authors, was compared and discussed taking into account the results reported in this paper. It was concluded that the thermal behaviour of this microcomposite prepared by chemical coating processing is different from pure sol-gel precursors and/or co-precipitated gel powders. This is an indication on the effects of processing conditions in the preparation of zirconium titanate reactive precursors with application in catalysis and ceramics as an advanced material.

* * *

Financial support by Junta de Andalucía (III Plan Andaluz de Investigación) to the Research Groups of reference FQM-181 (Prof. J. A. Navío) and TEP-204 (Dr. P. J. Sánchez-Soto), is greatfully acknowledged.

References

1 M. Murata, K. Wakino, K. Tanaka and Y. Hamakawa, Mater. Res. Bull., 11 (1976) 323.
2 K. Araka and K. Tanabe, Bull. Chem. Soc. Jpn., 53 (1980) 299.
3 I. Wang, W. F. Chang, R. J. Shiau, J. C. Wu and C. S. Chung, J. Catal., 83 (1983) 428.
4 F. P. Daly, H. Ando, J. L. Schmitt and E. A. Sturm, J. Catal., 108 (1987) 401.
5 Y. Hirashima and K. Nishiwaki, Bull. Chem. Soc. Jpn., 61 (1988) 1945.
6 A. E. McHale and R. S. Roth, J. Am. Ceram. Soc., 66 (1983) 18.
7 A. E. McHale and R. S. Roth, J. Am. Ceram. Soc., 69 (1986) 827.
8 F. J. Parker, J. Am. Ceram. Soc., 73 (1990) 929.
9 S. L. Swartz and T. R. Shrout, Mater. Res. Bull., 17 (1982) 1245.
10 F. Azough, A. Wright and R. Freer, J. Solid State Chem., 108 (1994) 284.
11 G. Wolfram and E. Göbel, Mater. Res. Bull., 16 (1981) 1455.
12 F. Hund, Z. Anorg. Allg. Chem., 525 (1985) 221.
13 G. Wilson and F. P. Glasser, Br. Ceram. Trans. J., 88 (1989) 69.
14 Y. Yoshikawa and K. Tsuzuki, J. Am. Ceram. Soc., 73 (1990) 31.
15 S. Hirano, T. Hayashi and A. Hattori, J. Am. Ceram. Soc., 74 (1991) 1320.
16 M. J. Muñoz-Aguado, M. Gregorkiewitz and A. Larbot, Mater. Res. Bull., 27 (1992) 87.
17 J. A. Navío, M. Macías and P. J. Sánchez-Soto, J. Mater. Sci. Letters, 11 (1992) 1570.
18 J. A. Navío, F. J. Marchena, M. Macías, P. J. Sánchez-Soto and P. Pichat, J. Mater. Sci., 27 (1992) 2463.

19 J. A. Navío, F. J. Marchena, M. Macías, P. J. Sánchez-Soto and P. Pichat, J. Thermal Anal., 40 (1993) 1095.

20 P. J. Sánchez-Soto, M. A. Avilés, G. Colón, M. Macías and J. A. Navío, Mater. Letters, 20 (1994) 339.

21 M. D. Sacks, N. Bozkurt and G. W. Scheiffele, J. Am. Ceram. Soc., 74 (1991) 2428.

22 J. A. Navío, F. J. Marchena, M. Macías and P. J. Sánchez-Soto, in: Ceramics Today-Tomorrow's Ceramics, p. 889, Ed. P. Vincenzini, Materials Science Monographs, 66B, Elsevier Science Publishers, Amsterdam (The Netherlands) 1991.

23 J. B. Peri, J. Phys. Chem., 69 (1965) 211.

24 J. M. Parera, Catal. Today, 15 (1992) 481.

25 E. Crucean and B. Rand, Br. Ceram. Trans. J., 78 (1979) 58.

26 X. Turrillas, P. Barnes, A. J. Dent, S. L. Jones and C. J. Norman, J. Mater. Chem., 3 (1993) 583.

27 M. I. Osendi, J. S. Moya, C. J. Serna and J. Soria, J. Am. Ceram. Soc., 68 (1985) 135.

28 J. Livage, K. Doi and C. Mazières, J. Am. Ceram. Soc., 51 (1968) 349.

29 S. L. Jones and C. J. Norman, J. Am. Ceram. Soc., 71 (1988) C-1909.

30 R. Srinivasan and B. H. Davis, Catal. Letters, 14 (1992) 165.

31 P. D. L. Mercera, J. G. van Ommen, B. M. Doesburg, A. J. Burggraaf and J. R. H. Ross, Appl. Catal., 57 (1990) 127.

32 A. Fernández, C. Bautista, J. Rubio and J. L. Oteo, in: Third Euroceramics, Vol. 1, p. 393, Eds P. Durán and J. F. Fernández-Lozano, Faenza Editrice Iberica S. L., Castellón (Spain) 1937.

33 G. Gimblett, A. A. Rahman and K. S. W. Sing, J. Chem. Tech. Biotechnol., 30 (1980) 51.