CHEMISTRY OF MATERIALS

VOLUME 17, NUMBER 8 APRIL 19, 2005

Communications

Preparation of Nanosized Perovskites and Spinels through a Silica Xerogel Template Route

T. Valdés-Solís,* G. Marbán, and A. B. Fuertes

Instituto Nacional del Carbón (CSIC), c/Francisco Pintado Fe, 26, 33011 Oviedo, Spain

Received December 27, 2004
Revised Manuscript Received March 3, 2005

Perovskite- (ABO_3) and spinel-type oxides (AB_2O_4, A being the cation of a larger size, e.g., A = Ca, La, Mg...; B = Mn, Fe, Al, Cr...) are materials of interest for a wide range of applications.[1] Thus, they have been extensively proposed as catalysts for many reactions, including CO and hydrocarbon oxidation,[2] pollution control (NO_x and SO_2 reduction),[1,3] hydrogenation and dehydrogenation reaction,[1,4] electrocatalysis,[5] and water−gas shift reaction.[2d,6] Additionally, noncatalytic applications have also been considered. For instance, perovskites have been proposed as electrode materials in solid oxide fuel cells[7] or as gas sensors[1,8] whereas spinels have been used as electrodes in lithium-ion batteries.[9] The magnetic properties of some spinels make them suitable for a number of applications, for example, as magnetic storage media or for magnetic resonance imaging.[10] There are several techniques available for producing high surface area metal oxides, as recently reported by Landau,[11] but in most of the cases, the high-temperature treatments needed to fabricate the spinels and perovskites lead to the sintering of the resulting particles, with the concomitant reduction in active surface area, typically in the range of a few square meters (<10) per gram. Thermal treatments can be avoided by the use of "chimie douce"-based nanotechnological approaches, such as microemulsion techniques,[12] but these are expensive procedures which, moreover, must integrate a number of different stages for the separation of organic solvents and surfactants. Therefore, innovative and low-cost methods for preparing nanosized oxidic catalysts are of great interest. Template methods with hard templates have been revealed as an interesting alternative for preparing high surface materials.[13] With this procedure, the synthesis of the nanoparticles takes place in a confined space formed by the porosity of the template, thus making it possible to avoid the uncontrolled growth of the material during the synthesis

* To whom correspondence should be addressed. E-mail: tvaldes@incar.csic.es.

(1) Tejuca, L. G.; Fierro, J. L. G.; Tascón, J. M. D. *Adv. Catal.* **1989**, *36*, 237.
(2) (a) Mehandjiev, D.; Naydenov, A.; Ivanov, G. *Appl. Catal., A* **2001**, *206*, 13. (b) Jansson, J.; Palmqvist, A.; Fridell, E.; Skoglundh, M.; Österlund, L.; Thormählen, P.; Langer, V. *J. Catal.* **2002**, *211*, 387. (c) Sekizawa, K.; Yano, S.; Eguchi, K.; Arai, H. *Appl. Catal., A* **1998**, *169*, 291. (d) Tanaka, Y.; Utaka, T.; Kikuchi, R.; Sasaki, K.; Eguchi, K. *Appl. Catal., A* **2003**, *242*, 287.
(3) (a) Sloczynski, J.; Janas, J.; Machej, T.; Rynkowski, J.; Stoch, J. *Appl. Catal., B* **2000**, *24*, 45. (b) Chen, L.; Horiuchi, T.; Mori, T. *Catal. Lett.* **1999**, *60*, 237.
(4) Sloczynski, J.; Ziolkowski, J.; Grzybowska, B.; Grabowski, R.; Jachewicz, D.; Wcislo, K.; Gengembre, L. *J. Catal.* **1999**, *187*, 410.
(5) Singh, J. P.; Singh, R. N. *J. New Mater. Electrochem. Syst.* **2000**, *3*, 137.
(6) Tanaka, Y.; Utaka, T.; Kikuchi, R.; Takeguchi, T.; Sasaki, K.; Eguchi, K. *J. Catal.* **2003**, *215*, 271.
(7) (a) Pudmich, G.; Boukamp, B. A.; González-Cuenca, M.; Jungen, W.; Zipprich, W.; Tietz, F. *Solid State Ion* **2000**, *135*, 433. (b) Fergus, J. W. *Solid State Ion* **2004**, *171*, 1. (c) Huang, X.; Pei, L.; Liu, Z.; Lu, Z.; Sui, Y.; Qian, Z.; Su, W. *J. Alloy Compd.* **2002**, *345*, 265.
(8) Alcock, C. B.; Doshi, R. C.; Shen, Y. *Solid State Ion* **1992**, *51*, 281.
(9) (a) Shui, J. L.; Jiang, G. S.; Xie, S.; Chen, C. H. *Electrochim. Acta* **2004**, *49*, 2209. (b) Horiba, T.; Hironaka, K.; Matsumura, T.; Kai, T.; Koseki, M.; Muranaka, Y. *J. Power Sources* **2003**, *119*−*121*, 893.
(10) (a) Kang, E.; Park, J.; Hwang, Y.; Kang, M.; Park, J. G.; Hyeon, T. *J. Phys. Chem. B* **2004**, *108*, 13932. (b) Manova, E.; Kunev, B.; Paneva, D.; Mitov, I.; Petrov, L.; Estournès, C.; D'Orléans, C.; Rehspringer, J. L.; Kurmoo, M. *Chem. Mater.* **2004**, *16*, 5689.
(11) Landau, M. V. Transition metal oxides. In *Handbook of porous solids*; Schüth, F., Singh, K. S. W., Weikamp, J., Eds.; Wiley-VCH: Weinheim, 2002; Chapter 4.7.3, pp 1677−1765.
(12) Weidenkaff, A. *Adv. Eng. Mater.* **2004**, *6*, 709.
(13) Schüth, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3604.

10.1021/cm0477321 CCC: $30.25
Published on Web 03/17/2005

and favoring the formation of nanostructures. Several metal oxides have been prepared by means of template methods using active carbon[14] and porous silica materials.[15] Active carbon is a cheap and readily available material for use as a template. However, the reactivity of carbonaceous materials in the presence of transition metal oxides (i.e., oxidation and reduction reactions) may limit its applicability. Indeed, at the high temperatures needed for the formation of ternary oxides, the oxidation of carbon (in an air atmosphere) or the reduction of oxides (in an inert atmosphere) prevents the formation of these kinds of compounds. For these reasons, a more inert hard template such as porous silica might be more appropriate. Recently, we proved that by using an inexpensive mesoporous silica xerogel as template, it is possible to prepare high surface-area single metal oxides.[15e] In this work, we have extented this synthetic approach to the preparation of spinels and perovskites with a large surface area. The advantages of this method will be evidenced by comparing the products obtained with those synthesized by using the well-established citrate method.

The synthesis of the silica xerogel was performed in a two-step process as described elsewhere.[16] To synthesize the mixed oxide, a solution of hydrated metal nitrates mixed in the appropriate proportion was prepared in ethanol (0.4−0.6 M). The silica xerogel was stirred with this solution at a moderate temperature (60 °C) until complete removal of the solvent. The impregnated sample was dried at 80 °C overnight and calcined in air at 5 °C/min up to the temperature required for the formation of the perovskite/spinel and then left for 4 h (unless otherwise stated). The calcination conditions (temperature and soaking time) of each formulation are listed in Table 1. The mixed oxides were obtained after dissolution of the silica framework in a NaOH solution (2 M) and final washing with distilled water to remove impurities.

Additionally, a single-step citrate method recently developed in our lab[17] was employed to prepare the same formulations for purposes of comparison. This procedure involved mixing a nitrate solution (1 M) with a citric acid solution (1.2 M) and keeping the mixture at 70 °C until dryness. The mixed oxide particles were then obtained after further calcination at the same conditions as those employed in the pore-confinement method.

Table 1. Preparation Conditions and Textural Characterization of Spinels and Perovskites Prepared by Citrate and Template Methods

		citrate method			template method		
		particle size, nm			particle size, nm		
formulation	T, °C	XRD	BET	S_{BET}, m^2/g	XRD	BET	S_{BET}, m^2/g
$LaMnO_3$[a]	850	18	33	40	14	32	41
$LaFeO_3$[b]	700	18	129	7	11	8	110
$CuCr_2O_4$[c]	800	24	39	14	14	6	90
$CuMn_2O_4$[d]	550	17	29	38	16	11	100
Co_3O_4	400	18	33	30	9	9	112
$NiMn_2O_4$	800	43	244	6.5	14	18	87

[a] Soaking time template method = 12 h. [b] Soaking time citrate method = 20 min. [c] Soaking time template method = 6 h. [d] Soaking time template method = 10 h.

The porosity of the silica xerogel employed as template is made up of mesopores in the 2−15 nm range. The values obtained from the nitrogen adsorption isotherms[18] for the BET surface area and pore volume are 510 m^2/g and 0.8 cm^3/g, respectively. Further characterization by TEM (not included) shows the existence of a disordered pore network.[16] In addition, the FTIR spectrum (not shown) evidences that silica xerogel contains an abundance of silanol groups that are essential for a good degree of impregnation.

The identification of the product obtained by the template technique was performed by X-ray diffraction (XRD) analysis in the wide-angle range ($2\theta = 10-90°$).[19] The XRD patterns for selected spinels and perovskites are shown in Figure 1. It can be observed that the main XRD peaks are broader for the materials prepared via the template method than for those prepared by the citrate method, due to the smaller crystallite or particle size of the former. The particle size values of these nanoparticles, estimated by using the Scherrer equation,[20] are on the order of 9−15 nm, as might be expected considering the pore size distribution of the original silica framework. The particle size values estimated by the Scherrer equation are summarized in Table 1 (particle size, XRD). It can be observed from these values that, in every case, the particle size estimated by the Scherrer formula is smaller for the materials prepared by the template method than for the materials prepared by the citrate method, even though in some cases longer periods of time at the final calcination temperatures are required to obtain the active phase via the template method. As might be expected, the differences between the particle sizes assessed by these two methods are more significant for the higher calcination

(14) (a) Schwickardi, M.; Johann, T.; Schmidt, W.; Schüth, F. *Chem. Mater.* **2002**, *14*, 3913. (b) Wakayama, H.; Itahara, H.; Tatsuda, N.; Inagaki, S.; Fukushima, Y. *Chem. Mater.* **2001**, *13*, 2392. (c) Li, W. C.; Lu, A. H.; Weidenthaler, C.; Schuth, F. *Chem. Mater.* **2004**, *16*, 5676. (d) Roggenbuck, J.; Tiemann, M. *J. Am. Chem. Soc.* **2005**, *127*, 1096. (e) Kang, M.; Kim, D.; Yi, S. H.; Han, J. U.; Yie, J. E.; Kim, J. M. *Catal. Today* **2004**, *93*−*95*, 695.

(15) (a) Tian, B.; Liu, X.; Yang, H.; Xie, S.; Yu, C.; Tu, B.; Zhao, D. *Adv. Mater.* **2003**, *15*, 1370. (b) Dong, A.; Ren, N.; Tang, Y.; Wang, Y.; Hua, W.; Gao, Z. *J. Am. Chem. Soc.* **2003**, *125*, 4976. (c) Laha, S. C.; Ryoo, R. *Chem. Commun.* **2003**, 2138. (d) Tian, B. Z.; Liu, X. Y.; Solovyov, L. A.; Liu, Z.; Yang, H. F.; Zhang, Z. D.; Xie, S. H.; Zhang, F. Q.; Tu, B.; Yu, C. Z.; Terasaki, O.; Zhao, D. Y. *J. Am. Chem. Soc.* **2004**, *126*, 865. (e) Fuertes, A. B. *J. Phys. Chem. Solids* **2005**, *66*, 741. (f) Zhu, K. K.; Yue, B.; Zhou, W. Z.; He, H. Y. *Chem. Commun.* **2003**, 98. (g) Yang, H. F.; Shi, Q. H.; Tian, B. Z.; Lu, Q. Y.; Gao, F.; Xie, S. H.; Fan, J.; Yu, C. Z.; Tu, B.; Zhao, D. Y. *J. Am. Chem. Soc.* **2003**, *125*, 4724. (h) Lee, K.; Kim, Y. H.; Han, S. B.; Kang, H. K.; Park, S.; Seo, W. S.; Park, J. T.; Kim, B.; Chang, S. B. *J. Am. Chem. Soc.* **2003**, *125*, 6844. (i) Wang, Y.; Yang, C. M.; Schmidt, W.; Spliethoff, B.; Bill, E.; Schüth, F. *Adv. Mater.* **2005**, *17*, 53.

(16) Fuertes, A. B. *Chem. Mater.* **2004**, *16*, 449. The procedure used to prepare the xerogel is schematically included here. The silica source (sodium silicate, Aldrich) was added under stirring to an aqueous solution of HCl. The molar composition of the synthesis mixture was sodium silicate/HCl/H_2O = 1/6/194. The solution was stirred in a closed Teflon vessel for 20 h at ambient temperature and subsequently heated to 100 °C for 2 days. The gel was then filtered and washed several times with water and acetone and finally dried at room temperature.

(17) Marbán, G.; Fuertes, A. B. *Appl. Catal., B* **2005**, *57* (1), 43−53; DOI: 10.1016/j.apcatb.2004.10.011.

(18) Nitrogen adsorption isotherms were performed at 77 K on a Micromeritics ASAP 2010 volumetric adsorption system. The BET surface area was deduced from the isotherm analysis in the relative pressure range 0.04 to 0.20.

(19) X-ray diffraction (XRD) patterns for the mixed oxide particles were obtained on a Siemens D5000 instrument operating at 40 kV and 20 mA and using Cu Kα radiation (λ = 0.15406 nm).

(20) ,Cullity, B. D.; Stock, S. R. *Elements of X-ray Diffraction*; Prentice Hall: Englewood Cliffs, NJ, 2001; p 170.

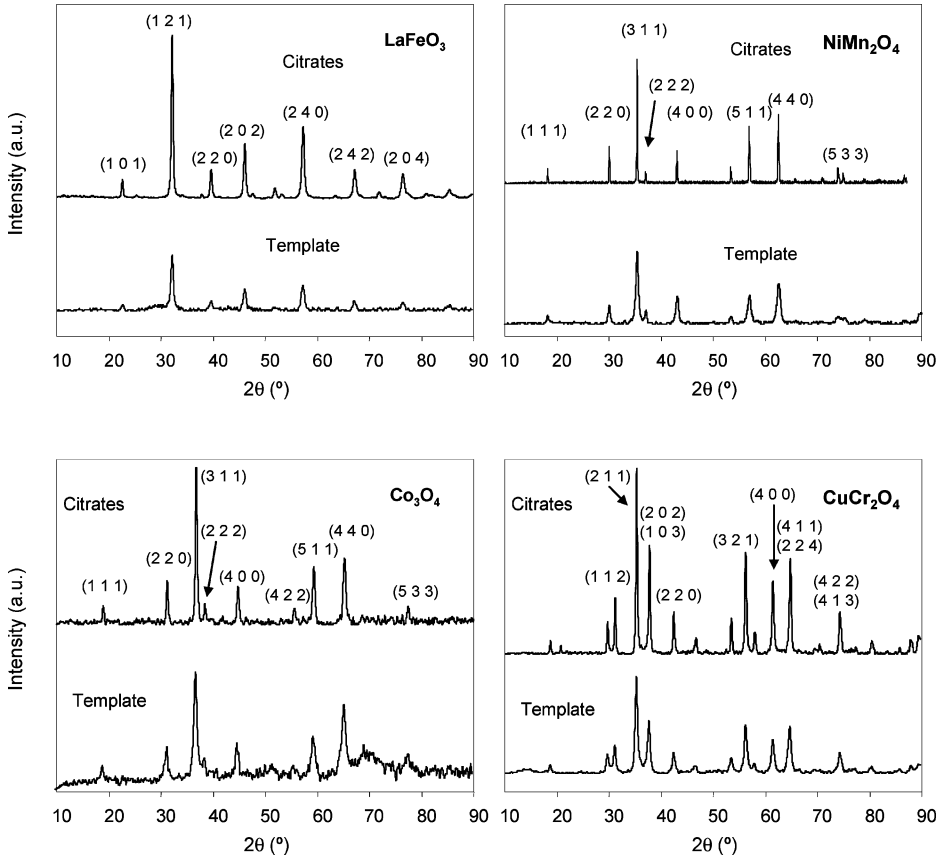

Figure 1. XRD patterns of various mixed oxides (perovskites and spinels) prepared by a citrate method and a template route.

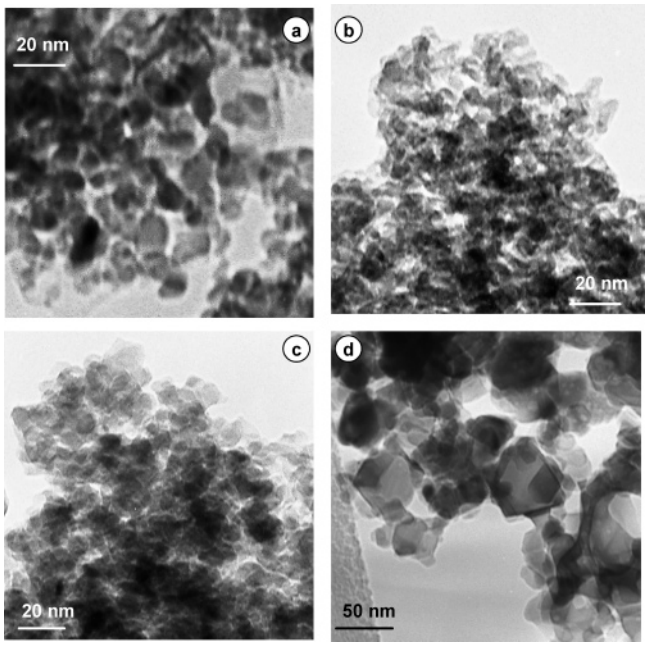

Figure 2. TEM images of selected spinels and perovskites: (a) $NiMn_2O_4$ (template); (b) $LaFeO_3$ (template); (c) $CuMn_2O_4$ (template); (d) $CuMn_2O_4$ (citrates).

temperatures. This finding is supported by the TEM[21] images in Figure 2. Thus, the particle size of $CuMn_2O_4$ prepared by the template method (Figure 2c, $d_p \sim 12$ nm) is approximately 3 times smaller than that of $CuMn_2O_4$ prepared via the citrate method (Figure 2d, $d_p \sim 35$ nm). The TEM images show that $NiMn_2O_4$ (Figure 2a), $LaFeO_3$ (Figure 2b), and $CuMn_2O_4$ (Figure 2c) prepared by the template method are formed by porous agglomerates of well-defined nanoparticles below 15 nm in size. The oxides produced by this method are quite uniform in particle size.

Nitrogen isotherms for the spinels and perovskites prepared by the template method are plotted in Figure 3. Using these isotherms, it is possible to calculate the values of the BET surface area (S_{BET}) that are included in Table 1. From Figure 3 it can be observed that the materials of a lower particle size exhibit a capillary condensation step, which is especially marked in the case of $LaFeO_3$ ($p/p_0 \sim 0.65-0.95$) and Co_3O_4 ($p/p_0 \sim 0.55-0.85$). TEM inspection (Figure 2) indicates that this step should be attributed to the aggregation of small nanoparticles, which favors the capillary condensation, and not to the existence of structural porosity (confined porosity in the framework of the oxide).

On the basis of these observations, we are able to estimate from geometrical relationships [$d_P = 6/(S_{BET} \times \rho)$, ρ being the density of the oxide] the particle size of the materials from the S_{BET} values, also included in Table 1. The particle size values determined by means of the nitrogen isotherms do not differ essentially from those obtained by XRD peak broadening in the case of materials prepared by the template route. The differences, however, are conspicuous when dealing with material prepared by the citrate route and are ascribed to the higher degree of agglomeration and sintering produced during the calcination step.

As mentioned above, the S_{BET} values of the perovskites and spinels prepared in this work are presented in Table 1.

(21) Transmission electron microscopy was performed in a JEOL Mod. 2000 EX II microscope (200 kV).

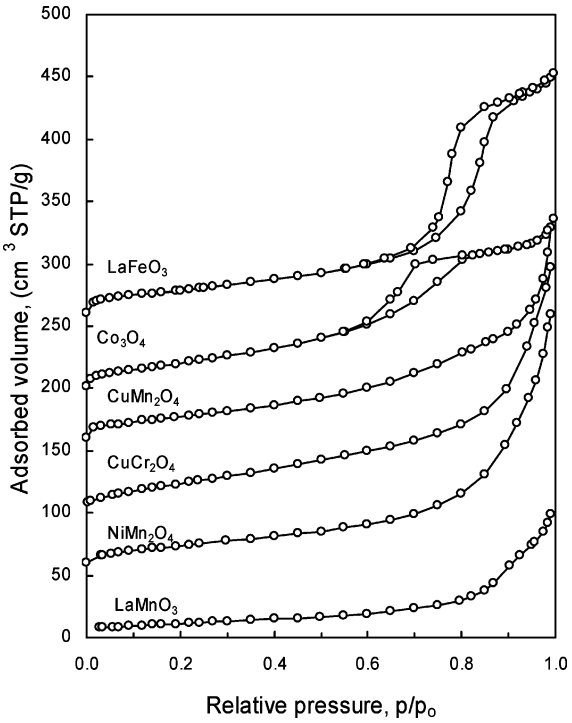

Figure 3. Nitrogen adsorption isotherms of spinels and perovskites prepared by using a silica template. Isotherms for $NiMn_2O_4$, $CuCr_2O_4$, $CuMn_2O_4$, Co_3O_4, and $LaFeO_3$ are vertically shifted 50, 100, 150, 200, and 250 cm^3/g respectively for clarity.

Except in the case of $LaMnO_3$ the S_{BET} values of the materials prepared by the template method are considerably higher than those obtained by the conventional citrate method. The difference is especially remarkable in the case of $LaFeO_3$ perovskite. This perovskite exhibits a surface area of 110 m^2/g when prepared by means of the silica xerogel template method, which is more than 15 times higher than the area of the perovskite achieved using the citrate method. $LaFeO_3$ perovskite has also been prepared by Schwickardi and coworkers[12b] following an active carbon template route, resulting in a material with a surface area of 48 m^2/g (700 °C, 20 min). In this work, we have managed to double this value, thereby confirming the better performance of the silica route over the carbon route in this case.

In summary, we have successfully demonstrated that nanosized and high surface area perovskites and spinels can be obtained by using porous silica as template. Porous silica is an inert, low-cost, and widely available material, whose pores can be used as nanoreactors for the preparation of an extensive variety of nanosized materials without any restriction of temperature or atmosphere during the synthesis. The ternary oxides of this work, prepared with a low-cost mesoporous silica xerogel template, are made up of aggregates of nanoparticles below 15 nm as deduced by different techniques (XRD, N_2 adsorption, and TEM). The specific surface areas obtained by the template method are, in general, considerably larger than those attained by other conventional methods (e.g., the citrate method).

Acknowledgment. T.V.S. acknowledges the CSIC-ESF for the award of an I3P postdoc contract.

CM0477321