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A general and low-cost synthetic route to high-surface area metal oxides through a silica xerogel template

Antonio B. Fuertes*

Department of Chemistry and Materials, Instituto Nacional del Carbón (CSIC), P.O. Box 73, 33080 Oviedo, Spain

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Abstract

Porous metal oxides with a large surface area are synthesised by means of a procedure based on the templating approach. An inexpensive porous silica xerogel synthesised at moderate temperatures (~100 °C) in order to preserve the silanol superficial groups was used as template. In a first step, the silica porosity was filled with a concentrated solution containing a metallic salt. Then, the impregnated sample was calcined in air at a temperature of 600 °C. Under these conditions, the metal oxides were synthesised within the confined space provided by the silica pores. Finally, the product was recovered after dissolution of the silica framework in 2 M NaOH solution. The materials obtained by this procedure are made up of aggregates of nanoparticles and/or 3D solid structures containing confined pores. In this work, the synthetic route proposed is illustrated by the preparation of various binary metal oxides (i.e. Fe_2O_3, Cr_2O_3, NiO, CeO_2, Mn_2O_3, Co_2O_3 and Al_2O_3). The BET surface areas measured for these materials are in the range of 100–270 $m^2\ g^{-1}$. The proposed method is not restricted to the binary metal oxides. It can also be used in the preparation of other inorganic materials such as metal sulphides or mixed metal oxides.

Keywords: A. Oxides, Nanostructures; B. Chemical synthesis; C. X-ray diffraction

1. Introduction

Recently, the preparation of high-surface area metal oxides (HSMO) has received widespread attention because they can be used in a high number of applications including catalysis [1–4], adsorption [5–7], as electrodes in electrochemical cells [8–10], as chemical sensors [11,12], etc. HSMO are currently prepared by procedures such as the precipitation of precursors, sol–gel techniques, crystallization, supramolecular chemistry, thermolysis, etc. An extensive survey of this subject has been recently reported by Landau [13]. Some of the synthetic procedures are quite complicated and/or involve the use of expensive reagents. Others give materials which have poor structural characteristics.

In recent years, a wide variety of porous materials (i.e. silica, carbon, metals, polymers, etc.) have been obtained by means of the template technique [14–18]. Two types of templates have been used for this purpose, i.e. soft templates (i.e. surfactants) and hard templates (i.e. porous solids such as silica or carbon). When hard templates are employed, the synthesis of the porous material takes place in a confined space formed by the porosity of the template. The use of a reduced space is of great importance because it restricts the growth of the material during the synthesis (i.e. by sintering) and facilitates the formation of nanostructures (i.e. nanoparticles, nanocylinders, etc.). Given that the synthesis of metal oxides usually requires high temperatures that induce the formation of large particles through sintering, the use of the template technique to prepare porous metal oxides is highly appropriate. Recently, several papers describing the preparation of HSMO by this technique have appeared. Two types of hard templates have been employed, i.e. active carbons [19–21] and mesostructured silica materials (MSM) [22–24]. Schwickardi et al. [20] described the use of commercial active carbons as templates to prepare different types of HSMO. Dong et al. [21] reported the preparation of monodisperse and porous spheres of

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* Tel.: +34 985 11 9090; fax: +34 985 29 7662.
E-mail address: abefu@incar.csic.es

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inorganic materials (i.e. oxides and phosphates) using submicrometric porous carbon spheres as templates. However, the use of active carbons as templates has certain limitations due to the fact that, at the high treatment temperatures employed during the synthesis, reactions may occur between the infiltrated salts and the carbon. When the heat treatment is performed in air, the carbon may be rapidly oxidised (ignition) even at relatively low temperatures due to the catalytic effect of infiltrated salts. On the other hand, some metallic salts may be reduced to metal when the heat treatment takes place under inert conditions. For these reasons, a more inert hard template such as porous silica could be more appropriate. Tian et al. [22,23] recently reported the fabrication of ordered porous inorganic materials (i.e. metal oxides, sulphides) by using various MSMs (i.e. SBA-15, SBA-16 and FDU-1) as templates. The authors emphasize the importance of preserving the silanol groups on the silica surface to attain a good degree of impregnation. With this objective they devised a special technique (microwave digestion) to eliminate the surfactant employed in the synthesis of MSM so as not to alter the presence of the silanol groups within the silica pores.

Although, the procedure proposed by Tian et al. [22] yields high-surface area metal oxides, it requires the use of expensive surfactants as templating agents for the synthesis of MSM and a sophisticated method to remove the surfactant. In short, this synthetic approach is too complex and costly for practical application. A low-cost route for manufacturing HSMO could be provided by using porous silica templates synthesised without the aid of surfactants (i.e. silica gels). Accordingly, in this work we propose a new approach based on the use of inexpensive silica xerogel as templating agent. The xerogel is obtained from a synthesis mixture formed exclusively by a silica source (sodium silicate), HCl and water. Furthermore, because the templated material is obtained without the aid of structure-directing agents (i.e. surfactants) and the synthesis takes place at a moderate temperature (100 °C), the surface silanol groups can easily be preserved. This procedure is illustrated here with the synthesis of various binary metal oxides.

2. Experimental section

The synthesis of silica xerogel was carried out in a two-step process according to a procedure reported elsewhere [25]. In a typical synthesis, the silica source (Sodium silicate, Aldrich, 27% SiO_2 + 14% NaOH) was added under stirring to an aqueous solution containing HCl. The molar composition of the synthesis mixture was: sodium silicate/HCl/H_2O = 1/6/194. In the first stage, the solution was stirred in a closed Teflon vessel for 20 h at room temperature. In the second stage, the mixture was maintained for 2 days at 100 °C. The resulting gel was filtered, washed several times with water and then with acetone and dried at room temperature.

For a typical synthesis of the templated metal oxides, hydrated metal nitrates were dissolved in ethanol (around 0.8–1.2 g nitrate/g ethanol). Afterwards, the silica xerogel was impregnated with this solution until incipient wetness was attained. The impregnated sample was dried at 80 °C. The impregnation-drying cycle was repeated up to three times for a high loading of the metal nitrate into the silica porosity. The impregnated samples were then calcined in air at 600 °C (2 °C/min) for 4 h. The metal oxide products were obtained after dissolution of the silica framework in 2 M NaOH solution.

The samples were characterised by nitrogen adsorption at −196 °C by using a Micromeritics ASAP 2010 volumetric adsorption system. The BET surface area was deduced from the isotherm analysis in the relative pressure range of 0.04–0.20. The total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The PSD was calculated by means of the Kruk–Jaroniec–Sayari method [26] applied to the adsorption branch. X-ray diffraction (XRD) analysis was carried out in a Siemens D5000 instrument operating at 40 kV and 20 mA and using Cu Kα radiation ($\lambda = 0.15406$ nm). The structure of the materials was characterised by transmission electron microscopy (TEM).

3. Results and discussion

The porosity of the silica xerogel used as template is made up of mesopores of quite uniform size within the 2–15 nm range. This is illustrated in Fig. 1 which shows the nitrogen sorption isotherm and PSD (inset) of this material. The values obtained for the BET surface area and pore volume are 510 $m^2\,g^{-1}$ and 0.8 $cm^3\,g^{-1}$, respectively. The TEM image (Fig. 1, inset) obtained for the silica xerogel shows a disordered pore network, which is characteristic of this type of material [27]. The FT-IR spectrum of the silica xerogel (not shown) exhibits a broad peak in the 3000–3800 cm^{-1} region, suggesting an abundance of silanol groups.

An energy dispersive X-ray analysis (EDX) of the synthesised metal oxides revealed that these samples only contain traces of silica. The identification of the product obtained by the templated technique was carried out by X-ray diffraction (XRD) analysis at the wide-angle range ($2\theta = 10$–$90°$). The XRD patterns for several templated oxides are shown in Fig. 2. In general, they contain broad diffraction peaks, indicating that the oxide is made up of very small particles. The size of these nanoparticles was estimated from the broadening of the XRD peaks according to the Scherrer formula. The values deduced are indicated in Table 1. The as-synthesised iron oxide exhibits an X-ray diffraction profile consisting of two very broad low-intensity reflections (Fig. 2a, lower). This spectrum is characteristic

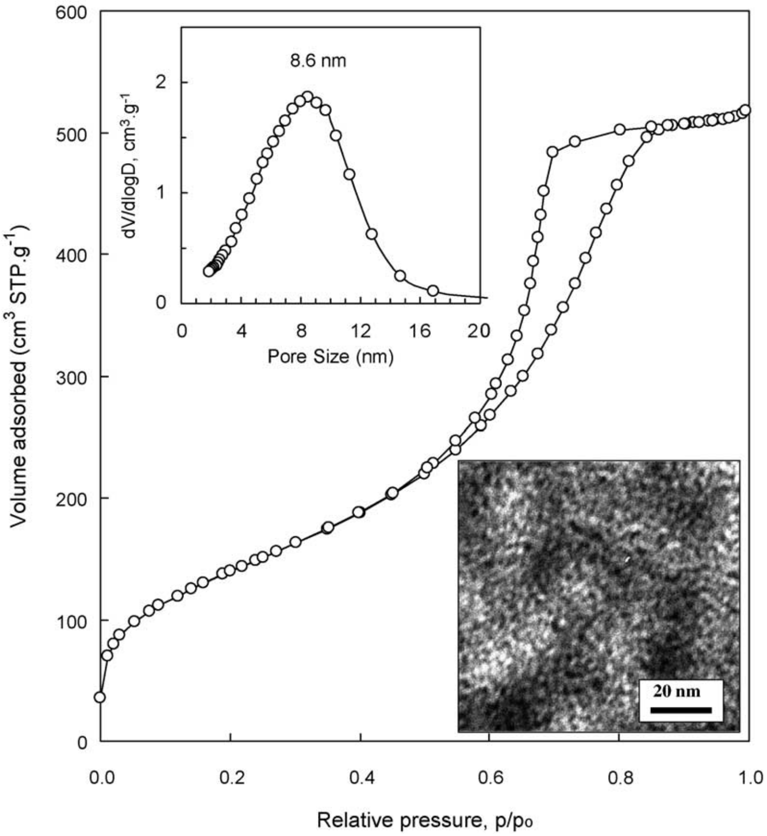

Fig. 1. Nitrogen sorption isotherm, pore size distribution (inset) and TEM image (inset) for the silica xerogel used as template.

of the poorly crystalline iron(III) oxide ferrihydrite [28]. This material is an excellent adsorbent for the elimination of traces of metallic ions (i.e. Zn (II), As (V), etc.) in contaminated water [29]. Moreover, ferrihydrite can be partially transformed into magnetic nanoparticles of γ-Fe_2O_3 (maghemite) by means of heat treatment at temperatures of around 350 °C [30]. Accordingly, the sample obtained here in this way is attracted by a magnet and its XRD pattern contains the peaks that are characteristic of γ-Fe_2O_3 (Fig. 2a, upper). Thus, this technique would be useful for making magnetic nanoparticles with a large surface area. The aluminium oxide obtained by means of this procedure exhibits an amorphous framework as was deduced by XRD. The other oxides show XRD patterns that are characteristic of the crystalline phases corresponding to the products listed in Table 1.

The physical properties of the metal oxides prepared by means of the templated technique are presented in Table 1. These materials exhibit BET surface areas of 96–270 $m^2\,g^{-1}$ and total pore volumes of 0.2–0.8 $cm^3\,g^{-1}$. The values calculated for the surface areas are larger than those reported for similar materials prepared by more complex techniques at similar calcination temperatures (i.e. ~600 °C) [13]. The metal oxides synthesised by the template method consist of aggregated nanoparticles or large particles, which enclose framework-confined pores. Accordingly, the porosity of the metal oxides may consist of two types of pores; i.e. pores arising from the voids between the nanoparticles (textural pores) and pores confined within the solid framework (structural pores). The TEM images obtained for different templated metal oxides illustrate this feature (Fig. 3). Thus, Fig. 3a clearly evidences the existence of structural pores in the iron oxide (ferrihydrite) sample. This structural porosity seems to be an inverse replica of the silica xerogel framework (Fig. 1, inset). Moreover, taking into account the density of Fe_2O_3 ($5.2\,g\,cm^{-3}$), the prepared iron oxide has a surface to framework volume ratio of $\sim 1.4 \times 10^7\,cm^{-1}$, which is close to that deduced for a mesoporous carbon obtained from the same silica template [25]. This clearly suggests that the structure of our iron oxide is a faithful replica of that of the silica template. The other TEM images in Fig. 3 shows that these products are made up of aggregates of nanoparticles with sizes below 20 nm. The sizes estimated from the TEM images are in good agreement with those obtained from XRD peak broadening (Table 1).

A more precise image of the structure of the synthesised materials can be obtained by means of N_2 sorption experiments. The existence of structural and/or textural

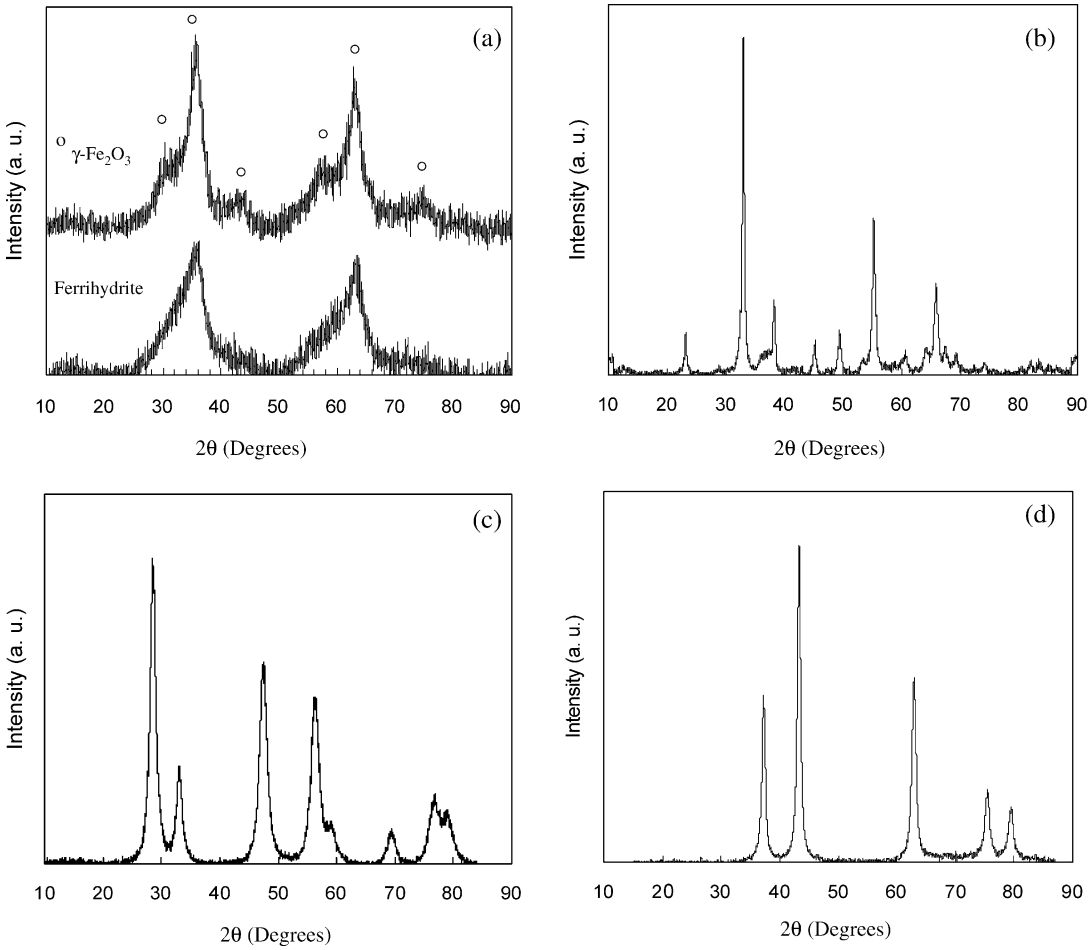

Fig. 2. XRD patterns of various templated metallic oxides: (a) Fe_2O_3; (b) Mn_2O_3; (c) CeO_2; (d) NiO.

porosities is evidenced by the analysis of N_2 sorption isotherms. Fig. 4 shows the isotherms and the PSDs (insets) for various representative metal oxides. The N_2 isotherm obtained for iron oxide/ferrihydrite (Fig. 4a) exhibits a capillary condensation step at $p/p_o \sim 0.6$–0.8. This clearly indicates that the material contains framework-confined mesopores (structural), the pore size being centred at ~6.5 nm (Fig. 4a, inset). Fig. 1a provides a TEM image that illustrates this porous structure. By applying the α_s-plot analysis to the N_2 adsorption data obtained for Fe_2O_3 (ferrihydrite), it was estimated that around 70% of the pore volume corresponds to the structural mesopores, whereas

Table 1
Structural properties of high-surface area metal oxides

Product (XRD)	S_{BET} ($m^2\,g^{-1}$)	V_t ($cm^3\,g^{-1}$)[a]	Structural porosity		Crystallite size (nm)[b]
			V_s ($cm^3\,g^{-1}$)[c]	Pore size (nm)[d]	
Fe_2O_3					
Ferrihydrite	270	0.45	0.32	6.5	–
Maghemite	176	0.44	0.32	11	–
Cr_2O_3	118	0.57	–	–	17
NiO	96	0.39	0.12	6.9	11
CeO_2	141	0.35	0.04	4.6	7
Mn_2O_3	117	0.26	0.08	4.6	18
Co_2O_3	98	0.21	0.14	8.6	10
Al_2O_3	153	0.78	–	–	–

[a] Total pore volume from N_2 adsorption at $p/p_o = 0.99$.
[b] Estimated from XRD peak broadening by using the Scherrer formula.
[c] Volume of structural pores.
[d] Maximum PSD for the structural pores.

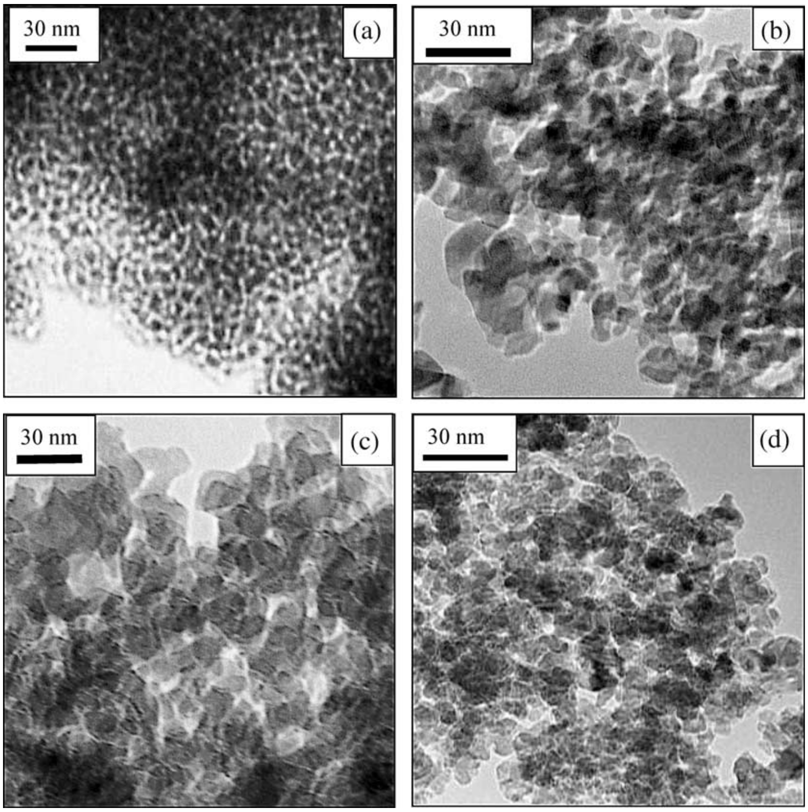

Fig. 3. TEM images of the various synthesised metallic oxides: (a) Fe_2O_3 (ferrihydrite); (b) Co_2O_3; (c) Al_2O_3; (d) NiO.

the rest can be assigned to interparticle voids (textural porosity). A similar balance structural/textural porosity is obtained for Fe_2O_3 (maghemite). This material exhibits in relation with ferrihydrite, a lower specific surface area and a larger pore size (see Table 1). The cobalt oxide shows a similar balance between structural and textural porosity. The N_2 sorption isotherm of CeO_2 (Fig. 4b) shows a capillary condensation step at $p/p_o \sim 0.4$–0.5, which reflects the existence of structural mesopores. These mesopores exhibit a narrow PSD centred at ~4.6 nm (Fig. 4b, inset). Unlike iron oxide, the structural porosity of CeO_2 only represents around 10% of the total pore volume, the rest corresponding to textural porosity (interparticle voids). Except for Cr_2O_3 and Al_2O_3, the other oxides exhibit some degree of structural porosity, suggesting the presence of 3D porous metal oxide structures. The values for structural pore size and pore volume estimated from the α_s-plot analysis are indicated in Table 1. The aluminium oxide shows an interesting structure as deduced from the N_2 sorption isotherm (Fig. 4d). Thus, it exhibits a pronounced capillary condensation step at a relative pressure of ~0.9, which is indicative of large, quite uniform large pores as is evidenced by the PSD (Fig. 4d, inset). This shows that the porosity in the aluminium oxide is made up of pores centred at ~37 nm. It is also clear from the TEM image in Fig. 3c, which shows that this material is made up of the aggregation of uniform nanoparticles with sizes within the 10–20 nm range.

In addition to binary metal oxides, the template procedure can be extended to the preparation of multi-component metal oxides and other compounds such as metal sulphides. Thus, our laboratory has prepared various porous mixed oxides like CuO–CeO_2, which are currently under study as catalysts for CO-oxidation. In principle, the only limitation to the use of this technique concerns those compounds, which are affected by the agent used to remove the silica template. As an example, ZnO is dissolved by the NaOH solution and consequently it cannot be prepared by means of this procedure.

4. Conclusions

In summary, a novel synthetic route to obtain porous metal oxides that exhibit a large surface area is reported. The method presented is based on the templating approach. An inexpensive porous silica xerogel that contains abundant superficial silanol groups is used as template. This facilitates the filling of the silica porosity by the infiltrating solution. The metal oxides are synthesised in a confined space provided by the silica porosity. As a result, the solid formed will be made up of

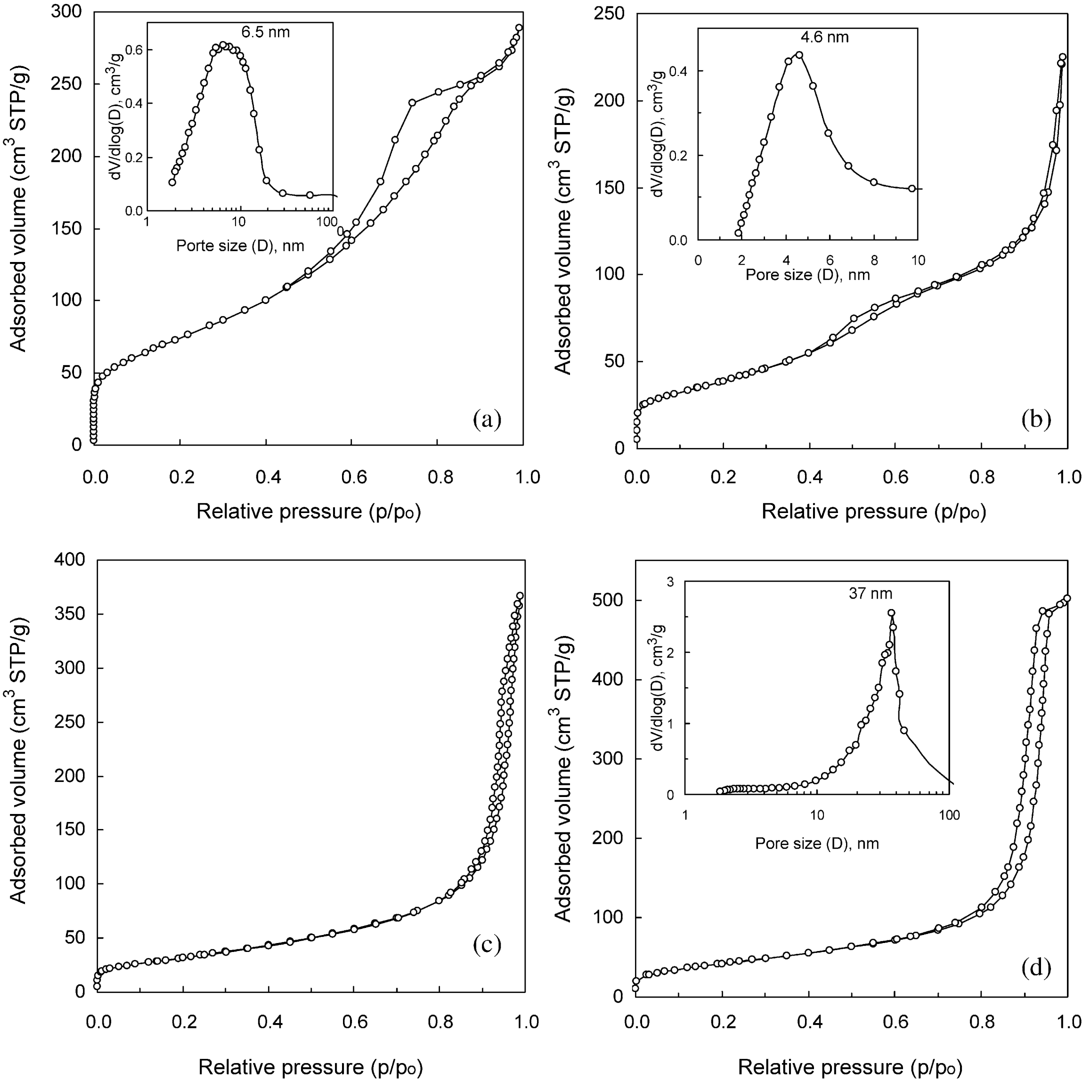

Fig. 4. Nitrogen sorption isotherms and PSDs of structural pores (insets) of several representative metallic oxides synthesised by means of the templating technique. (a) Fe_2O_3 (ferrihydrite); (b) CeO_2; (c) Cr_2O_3; (d) Al_2O_3.

aggregates of nanoparticles and/or 3D solid structures containing confined pores. The solid therefore exhibits a textural porosity arising from the interparticle voids and a structural porosity made up of the framework-confined pores. The synthetic route proposed in this work is illustrated by the preparation of several binary metal oxides. However, this method can be extended to other inorganic materials such as metal sulphides, mixed metal oxides, etc.

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