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Titania coatings on high and low surface area spherical silica particles by a sol–gel method

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Spherical particles of porous silica were coated with titania by the sol–gel method starting from titanium isopropoxide. The silica samples used were of high and low surface area (about 250 and 19 $m^2 g^{-1}$, respectively). The coated particles were generally calcined in air at 500 °C for 2 h. X-Ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used before and after erosion with Ar^+ ions at 4 keV. Silica with a high surface area was partially coated with a thin (below 1 nm) TiO_2 layer, whereas the low surface area silica resulted in a better coating. In this case, XPS and AES, in combination with silica and titanium chemical analysis, suggest that the particles were coated with nearly one monolayer of titania. High surface area samples exhibited a small decrease of BET area after deposition of the titanium dioxide, whereas no significant change of BET area was observed in low surface area silica. Porosity analysis showed, in both cases, a minor decrease of micropore volume and area after the coating process. This suggests that titania oligomers contained in the titania precursor sol do not penetrate significantly into the micropores and therefore the pore plugging process is a rather limited one. X-Ray diffraction showed that the titania layer is amorphous but begins to crystallize in the anatase form after about 6 h at 700 °C in those samples with the larger TiO_2 content.

Introduction

Titania presents increasing interest as a catalyst or support.[1–3] However, its low surface area is an important disadvantage for catalytic applications. This has been partially overcome by the application of new synthesis procedures in order to obtain titania with a high specific area.[4–6] Nevertheless, for many applications, supported oxides are more efficient as thin layers on the surface of a different support, and therefore titania supported silica is also interesting as a catalyst as well as a support.

Important aspects such as thickness, distribution and morphology of the layers deposited on particles of inorganic oxides are not well known. The direct grafting of precursors by means of reaction with the surface hydroxyl groups of the support is a convenient way to disperse an active element while it stays strongly joined to the oxide support.[7,8] In a state of monomolecular dispersion, the deposited layer is strongly influenced by the support.[9] By applying the Chemical Vapor Deposition (CVD) method, starting from titanium tetraisopropoxide (TTIP), the formation of a monolayer of TiO_2 covalently bonded to the silica surface has been achieved.[10,11] It is well known that the synthesis conditions determine to a great extent morphological characteristics such as homogeneity, size, and distribution of pores of the coated product. Several works deal with the coating of porous high area supports with titania using solution chemistry based methods.[12–20] The deposition of TiO_2 onto high area silica has been studied by means of precipitation, grafting with $TiCl_4$, and grafting (or impregnation) with TTIP.[13–16] The best dispersion of TiO_2 on the surface was achieved with the impregnation and grafting with titanium alkoxide.[15] The existence of a strong interaction between titania and silica due to the formation of Ti–O–Si bonds was established. Several authors[21–27] have reported the preparation of titania films by the sol–gel method, and this is an alternative way of covering silica particles with a thin film of titania. This method involves hydrolysis and condensation reactions of organometallic precursors where the resulting sol, containing inorganic oligomers, can be deposited on the substrates by spinning or dipping. The resultant amorphous film is then annealed at relatively low temperatures (500–800 °C) to achieve densification and crystallization. The most widely used sol–gel systems are based on metal alkoxides, $M(OR)_n$. The key steps in the sol-forming reactions can be summarized as follows:

$$\equiv M\text{–}OR + H_2O \rightarrow \ \equiv M\text{–}OH + ROH \text{ (Hydrolysis)}$$
$$\equiv M\text{–}OH + RO\text{–}M\equiv \rightarrow \ \equiv M\text{–}O\text{–}M\equiv + \ ROH \text{ (Condensation)}$$

Under controlled reaction conditions nearly linear or branched soluble oligomers are first obtained (sol). Further condensation reactions between oligomer chains lead to gelification (crosslinking). Condensation reactions between M–OH groups, leading to the formation of new M–O–M bonds, are important during the densification of the gel. In addition to the low temperature process, the sol–gel method provides the advantage of reproducible coating thickness and compositions.

In the present study titania sols were used in order to coat silica particles of spherical morphology. The aim of the work was to deposit a very thin film, ideally a monolayer of titania, on the surface of the silica without altering significantly the morphology or porosity characteristics of the support. In the preliminary experiments the hydrolysis of the titanium alkoxide was performed in the presence of the silica sample. It was found that after the process a great decrease in BET area took place in the HA-silica sample (up to about 90 $m^2 g^{-1}$). Therefore, this coating procedure was discarded and preformed titania sols were used as described next.

It has been established that when depositing a titania sol on such substrates as fused silica or rutile, with a flat and uniform surface, the formed layer covers the surface completely.[25,28] One can expect a similar result when depositing titania on solid

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spheres of silica, provided that titania can be covalently bonded to the surface. However, the presence of pores and pleats, characteristic of materials with large surface areas, can promote the formation of inhomogeneous and incomplete deposits on the surface of the substrate. In order to obtain information on the influence of these morphological properties on the coating characteristics, two different types of silica were used as substrates for the coating process. Both silicas were of spherical morphology but one was a high surface area (HA, about 250 $m^2 g^{-1}$) and the other was a lower surface area type (LA, about 19 $m^2 g^{-1}$).

Experimental

Reagents

Titanium(IV) isopropoxide (97%), isopropanol (99+%) and diethanolamine (99%) were used as received from Aldrich. Porous silica samples with high BET surface area (HA) ES-70X (Crossfield) (about 250 $m^2 g^{-1}$) and low BET surface area (LA) silica (about 19 $m^2 g^{-1}$) provided by Fabrica Carioca de Catalizadores (Rio de Janeiro, Brasil) were used as substrates. Both silicas were of spherical morphology with diameters in the range 20–50 μm (HA-silica) and 15–40 μm (LA-silica)

Titania sols

To a solution of diethanolamine (3.2 g, 0.03 mol) in 22.3 ml isopropanol (17.4 g, 0.29 mol) was added 9.23 ml of TTIP (8.5 g, 0.03 mol) under dry nitrogen. Thereafter, 0.5 ml (0.027 mol) of water, dissolved in 22.3 ml isopropanol (17.4 g, 0.29 mol), was slowly added under nitrogen with stirring by means of a dropping funnel. The solution was stirred at room temperature for 4–6 h and then hermetically sealed and kept refrigerated until use. The concentration of the prepared sol was 0.7 M. Diethanolamine was used in order to control the hydrolysis rate and to stabilize the sol from gelation.[22,25]

To carry out the coating process, sols with different amounts of titania precursors with respect to the quantity of silica were used. These amounts were estimated following previous work[13–15] where the theoretical quantity necessary to form a TiO_2 monolayer on the total surface of the silica particles was calculated by considering the density of the (010) plane of anatase (5.5 Ti^{4+} nm^{-2}). The authors calculated that for silica particles with an area of 320 $m^2 g^{-1}$ 19 wt% TiO_2 is required with respect to the weight of SiO_2. Naturally, the amount of titania required is proportional to the total area of the corresponding silica sample. From the concentration of the prepared sol it can be calculated that 1 ml of solution corresponds to 0.04 g of TiO_2. In this case the quantity applied was calculated as that necessary to coat 100, 80, and 50% of the BET area.

For the preparation of the titania sol, the quantity of water used was slightly lower than the amount calculated to hydrolyze two of the four ethoxide groups of TTIP. This was done in order to produce mainly linear oligomers. The contact time between the phases was 30 min. This contact period was chosen on the basis of a series of preliminary experiments where it was demonstrated that at room temperature the amount of titania incorporated did not change after 15–20 min.

Silica coating

In order to eliminate adsorbed water and diminish the amount of surface –OH groups both types of silica were first calcined in air at 500 °C for 2 h before deposition of titania. The silica (about 1 g) was added to solutions (sols) containing a predetermined amount of titania precursor, ranging from 50 to 100% of the calculated amount required to coat the silica surface with one monolayer of titania.[29] The suspensions were held and shaken in a flask shaker at room temperature over a period of 30 min at about 300 oscillations min^{-1}. Thereafter, the solid was separated by filtration using a Normag pressure filter funnel and washed thoroughly with isopropanol under nitrogen in order to remove those titania oligomers that were not covalently bound to the silica surface and then dried at 80 °C for 20 h.

Calcination treatment

A forced convection, temperature programmed Nabertherm S27 furnace was used. The samples were calcined in air at a predetermined temperature (500–700 °C) for 2 h.

Characterization

BET area determinations and porosity analyses were carried out using a Micromeritics ASAP 2010 apparatus at −196 °C using nitrogen as the adsorption gas. Powder X-ray diffraction analyses (XRD) were carried out with a Siemens D-5000 instrument. Morphologies were examined on micrographs obtained by scanning electron microscopy (SEM, Philips EM 300).

X-Ray photoelectron spectroscopy (XPS) measurements were performed at room temperature using a Physical Electronics 1257 system with a hemispherical analyzer and non-monochromatized radiation (Al-Kα, 1486.6 eV) operating at 200 W. The pass-energy was set to 50 eV and no flood gun was used for charge compensation. The sensitivity factors used for quantitative estimates and the values of binding energies were taken from available data.[30] The powder was supported with double sided adhesive tape. The analysis area was approximately 0.4 cm^2. These analyses were performed at room temperature, but irradiation from the X-ray source can increase the sample temperature. Measurements were carried out before and after erosion with Ar^+ ions at 4 keV. The surface charging effects ($\approx$0.5 eV) were corrected by using the C 1s peak at 284.5 eV.[30] Numerical analysis of the peaks was performed using the MULTIPACK software for data analysis, from Physical Electronics, Inc., which evaluates the peak area and uses tables of sensitivity factors for quantitative calculation in the standard way.

Auger electron spectroscopy (AES) was performed with the same instrument by exciting the samples with an electron current of 30 nA at 3 kV. Larger currents lead to run-away charging effects. The analysis area was approximately 0.01 cm^2. AES measurements were performed before and after erosion with Ar^+ ions, as for the XPS measurements described above.

Si and Ti contents of the samples were determined trough Inductively Coupled Plasma measurements using a Perkin-Elmer P-400 ICP-OES instrument.

Results and discussion

In the sol–gel method precursors with more than two ligands such as silicon or titanium alkoxide can form a nearly linear chain structure when the reactions are carried out using acid catalysts (normally HCl) with a molar ratio of water to precursor of *ca.* 2.0. Excess water increases the functionality of polymerization,[31] since the formation of lateral M–OH groups with respect to the main chain allows branching and/or crosslinking reactions. In the case of titanium alkoxides, due to the great reactivity of Ti–OR bonds towards hydrolysis, the presence of chelating agents, such as alkanolamines[25] is necessary in order to control the degree of hydrolysis and subsequent polymerization reactions. In this work, the preparation of the titania sol was carried out under linear growth conditions, that is with a relatively low amount of water, and diethanolamine. The sols were stable for months

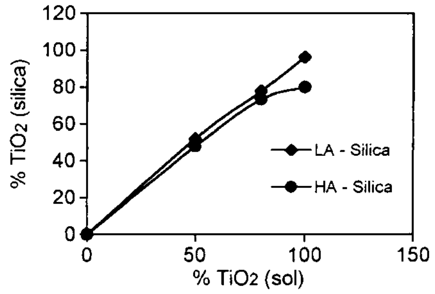

Fig. 1 Relationship between the amount of titania present in the sol and that deposited on the surface of silica samples with high (HA-silica) and low (LA-silica) BET areas. Values are expressed as percentages of the amount calculated to coat the silica surface with a monolayer of titania.

indicating that no free Ti–OH groups are present in the oligomers contained in the stabilized sol. By bringing into contact both phases (silica and titania sol), –Ti–OR groups can react with Si–OH groups present in the silica surface forming –Ti–O–Si–O– bonds. Through this condensation reaction titania oligomers are covalently bonded to silica forming a titania layer during the subsequent steps of drying/calcination. Those titania precursor oligomers not covalently bonded to the silica surface were rinsed with isopropanol in order to avoid the formation of titania aggregates.

Fig. 1 shows the relationship between the amount of titania in the sol and the quantity effectively deposited on the surface of the silica according to data obtained from chemical analysis. It can be observed that a high proportion of the titania contained in the sol is deposited and that this relationship is almost linear up until 80% of the theoretical amount. In both silica types it is observed that, for coatings applying 100% of the theoretical quantity to form a monolayer, the deposited amount reaches about 75% of the titania present in the sol. This would indicate that part of the area is not available or accessible for coating with the precursor titania oligomers contained in the sol. However, if only the external area is considered, that is excluding the area of the micropores (Table 1), the deposited quantity corresponds nearly to the theoretical one in the case of the LA-silica and around 80% of the theoretical value in the case of the HA-silica (Fig. 1).

On the other hand, as shown in Table 1, a decrease in the micropore area in the LA-silica is not observed, while in the HA-silica the micropore area decreases between 15 to 25%. Moreover, the decrease depends only slightly on the quantity of TiO_2 present in the sol for the studied range. These facts suggest that the oligomers contained in the titania sol do not penetrate the micropores in the case of the LA-silica and only penetrate the micropores to a small degree in the case of the HA-silica. For this reason, in the case of the LA-silica, a decrease of the BET area is not observed. In the case of the HA-silica there is a decrease in BET area of around 7%, which is almost independent of the relative quantity of TiO_2 used for the coating process. This decrease in BET area is notably smaller than that reported by Castillo *et al.*[15] when using TTIP directly without prehydrolysis. The decrease in BET area reported by those authors is approximately 12% when applying the quantity of TiO_2 calculated to coat 100% of the area. Moreover, they found, in contrast to our results, that the BET area diminishes gradually on increasing the relative amount of titania used. This fact can be attributed to extensive pore plugging due to the small titanium alkoxide molecule and/or to the presence of titania which is not covalently bonded, because this was not removed by washing prior to drying the coated product.

Surface analysis

HA-Silica sample coated with TiO_2. The XPS analysis of the surface of a HA-silica sample coated with titania is presented in Fig. 2a. The Ti 2p3/2 peak is located at 458.0 eV, which is the energy corresponding to TiO_2.[22] The O 1s peak exhibited two maxima, one at 531.5 eV attributed to OH groups and the second at 529.5 eV attributed to oxygen in the oxide.[30] The Si 2p peak at 104.5 eV is attributed to SiO_2, usually in the range 103–104 eV.[30] An estimate for the average Ti : Si ratio performed using the available sensitivity factors leads to Ti : Si ≈ 1.6, an estimate that assumes a homogeneous sample. Since photoelectrons emitted by silicon have a kinetic energy of about 1200 eV, their mean free path is of the order of 10 monolayers.[23] Along with the fact that the mean free path depends on the material, this means that the XPS spectrum is consistent with a homogeneous TiO_2+SiO_2 mixture as well as with a structure of SiO_2 grains coated with a few monolayers of TiO_2.

Fig. 3a shows the AES spectrum of the surface of the as-received HA-silica sample. The shape of the Si peak corresponds to oxidized silicon. A rough estimate using the sensitivity factors for the peak to peak amplitudes[32] leads to a Ti : Si ≈ 1 : 2 ratio, roughly similar to the XPS estimate, but larger than that reported by Castillo *et al.*[14] The mean free path of the Auger electrons emitted by silicon (≈100 eV) is of the order of 1 monolayer.[33] A nearly complete coating of the silica grains by a TiO_2 layer would decrease the silicon intensity to a lower degree than that observed. Therefore, a partial coating of the silica grains by titania is a consistent interpretation.

After erosion with doses of 0.3 mC cm^{-2}, which is able to remove about 1 nm of SiO_2 as calibrated on the same system, the AES spectrum exhibits a large relative increment in the silicon signal from SiO_2, as shown in Fig. 3b. After removal of the TiO_2, the sputtering process possibly reduces some SiO_2 leading to elemental silicon, with a sensitivity twice as high as Si in SiO_2.[32] The large silicon LVV Auger signal in Fig. 3b precludes the observation of titanium and oxygen which are below the instrumental sensitivity. A scan with different acquisition parameters, shown in Fig. 3c, showed that both elements, titanium and oxygen, were still present in small amounts. Since the Auger spectra from Fig. 3b and Fig. 3c were recorded with different pass-energy values, no quantitative estimate is possible.

Table 1 BET area and porosity characteristics of silica samples coated with different amounts of titania, expressed as a percentage of the amount necessary to form a monolayer on the external area

Sample	TiO_2 (%)	BET area /m^2 g^{-1}	Micropore volume/cm^3 g^{-1}	External surface/m^2 g^{-1}	Pore volume/cm^3 g^{-1}	Micropore area/m^2 g^{-1}	Pore diameter/Å
LA-1	0	20	0.0029	13.4	0.1	6.6	96
LA-2	52	19	0.0026	13.2	0.095	5.9	93
LA-3	79	19	0.0026	13.2	0.092	6.0	93
LA-4	96	21	0.0033	13.5	0.075	7.5	86
HA-1	0	253	0.013	217	1.59	35.2	246
HA-2	48	241	0.0097	213	1.39	27.8	229
HA-3	73	240	0.0078	216	1.39	23.8	222
HA-4	80	234	0.0101	206	1.29	28.2	214

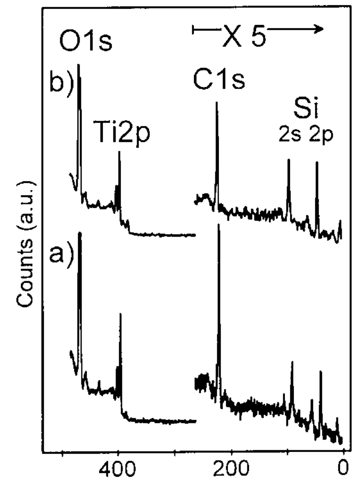

Fig. 2 XPS surface survey of the samples: a) HA-silica, b) LA-silica.

The preceding results strongly suggest that a very thin (below 1 nm) layer of TiO_2 was partially deposited on the silicon dioxide substrate. The persistence of some titanium in the spectrum after sputtering is due to the rough and porous surface of the sample, which did not allow homogeneous removal by sputtering.

LA-Silica sample coated with TiO_2

The XPS analysis of a low BET area silica sample coated with titania is shown in Fig. 2b. The analysis was qualitatively similar to the preceding sample, but with a somewhat lower titanium content: the estimated titanium to silicon ratio is $Ti : Si \approx 0.8$. However, the absolute values of these estimations are rather uncertain since there is a significantly lower signal from titanium in this sample. This could be interpreted on the basis of a comparatively minor amount of titanium or an incomplete coating of the substrate.

In the AES spectrum of the LA-silica sample presented in Fig. 4a the titanium signal is clearly observable, whereas silicon is barely detectable, opposite to what was observed with HA-silica. This can indicate a more homogeneous coating of the substrate. On the other hand, after ion erosion a strong silicon peak was observed along with a weak titanium signal, both detected on the same scale. The titanium signal can be attributed to titanium remaining inside the pores which would therefore be difficult to eliminate by the erosion process. These observations suggest the existence of a very thin layer of titania coating homogeneously the silica surface. Since the titania determined by chemical analysis is consistently close to the amount theoretically needed to totally cover the silica surface with a monolayer, it is safe to suppose that the LA-silica particles were coated with nearly one monolayer of TiO_2.

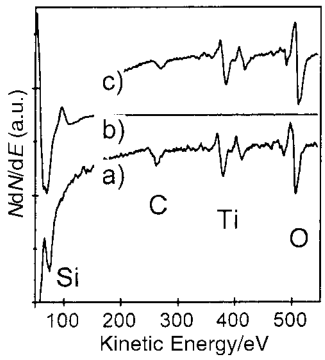

Fig. 3 AES spectra from the HA-silica sample. a) Sample as-received. b) After erosion (dose equivalent to the removal of a 1 nm SiO_2 layer) showing the Si LVV signal. c) The same as b) showing Ti and O, recorded with a higher pass-energy.

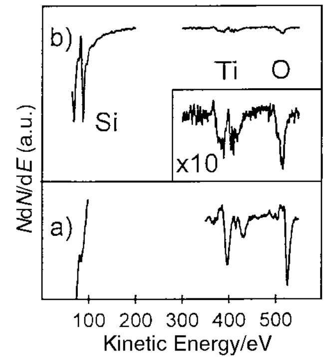

Fig. 4 AES spectra from the LA-silica sample. a) Sample as-received. b) After erosion (dose equivalent to the removal of a 10 nm layer of SiO_2).

X-Ray diffraction

XRD showed only the characteristic broad peak of SiO_2 in all silica samples coated with titania after calcination at 500 °C for 2 h indicating that crystalline TiO_2 particles were not formed on the silica surface. The same results were obtained at 700 °C after 2 h heating. Very weak reflections associated with the anatase phase were found only after heating for 6 h at 700 °C in the HA-silica samples with the greater amount of titania (10.3% TiO_2). No XRD diffraction peaks due to anatase were observed in coated LA-silica samples after 2 h at 800 °C. These results are similar to those obtained by Asakura *et al.*[11] studying the structure of a layer of TiO_2 on SiO_2 prepared by the CVD method. This has been attributed to the formation of one atomic titania layer on the silica surface.

SEM

SEM micrographs showed that HA-silica as well as LA-silica particles had a considerable size dispersion. Therefore, it is difficult to determine if a significant change in the diameter of the spherical particles occurred after deposition of titania. However, it could be noted that the particles appeared to maintain their average dimensions and morphology after the coating process.

Conclusions

A variation of the method for coating silica particles with titania *via* a sol–gel approach has been developed. This uses stabilized titania sols that contain mainly linear oligomers, which are covalently bonded to the silica through reaction with surface –OH groups. In order to avoid the formation of TiO_2 aggregates, the unreacted oligomers were removed by rinsing with isopropanol prior to calcination. This method allows the formation of a very thin and homogeneous layer of titania, probably a monolayer, on the external surface, that is to say excluding the micropores, of silica particles of relatively low specific area. When applying this method to coat the surface of particles with high specific areas, only a partial coating of the surface with a thin layer of titania was achieved. These results suggest that in this case part of the surface of this silica is not accessible to the oligomers contained in the titania sol, probably due to their size.

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References

1 A. Fernandez, J. Leyrer, A. Gonzalez, G. Munera and H. Knozinger, *J. Catal.*, 1988, **112**, 489.
2 Z. Wei, Q. Xin, X. Guo, E. Sham, P. Grange and B. Delmon, *Appl. Catal.*, 1990, **63**, 305.
3 P. Wauthoz, M. Ruwet, T. Machej and P. Grange, *Appl. Catal.*, 1991, **69**, 149.
4 G. M. Pajonk, *Appl. Catal.*, 1991, **72**, 217.
5 E. I. Ko, *Chemtech.*, 1993, **4**, 31.
6 J. Retuert, R. Quijada and V. Arias, *Chem. Mater.*, 1998, **10**, 3923.
7 M. Ichikawa, *Adv. Catal.*, 1992, **38**, 283.
8 A. Zecchina and C. O. Arean, *Catal. Rev. Sci. Eng.*, 1993, **35**, 261.
9 G. C. Bond and S. F. Tahir, *Appl. Catal.*, 1991, **71**, 1.
10 T. M. Salama, T. Tanaka, T. Yamaguchi and K. Tanabe, *Surf. Sci. Lett.*, 1990, **100**, 227.
11 K. Asakura, J. Inukai and Y. Iwasawa, *J. Phys. Chem.*, 1992, **96**, 829.
12 C. J. Brinker, T. L. Ward, R. Sehgal, N. K. Raman, S. L. Hietala, D. M. Smith, D. W. Hua and T. J. Headley, *J. Membrane Sci.*, 1993, **77**, 165.
13 R. Castillo, B. Koch, P. Ruiz and B. Delmon, *J. Mater. Chem.*, 1994, **4**, 903.
14 R. Castillo, B. Koch, P. Ruiz and B. Delmon, in *Proceedings of the 6th International Symposium on the Preparation of Heterogeneous Catalysts*, Louvain la Neuve, Belgium, September 1994, eds. G. Poncelet, P. A. Jacobs, P. Grange and B. Delmon, Elsevier, Amsterdam, 1995, p. 291.
15 R. Castillo, B. Koch, P. Ruiz and B. Delmon, *J. Catal.*, 1996, **161**, 524.
16 K. Schrijnemakers, N. R. Impens and E. F. Vansant, *Langmuir*, 1999, **15**, 5807.
17 M. L. Liu and D. S. Wang, *J. Mater. Res.*, 1995, **10**, 3210.
18 K. S. Chou, K. B. Kao, C. D. Huang and C. Y. Chen, *J. Porous Mater.*, 1999, **6**, 217.
19 A. Fernandez, J. Leyrer, A. Gonzalez, G. Muñera and H. Knözinger, *J. Catal.*, 1988, **112**, 489.
20 Y. A. Yan, S. R Chaudri, D. G. Chen and A. Sarkar, *Chem. Mater.*, 1995, **7**, 2007.
21 Y. A. Yan, S. R. Chaudri and A. Sarkar, *J. Am. Ceram. Soc.*, 1996, **79**, 1061.
22 H. Dislich and E. Hussmann, *Thin Solid Films*, 1981, **77**, 129.
23 C. Sanchez, J. Livage, M. Henry and F. Babonneau, *J. Non-Cryst. Solids*, 1988, **100**, 65.
24 G. Yi and M. Sayer, *Ceram. Soc. Bull.*, 1991, **70**, 1173.
25 Y. Takahashi and M. Matsuoka, *J. Mater. Sci.*, 1988, **23**, 2559.
26 U. Selvaraj, A. V. Prasadarao, S. Komarneni and R. Roy, *J. Am. Ceram. Soc.*, 1992, **75**, 1167.
27 Y. Ohya, H. Saiki, T. Tanaka and Y. Takahashi, *J. Am. Ceram. Soc.*, 1996, **79**, 825.
28 U. Selvaraj, A. V. Prasadarao, S. Komarneni and R. Roy, *J. Am. Ceram. Soc.*, 1992, **75**, 1167.
29 A. Muñoz and G. Munera, in *Studies in Surface Science and Catalysis, No. 63. Preparation of Catalysts V*, eds. G. Poncelet, P. A. Jacobs, P. Grange, and B. Delmon, Elsevier, Amsterdam, 1991, p. 627.
30 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of Photoelectron Spectrometry*, Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1992.
31 E. J. A. Pope and J. D. MacKenzie, *J. Non-Cryst. Solids*, 1998, **101**, 198.
32 L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach and R. E. Weber, *Handbook of Auger Electron Spectroscopy*, Physical Electronic Industries, Inc., Eden Prairie, Minnesota, 1976.
33 J. M. Walls, *Methods of Surface Analysis*,Cambridge University Press, Cambridge, 1990.