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Phosphoric Acid Adsorbed on Silica-Ceria Matrix Obtained by Sol-Gel Method: Studies of Local Structure, Texture and Acid Property

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Óxidos mistos de SiO_2/CeO_2 (designados como SC) contendo quantidades variáveis de céria, SC1 = 5,6, SC2 = 8,0 e SC3 = 13,0 (% em massa), foram preparados pelo método de processamento sol-gel e obtidos como sólidos amorfos possuindo áreas superficiais específicas de SC1 = 463, SC2 = 474 e SC3 = 460 m^2g^{-1}. Íons fosfatos foram imobilizados na superfície destes sólidos, através da ligação química Ce-O-P, pela imersão de SC em uma solução de ácido fosfórico. Este procedimento produziu sólidos com as seguintes quantidades de P adsorvidas na superfície (em % atômica): SCP1 = 0,60, SCP2 = 0,71 e SCP3 = 1,63. A energia de ligação P $2p_{3/2}$, obtida por XPS, e o único pico observado em -10 ppm, por NMR de ^{31}P, revelaram que o fosfato adsorvido na superfície é a espécie $H_2PO_4^-$. Utilizando-se piridina como sonda molecular, somente sítios ácidos de Brønsted foram detectados. A determinação das quantidades destes sítios ácidos, feita pela adsorção de NH_3 gasosa sobre a superfície, revelou os seguintes valores para cada sólido tratado com o íon fosfato: SCP1 = 0,37, SCP2 = 0,43 e SCP3 = 0,51 mmol g^{-1}.

SiO_2/CeO_2 mixed oxide (designated as SC) with variable ceria contents, SC1 = 5.6, SC2 = 8.0 and SC3 = 13.0 wt%, prepared by the sol-gel processing method, were obtained as amorphous solids possessing specific surface areas of SC1 = 463, SC2 = 474 and SC3 = 460 m^2g^{-1}. Phosphate ions were immobilized onto the surface of these solids through Ce-O-P bonding by immersing SC into a phosphoric acid solution. Solids with the following P contents were obtained (in atom %): SCP1 = 0.60, SCP2 = 0.71 and SCP3 = 1.63. The binding energy peak P $2p_{3/2}$ at *ca.* 134.0 eV, observed by XPS, and the ^{31}P MAS NMR single peak, observed at *ca.* -10 ppm, revealed that $H_2PO_4^-$ is the species present on the surface of the matrices. Using pyridine as a molecular probe, only Brønsted acid sites could be detected. The amount of these acid sites, determined by ammonia gas adsorption on the surface, reached the following values for each phosphate-treated solid: SCP1 = 0.37, SCP2 = 0.43 and SCP3 = 0.51 mmol g^{-1}.

Keywords: silica-ceria, silica-ceria-phosphate, sol-gel method, acid sites

Introduction

Cerium(IV) phosphate can be prepared by reacting phosphoric acid with diammonium cerium(IV) nitrate, by an acid sol-gel process involving controlled precipitation,[1] or by using a chelating agent to obtain nanocrystalline mesoporous solids with controlled pore size.[2] It can also be obtained by hydrothermal synthesis from the reaction of CeO_2 and phosphoric acid.[3] A recent interesting process described in the literature consists of a reproducible and controllable route to produce cerium phosphate nanotubes.[4]

Cerium phosphate can have many applications as ceramic material,[5] as a glass presenting optical[6] and luminescent[7] properties, as ion exchanger[8] and catalyst.[9] It can also be prepared as phosphate particles dispersed in hybrid organic-inorganic matrices, aiming at their use in filtering process.[10,11]

Processes to prepare metal oxides incorporated into a silica matrix have been described in recent years. Mixed oxides of the SiO_2/M_xO_y type have been obtained by the sol-gel processing method, where the metal oxides are incorporated into the silica matrices as very fine and

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homogeneously dispersed particles.[12-15] SiO_2/M_xO_y obtained by this method normally presents high thermal and mechanical stability provided by the silica framework.[13,16] Despite this rigid structure, the metal oxide M_xO_y presents reactive MOH groups on the surface which can easily react with organic or inorganic acids forming a stable linkage.[17]

In this work, the preparation of microporous SiO_2/CeO_2 mixed oxide by the sol-gel process and the subsequent immobilization of phosphate groups onto the surface of this matrix are reported. The objective was to obtain cerium(IV) confined in a silica matrix and attached to phosphate species by Ce-O-P bonds. The textural, thermal stability, local structure and acidic properties of SiO_2/CeO_2/Phosphate were investigated by XRD, XPS, FTIR and SEM/EDS techniques.

Experimental

Preparation of SiO_2/CeO_2 by the sol-gel method

The silica/ceria mixed oxide, SiO_2/CeO_2, was prepared by the sol-gel method. In a reaction flask containing 150 mL of absolute ethanol (Synth), 175 mL of tetraethylorthosilicate (TEOS-Aldrich), 16 mL of twice distilled H_2O and 2.3 mL of concentrated nitric acid were added and the resulting solution was heated with constant stirring at 353 K for 3 hours. After cooling the solution, different amounts of $(NH_4)_2Ce(NO_3)_6$ (0.014, 0.027 and 0.040 mol), dissolved in mixtures containing 100 mL of ethanol and 25 mL of twice distilled water, were added. The mixtures were stirred for additional 3 hours at 298 K. Then, 1.3 mL of concentrated HNO_3 in 9.5 mL of distilled water were added and the solution was stirred for other 2 hours. The solvent was evaporated from the mixtures at 373 K, producing gelatinous materials. The gels obtained were heated at 473 K under constant air flow for two hours. The materials obtained with increasing amount of ceria will be hereafter designated as SC1, SC2 and SC3.

The thermal stabilities were investigated submitting SC1, SC2 and SC3 to heat treatment at 473, 673, 873, 1073 and 1273 K, with a plateau of 8h for each temperature.

Phosphate adsorption on the SiO_2/CeO_2 mixed oxide

About 1.5 g of each SC were immersed in 40 mL of a 0.1 mol L^{-1} H_3PO_4 solution and allowed to stand, with occasional shaking, for 72 hours. The mixtures were filtered, washed with water and dried at room temperature. They were designated as SCP1, SCP2 and SCP3, respectively.

X-ray diffraction and X-ray fluorescence

X-ray diffraction patterns were obtained on a Shimadzu XRD-6000 diffractometer by using Cu K_α radiation ($\lambda = 0.154$ nm, 40kV *per* 30 mA) and a sweeping velocity of 2 degree min^{-1} (units of 2θ).

The amount of cerium in the silica matrix was determined by X-ray fluorescence analysis. Mechanical mixtures of finely powdered SiO_2 (Merck) and CeO_2 (Carlo Erba), containing different ratios of Si/Ce, were used to obtain the calibration curve. The measurements were carried out on a SHIMADZU EDX-700 using a rhodium X-ray anode (50 kV) as source.

Specific surface area (S_{BET}) and average pore size

Samples of the SC and SCP materials were previously heated at 343 K under vacuum (1.3×10^{-3} Pa) for 1 h. The specific surface areas were determined by the BET method, while the average pore size was determined by nitrogen adsorption-desorption isotherms (using the BJH method) on an ASAP 2010 apparatus from Micromeritics.

Scanning electron microscopy (SEM) and X-ray emission analyses (EDS)

Samples were fixed onto a double faced tape adhered to an aluminum support and coated with a layer of gold (*ca.* 15 nm) by a BalTec SCD 050 Sputter Coater apparatus (60 mA current for 60 s). The scanning electron microscopy analysis (SEM) was carried out using low vacuum microscopy on a JSM 5900LV equipment operating at an accelerating voltage of 25 kV. Images were obtained by using secondary electrons. X-ray emission spectroscopy (EDS) was used for elemental mapping with a Noram Voyager instrument. The micrographs and the elemental maps were obtained for all contents of CeO_2 oxide supported by silica.

High power decoupling-magic angle spinning ^{31}P NMR

The high power decoupling magic angle spinning (HPDEC-MAS) ^{31}P NMR spectra of all solids were obtained at room temperature on a Bruker AC300/P spectrometer operating at 121 MHz. Conditions used were a sequential pulse with an acquisition time of 41 ms and a relaxation time of 4 seconds. Phosphoric acid (85 wt%; $\delta = 0$ ppm) and sodium hydrogen phosphate ($\delta = 0.9$ ppm) were used as primary and secondary references for the chemical shifts, with a spectral width of 50×10^3 Hz.

X-ray Photoelectron Spectroscopy (XPS)

Spectra were recorded on a VSW HA-100 Spherical Analyzer operating with pass energy of 44 eV and an Al-K_α radiation source (1486.6 eV). Samples were prepared as powder pressed into pellets, fixed to a stainless steel sample holder with double-faced tape and analyzed as prepared. The binding energies were referenced to the C 1s line at 284.6 eV and the photoemission lines were simulated with Gaussian line shapes. The relative surface compositions were calculated from the photoelectron peak areas after correction for the photo-ionization cross section and the difference in the electron escape depth.[18] The atomic compositions were estimated from the C 1s, O 1s, Si 2p, P 2p and Ce $3d_{5/2}$ integrated peak areas.

Infrared spectrometry for determining acidic properties

The Brønsted acid sites on the surface of all SC and SCP samples were studied by analyzing the infrared spectra of pyridine as a probe molecule. About 100 mg of the ground sample were wetted with liquid pyridine at room temperature and the samples were then submitted to vacuum (1.3×10^{-5} Pa), initially at room temperature, to eliminate physically adsorbed pyridine. The self-supported pressed disks were heated under vacuum at 373 and 473 K and, for each temperature, spectra were obtained at room temperature on a Bomen Hartmann & Braun (MB-Series) spectrophotometer. FTIR spectra of samples as prepared and of the heated materials were obtained on the same spectrophotometer, using pressed KBr pellets containing 1 wt% of the material.

Ammonia gas adsorption

A 250 mL erlenmeyer flask with about 1 g of each SCP material was filled with NH_3 gas and closed for 30 minutes at room temperature. The excess of gas was pumped off at 1.3×10^{-3} Pa at room temperature. The amount of ammonia adsorbed in the material was determined by the Kjeldhal method.

Results and Discussion

Characteristics of the samples

The X-ray fluorescence analyses of the samples showed the following amounts of CeO_2 for the three SC mixed oxides (in wt%): 5.6, 8.9 and 13.0, which correspond to 0.33, 0.53 and 0.76 mmol of Ce *per* gram, respectively. The specific surface areas, S_{BET}, and the average pore diameters, $\bar{r}$, are presented in Table 1.

Table 1. Values of specific surface area, S_{BET}, and average pore diameters, $\bar{r}$

Material	Designated as	S_{BET} / ($m^2\ g^{-1}$)	$\bar{r}$ / nm
SiO_2 / 5.6% CeO_2	SC1	463	1.7
SiO_2 / 8.9% CeO_2	SC2	474	1.7
SiO_2 / 13% CeO_2	SC3	460	1.7
SiO_2 / 5.6% CeO_2 / P*	SCP1	473	1.9
SiO_2 / 8.9% CeO_2 / P*	SCP2	477	1.7
SiO_2 / 13% CeO_2 / P*	SCP3	539	1.7

*P = phosphate.

The specific surface areas of SC1, SC2 and SC3 remained practically constant when compared with the corresponding modified solids SCP1, SCP2 and SCP3, except for SCP3, where a slight increase was observed. These results indicate that reaction of phosphoric acid with CeO_2, resulting in formation of phosphate species on the surface, is not blocking the finest pores. Otherwise, a decrease of the specific surface areas by the species formed should be observed.[19]

Contents of P, Ce, Si and O on the surface of the SCP solids were determined by the XPS technique. Table 2 lists the results obtained.

Table 2. Elemental contents on SCP surface (in atom %), determined by XPS

Elements	SCP1/atom %	SCP2/atom %	SCP3/atom %
P	0.60	0.71	1.63
Ce	0.22	0.31	0.60
Si	36.8	39.7	36.4
O	48.2	50.3	51.4

As the amount of surface Ce increases on the surface, the quantity of P also increases, evidencing that phosphoric acid is retained by the reaction with the metal oxide sites on the surface.

Figure 1 shows the IR spectra of SC and pure SiO_2 treated at 473 K and compared with SC3 calcined at 1273 K. For pure SiO_2, the band observed at 975 cm^{-1} (Figure 1d) is assigned to the Si-O stretching mode (νSiO) of free silanol, ≡Si-OH, group.[20] In the mixed oxide this frequency is shifted to 948 cm^{-1} (Figures 1a-c), due to the Si-O-Ce linkage formation.[21,22] This band disappears on heating SC3 (taken as a model material) at 1273 K, presumably due to the breaking of the Si-O-Ce bonding as a consequence of the increase in SiO_2 and CeO_2 particles size.

X-ray Diffraction patterns

Figure 2 shows the XRD patterns for SC1, SC2 and SC3 samples submitted to thermal treatments at 473, 673,

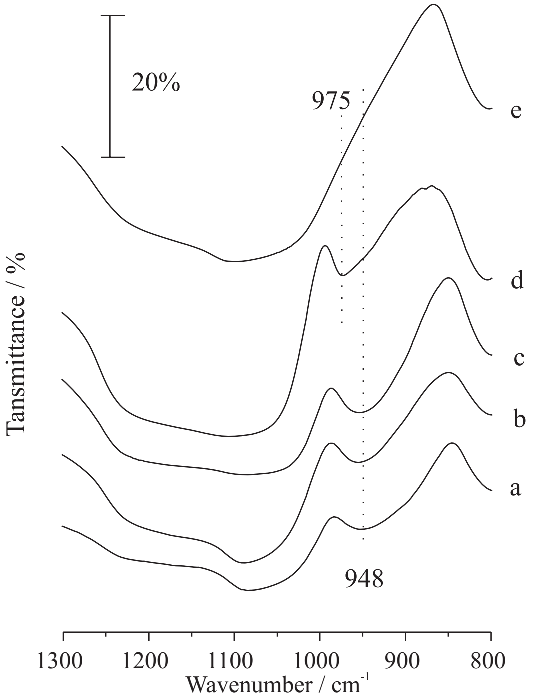


Figure 1. FTIR spectra of (a) SC1, b) SC2, (c) SC3, (d) SiO_2 thermally treated at 473 K and (e) SC3 calcined at 1273 K.

873, 1073 and 1273 K. Comparing the corresponding diffraction peaks, particles of CeO_2 incorporated into the mixed oxide present some degree of crystallinity, which increases as the temperature is raised from 473 up to 1273 K. For SC2 and SC3, which contain more ceria, at 1273 K (Figures 2c and 3c) peaks at 28.5, 47.0 and 56.0 (in 2q) match with CeO_2 cerianite structure (JCPDS, file number 34-0394). SiO_2 particles remain amorphous at this temperature.

Scanning Electron Microscopy (SEM) and X-ray emission analysis (EDS)

Figure 3 shows the SEM micrographs and the corresponding cerium analyses by EDS (white points) for SCP3 (taken as the representative sample) thermally treated at 473 and 1273 K. The elemental mappings as a function of the thermal treatment temperature reveal that the cerium oxide is, within the magnification used, well dispersed in the silica matrix. Such a degree of dispersion is important, since it enables a uniform distribution of phosphate species on the surface in the adsorption process.[17,23]

^{31}P NMR analysis

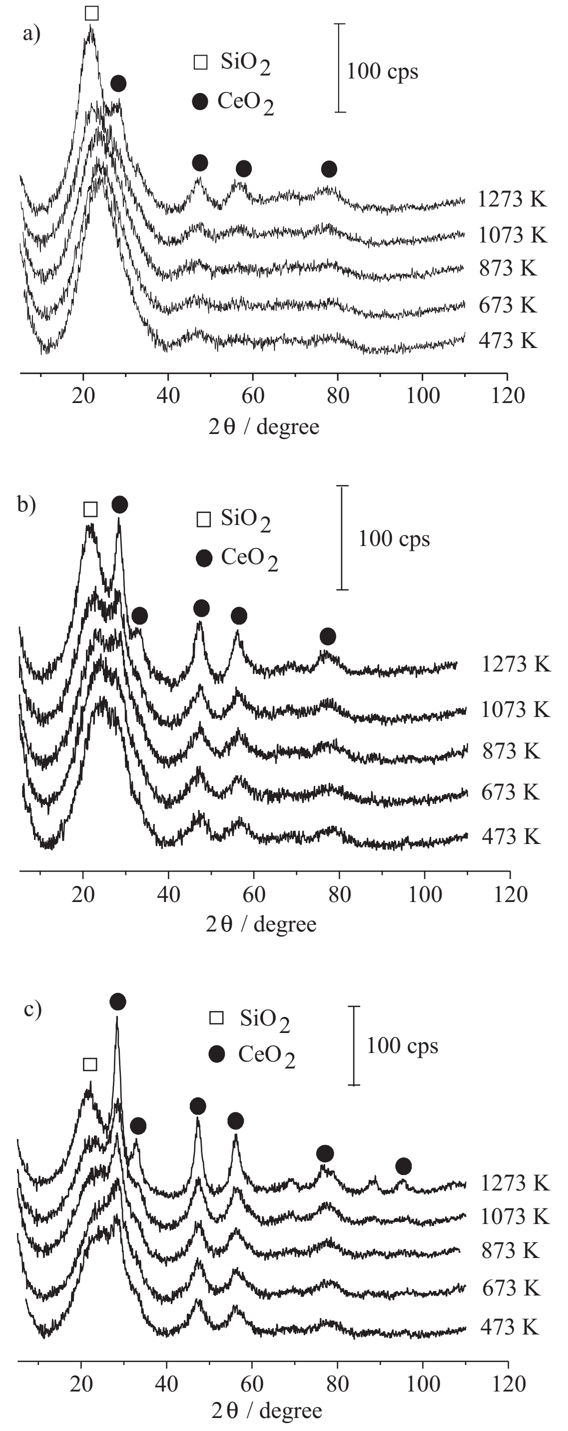


Figure 2. X-ray diffractograms of a) SC1, b) SC2 e c) SC3 samples, calcined at 473, 673, 873, 1073 and 1273 K.

^{31}P MAS NMR spectroscopy is a powerful technique for studying the environment of metal phosphates, since the chemical shift of the phosphate group is very sensitive to its local environment. In the present case, the spectra recorded for SCP1, SCP2 and SCP3 showed a single peak at *ca.* –10 ppm (Figure 4). In comparison with crystalline pure cerium phosphate, the observed chemical shift can be assigned to the dihydrogen phosphate species bonded to the ceria particle, Ce-O-P(O)$(OH)_2$.[24] This assignment

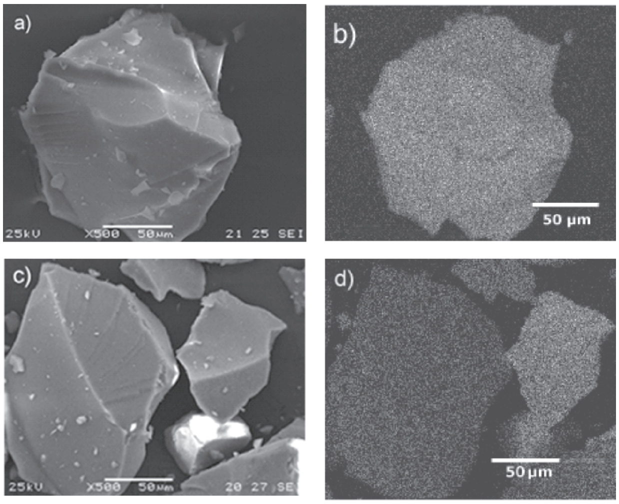


Figure 3. a) Images obtained by MEV, b) the respective cerium mapping by EDS (white points), for SCP3 thermally treated at 473 K and c) MEV and d) the respective cerium mapping for SCP3 thermally treated at 1273 K.

is also consistent with the presence of dihydrogen phosphate species in various M-phosphates (M= Nb, Ti, Zr and Al).[17,25-27]

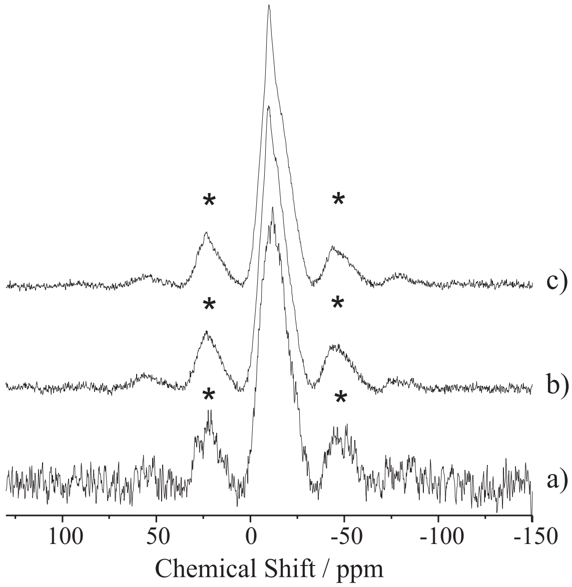


Figure 4. Solid-state ^{31}P MAS/NMR for (a) SCP1, (b) SCP2 and (c) SCP3 thermally treated at 473 K. * side bands.

X-ray Photoelectron Spectroscopy (XPS)

Table 3 lists the XPS binding energy values (BE) for SCP1, SCP2 and SCP3 thermally treated at 473 K.

The phosphate-adsorbed mixed oxide presented an average binding energy value for the Si 2p peak at *ca.* 103.5 eV, with a width at half-maximum of 2.4 eV, similar to results from the literature for pure silica.[23,28,29] All the samples had the XPS spectrum of the O 1s level at 530.6 and 532.4 eV, with full width at half-maximum of 2.2 and 2.3 eV, attributed to the oxygens present in SiO_2[28,29] and in CeO_2,[30] respectively.

The XPS of the Ce 3d level is complex, since photoemission provokes the re-arrangement of the electrons from the valence level and the resulting final states contain different hybridizations. In Table 3, ν” and ν’’’ for CeO_2 BE peaks refer to the bonding and antibonding states due to the Ce 4f final state hybridized with the O 2p orbital [the $3d^9 4f^1$(O $2p^5$)] electronic configurations and the [$3d^9 4f^0$(O $2p^6$)] final state (ν’’’), respectively. The SCP samples present cerium as Ce^{4+}.[30-34]

Phosphorus presented only one photoemission peak, which is assigned to the P $2p_{3/2}$ binding energy at *ca.* 134.0 eV (average value). This binding energy value is assigned to the $H_2PO_4^-$ species on the surfaces of the three mixed oxides. These values are very close to that observed for phosphate ions adsorbed as $H_2PO_4^-$ species on the surfaces of SiO_2/Nb_2O_5 [17] and SiO_2/ZrO_2 (134.5 eV)[16] sol gel matrices. It is interesting to observe that P/Ce atomic ratios obtained were: SCP1 = 2.8, SCP2 = 2.3 and SCP3 = 2.7. These values are not far from P/Ce = 2 ratio expected, if we consider that almost all ceria centers reacted and the species formed is the dihydrogen phosphate species.

The Ce/Si atomic ratios calculated for SCP1, SCP2 and SCP3 (Table 3) increased proportionally, taking into account an error of 8% in the calculation, as the ceria amount increased in these three matrices.

Table 3. Ce/Si and P/Ce atomic ratios (error of 8%) and binding energy (BE) values obtained for SCP samples thermally treated at 473 K

Samples	Atomic ratios		BE / eV					
	Ce/Si	P/Ce	Si $2p_{3/2}$	O 1s		P $2p_{3/2}$	Ce $3d_{5/2}$	
				Si-O	Ce-O		v’’’	v’’
SCP1	0.006	2.8	103.8(2.5)[a]	531.2(2.3)	533.1(2.4)	134.3(2.5)	900.3(3.0)	887.9(3.0)
SCP2	0.008	2.3	103.5(2.4)	530.5(2.0)	532.7(2.3)	134.0(2.4)	899.6(3.0)	887.6(3.0)
SCP3	0.016	2.7	103.3(2.4)	530.2(2.4)	532.4(2.5)	133.8(2.5)	899.1(3.0)	888.3(3.0)
CeO_2[b]	-	-	-	-	532.0(2.5)	-	898.2(3.0)	888.4(3.0)

[a]in parenthesis: full widths at half-maximum; [b]standard CeO_2.

Acidic properties

An investigation of the acidic properties of the SC and SCP materials was made by using pyridine as a probe molecule. Figure 5 presents the FTIR spectra obtained for the SC3 and SCP3 samples, taken as representatives of the other materials, which did not present any significant difference. The bands at 1599 and 1444 cm^{-1} are assigned to the 8a and 19b vibrational modes, respectively, of the pyridine molecule bonded to the surface by hydrogen bonds, possibly to the free silanol (≡SiOH) groups.[35,36] We observe in Figures 5(I) and 5(II) that the intensities of these bands decrease on heat treatment under vacuum at 473 K. The band at 1490 cm^{-1} is assigned to the 19a vibrational mode and it is always present for all kinds of pyridine adsorption.

The band observed at 1546 cm^{-1} in Figure 5(II) is assigned to the 19a vibrational mode of the pyridine molecule adsorbed on Brϕnsted acid sites.[37,38] These Brønsted acid sites are due to the $H_2PO_4^-$ species bonded to the matrix surface by Ce-O-P linkages. The result agrees with the conclusion from X-ray photoelectron spectroscopy, where the spectra of phosphorus presented only one photoemission peak due to the dihydrogen phosphate species on the surface of the mixed oxides. We also observe that they are very stable, since they are present on the surface even after heating the sample at 473 K. In Figure 5(I), for the SC3 sample, the vibrational mode due to pyridine molecules adsorbed on the Brønsted acid sites is not observed. The broadened feature of the band in this region is due to the OH deformation mode of free silanol (≡SiOH) and the attached residual CeOH groups.

Ammonia gas adsorption

The infrared spectra of SCP1/NH_3, SCP2/NH_3 and SCP3/NH_3 (solids with adsorbed NH_3) show a band observed at ≈1454 cm^{-1}, as seen in Figure 6. This vibration mode is assigned to the δNH_4^+ deformation mode (F_2 mode) of the ion having a T_d symmetry.[39] The three SCP pure samples do not show this band. Chemical analyses carried out on SCP/NH_3 showed the following amounts of ammonia adsorbed on the surfaces: SCP1/NH_3 = 0.37, SCP2/NH_3 = 0.43 and SCP3/NH_3 = 0.51 mmol g^{-1}.

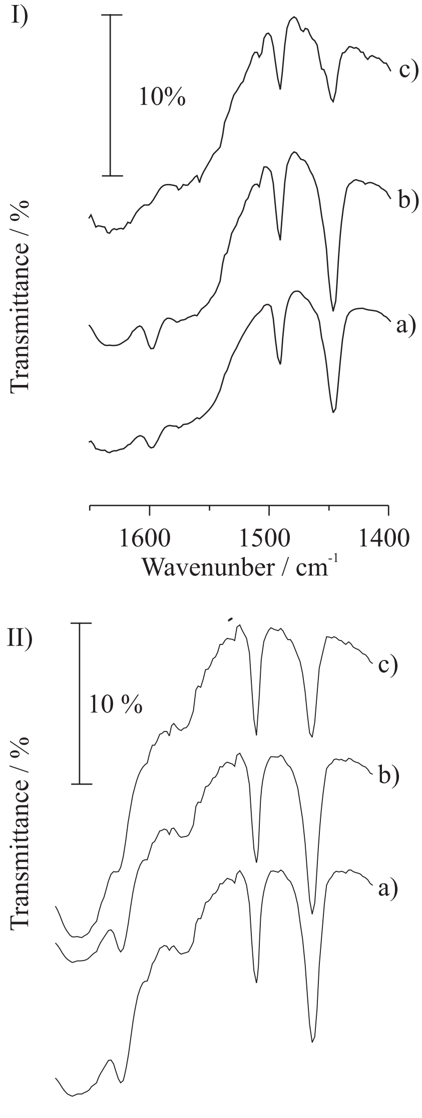


Figure 5. Infrared spectra of pyridine adsorbed on (I) SC3 and (II) SCP3: a) room temperature, b) heated at 373 K and c) heated at 473 K.

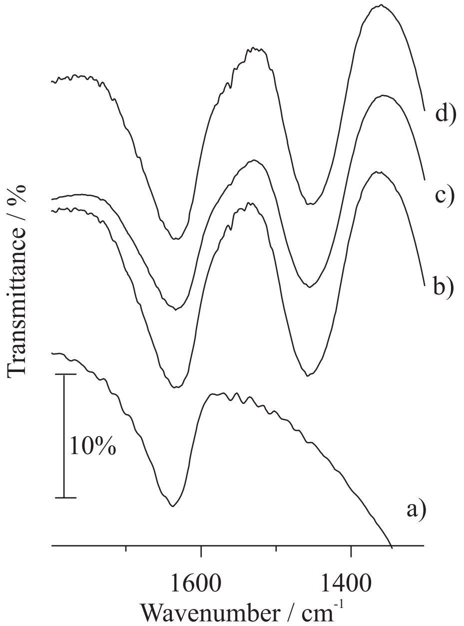
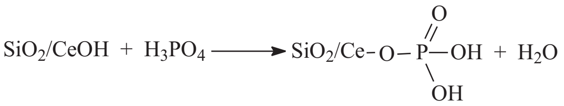


Figure 6. Infrared spectra of a) SCP3 and with ammonia adsorbed on b) SCP1, c) SCP2 and d) SCP3.

Conclusions

SiO_2/CeO_2 mixed oxide is obtained as a porous solid in which CeO_2 particles interact, through Si-O-Ce bonds, with the SiO_2 environment. This assumption is based on the IR absorption band observed at 948 cm^{-1}, assigned to the ν(Si-O) mode of the Si-O-Ce bond. The SEM and EDS images suggest that, within the magnification used, CeO_2 particles inside the silica matrix are homogeneously dispersed.

Phosphoric acid reacted with the CeOH group, resulting in dihydrogen phosphate species attached to the matrix surface, according to the following equation:



$$SiO_2/CeOH + H_3PO_4 \longrightarrow SiO_2/Ce{-}O{-}\underset{\displaystyle \backslash \atop OH}{\overset{\displaystyle O \atop /\!/}{P}}{-}OH + H_2O$$

The average pore diameters of SC and SCP are the same, *i.e.* 1.7 nm, except in the case of SCP2 where a small increase is observed, *i.e.* 1.9 nm. This indicates that the formation of cerium phosphate attached to the surface does not block the finest pores of the matrices.

Quantification of NH_3 gas adsorbed on the SCP matrices surface, assuming a homogeneous surface, indicated the following surface densities of acid sites on the surface: SCP1 = 0.78×10^{-10}, SCP2 = 0.90×10^{-10} and SCP3 = 0.95×10^{-10} mol cm^{-2}, which correspond to *ca.* 0.5 Brønsted acid sites *per* nm^2.

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