Effect of inductively coupled plasma surface treatment on silica gel and mesoporous MCM-41 particles

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Received 28 November 2017, revised 27 January 2018
Accepted for publication 30 January 2018
Published 30 April 2018

Abstract
Silica gel and MCM-41 synthesized mesoporous materials were treated with either oxygen (O₂), hexamethyldisiloxane (HMDSO) and organic vapors like ethanol (EtOH), and acrylonitrile (AN) inductive plasma. The radiofrequency power for the modification was fixed to 120 W and 30 min, assuring a high degree of organic ionization energy in the plasma. The surface properties were studied by infrared spectroscopy (FTIR), scanning electron microscopy, x-ray photoelectron spectroscopy and dynamic light scattering technique was used for characterizing size distributions. When the silica and MCM-41 particles were modified by AN and HMDSO plasma gases, the surface morphology of the particles was changed, presenting another color, size or shape. In contrast, the treatments of oxygen and EtOH did not affect the surface morphology of both particles, but increased the oxygen content at the surface bigger than the AN and HMDSO plasma treatments. In this study, we investigated the influence of different plasma treatments on changes in morphology and the chemical composition of the modified particles which render them a possible new adsorbent for utilization in sorptive extraction techniques for polar compounds.

Keywords: silica, MCM-41 nanoparticles, plasma treatment

1. Introduction
Inorganic nanoparticles have shown great potential for various applications in various fields, such as medicine, agriculture, optics, food packaging, optoelectronic devices, environmental-adsorbent of gases (CO₂), aerospace, catalysis, among others [1, 2]. However, one of its limitations is the difficulty of obtaining well-dispersed inorganic materials because of the strong tendency of aggregation among nanoparticles, which may depress the physical–chemical properties and its compatibility [2]. Because of the above-mentioned, the surface modification of inorganic nanoparticles has attracted great attention for aspects as improve the hydrophilic characteristics and prevents agglomeration of particles, and produces excellent integration and an interface improvement between nanoparticles and polymer matrices [2].

Chemical treatments, grafting of synthetic polymers to the surface, ligand exchange technique and other methods have been used for this purpose, with some advantages and limitations [3, 4]. A more varied and powerful approach to surface modification is represented by cold plasma discharges, which may be controlled to implant reactive groups into inorganic nanoparticles [5]. The plasma chemistry plays an important role in production of many active species, and
therefore, the inorganic nanoparticles surface during processing is exposed to highly reactive regimes with some strong bonds broken or disturbed [6]. On the other hand, it is generally known that plasmas can be generated inductively and/or capacitively in vacuum treatment chambers. An inductive plasma is a low-pressure, high density plasma in which the radiofrequency (RF) power is coupled from a non-resonant inductive coil across the Pyrex quartz reactor which serves as a dielectric window [7]. The plasma is driven by the induced electric field within the RF generator (13.56 MHz) which powers the coil surrounding the Pyrex quartz generator.

The inductive plasma has been extensively studied and widely used to surface modification of various kinds of materials like metals and polymers. However, and although there are a few studies on plasma modification of inorganic particles (like silica and MCM-41), they focus only on characterization and not on the effects caused by each gas-plasma-treatment.

The main objective of the present study was to assess the potential application of low-temperature plasmas for treating silica gel and mesoporous silica, MCM-41 surfaces.

2. Materials and methods

Silica gel chromatography grade 70–230 mesh, 60 Å, and all chemicals used in this study were purchased at reagent grade from Sigma-Aldrich and used without further purification unless otherwise specified.

2.1. Synthesis of MCM-41 mesoporous materials

Synthesis of MCM-41 silica particles was carried out by means of the sol–gel process [8, 9]. For this, 0.2 g of cetrimonium bromide was dissolved in 96 ml of distilled water and 0.7 ml of NaOH 2 M, this solution was stirred magnetically and heated to 80 °C, 1.4 ml of tetraethyl orthosilicate dissolved in 3 ml of ethanol was then added slowly and maintained in agitation at 80 °C for 2 h; after which the solution was filtered and left to dry at room temperature overnight. In order to extract the surfactant, the product was re-suspended in ethanol and 1 ml of pure hydrochloric acid and allowed to sit in reflux for 24 h. Subsequently, the solution was filtered and the nanoparticles obtained were washed with ethanol and dried in an oven at 100 °C overnight.

2.2. Plasma treatment of silica and MCM-41 particles

Silica and MCM-41 particles were treated with either oxygen (O₂), hexamethyldisiloxane (HMDSO), ethanol (EtOH) or acrylonitrile (AN) plasmas in a RF plasma reactor (figure 1). During the plasma treatment, silica and MCM-41 particles were stirred separately using a stirring bar. Plasma source was obtained with a 13.56 MHz Cesar Radio Frequency Power Supply (Advanced Energy, USA). A custom-designed matching network (Advanced Energy, USA) was built to inductively coupled to the glass reactor. Vacuum was generated in the plasma system using a mechanical pump to reach a base pressure of the vacuum system minimum pressure was approximately 1 × 10⁻² Torr.

Conventional silica and MCM-41 mesoporous particles samples of 1 g were treated at 30 min at a plasma input power of 120 W.

2.3. Silica and MCM-41 particles characterization

2.3.1. Surface morphology analysis. Surface morphology was investigated using a JSM-760 IF scanning electron microscope (JEOL, USA) operated at 10–20 keV was used to image silica and MCM-41 particles after plasma treatment. Samples were gold-coated to improve the conductivity of the samples and thus the quality of the SEM images.

2.3.2. Size distribution profile. The size and size distribution of MCM-41 particles dispersed in water were measured by dynamic light scattering analysis (DLS, Malvern Nano Zen 3600, UK) equipped with a 10 mW He–Ne laser (633 nm) and operating at an angle of 90° and a temperature of 25 °C.

2.3.3. Surface chemistry analysis. Pristine and plasma modified silica and MCM-41 particles were studied by Fourier transform infrared spectroscopy in attenuated total reflectance (FTIR-ATR) mode. FTIR spectra were recorded
on a Frontier MIR/NIR (Perkin Elmer, USA) equipment. The reported spectra are the average of 50 scans at 4 cm\(^{-1}\) resolution accumulated in the 4000–400 cm\(^{-1}\) wavenumber range using an ATR diamond crystal.

2.3.3.1. X-ray photoelectron spectroscopy (XPS) measurements. XPS was carried out on the samples, before and after modification, using an ESCA/SAM equipment, model S60 (Perkin-Elmer, USA) with a radiation of MgKα at 600 W (10 kV-60 mA) and an angle of analysis of 50°. Spectra were obtained under two different conditions: (i) a survey spectrum mode of 0–1200 eV to examine the composition of the elements present (in atomic percentage), and (ii) a multiplex repetitive scan mode was conducted through the O1s, C1s and N1s windows. A scanning step of 1 eV/step and 0.2 eV/step with an interval of 50 ms was utilized for survey and multiplex modes, respectively. Deconvoluted functions (Lorentzian-Gaussian) [10] with Origin 2015 (OriginLab Corp., Northampton, MA) software was employed.

3. Results and discussion

3.1. Effect of the type of plasma on the silica and MCM-41 particles surface properties

In the present study, for both silica gel and MCM-41 particles, treatment with HMDSO and AN plasmas significantly changed the surface morphology and surface chemistry of the particles. These modifications were the result of the surface association of HMDSO or AN species on organic or organically coated particle surfaces.

On the other hand, the O\(_2\) and EtOH treatments do not show any clear changes or improvements. Generally, with O\(_2\) treatment, polar functional groups can (or could) be induced on the surface of the particles, resulting in higher surface wettability [11]. Therefore, results of this study suggested that the induction of polar functional groups probably did not apply to the O\(_2\)-treated silica gel and MCM-41 particles.

With respect to EtOH treatment, CO\(_2\) and H\(_2\), which are two of the main reaction products of the plasma process [12], were not observed, however, and discussed later C=O interactions were evident.

3.2. Structural characterization

The shape and surface morphology of the silica gel and MCM-41 particles were investigated by SEM. Figure 2(a) shows SEM image of the surface morphology of silica without treatment where the particles range in size from 70 to 90 μm and are morphologically irregular with respect to size and shape, the size of commercial SiO\(_2\) (silica gel) is in the range of 75–150 μm.

Figures 2(b)–(e) present SEM micrographs of the modified silica surfaces and where exposure to different plasmas, showing numerous embedded fragments of eroded particles probably induced by the inter-particles friction during treatment. Moreover, as mentioned earlier, an organically coated surface and a particle size reduction were observed after exposure to AN and HDMS plasmas (figures 2(d) and (e)).

The SEM images of MCM-41 samples are presented in figures 3(a)–(e). The results show that untreated and treated MCM-41 particles have spherical agglomerates shape, with sizes ranging in the micrometer region and slightly below. Comparison of the images shows how the exposure to different plasma treatments resulted in non-significant changes in comparison with the untreated MCM-41 particles. The agglomeration of particles is not significantly reduced, and no morphological modifications were observed on the surface.

By dynamic light scattering the size distribution of the MCM-41 particles were determined. The obtained results are presented in figures 4(a)–(e).

Since the surface of the mesoporous MCM-41 particles has a high surface area covered by hydrophilic silanol groups; these are easily adhering to each other via hydrogen bonding and tend to form irregular agglomerations [2]. Figure 4(a) shows the particle size distribution curves for pure colloidal MCM-41, as can be seen has a wide range from 80 to 1500 nm with two strong peaks at 250 and 900 nm indicating that untreated MCM-41 has a high grade of agglomeration. Although it is difficult to statistically estimate the precise diameter, the mean diameter of the first peak (narrowest peak) was approximately of 105.7 nm and it could be used only as an approximate estimation of MCM-41 particle size.

A similar agglomeration behavior was observed for colloidal MCM-41 treated with all plasmas (figures 4(b)–(e)). The size of the agglomerates varies between 425 and 725 nm for AN-treated MCM-41 particles and up to 2700 nm for MCM-41 treated with EtOH-plasma. After MCM-41 particles modification with AN-plasma, the external hydrophilic surface is changes into a hydrophobic surface. This treatment reduced silica–silica interactions and promote silica-acrylonitrile interactions, thus reducing the formation of agglomerates [13].

Unlike the treatments with EtOH and O\(_2\)-plasma, increases the silica–silica interactions that promotes the aggregates formation because the intermolecular hydrogen bonds between hydroxyl groups on the surface of silica are very strong [14].

Finally, two groups of particles with sizes ranged 164.2–295.3 nm, and 342–1281 nm were present for MCM-41 treated with HMDSO-plasma, as shown in figure 4(d).

For the silica gel the size distribution could not be measured by DLS because these samples presented large particle sedimentation, whose sizes would be higher than the upper limit of detection of the equipment (6 μm).

3.3. Surface chemistry

To understand the surface chemical changes, FTIR-ATR and XPS were used for this study.

Figures 5(a)–(e) display the FTIR spectra of pure and pristine silica gel and the plasma-treated silica samples. The untreated silica spectrum (figure 5(a)) is well-known [15] and

Figure 2. Scanning electron micrographs (SEM) untreated images of silica gel (a), ethanol treatment (b), oxygen treatment (c), HMDSO treatment (d) and Acrylonitrile treatment (e).

Figure 3. Scanning electron micrographs (SEM) untreated images of MCM-41 (a), ethanol treatment (b), oxygen treatment (c), HMDSO treatment (d) and Acrylonitrile treatment (e).
can easily be compared to our experimental data. The spectrum shows a broad and strong band between 2500 and 4000 cm\(^{-1}\), attributed to the stretching vibrations of silanols groups (SiOH) attached to silica gel surfaces. The sharp band at 3739 cm\(^{-1}\) is related to free silanols.

Between 2500 and 1500 cm\(^{-1}\), weak absorption band appear around 1626–1633 cm\(^{-1}\). The absorption band has been assigned to the angular vibration of water, which is characteristic of the adsorbed water in inorganic particle surfaces or incorporated water into the crystal lattice [16].

Figure 4. Size distribution obtained by dynamic light scattering of MCM-41 with different plasma treatments (a) pure MCM-41, (b) EtOH-plasma, (c) O\(_2\)-plasma, (d) HMDSO-plasma and (e) AN-plasma.
Below 1500 cm$^{-1}$, an intense peak at 1068–1085–1110 cm$^{-1}$ is related to the siloxane stretching (Si–O–Si) [17], and a less intense band at 806 cm$^{-1}$, associated with the Si–O–Si symmetric stretching vibrations is also noticed.

On the other hand, figures 5(b)–(e) shows the FTIR spectra of the silica treated by O$_2$, HMDSO, EtOH and AN plasma respectively. The main absorptions are similar to the untreated silica i.e. a Si–OH (broad band in the region of 4000–2500 cm$^{-1}$ with a pronounced shoulder at 3739 cm$^{-1}$) and Si–O (1100–1000 cm$^{-1}$) and (806 cm$^{-1}$). This behavior was not observed for the spectrum with O$_2$-plasma, however the appearance of new signals was observed.

For the spectrum of EtOH-plasma-treated silica particles (figure 5(b)), the appearance of a band near 1700 cm$^{-1}$ corresponds to the carbonyl stretching and therefore, it is suggested the formation of carboxylic functional groups at the silica surface. Additionally, the broad band ranging from 3600 to 3000 cm$^{-1}$ corresponding to the OH stretching vibrations looks slightly modified.

With respect to HMDSO-plasma treatment, a strong increase in the intensities of absorption bands corresponding to CH$_2$ and CH$_3$ vibrational bands (2950–2800 cm$^{-1}$) suggesting an evidence of the deposition of organic carbon material on the silica gel particles surface. The infrared spectra of HMDSO is also typically characterized by absorption regions at 980–780 cm$^{-1}$ (Si–CH$_3$, Si–CH$_2$ symmetric and asymmetric rocking), 1200–1000 cm$^{-1}$ (Si–O–Si, Si–O–C stretching), 1270–1240 cm$^{-1}$ (CH$_2$, CH$_3$, and Si–(CH$_3$)$_2$) symmetric deformation [18].

In the case of AN-plasma treatment (figure 5(e)), two peaks were obtained at 2199 cm$^{-1}$ of conjugated imine and a band near to 1660 cm$^{-1}$ due to N–H deformation of amide or C=O of amide or possibly due to non-conjugated C=C and C=N. This shows that for acrylonitrile plasma treatment amine as well as amide groups are formed [19].

Regarding to the FTIR spectra of untreated and plasma-treated MCM-41 particles are presented in figures 6(a)–(e). Untreated MCM-41 particles (figure 6(a)), exhibit a broad absorption band located in the 3700–2700 cm$^{-1}$ interval and assigned to hydrogen-bonded SiOH groups with adsorbed water. The weak band at ca. 3740 cm$^{-1}$ is ascribed to single and geminal SiOH groups. The spectrum also exhibits a typical band at 1640 cm$^{-1}$ corresponding to the adsorbed water (OH bending). Reference [20] Bands between 1400 and 400 cm$^{-1}$ have been allocated for lattice vibrations. The band at 1093 cm$^{-1}$ reflects the siloxane (–Si–O–Si–) group stretching vibrations, while those at 806 and 466 cm$^{-1}$ correspond to symmetric O–Si–O stretching vibrations and the O–Si–O bending mode, respectively. Finally, the frequency at 960 cm$^{-1}$ has been assigned to a SiOH vibration [20].

The particular case of the spectra of MCM-41 treated by O$_2$- and EtOH-plasmas (figures 6(b) and (c) respectively), did not show changes and/or the appearance of new bands after treatments. This may be due to the low surface energy of the modified MCM-41 particles [21].

On the other hand, FTIR spectra of the MCM-41 particles with HMDSO-plasma (figure 6(d)), exhibits characteristic absorption bands at 2960 cm$^{-1}$ of CH-stretching and 845 cm$^{-1}$ and 793 cm$^{-1}$, corresponding to Si–C rocking [22]. In the same way, the absorption bands of C≡N triple bond stretching vibration (2270–2240 cm$^{-1}$) and C≡C double bonds in the 1655 cm$^{-1}$ region [23] (figure 6(e)) were observed in the FTIR spectrum of MCM-41 particles surface treated by acrylonitrile plasma.

The presence of these groups of bands suggests the coating and/or functionalization of MCM-41 particles surface.

Finally, XPS results obtained for silica gel and MCM-41 particles are shown in figures 7 and 10 respectively. In both cases, the Si 2p band was observed at 103.8 eV binder energy (B.E.), and an O 1s shoulder at 532 eV B.E. These spectral features are associated to the four corners of the SiO$_4$ tetrahedron, linked by –Si–O–Si– bonds [24]. The general scan XPS spectrum of both cases showed also the presence of C 1s (285.0 eV) core levels with no evidence of impurities.
XPS spectra of the silica treated by EtOH, O₂, HMDSO and AN plasma, are shown in figures 7(b)–(e). For all cases the Si 2p and O 1s regions were relatively identical, and they correspond with the assignments given for untreated silica. To confirm the above assertion, the elemental surface composition of pure silica and modified silica is given in table 1. The data for EtOH-plasma and O₂-plasma show that both treatments does not alter the surface oxygen composition relative to pure silica sample.

On the other hand, it was also noted that the increase in the C 1s peak intensity in the spectrum of the silica treated with EtOH, HMDSO and AN-plasmas (figures 7(b), (d), (e)) with respect to that measured for the untreated silica is consistent with the generation of carbon on the particles’ surface by plasma deposition. The surface composition of C percentage determined from the peak intensities of carbon is 48.7% for silica treated by AN-plasma.

Silica treated with AN-plasma shows the presence of N 1s at 400 eV BE re-confirming the particles N-functionalization (figure 7(e)).

The silica surface contains several kinds of functional group: siloxane (Si–O–Si), silaketone (Si=O), silanol (Si–OH) and siloxide (Si–O−) [25]. Therefore, to understand the modification on the chemical state on the surface, a detailed deconvolution by curve fitting of the C 1s, Si 2p and N 1s peaks were performed.

Figures 8(a)–(c) shows the deconvoluted XPS spectra of the C 1s peak for the EtOH, HMDSO and AN-plasma-treated silica particles. According to the literature [26], the binding energy of C 1s for silica-plasma-modified, which is located at 288.5 eV, indicates the presence of carboxyl groups.

For example, according to figure 8(c), EtOH plasma-treated silica, the C 1s peak can be deconvoluted into three peaks at 285.0, 286.6 and 288.1 eV. The lowest binding energy peak (285.0 eV) can be assigned to C–H/C–C species.
In addition, the peaks at 286.6 and 288.1 eV suggest the formation of C–OH and C=O groups, respectively [27].

The C 1s core-level spectrum of HMDS plasma-treated silica (Figure 8(b)) consists of two peak components with binding energies at about 283.0 and 285.0 eV, which can be attributed to C–H/C–C and C–Si, respectively. The C–Si species are related to the CH₃ groups introduced by HMDSO-plasma treatment.

As expected, the C 1s core-level spectrum of AN plasma-treated silica (Figure 8(a)) can be fitted with three peak components at binding energies of 284.4, 285.0 and 286.4 eV, which are attributed to C=≡C, C=H/C–C and CN (sp C=N) species, respectively, the latter confirms the presence of acrylonitrile units in the modified silica surface. Furthermore, in the case of O₂ plasma-treated silica, C 1s signal was not present.

On the other hand, the binding energy corresponding to Si–O, Si–OH of Si 2p level did not change, in comparison to the original silica gel, i.e. without any plasma treatment.

The XPS N 1s peak for the nitrogen implanted is shown in Figure 9. As mentioned earlier, a small and broad N 1s peak at 399.2 eV is found. It has also been reported that N 1s peak position for nitrile (–C≡N) is at 399.4 eV [28]. Therefore, the peak at 399.2 eV of the treated silica can be related to two overlap peaks (398.3 and 400.2 eV) or corresponds to nitrile.

In order to gain further insight into the surface composition and the valence states of MCM-41, the XPS spectra of untreated MCM-41 and plasma modified MCM-41 samples were obtained. The analysis of the spectra for MCM-41 particles treated by EtOH, O₂, HMDSO and AN plasma also revealed that for all cases, the Si 2p and O 1s regions were
similar, and they correspond with the assignments given for pure MCM-41 particles (figures 10(b)–(e)).

Specifically, the composition of the MCM-41 particles analyzed in this study, showed a higher content of carbon than the reported in the literature, this may be due to the surfactant presence within the pores of MCM 41. In the same way, and analogous to silica particles, MCM-41 treated with AN-plasma shows the presence of N 1s at 400 eV BE re-confirming the particles N-functionalization (figure 10(e)) [29].

The oxygen content also varies slightly, and it suggests that these phenomena are associated to surfactant presence and not to plasma interaction.

Finally, the XPS spectra with a detailed deconvolution by curve fitting of the C 1s, Si 2p and N 1s peaks were examined. Figures 11(a), (b) show the C 1s spectra of EtOH and AN-plasma shows the presence of N 1s at 400 eV BE re-confirming the particles N-functionalization (figure 10(e)) [29].
HMDSO-plasma-treated MCM-41 samples. The deconvoluted spectra of both samples show the presence of two different C species with their C 1s binding energies which can be fitted with two peaks which distinguish CH/CC (285.0 eV), which is a common signal for both treatments and C–OH (286.6 eV) for EtOH treatment and C-Si (283.2 eV) for HMDSO treatment respectively [30].

In the C–N peak (figure 11(c)), one can also distinguish at least three different chemical states for carbon in the C 1s spectrum at 286.4 eV (C–N), 285.0 eV (CH/CC) and 283.4 eV (C=C), respectively. The inspection of the O 1s peak in the O2-plasma-treatment showed an excess (≈41.6%) hydroxide which suggests the presence of C–OH bonds, probably caused again by the presence of surfactant in the MCM-41 particles.

The analysis of Si 2p spectra (figure 12) confirmed the characteristic peaks related to Si–O (103 eV), Si–OH (105.2 eV) and Si–C (100.5 eV), which correspond to MCM-41 silicates.

Finally, the signal for acrylonitrile on MCM-41 are reported in figure 13. Even though the molecule possesses only one nitrogen atom, the N 1s spectrum is made of two features, a main line at 399.0 eV, and a weak component (15% of the spectral weight) at lower binding energy, 398.0 eV [31].

4. Conclusion

Inductively coupled plasma treatments modified the surface chemistry without changing the irregular geometry or spherical form of silica and MCM-41. Surface modification with oxygen plasma could remove organic compounds especially with MCM-41 where the organic was attributed to the remaining surfactant and oxygen plasma promoting the carbonyl formation moreover methanol plasma was able to increase the carbonyl groups. However after AN and HMDSO plasma treatment the surface of treated materials showed the characteristics groups of monomer. Finally, regardless of the substrate either silica or MCM-41 behave the same upon different plasma treatments showing the same surface chemistry. From these data we conclude that the related effect of treatments on both particles is due the similar surface composition mainly silanols.

Acknowledgments

This work was supported by CONACYT Ciencia Básica project 176544. SEM and XPS measurements were performed at LANINBIO Cinvestav Mérida, under support from projects FOMIX-Yucatán 2008-108160, CONACYT LAB-2009-01 No. 123913. Technical help is acknowledged to MSc. D Huerta and Ing. W Cauich.

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