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Combined modeling and experimental studies of hydroxylated silica nanoparticles

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Abstract Nanotechnology offers several opportunities to solve problems related with Oil and Gas industry. One of them is the possibility to use hard nanoparticles to control the wettability phenomena between the three-phase system (oil–water–minerals) at reservoir conditions of temperature, pressure, and salinity. Here, we present a combined experimental and modeling study of hydroxylated silica nanoparticles as candidate for improved oil recovery applications. In this work, we mainly focus on development of more realistic SiO_2-nanoparticle models and validating them against the experimental data. An efficient Monte Carlo scheme is proposed to generate realistic SiO_2 nanoparticle atomistic models (3–5 nm). Structural and spectroscopic properties such as Raman and Infrared were obtained through Molecular Dynamics (MD) calculations using a force field that mimics an ab initio data. We have also used Fourier transform infrared spectroscopy to identify chemical functional groups present in 5 nm unmodified (bare) silica nanoparticle dispersions. A good agreement between the MD simulations and experiments has been observed.

Introduction

Nanotechnology opens several opportunities on applications in the Oil and Gas industry [1, 2]. Particularly, subsurface applications of nanotechnology seem to be promising in modifying and monitoring reservoir properties, such as wettability and interfacial tension between rock and fluids [2]. Surfactant aggregates, which can be characterized as soft nanoparticles, have been extensively studied as effective wettability modifiers. However, most of them exhibit relatively low tolerance to divalent ions and salinity [3, 4]. Other types, high performance surfactants greatly lower oil/water interfacial tension, but do not favor capillary driven imbibitions during water flooding [5–8]. Recent advances in hard nanoparticle engineering have indicated a great potential for the use of nanoparticles as a more robust wettability modifier under broader reservoir conditions than conventional soft nanoparticles [5].

A better understanding of behavior of hard nanoparticles and their interactions with the three-phase interface (mineral–oil–water) under realistic conditions of reservoirs is essential for any possible applications of nanoparticles as an improved oil recovery agent. To understand these effects at molecular level, we have applied molecular simulations to model the structural, vibrational, and dynamic properties of hydroxylated SiO_2 nanoparticles. An advantage of this modeling work is to predict transport phenomena of nanoparticles in porous media under subsurface conditions (high temperature, pressure, and salinity).

In order to perform these simulations, a realistic model for SiO_2 nanoparticles is needed. Several atomistic models

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for SiO_2 nanoparticles have been suggested in the literature [9–11]. However, those models are either built by using simple potentials that cannot capture fully the complexity of SiO_2 systems [12, 13], particularly for hydroxylated and amorphous cases, or limited in size in case of fully ab initio based models [14, 15]. In this work, we mainly focus on an efficient way to generate atomistic hydroxylated SiO_2 nanoparticle models based on accurate ab initio force fields and validated the models using experimental techniques such as Fourier transformed infrared spectrometry (FTIR).

Methodology

The physical–chemical properties of isolated SiO_2 nanoparticles have been investigated by experimental and modeling methods. In the modeling study, a combined Molecular Dynamics (MD) and Monte Carlo (MC) techniques were applied to generate and characterize structural and spectroscopic properties of SiO_2 nanoparticles.

In order to model the atomic interactions of hydroxylated SiO_2 systems, we have used the recently proposed FFSiOH force field based on ab initio calculations [16]. This potential is a partial charge shell-ion model and was parameterized to describe silica polymorphs and their hydroxylated surfaces self-consistently with periodic B3LYP results. In particular, this potential correctly captures the OH stretching vibrational frequencies and the geometries of silanol groups in the amorphous silica surfaces [16]. Those properties are essential for the description of SiO_2 nanoparticles. Details of the FFSiOH force field functional form and its parameters used can be found in reference [16].

Computational methods

Nanoparticle models were obtained from amorphous SiO_2 atomistic samples and their surface structure was modified to capture experimental observations. Roughly spherical nanoparticle models with several diameters (3–5 nm) were cut out from large well-relaxed periodic models of vitreous SiO_2 samples (up to 20,000 SiO_2 molecules) [17]. These amorphous matrix structures do not contain any coordination defect. To guarantee the nanoparticle charge neutrality, we proceed with a two step process: (a) cuts were taken in accounting for only oxygen terminated surface (no under-coordinate Si on the surface), and (b) hydrogen atoms were attached next to all terminated oxygen within a 0.96 Å distance to keep charge balance, neutral.

The presence of hydrophilic silanol groups (Si–OH) on silica surface acts as binding sites for water. However, under proper conditions (dehydroxylation at high temperatures) silanol groups may turn into hydrophobic siloxane groups (Si–O–Si). Based on experimental results, Zhuravlev [18] argued that silanol group was the most probable compound on the surface of amorphous fully hydroxylated silica and that one OH group corresponded to one surface Si atom. It is known experimentally that SiO_2 amorphous surfaces contains a high (small) concentration of silanol (i.e., $Si–(OH)_2$) groups and barely any concentration of $–Si–(OH)_3$. This value was found to be independent of the origin and structural characteristics of amorphous silica and hence was accepted as a physical-chemistry constant (Fig. 1).

In order to guarantee a realistic hydroxylated terminal group distribution on the surface description of the SiO_2 nanoparticles, we propose a MC scheme that reproduces the experimentally observed concentrations of terminal groups. Our proposed MC flowchart scheme is shown in Fig. 2. First, near surface silicon atoms were labeled as the ones, which linked to, terminated oxygen. The MC trial is to remove surface type silicon and the O–H groups bonded to them. Figure 2 shows the example case where the proportion of SiOH increases by this trial. In order to optimize the process, a cost function was applied during the MC scheme through a Metropolis algorithm. This cost function was defined by the weighted difference (ω) between the present proportion in the model (m) and target (t) value:

$$\mathrm{Cost} = \omega_{\alpha}(\alpha_{\mathrm{t}} - \alpha_{\mathrm{m}}) + \omega_{\beta}(\beta_{\mathrm{t}} - \beta_{\mathrm{m}}) + \omega_{\gamma}(\gamma_{\mathrm{t}} - \gamma_{\mathrm{m}}), \qquad (1)$$

where α, β, and γ are proportion of SiOH, $Si(OH)_2$, $Si(OH)_3$ concentrations, respectively. In our simulations, we have used $\omega_{\alpha} = 1$, $\omega_{\beta} = 1$, and $\omega_{\gamma} = 10$. The trial is accepted if the cost function decreases ($\mathrm{Cost} < 0$) in the MC step, and rejected with Boltzmann probability if the cost function increases ($\mathrm{Cost} > 0$).

By using this scheme, models with any given proportion can be obtained. Particularly, we have applied realistic proportion of these functional groups SiOH (83%), $Si(OH)_2$ (17%), $Si(OH)_3$ (0%) to the models obtained using this protocol. Figure 2c shows the efficiency of this MC scheme. Typically, we could observe that with less than 100 MC steps the target proportion is achieved.

Using the procedure described above, five different samples with different sizes (3, 4, and 5 nm) were generated varying from 300 up to 5,000 atoms. The atomic structures were further optimized by minimizing the energy using the Newton–Raphson method [19] as it is implemented in GULP code. These initial structures were heated up to 250 K by 50 K increments within 12.5 ps using classical MD. The internal energy with time during the heating and cooling process of 3 nm SiO_2 nanoparticle model is shown in Fig. 3, as an example of this procedure.

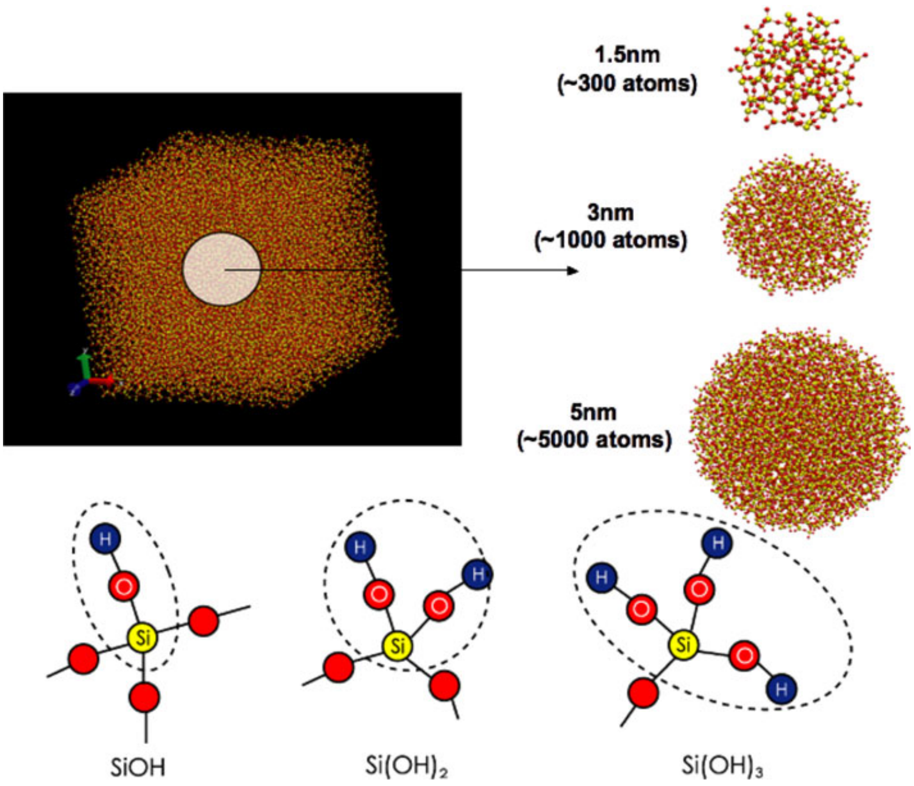

Fig. 1 **a** Nanoparticle models with diameters varying from 2 nm to 5 nm and typical functional groups on hydroxylated SiO_2 amorphous surfaces

A further structural energy optimization is performed in the quenched sample.

Experiments

We have used 100 FTIR spectrometer purchased from Perkin Elmer to identify chemical functional groups present in nanoparticles. Surface unmodified silica particles dispersed in water were provided by 3M Company with a mean diameter of 5 nm. Silica dispersions are positioned in direct contact with an attenuated total reflectance (ATR-FTIR) diamond crystal. Then, the ATR-FTIR spectra are recorded from 4,000 to 600 cm^{-1} at a resolution of 2 cm^{-1}. Baseline correction is applied to ATR-FTIR spectra before each measurement. The concentration of nanoparticle in the dispersion is kept constant throughout for all experiments.

Results and discussion

Several physical-chemistry properties can be directly obtained from MD simulations. Here, we have focused on the structural and spectroscopic properties of the computationally generated SiO_2 nanoparticles. These properties allow a direct comparison between the atomistic models and experimental data.

Structural properties

In order to analyze the structures of nanoparticle models, we have calculated radial distribution functions (RDF) of optimized systems. RDFs of 3 nm particle models for silicon–oxygen, silicon–silicon, and for oxygen–oxygen distances are shown in Fig. 4, respectively, compared with the α-quartz SiO_2. Due to the finite structure, these functions are close to zero around distance at 3 nm. The first peaks for the partial RDFs are found to be 0.152, 0.254, and 0.302 nm for Si–O, O–O and Si–Si distances, respectively. The second and third peaks show the amorphous nature of nanoparticle models. Partial RDFs for Si–O surface were also calculated to infer if the volume relaxation of these surface groups compared with the bulk ones would expand or shrink their diameters. No significant variation was observed in all sizes studied.

Vibrational properties

Yalamanchili et al. [20] used internal reflectance spectroscopy FTIR/IRS to study the water structure next to a hydrophilic silicon surface. Hydrogen bonded ice-like structure was detected next to the hydrophilic surface from the symmetric OH stretching associated with tetrahedral coordinated water molecules at 3,200 cm^{-1}. Asay and Kim [21] also observed the presence of hydrogen bonded

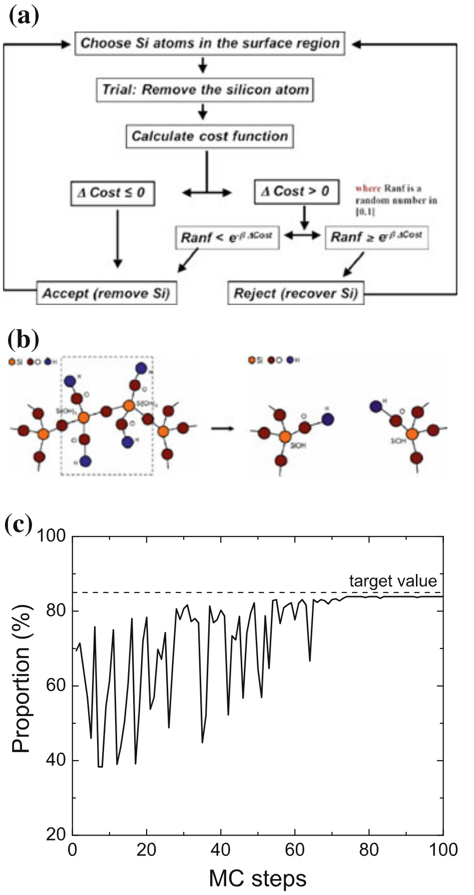

Fig. 2 Monte Carlo proposed method to generate realistic SiO_2 nanoparticle models. **a** Flow chart and **b** molecular mechanism trial to increase SiOH by removing $Si(OH)_2$ terminal groups, **c** performance of the method

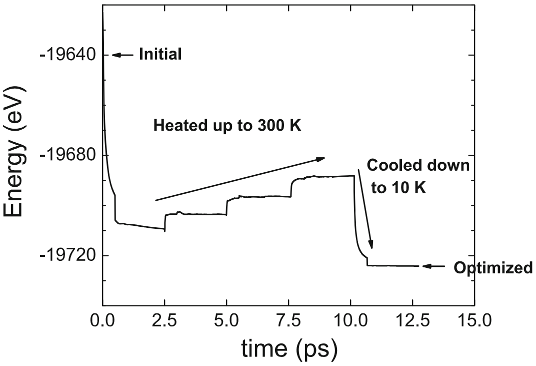

Fig 3 Potential energy during heating and cooling process

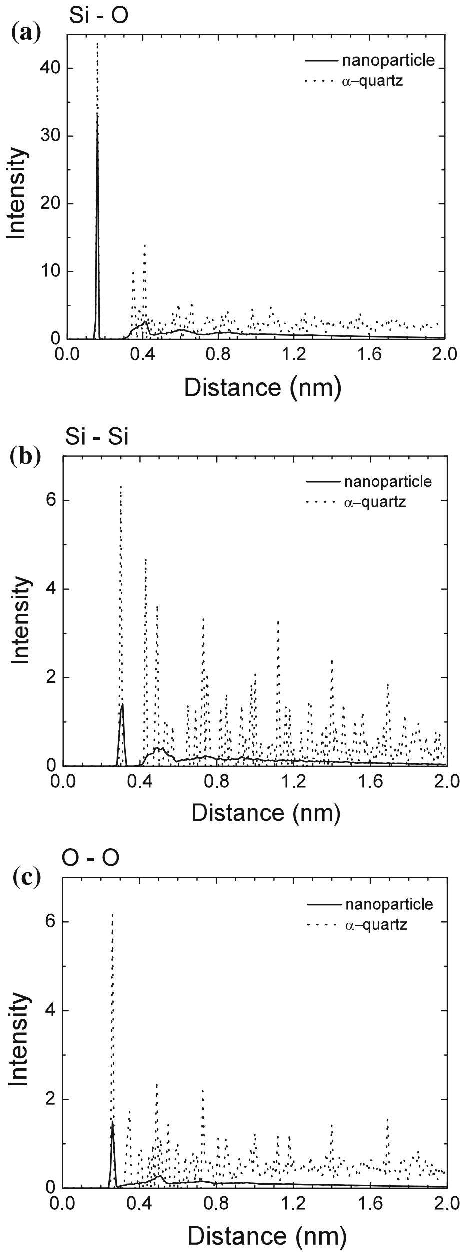

Fig. 4 Radial distribution function for 3 nm nanoparticle model compared with α-quartz for **a** Si–O, **b** O–O and **c** Si–Si distances

ice-like water next to a hydrophilic silica surface by using attenuated total reflectance infrared (ATR-FTIR) spectroscopy. Morrow and Molapo [22] observed the infrared absorption of a silica thin film at 1,100, 800, and 480 cm^{-1}.

The spectroscopic properties such as Raman and Infrared spectrum of the generated SiO_2–OH nanoparticle models were obtained through the calculation of the vibrational modes of the system by determination and diagonalization of the force constant matrix, given by the second derivatives of energy with respect to the displacement of the atoms for different wave vectors. In order to compare the calculated phonon spectra and experiment, it is important to discuss the intensity of the vibrational modes. Our intensity values for infrared spectra were determined as implemented on the GULP code [19, 23].

Raman and infrared spectra of 3-nm particle model and experimental ones (unmodified surface silica nanoparticles) are plotted in Fig. 5. Peaks around 4,000 cm^{-1}, which

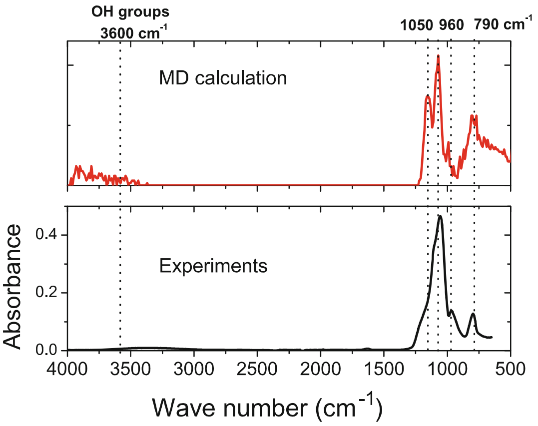

Fig. 5 Experimental and simulated vibrational spectra for SiO_2 nanoparticles

appears only in model, shows O–H groups, which we added to keep charge balance, neutral. We observe a good agreement on the frequencies peaks around 790, 960, and 1,150 cm^{-1}. Based on these results, our structural models for SiO_2–OH nanoparticles and the interatomic potential used are able to reproduce our experimental results for SiO_2 unmodified nanoparticles.

Conclusions

In this work, we have constructed realistic models of SiO_2 nanoparticles by computer simulations with the purpose to understand transport phenomena in subsurface systems. We propose an efficient MC scheme to reproduce the observed terminal group distribution on the hydroxylated amorphous SiO_2 surfaces. Those models were further relaxed and optimized by using MD simulations based on GULP program. The structural and spectroscopic properties were calculated for different atomistic size models and their results compared with our experimental FTIR measurement for unmodified 5-nm SiO_2 nanoparticles. Our results indicate a very good agreement between the experimental data and the atomistic models. Based on this validated models, we are currently studying the behavior of the SiO_2 nanoparticles models within H_2O with different NaCl concentrations under subsurface conditions. Atomic structures of the nanoparticle models are available upon request from the authors.

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