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Incorporation of trivalent cations in NaX zeolite nanocrystals for the adsorption of O₂ in the presence of CO₂

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The O₂ and CO₂ sorption properties of nanosized zeolite X with faujasite type structure through a partial ionic exchange of sodium (Na⁺) by trivalent cations (Gd³⁺ and Ce³⁺) were evaluated. Three faujasite samples were studied, the as-synthesized Na-X possessing Na⁺ solely, and the modified samples Na-Gd-X and Na-Ce-X containing Gd³⁺ (1.8 wt%) and Ce³⁺ (0.82 wt%), respectively. Incorporating scarce amounts of trivalent cations modified the adsorption affinity of zeolites towards O₂ and CO₂ as demonstrated by *in situ* Fourier-transform infrared spectroscopy (FTIR). While Na-Ce-X encounters the highest O₂ physisorption capacity, the Na-Gd-X is adsorbing the highest quantities of molecular CO₂. All three samples exhibit the chemisorbed CO₂ in the form of carbonates, while the Na-X stores carbonates in monodentate and polydentate forms, the Na-Gd-X and Na-Ce-X allow the formation of polydentate carbonates only. Density functional theory (DFT) calculations revealed that trivalent cations tend to adsorb gases through two cations simultaneously which explains the presence of polydentate carbonates exclusively in the corresponding modified zeolites. The DFT results confirmed the higher affinity of Na-Gd-X and Na-Ce-X nanocrystals towards O₂ in the presence of CO₂. The affinity of Na-Gd-X and Na-Ce-X nanocrystals towards O₂ opens the door of their use as oxygen transporters for medical applications where CO₂ is constantly present. The toxicity of the nanosized zeolites and their performance in O₂ release are reported too.

Introduction

Zeolites are crystalline materials with well-defined framework structures consisting of pores and cages of different sizes and shapes. The large micropore volume, high external surface area¹ and the exchangeable charge compensating cations are fascinating features of zeolites. The systematic control of these parameters allows a facile modulation of the physical and chemical properties of zeolites to tailor them towards target applications, such as selective gas sensors, separation membranes, medical applications, hosts for guest molecules, and even gas carriers.^{2,3}

Faujasite type zeolite (zeolite X) is widely used in the adsorption and the separation processes owing to the large free volume available to accommodate desired gases and various metal cations.⁴ Additionally, template free zeolites have shown non-toxic behaviour thus promoting the interest in their use for biological and biomedical applications^{5,6} such as

the storage and transportation of respiratory gases including carbon dioxide and dioxygen.^{7,8} We have recently reported on the synthesis and sorption properties of faujasite zeolite nanocrystals.^{6,9}

Herein, we report experimental results and theoretical DFT calculations on the impact of trivalent cations in the faujasite zeolite nanocrystals on their sorption capacities for O₂ and CO₂. The as-synthesized sodium form of faujasite zeolite (sample Na-X) is used as a reference and compared with samples containing trivalent metal cations Ce³⁺ (sample Na-Ce-X) and Gd³⁺ (sample Na-Gd-X). We have already shown that cerium (Ce³⁺) can improve the oxygen loading capacity of the zeolites.⁶ Therefore cerium and gadolinium were selected to be introduced in the zeolite nanocrystals; such properties of Ce- and Gd- containing zeolites will allow localizing the nanocrystals in the tissues and reveal the regions of action as well as the regions of their accumulation after releasing the O₂. The crystallinity, composition, stability, and textural properties of the as-synthesized and ion-exchanged faujasite samples were characterized by various means including X-ray diffraction (XRD), thermogravimetric analysis (TG), dynamic light scattering and zeta potential (DLS), inductive coupled plasma (ICP), and N₂ sorption analyses. Furthermore, the adsorption behaviour of zeolite nanocrystals toward oxygen and carbon dioxide was evaluated using *in situ* FTIR spectroscopy. Our data revealed the high sorption capability and reversible adsorption/desorption of respiratory gases (CO₂

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and O₂) of nanosized zeolites; the quantity of loaded gases being controlled by the charge compensating cations, thus generating selective gas storage and controlled delivery. The selective adsorption of O₂ in the presence of CO₂ is very challenging, as most of zeolites will adsorb preferably CO₂.^{10–14} The experimental results were supported by DFT calculations, which in turn highlight that the adsorption selectivity of O₂ towards CO₂ may be largely enhanced if Ce³⁺ cations pairs are embedded in the nanosized zeolites.

Experimental part

Preparation of nanosized faujasite zeolite

The as-synthesized nanosized faujasite zeolite, Na-X (particle size of 10 - 20 nm) with Si /Al = 1.32, was prepared following the originally reported procedure by our group.¹⁵ The zeolite nanocrystals were purified by centrifugation and then subjected to freeze drying prior further characterization. No calcination of the samples was carried out due to the absence of organic template.

Ion exchange of nanosized faujasite zeolite

The as-synthesized zeolite (Na-X) was ion-exchanged with gadolinium (III) nitrate hexahydrate Gd(NO₃)₃·6H₂O (sample Na-Gd-X) and cerium (III) chloride pentahydrate CeCl₃·5H₂O (sample Na-Ce-X).

25 mL of Gd(NO₃)₃·6H₂O (3 mM) or CeCl₃·5H₂O (3 mM) were added in 5 ml of Na-X suspensions (2.5 %). The suspensions were then kept under stirring at room temperature for 1 h and then washed by double distilled water. This procedure was performed once to obtain sample Na-Gd-X and repeated twice to obtain sample Na-Ce-X.

Characterization

Dynamic light scattering (DLS) and zeta potential

The size of the nanoparticles was measured by a Malvern Zetasizer Nano instrument using a backscattering geometry (scattering angle of 173°, He-Ne laser with a 3 mW output power at a wavelength of 632.8 nm). The DLS analyses were performed on samples with a solid concentration of 1 wt %. The surface charge of the crystals was determined by measuring the zeta potential value of zeolite nanocrystals in water suspensions at a constant solid concentration (1 wt %) and pH = 8.5.

X-ray diffraction (XRD)

The crystallinity of the zeolite powder samples (Na-X, Na-Gd-X and Na-Ce-X) was studied by XRD; the XRD patterns were recorded by a PANalytical X'Pert Pro diffractometer with CuK α monochromatized radiation (λ = 1.5418 Å).

Inductively coupled plasma (ICP)

The chemical composition of the zeolites was determined by inductively coupled plasma optical emission spectroscopy using a Varian ICP-OES 720-ES.

N₂ sorption analysis

The porosity of the samples was measured using a Micrometrics ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 275 °C under vacuum overnight before the measurement. The external surface area and

micropore volume were estimated by the alpha-plot method using Silica-1000 (22.1 m² g⁻¹ assumed) as a reference. The micropore and mesopore size distributions of solids were estimated by the Nonlocal Density Functional Theory (NLDFT) and Barret-Joyner-Halenda (BJH) method using the desorption branch, respectively.

Thermogravimetric analysis (TGA)

The water content and stability of the samples were investigated using a SETSYS instrument (SETARAM) analyzer (heating rate of 5 °C min⁻¹ under 40 ml.min⁻¹ flow of air).

In situ FTIR spectroscopy

Powder zeolite samples (Na-X, Na-Gd-X and Na-Ce-X) were pressed (~10⁷ Pa) into self-supported disks (2 cm² area, 20 mg.cm⁻²). *In situ* IR spectra were recorded using a Nicolet 6700 IR spectrometer (ThermoScientific, Villebon sur Yvette, France) equipped with a mercury cadmium telluride (MCT) detector and an extended KBr beam splitter. Spectra were recorded in the 400-5500 cm⁻¹ range at 4 cm⁻¹ with 128 scans. A homemade IR cell was used to evacuate the samples, then samples were heated up to 200 °C for 2 h under vacuum prior to the measurements, and cooled down to -196°C. Various amounts of oxygen (0–102 Torr) and carbon dioxide (0-1.5 Torr) were introduced into the cell and kept in equilibrium for 5 min in the case of O₂, and 1 min in the case of CO₂ before recording each spectrum. The zeolites were loaded with increasing amounts of O₂ and CO₂ till their corresponding FTIR bands reached saturation. To allow the comparison of different samples, all spectra were normalized to the samples' mass and plotted as absorbance per gram over the wavelength.

DFT calculations

The adsorption modes and interactions energies of CO₂ and O₂ and cationic-exchanged zeolites have been investigated through density functional theory (DFT). All the calculations were performed using the Vienna Ab initio Simulation Package (VASP),¹⁶ with a planewave basis set and projector augmented wave (PAW) pseudopotentials.¹⁷ The PBE functional¹⁸ was used combined with the D2 correction to account for dispersion forces.^{19,20} The plane wave cutoff energy was set to 500 eV, and the Brillouin zone sampling at the Γ -point. The Kohn-Sham equations were solved self-consistently until energy difference between cycles become lower than 10⁻⁶ eV, and the atomic positions have been fully optimized until all forces were smaller than 0.03 eV/ Å per atom. For open-shell cations, the DFT+U method of Hubbard²¹ was used with U = 6.7 and 5 eV for cerium and gadolinium, respectively.²² Previous work has also shown that the correct localization of excess electrons on Ce ions is only achieved for U = 5 eV and higher.²³

In the present study, we use a primitive rhombohedral cell of FAU containing around 165 atoms to reduce computational effort.^{24–27} It can be seen in Figure 1 that the primitive cell of faujasite contains two supercages and eight hexagonal windows connecting the sodalite with the supercage.^{25,28}

Figure 1. Periodic model used for faujasite sample Na-X (Si/Al=1.28): primitive cell, 165 atoms (21 Na, 21 Al, 27 Si, 96 O).

Interaction energies have been calculated according to the following equation:

$$\Delta E_{int} = E_{FAU-M} - (E_{FAU} + E_M)$$

Where ΔE_{int} is the adsorption energy, E_{FAU+M} is the total energy of the zeolite with the adsorbate, and E_{FAU} and E_M are the total energies of isolated adsorbate and bare zeolite, respectively.

Cell lines

A human glioblastoma cell line, U87-MG purchased from American Type Culture Collections (ATCC, Manassas, VA, USA) was used. Cells were cultured in Dulbecco's Modified Eagle Medium (DMEM, Sigma-Aldrich, France). DMEM was supplemented with 10 % fetal bovine serum (Eurobio, France), 2 mM glutamine (Sigma-Aldrich, France) and 100 U/ml penicillin/streptomycin (Sigma-Aldrich, France). Cells were maintained in culture at 37 °C with 5 % CO₂ and 95 % humidity.

Primary culture of astrocytes

Cerebral cortices were isolated from neonatal (1 to 3-day-old) mice (Swiss, CURB, France) carefully stripped of the meninges and dissociated to generate a single-cell suspension. Cultures were allowed to grow in a humidified 5 % CO₂ incubator at 37 °C to confluency (15-20 days) prior to use in DMEM supplemented with 10 % foetal bovine serum (Eurobio, France), 10 % horse serum (Eurobio, France), 2 mM glutamine (Sigma-Aldrich, France) and 100 U/ml penicillin/streptomycin (Sigma-Aldrich, France). At about 80 % confluence, the growth medium was replaced by the same medium.

Cells exposure to nanosized zeolites

Cells were exposed to nanosized zeolites (Na-X, Na-Ce-X, and Na-Gd-X) up to 48 h. Zeolites were diluted in culture medium at a concentration of 50, 100 or 400 µg/ml and added directly into the wells. Control tests (distilled water) in the wells with the same volumes were performed.

Cell viability

The concentration range to test was determined using the following assumption: the average blood volume of a rat is ~64 mL/kg. Given that 250-300 mg animals were used in the in vivo experiments, the rats had 16-19 ml of blood. 300 µl of a 1 wt % solution, which is 3 mg of material, equates to a maximum of ~156-188 µg zeolite/mL of blood.

Cells were seeded in 24-wells plates to achieve 80 % confluency for the control on the day of the analysis. Cell viability was assessed 48 h following the exposure to zeolites

with the WST-1 assay (Roche, France) according to the manufacturer's instructions.

Release of oxygen in aqueous and hypoxic conditions

A hypoxia workstation (IN VIVO2 500, 3M) was used to obtain a stable and controlled gas composition of the atmosphere with a precision of 0.1 % O₂ by adapting the amount of N₂. Phosphate buffered saline (PBS, Sigma-Aldrich) solution was equilibrated in the hypoxia chamber for 1 h prior to the experiment. A closed reaction vessel containing 12 ml of equilibrated PBS at 37 °C, and a dissolved oxygen sensor (SevenGo (Duo) pro™ / OptiOx™, Mettler Toledo) was used inside the hypoxia chamber. Prior to the experiments, the baseline was established by measuring the oxygen saturation in the system for 30 min. Nanosized zeolites (Na-X, Na-Gd-X, and Na-Ce-X) were then added to the system, and the oxygen dissolved in the PBS solution was measured continuously for 1h. The oxygen release capacity of nanosized zeolites (Na-X, Na-Gd-X and Na-Ce-X) was compared to the baseline situation and expressed as a change relative to baseline.

Statistical analyses. Data are presented as mean ± s.d. HSD Tuckey post-hoc test using a two-way ANOVA with the JMP programs (SAS Institute)

Results and Discussion

XRD patterns reflecting the crystallinity and purity of phases with Bragg peaks typical of faujasite zeolite structure were recorded for the as-synthesized (Na-X), the cerium (Na-Ce-X), and the gadolinium (Na-Gd-X) ion-exchanged zeolite samples (Figure 2). The crystallinity of the as-synthesized Na-X zeolite is highly preserved throughout the ion-exchange process.

Figure 2. XRD patterns of the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples.

The as-synthesized and ion exchange samples contain discrete nanoparticles of 10-20 nm with narrow and monomodal particle size distribution (Figure S1). These nanocrystals are highly stable in water suspension which is confirmed by the measured zeta potential values of -39 mV (Na-Gd-X) to -43 mV (Na-Ce-X) (Figure S2). Besides, the partial replacement of Na⁺ by Ce³⁺ or Gd³⁺ does not seem to affect the crystallinity of the zeolites; the Si/Al ratio is almost constant for all samples, as shown by ICP (Table 1).

The TG curves contain peaks that correspond to the removal of water molecules solely (Figure 3). For instance, a main mass loss was detected at 85 °C in the case of Na-X and Na-Ce-X samples corresponding to the removal of the physisorbed water. A second important loss was identified at 135 °C (Na-X) or at 119 °C (Na-Ce-X) which is linked to the water molecules adsorbed in the channels of the zeolite that is strongly related with the presence of cations. A different behaviour was recorded for Na-Gd-X with

Figure 3. (A) Thermogravimetric analysis and (B) differential thermogravimetric analysis curves of the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples.

one single weight loss at 119 °C (Figure 3). The ion exchange modification of nanosized faujasite samples induced a slight increase in their hydrophobicity, and the water content decreases following the order: Na-X (23.5 % H₂O) > Na-Ce-X (21.3 % H₂O) > Na-Gd-X (20.7 % H₂O).

Sample	Chemical composition (wt %)				
	Si (wt %)	Al (wt %)	Na (wt %)	*M (wt %)	Si/Al
Na-X	19.9	15.1	11.2	0	1.32
Na-Ce-X	17.6	13.5	11.0	0.82	1.30
Na-Gd-X	17.9	13.8	10.7	1.80	1.30

Table 1. Chemical composition of the as-synthesized Na-X, gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples.

The chemical formula based on the ICP results for the samples were calculated: Na-X: [Na₈₅(H₂O)₂₂₈ [Si₁₀₇Al₈₅O₃₈₄], Na-Ce-X: [Na₈₄Ce₁(H₂O)₂₀₁ [Si₁₀₇Al₈₅O₃₈₄], and Na-Gd-X: [Na₇₉Gd₂(H₂O)₁₈₈ [Si₁₀₇Al₈₅O₃₈₄].

Nitrogen sorption analyses of sample Na-X revealed Type I isotherm with high N₂ uptake at low partial pressure (P/P₀) characteristic for microporous materials, and another high uptake at P/P₀ > 0.8 attributed to the high textural mesoporosity resulting from the closely packed zeolite nanoparticles with similar particle sizes (Figure 4). These properties were highly preserved upon the incorporation of the various charge compensating cations. More specifically, the high surface area (760 m².g⁻¹) and large micropore volume (0.28 cm³.g⁻¹) calculated for Na-X (Table 2) were very close to

those of Na-Gd-X and Na-Ce-X zeolite samples.

Figure 4. Nitrogen isotherms (full circles: adsorption/ empty circles: desorption) of the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples.

Table 2. Surface area and pore volume of the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples.

Sample	S _{BET} (m ² .g ⁻¹)	V _{mic} (cm ³ .g ⁻¹)	V _{total} (cm ³ .g ⁻¹)
Na-X	760	0.28	1.39
Na-Ce-X	753	0.26	1.21
Na-Gd-X	749	0.26	1.18

CO₂ adsorption properties of zeolite nanocrystals

The CO₂-zeolite interaction is known to take place via the zeolite charge compensating cations. The incorporation of alkaline earth or alkali metals on the surface and/or in the voids of zeolite promotes their basic character and increases further the zeolite affinity towards such acidic gas.^{29,30} Carbon dioxide can be adsorbed on the zeolite in two different forms (Figure 5): (1) the physisorbed CO₂ where the gas is immobilized in its molecular form following weak interactions with the zeolite, and (2) the chemisorbed CO₂ where it is stored as carbonates chemically bonded to the zeolite. In regards to the limited space available on the surface and channels of the zeolite, the formation of carbonates is expected to reduce the free space available for the adsorption of molecular CO₂. Several additional factors can eventually

affect the zeolite affinity towards the adsorption of carbon dioxide, including the zeolite structure, zeolite hydrophilicity (hence the quantity of available water), the size, the type and the quantity of charge compensating cations.^{31,32}

Figure 5. FTIR spectrum of CO₂ adsorbed on as-synthesized Na-X zeolite (25°C).

Experimental results revealed the adsorption of CO₂ in both physisorbed and chemisorbed modes on all zeolite samples (Figure 6). The former appears as an intense band centered at 2354 cm⁻¹, while the different carbonate species are distinguished as a set of bands extending from 1750 cm⁻¹ to 1300 cm⁻¹.

The impact of charge compensating cations on the physisorption of CO₂ is illustrated in Figure 7. Incorporating gadolinium (Na-Gd-X) induce an increase of CO₂ loading by 11 % while the cerium (Na-Ce-X) reduced the zeolite affinity towards CO₂ by 15 %.

CO₂ can chemically bind to zeolite in a quasi-irreversible process giving rise to different carbonate species such as mono-, bi-, and polydentate carbonates.^{33,34,35} In our case, polydentate carbonates also referred to as "bridged bidentate carbonates" identified by the IR bands at 1710 cm⁻¹ and 1364 cm⁻¹^{19,36} (Figure 6); the bridged bidentate carbonates were recorded in all three samples with the highest levels for the Na-Gd-X sample. On the other hand, the monodentate species appeared as well; the IR bands at 1485 cm⁻¹ and 1430 cm⁻¹ with comparable intensities to polydentate appeared only for sample Na-X (Figure 8).³⁶ Apparently, the monovalent Na⁺ favours the formation of monodentate carbonates, whereas trivalent Gd³⁺ and Ce³⁺ cations favour the formation of polydentate species with no traces of monodentate being detected.

O₂ adsorption properties of zeolite nanocrystals

The exposure of the zeolite samples to O₂ pressure generates an IR band at 1554 cm⁻¹ (Figure 9). This is clear evidence of the successful adsorption of the symmetrical O₂ molecules on the zeolite, and consequently, the altering of its symmetry that prevents any detectable IR band in its gas phase.⁶ Different sites of zeolites are available for the oxygen adsorption including, the Brønsted acid sites, and the charge compensating cations³⁷ identified by the FTIR bands at 1553 cm⁻¹ and 1557 cm⁻¹, respectively. In our case, broadband

extends from 1570 cm⁻¹ to 1545 cm⁻¹. Considering that the zeolite samples used in this study are present in the cationic form and not in the H-form, the oxygen is believed to adsorb on the Na⁺ for (Na-X), Na⁺ and Ce³⁺ for (Na-Ce-X), and Na⁺ and Gd³⁺ cations for (Na-Gd-X). Repetitive adsorption/desorption cycles resulted in the reproducible appearance/disappearance of the band at 1554 cm⁻¹ with no remarkable decrease in intensity, thus confirming (1) its attribution to O₂ adsorption, and (2) demonstrating the high capability of the zeolite

samples for O₂.

Figure 6. Evolution of the IR spectra of the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples during the CO₂ adsorption. All spectra were subtracted from the IR spectrum of the corresponding samples after activation at 250°C under vacuum.

Figure 7. Physisorbed CO₂ FTIR band area normalized to the mass of the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples at various CO₂ pressure of 0.1-1.5 Torr.

Figure 8. Different carbonate species detected on the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples by FTIR.

Figure 9. FTIR spectra of as-synthesized Na-X before and after adsorption of various O₂ pressures at -196 °C.

The trivalent cations are found to slightly enhance the capacity of zeolite nanocrystals towards O₂ (Figure 10); the affinity towards O₂ increased by 5% and 13% following the incorporation of Gd³⁺ (Na-Gd-X) and Ce³⁺ (Na-Ce-X) in the zeolite samples, respectively. This is ascribed to the fact that introducing one trivalent cation requires the removal of three Na⁺ cations, which releases additional volume available to host more molecules. In addition to the higher O₂ loading, the trivalent cations in samples Na-Gd-X and Na-Ce-X promote a faster loading of O₂ as revealed by the higher slope of the curve presenting the area of oxygen versus pressure introduced (Figure 10).

Figure 10. O₂ FTIR band area normalized to the mass of the as-synthesized (Na-X), gadolinium ion-exchanged (Na-Gd-X) and cerium ion-exchanged (Na-Ce-X) zeolite samples as a function of O₂ pressures.

Density functional theory (DFT) calculations

In the first step, DFT calculations were performed for the three zeolite models: Na-Na which contains 21 Na⁺ cations for two supercages (Na-X experimental sample); Na-Ce which contains 18 Na⁺ cations and one Ce³⁺ cation (Na-Ce-X experimental sample); Na-Gd which contains 18 Na⁺ cations and one Gd³⁺ cation (Na-Gd-X experimental sample). We consider isolated trivalent cations surrounded by sodium cations. The two latter models were designed to respect the relative amount of cations measured in the samples by ICP-MS (Table 1). The possible O₂ and CO₂ adsorption modes revealed that these gases adsorbed on zeolite via two or three cations simultaneously (Figure 11). Owing to the short distance across

the different charge compensating cations within Na-X, O₂ preferably adsorb by two cations located in the proximity and CO₂ by three cations. Na-X has a stronger affinity for CO₂ rather than O₂ by around 20 kJ/mol (Figure 12). Introducing one trivalent cation (M³⁺) in the faujasite leads to a change of affinities, provoking the interaction of zeolites with O₂, and the interaction energies of both adsorbed CO₂ and O₂ increase; this enhancement was more pronounced for O₂ (see Figure 7). Higher O₂ adsorption is calculated for the faujasite zeolite nanocrystals containing trivalent cations (Na-Gd-X, Na-Ce-X) in comparison to the as-synthesized Na-X. A similar trend for adsorption of O₂ and CO₂ on the samples was found by *in situ* FTIR study (see Figure 10).

Figure 11. DFT computed adsorption modes of CO₂ in (a) Na-X, (b) Na-Ce-X, and (c) Na-Gd-X, and O₂ in (d) Na-X, (e) Na-Ce-X, and (f) Na-Gd-X samples.

Figure 12. DFT computed interaction energies (ΔE_{int} in kJ/mol) of CO₂ and O₂ on pure Na-X, the partially exchanged faujasite samples with trivalent cations (Na-Ce-X, Na-Gd-X) (corresponding to the experimental samples on this work) and the hypothetical fully exchanged zeolite (Ce-X, Gd-X) samples.

To evaluate the potential of fully exchanged zeolites, we have then considered pure Ce-X and Gd-X models (Figure 13). In contrast to the sample Na-X with a higher affinity towards CO₂ over O₂, the Na-Ce-X and Na-Gd-X zeolites preferably bind to O₂ in the presence of CO₂. This is a highly desirable feature of zeolite nanocrystals for biological applications especially for preferential O₂ delivery where both gases (O₂ and CO₂) are available in the bloodstream. The difference in interaction energy between CO₂ and O₂ over fully exchanged zeolites are very high compared to partially exchanged zeolites (Figure 12). Pure Na-Gd-X zeolite is expected to adsorb O₂ more strongly than CO₂ by 40 kJ/mol, while the pure Na-Ce-X zeolite is expected to adsorb O₂ more strongly than CO₂ by 50 kJ/mol. These results would be further used to motivate the synthesis works to increase the incorporation of trivalent cations in nanozeolites in order to improve their capacity toward O₂.

Figure 13. DFT computed adsorption modes of CO₂ in (a) Ce-X, (b) Gd-X; and O₂ in (c) Ce-X, (d) Gd-X samples.

Toxicity of nanosized zeolites

To evaluate further the potential use of nanozeolite for biomedical applications, we performed toxicity measurements on a cell line and a primary cell culture. These cells were exposed to increasing dose of zeolite nanocrystals with either Na-X, Na-Ce-X, and Na-Gd-X zeolite samples. No toxicity was observed on the glioblastoma cell line at all the tested zeolite concentrations (Figure 14).

Figure 14. Toxicity measurements of nanosized Na-X, Na-Ce-X, Na-Gd-X zeolites using (a) glioblastoma cell line and (b) primary brain culture for 24 h and 48 h.

For the primary culture, a decrease in cell number was noticed only after 48 h and for the highest dose used (400 µg/ml). Interestingly, no change in the toxicity of the samples was noticed when different cations were introduced in the zeolite samples.

We then measured the ability of zeolite samples to release the oxygen in liquid media. After adding Na-X preloaded with O₂, the changes in oxygen content in the solution measured were 3.17 fold while for Na-Gd-X was 3.4 fold (Figure 15).

Figure 15. Changes in the oxygen content of a PBS solution maintained in hypoxia at 0.2% of O₂ in the workstation following the addition of Na-X or Na-Gd-X zeolites preloaded with O₂. Results are extrapolated for sample Na-Ce-X based

on the results from Figure 10.

Conclusions

The influence of different cations (Na⁺, Ce³⁺, and Gd³⁺) on the CO₂ and O₂ sorption properties of faujasite zeolite nanocrystals was studied experimentally and by DFT theoretical calculations. The structural and textural properties of the as-synthesized and ion-exchanged zeolite samples were highly preserved. The Na-Gd-X zeolite demonstrated the highest CO₂ physisorption capacity. In contrast, the Na-Ce-X adsorbed 15 % less CO₂ compared to the as-synthesized Na-X zeolite. The incorporated trivalent cations Ce³⁺ and Gd³⁺ favored the

formation of polydentate carbonate over the monodentate one that disappeared completely. These experimental data were validated by theoretical DFT calculations that showed a similar trend toward O₂ and CO₂. Additionally, the easier formation of bi-(poly)dentate carbonates in the presence of trivalent cations (samples Na-Ce-X and Na-Gd-X) is demonstrated. The DFT results show that pure Na-Gd-X zeolite will adsorb O₂ more strongly than CO₂ by 40 kJ/mol, while the pure Na-Ce-X zeolite will adsorb O₂ more strongly than CO₂ by 50 kJ/mol.

Toxicity tests were performed and no toxicity was observed for all three samples using glioblastoma cell line and primary culture; zeolite suspensions with various concentrations were used and the duration of the toxicity test varied from 24 to 48 h. Finally, the potential application of nanosized zeolites with different cations as a transporter for oxygen was demonstrated.

Conflicts of interest

"There are no conflicts to declare".

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