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# Microporous and Mesoporous Materials

## CO<sub>2</sub> adsorption in nanosized RHO zeolites with different chemical compositions and crystallite sizes --Manuscript Draft--

<b>Manuscript Number:</b>	MICMAT-D-20-00636R1
<b>Article Type:</b>	VSI:Enigma of Zeolites*
<b>Keywords:</b>	Na-Cs RHO, nanosized, CO <sub>2</sub> adsorption, in situ XRD, in situ IR spectroscopy
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<b>Abstract:</b>	<p>In this work, nanosized RHO zeolite samples with different Si/Al ratios were synthesized and tested for CO<sub>2</sub> adsorption by combining in situ IR spectroscopy and in situ X-ray powder diffraction using synchrotron radiation. The structural changes of the RHO nanosized zeolites subjected to high temperature treatment (350 °C) and CO<sub>2</sub> adsorption (1 and 5 Bars) studied by high-resolution X ray powder diffraction indicated the presence of two phases with different cell parameters in both samples. The combination of the X-ray technique with IR allowed evaluation of the CO<sub>2</sub> adsorption capacity of the samples and their adsorption dynamic. The results indicated that the CO<sub>2</sub> adsorption capacity is mainly related to the sodium content in the nanosized RHO crystals. The adsorption experiments performed showed that 1 bar CO<sub>2</sub> is sufficient to saturate the RHO samples at room temperature; no change in the CO<sub>2</sub> adsorption capacity at 5 bars was observed.</p>



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Modena May27<sup>th</sup> 2020

Dear Editor,

Thank you for the letter and the reviewers' comments concerning our manuscript entitled "CO<sub>2</sub> adsorption in nanosized RHO zeolites with different chemical compositions and crystallite sizes" by Confalonieri et al.

In the following we have answered all the question raised by the referee and we have modified the manuscript accordingly (changes are highlighted).

**Reviewers' comments:**

Reviewer #1:

**1. At one point in the paper Pa is used instead of bar as the pressure unit. It would be better to always use the same unit.**

*The unit (bar) was used in the manuscript only*

**2. A table summarizing the unit cell parameters would be helpful, especially to follow the section on the hydrated and dehydrated materials.**

*The table of unit cell values, previously deposited in SI, now is reported in the manuscript as Table 1*

**3. A few typographical errors need to be corrected.**

*All the manuscript was carefully corrected*

Reviewer #2:

**1. There are a few grammatical and typo errors that should be rectified. For examples:**

"P/P<sub>0</sub>"; 0 should be in subscript

"patters"; should be patterns

"In the current study, the sorption capacity of the RHO zeolite towards CO<sub>2</sub> at different concentrations was investigated only"; the sentence is with dangling clauses.

*The grammatical and typos errors were corrected across the text*

**2. The authors may want to determine if all the diffraction peaks of RHO-2 r.t. have shifted to higher 2theta, or only some of the peaks, in relative to RHO-1 r.t. This will give information whether all the lattice parameters have been affected or only certain lattice planes are affected by the different Si/Al (Na/Cs) ratio.**

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### **DIPARTIMENTO DI SCIENZE CHIMICHE E GEOLOGICHE**

*We thank the author for the comment, but in this case is not possible to see differences in the variation of different lattice parameters since the phase is cubic (see answer to point 4)*

**3. By looking at Figure 3, the diffraction peak of RHO-2 350C have also shifted, in relative to RHO-1 350C. However, the shifting is not that much as compared to the shifting during hydrated condition. Maybe the authors can provide an explanation on how the water molecules have affected the degree of lattice change due to different Na/Cs.**

*A more detailed interpretation of cell parameter variations after dehydration was added to the manuscript*

**4. Other than changes in peak position, changes in peak intensity also could be informative and be related to a number of things, such as a composition change in the unit cell or a change in ordering. The authors may want to determine if there are hkl dependent peak intensity change (can be done if there are XRPD recorded on an additional temperature) so that any anisotropic thermal effects on certain lattice planes could be determined.**

*The changes in the peak intensities are mostly related to the intensity of the first peak (110 reflection in RHO) with respect to the others and this is mainly linked to the process of dehydration (i.e. ordering) in the channels. As stated in point 2, it is not possible to link these variations to anisotropic thermal effects since the phase is cubic. The Figures S1 and S2 have been modified to enhance these small variations*

**5. The in situ IR results show that RHO-2 has higher CO<sub>2</sub> capacity and the elemental analysis result reveals that RHO-2 has lower Na content. Therefore, the authors have suggested that the high content of Na in the RHO leads to a reduced CO<sub>2</sub> capacity, i.e. the CO<sub>2</sub> adsorption capacity of the RHO zeolite might be controlled by the sodium content. However, one might question if the CO<sub>2</sub> uptake could be related to particle size and hence the external surface area available. Therefore, to make their suggestion more convincing, the authors might include related N<sub>2</sub> sorption data (e.g. Fig S3) in the manuscript, and give a brief discussion in Section 3.3 that RHO-2 does not possess greater external surface area nor interparticles mesoporosity.**

Figure 2 is now reported in the manuscript and a brief discussion was added to the text.

We hope the revised manuscript is appropriate for publication in MMM.

Looking forward to hear from you.

On behalf of the co-authors

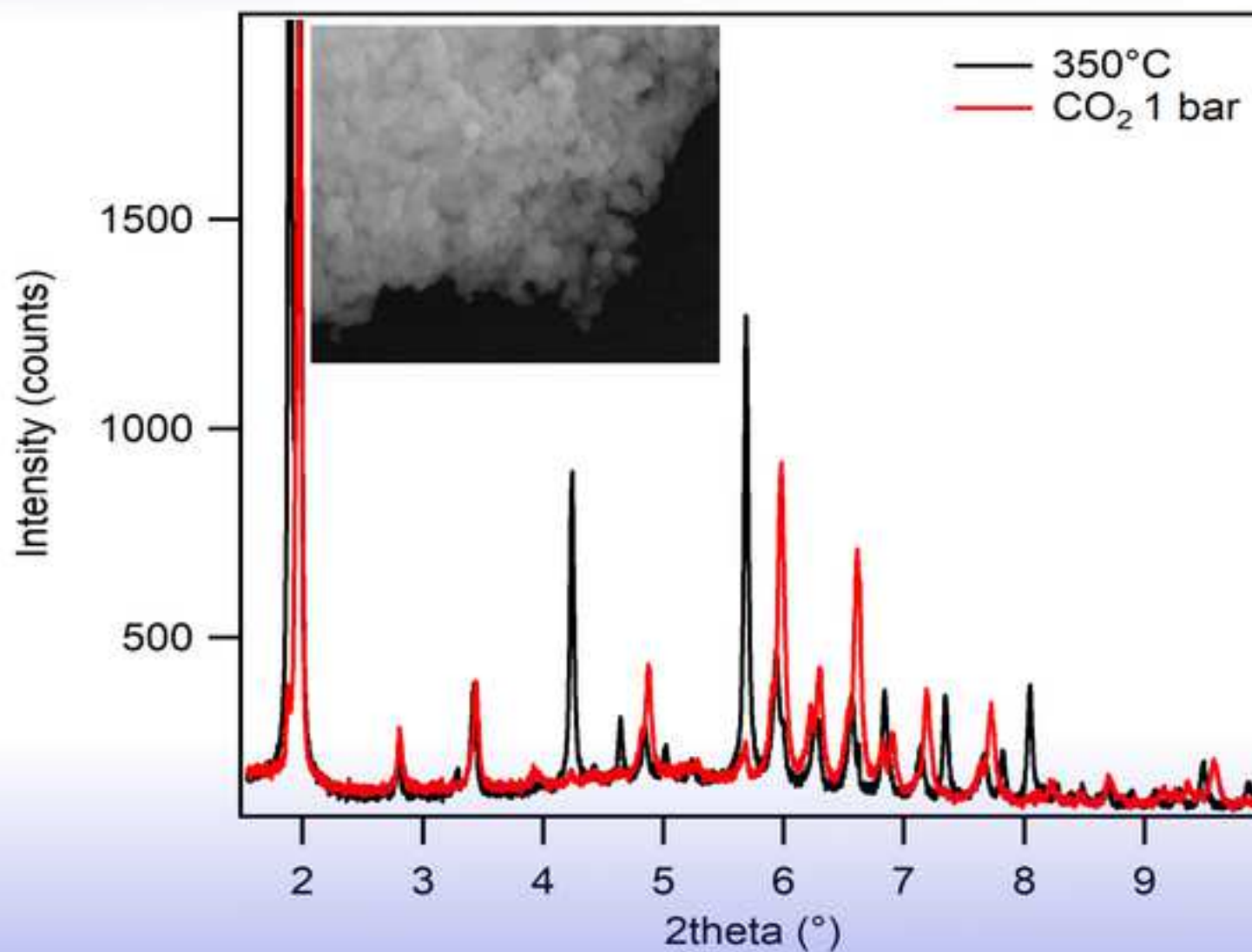
Prof. Rossella Arletti



**Highlights:**

- Two RHO nanosized zeolite samples with different particle sizes and cations content were synthesized.
- The biphasic nature of RHO zeolite upon dehydration and adsorption of CO<sub>2</sub> is due to the presence of mobile inorganic (Na and Cs) cations.
- The content of charge compensating Na cations influence the CO<sub>2</sub> adsorption of RHO.

# Structural changes of RHO zeolite under CO<sub>2</sub> adsorption



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## CO<sub>2</sub> adsorption in nanosized RHO zeolites with different chemical compositions and crystallite sizes

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### Abstract

In this work, nanosized RHO zeolite samples with different Si/Al ratios were synthesized and tested for CO<sub>2</sub> adsorption by combining *in situ* IR spectroscopy and *in situ* X-ray powder diffraction using synchrotron radiation. The structural changes of the RHO nanosized zeolites subjected to high temperature treatment (350 °C) and CO<sub>2</sub> adsorption (1 and 5 Bars) studied by high-resolution X ray powder diffraction indicated the presence of two phases with different cell parameters in both samples. The combination of the X-ray technique with IR allowed evaluation of the CO<sub>2</sub> adsorption capacity of the samples and their adsorption dynamic. The results indicated that the CO<sub>2</sub> adsorption capacity is mainly related to the sodium content in the nanosized RHO crystals. The adsorption experiments performed showed that 1 bar CO<sub>2</sub> is sufficient to saturate the RHO samples at room temperature, and no change in the CO<sub>2</sub> adsorption capacity at 5 bars was observed.

**Keywords:** Na-Cs RHO, nanosized, CO<sub>2</sub> adsorption, *in situ* XRD, *in situ* IR spectroscopy

### Highlights:

- Two RHO nanosized zeolite samples with different particle sizes and cations content were synthesized.
- The biphasic nature of RHO zeolite upon dehydration and adsorption of CO<sub>2</sub> is due to the presence of mobile inorganic (Na and Cs) cations.
- The content of charge compensating Na cations influences the CO<sub>2</sub> adsorption of RHO.

## 1. Introduction

The rise of carbon dioxide and of other greenhouse gases in the atmosphere is believed to be one of the major causes of the global warming [1-4]. CO<sub>2</sub> capture in solid systems provide a way to permanently store, easily transport and, possibly, extract if needed. Several materials such as carbon, polymers, salts, zeolites, calcium oxides for CO<sub>2</sub> adsorption, have been tested [5,6]. Zeolites has demonstrated to be excellent candidate for separation of carbon dioxide [7-15] not only because of their high adsorption capacity but also because of their properties *i.e.* crystal size, pore architecture, chemical composition, and nature of extra-framework cations. On the basis of these, there is an increasing demand for porous materials for the separation of natural gas components (*i.e.* mainly CH<sub>4</sub> and CO<sub>2</sub>). Flexible small pore zeolites are interesting candidates due to their high sorption capacity and selectivity [16] and many works focused on their characterization and more specifically on finding the relationship between type of framework, structure and sorption properties. Interesting observations come from X-Ray Powder Diffraction (XRPD). Indeed, this technique is particularly useful since it allows to quantify and localize the adsorbed CO<sub>2</sub> molecules into the zeolite porosities using *in situ* approach during the CO<sub>2</sub> adsorption, thus unravelling the relation among adsorption and structural and chemical characteristic of the host material.

For example, the capacity of Na<sub>12-x</sub>K<sub>x</sub>-A was demonstrated to be strongly related to the occupancy of the so-called site I, where CO<sub>2</sub> is absorbed bridging the two cations placed in the neighboring 8-rings [17]. Structural studies on Li<sup>+</sup>, Na<sup>+</sup>, and K-CHA reveal a preferential CO<sub>2</sub> adsorption site, located in the 8-membered ring due to high van der Waals and quadrupole interactions [18]. In the work of Pham and co-workers, a detailed structural description of CO<sub>2</sub> adsorption was given for ZK-5 exchanged with different cations [19]. Independently from the extra framework cations, three sites were recognized for the CO<sub>2</sub> molecules, the first between the flat eight-membered rings, the second in the  $\alpha$ -cage and the third in the  $\gamma$ -cage. In particular, in Li<sup>+</sup>-Na<sup>+</sup>-Mg<sup>2+</sup>-ZK-5 zeolites, the XRD analysis showed the formation of metal-CO<sub>2</sub> complexes upon gas pumping, due to a shift of the cations away from the double six-membered rings toward  $\alpha$ -cage. As well as in the above reported example, XRPD was also exploited to investigate nanocrystalline FAU zeolites upon CO<sub>2</sub> adsorption [20]. Structural results showed a different amount of adsorbed CO<sub>2</sub> molecules in nanosized Na-Y and Na-X zeolites supported by the *in situ* IR study revealing the different ratio of chemisorbed and physisorbed CO<sub>2</sub> molecules.



Among different zeolites possibly exploitable in the CO<sub>2</sub> adsorption and/or separation, the RHO-type zeolite [8] is of great interest due to the particular 3D structures consisting of cages and small pore openings. Their selectivity comes from their narrow pore sizes and shapes which can be tuned by the introduction of different extra-framework cations such as K<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>. Indeed, the extra-framework cations selectively block the access of CO<sub>2</sub> molecules to pores and cages of the zeolite [21].

In this work, we tested the CO<sub>2</sub> capture effectiveness of two nanosized RHO samples with a different grain size and Si/Al ratios and thus with a different amount of extra framework cations occupying the cages to evaluate their effect on the sorption properties. The study was carried out combining *in situ* XRPD using synchrotron radiation and *in situ* IR spectroscopy to reveal the nature and the amount of the CO<sub>2</sub> trapped in RHO zeolites at different pressure (1 and 5 Bars CO<sub>2</sub>).

## 2. Experimental section

### 2.1. Synthesis of RHO type nanosized zeolites

The reagents used for the hydrothermal synthesis of RHO type nanosized zeolites included the following chemicals without further purification: sodium aluminate (53% Al<sub>2</sub>O<sub>3</sub> 47% Na<sub>2</sub>O by mass, Sigma-Aldrich), colloidal silica LUDOX AS40 (40% by mass in water, Sigma-Aldrich), sodium hydroxide (99%, Sigma-Aldrich) and cesium hydroxide (98%, Alfa-Aesar).

Two initial precursor suspensions were prepared and used for the synthesis of two RHO zeolite samples with different particle sizes and chemical compositions:

**RHO-1:** 10 SiO<sub>2</sub> : 0.8 Al<sub>2</sub>O<sub>3</sub> : 8 Na<sub>2</sub>O : 0.58 Cs<sub>2</sub>O : 100 H<sub>2</sub>O

**RHO-2:** 10 SiO<sub>2</sub> : 0.8 Al<sub>2</sub>O<sub>3</sub> : 6.6 Na<sub>2</sub>O : 0.33 Cs<sub>2</sub>O : 100 H<sub>2</sub>O

The precursor aqueous suspensions were aged on a magnetic stirrer for 14 h at room temperature. Doubly deionized water was used throughout the synthesis and post-synthesis treatments. Syntheses were carried out in 100 cm<sup>3</sup> polypropylene bottle (PP bottle) at autogenous pressure without agitation at 90 °C for 1 h. The solid products were separated and recovered by high-speed centrifugation (20000 rpm, 60 min) and purified until the pH of the decanting water was about 7.5.

### 2.2. General characterization

*Scanning Electron Microscopy:* The surface features, morphology, homogeneity and size of RHO zeolite nanocrystals were characterized by field-emission scanning electron microscope (SEM) using a MIRA-LMH (TESCAN) fitted with a field emission gun using an accelerating voltage of 30.0 kV. All samples before the SEM characterization were covered with a Pt conductive layer.

*Inductively Coupled Plasma Analysis:* The chemical composition of the samples was determined by inductively coupled plasma (ICP) optical emission spectroscopy using a Varian ICP-OES 720-ES; the Si/Al ratio of the samples was confirmed by deconvolution of the  $^{29}\text{Si}$  solid state MAS NMR signals using DMFIT software.

*Thermogravimetry Analysis:* Thermogravimetry analyses (TGA) of the samples were carried out on a SETSYS 1750 CS evolution instrument (SETARAM). The samples were heated from 25 °C to 800 °C with a heating ramp of 5 °C /min (air flow rate: 40 mL/min).

*X-Ray Powder Diffraction Data Collection and Analysis.* Data collection was performed at ID22 beamline, ESRF, Grenoble, France. Diffracted intensity was detected by a bank of nine detectors, each preceded by a Si(111) crystal analyser. The beam wavelength ( $\lambda = 0.3544 \text{ \AA}$ ) was set by a channel-cut Si(111) crystal monochromator. Measurements were performed as follows: i) at room temperature (labelled *sample r.t.*) ii) samples were then carefully dehydrated at 350°C using a gas blower sample-environment for 3 hours and a further collection was performed (labelled *sample 350 °C*). Diffraction patterns are reported in Figure S1 and S2. Data refinements were performed by GSAS-II program [22] using Le Bail method.

### **2.3 Adsorption of CO<sub>2</sub> in nanosized zeolites**

*Volumetric Adsorption Analysis:* The adsorption of carbon dioxide on the nanosized RHO zeolite samples was measured at 0 °C using a Micrometrics Model ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 250 °C under vacuum for 12 h prior analysis.

*Thermogravimetry Analysis:* CO<sub>2</sub> adsorption on the nanosized RHO zeolites after activation at 350 °C for 2 h (water desorption) was performed; the RHO zeolites were kept at room temperature under a continuous flow of CO<sub>2</sub> (flow rate: 40 mL/min, 1 bar) for 9 h. The quantity of CO<sub>2</sub> absorbed in the RHO zeolites was determined using the mass increase compared to the total mass of the initial activated samples.

*In situ Infrared Spectroscopy:* Zeolite self-supported pellets (10 mg.cm<sup>-2</sup>) were prepared, and the transmission IR spectra with a Nicolet Avatar spectrometer were recorded. IR-cell equipped with

a heating device was used to activate the samples prior to the measurements. The cell was connected to a high vacuum line with a reachable pressure of  $10^{-10}$  bar. The sample was activated at 100 °C for 0.5 h followed by heating at 350 °C for 3.0 h. All the above steps were performed under secondary vacuum. The IR spectra were recorded at room temperature, and the IR spectrum recorded in empty transmission cell under secondary vacuum at room temperature was used as a background.

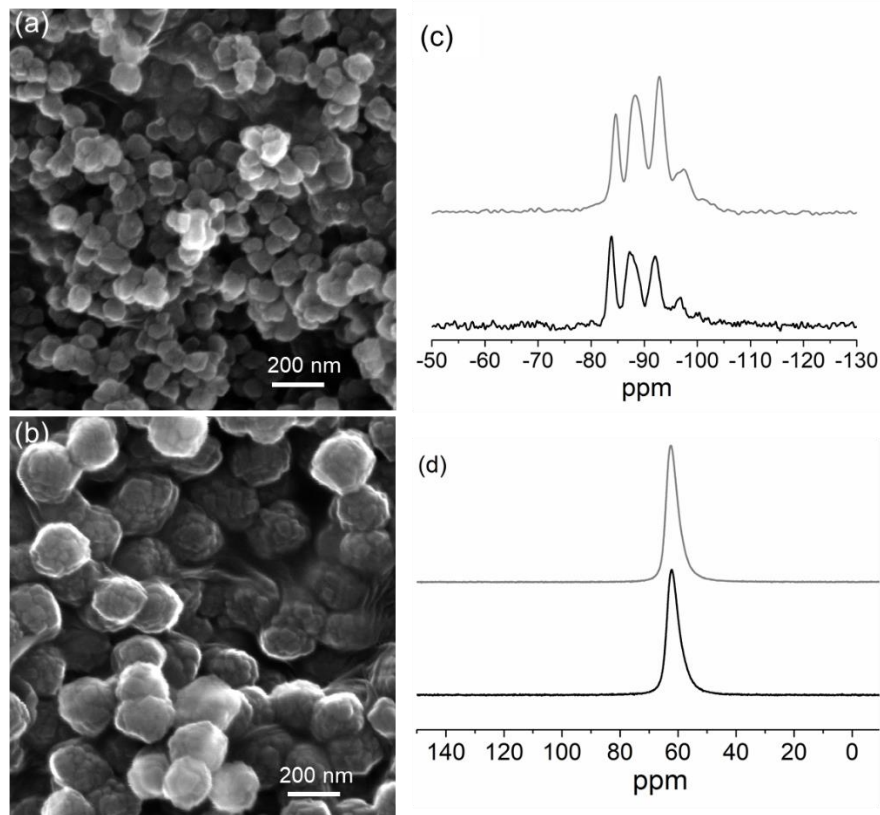
*In situ X-Ray Powder Diffraction Data Collection and Analysis:* CO<sub>2</sub> adsorption was performed after the dehydration of RHO zeolite samples (see general characterization XRPD section): i) room temperature was restored and CO<sub>2</sub> was pumped at 1 bar using a Gas-handling capillary cell, and data was recorded after 1 hour of pumping (labelled *sample CO<sub>2</sub> 1 bar*) and ii) CO<sub>2</sub> was then pumped at 5 bar and data collection was performed after 1 hour of pumping (labelled *sample CO<sub>2</sub> 5 bar*). Beamline used setup is the same as the reported one for the measurements at room temperature (r.t.) and at 350°C; diffraction patterns are presented in Figure S1 and S2. The acentric space group  $I\bar{4}3m$  is the preferred for RHO zeolites with a cell parameter lower than 14.95 Å according to Ref. [23], therefore Le Bail analysis of the RHO samples was performed using acentric space group for both samples.

### **3. Results & discussions**

#### **3.1. Characterization of as-synthesized nanosized RHO zeolite samples**

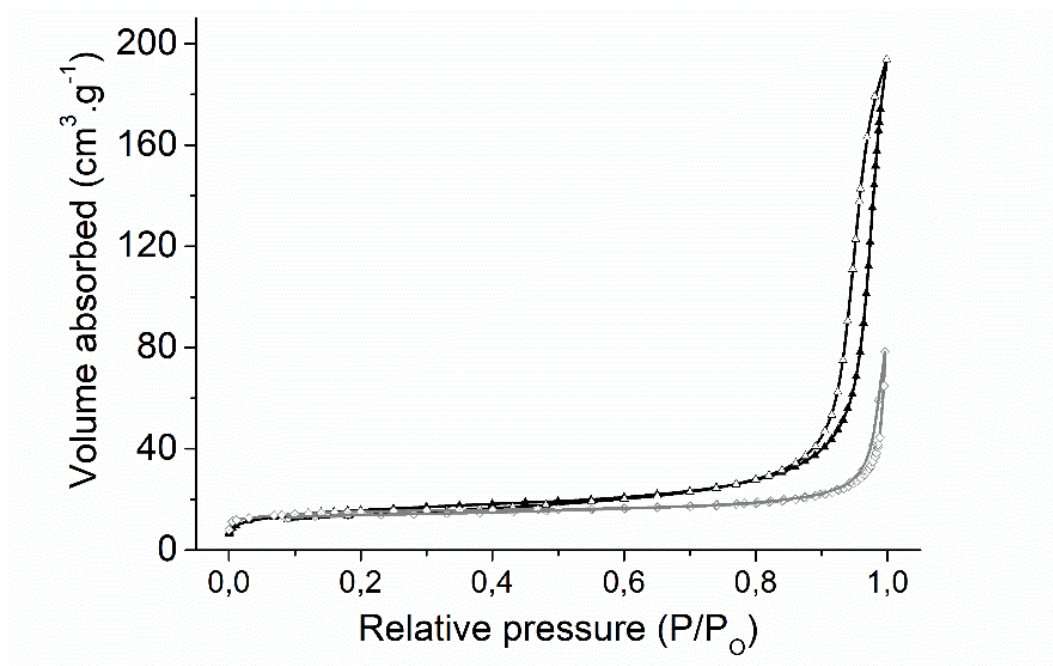
##### *Morphology and porosity.*

The SEM images reveal the presence of homogeneous RHO crystals with regular round-shapes in both samples RHO-1 and RHO-2 (Figure 1).



**Figure 1.** SEM images of (a) RHO-1 and (b) RHO-2 samples and (c)  $^{29}\text{Si}$  MAS NMR and (d)  $^{27}\text{Al}$  NMR spectra of RHO-1 (black) and RHO-2 (grey) samples.

Indeed, RHO-1 zeolite sample has a particle diameter of around 80 nm while RHO-2 is formed by smaller particles forming aggregates of around 200 nm. The presence of small discrete nanoparticles in sample RHO-1 is further confirmed by the  $\text{N}_2$  sorption isotherm revealing the presence of high textural porosity due to the presence of nanosized homogenous crystals (Figure 2). The hysteresis loop above 0.8  $P/P_0$  in the  $\text{N}_2$  sorption isotherm of RHO-1 corresponds to the interparticles mesoporosity, while this is not well-pronounced for sample RHO-2; this is explained with the aggregates having bigger ultimate particle size. The agglomerated RHO-2 crystals do not possess high external surface area nor interparticles mesoporosity as clearly shown by the low intensity of the hysteresis loop above 0.8  $P/P_0$ . The total pore volume of RHO-1 sample is higher than for RHO-2, and the absence of microporosity for both samples is expected since the pores are blocked with the cations used for the synthesis of the RHO-1 and RHO-2 samples (Figure 2).



**Figure 2.** Nitrogen adsorption-desorption isotherms of nanosized RHO-1 (black) and RHO-2 (grey) zeolites (closed symbols: adsorption and open symbols: desorption).

#### *Chemical Composition.*

The ICP analysis for samples RHO-1 and RHO-2 reveal the molar Si/Al ratio of 1.46 and 1.71, respectively. More precisely, the overall chemical composition of both samples has been determined based on ICP results:

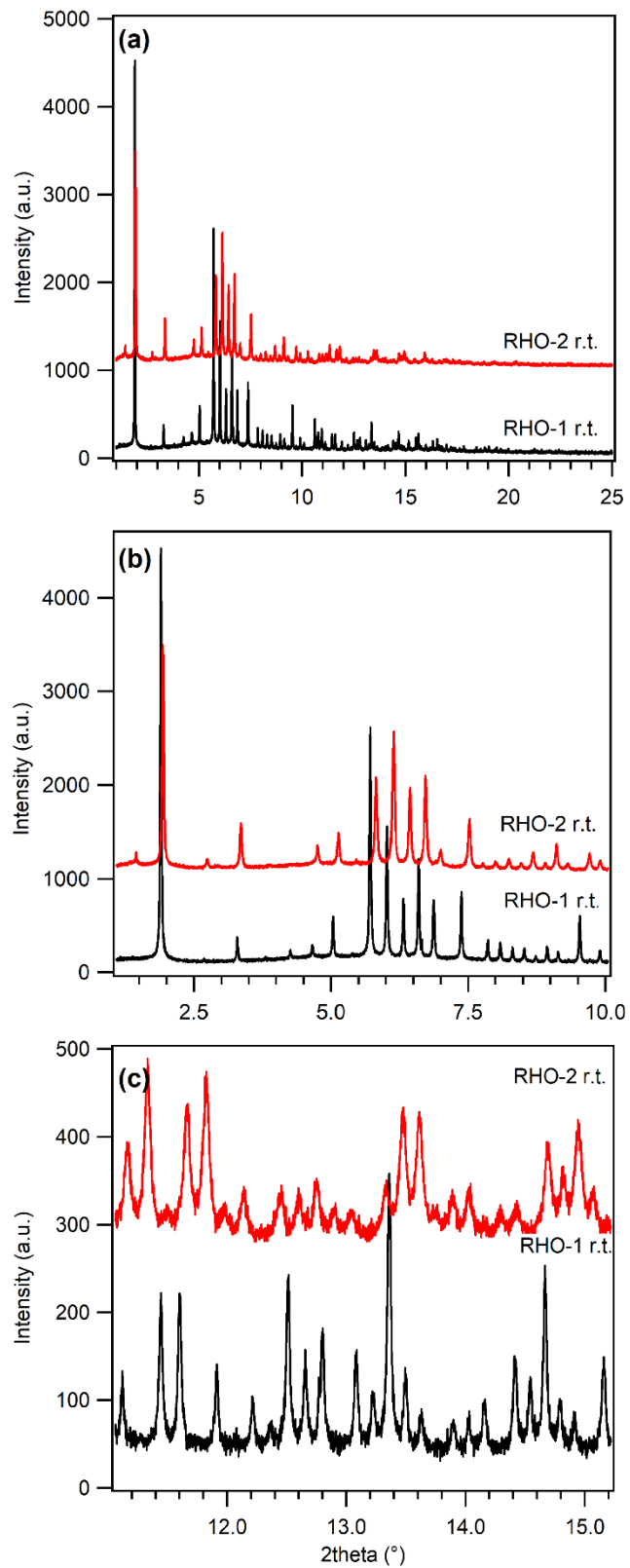


The  $^{29}\text{Si}$  MAS NMR spectra were used to verify the Si/Al ratio of the materials (Figure 1c). Peaks at -84 ppm, -88 ppm, -92 ppm, -98 ppm and -102 ppm correspond to  $\text{Q}^0$  (4Al),  $\text{Q}^1$  (3Al),  $\text{Q}^2$  (2Al),  $\text{Q}^3$  (1Al) and  $\text{Q}^4$  (0Al) types of silicon in tetrahedral positions. After being normalized with the mass of samples, those peaks have been deconvoluted and their respective areas allowed to calculate the molar Si/Al ratio of 1.55 for RHO-1 and 1.75 for RHO-2. No peak corresponding to octahedral aluminum at 0 ppm in  $^{27}\text{Al}$  MAS NMR spectra of both samples was observed, thus confirming that no amorphous alumina was present (Figure 1d).

The RHO-1 material has a lower Si/Al ratio compared to RHO-2, probably due to the highest content of cations in the initial precursor suspension. It is interesting to notice that Cs<sup>+</sup> cations content is rather similar in both samples. While the Na<sup>+</sup> content is higher in RHO-1 sample, which is expected since they must compensate the high Al loading.

*X-Ray Powder Diffraction Analysis.*

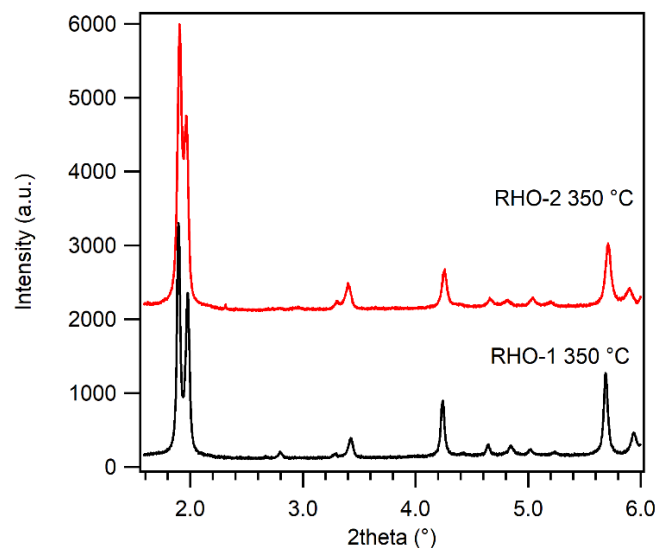
Highly crystalline RHO materials were obtained as proved by the two diffraction patterns shown in Figure 3 (top and medium panel). RHO-1 and RHO-2 present two different peak broadening and signal dampening (Figure 3, bottom panel) due to the smaller domain size (*i.e.* crystallite dimension) of the second sample, which is consistent with the SEM analysis. Indeed, as previously reported, the RHO-2 sample consists of aggregates (200 nm) formed by smaller nanocrystallites of about 30-40 nm. Minor impurities were detected in both samples, the presence of only few low intensity peaks did not allow the phase identification.



**Figure 3.** Diffraction patterns of RHO-1 and RHO-2 collected at room temperature before dehydration in the range (a) 1-25 ° 2theta, (b) 2-10 ° 2theta and (c) 11-15 ° 2theta.

### 3.2. Characterization of dehydrated nanosized RHO zeolite samples

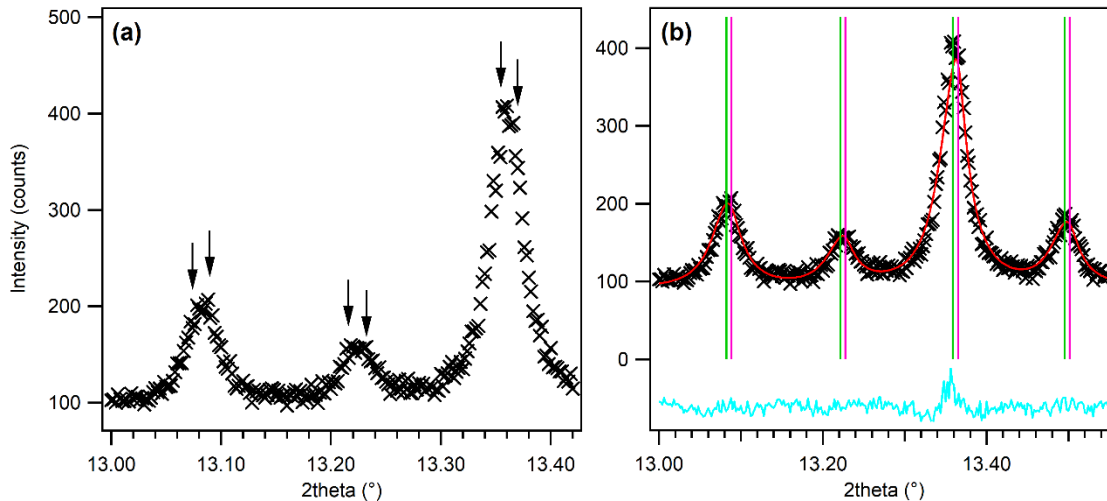
Figure 4 shows the diffraction patterns of RHO-1 and RHO-2 samples after dehydration (see experimental section). After dehydration, the XRPD patterns of both RHO-1 and RHO-2 samples present split peaks indicating the presence of two phases with different cell parameters.



**Figure 4.** XRPD patterns of nanosized RHO-1 and RHO-2 zeolite samples collected after dehydration at 350 °C.

Parise and co-workers already reported this behaviour in Cd exchanged RHO zeolite [24]. This zeolite, indeed, upon dehydration, presents a transformation from  $I\bar{4}3m$  to  $Im\bar{3}m$  space group with a displacement of  $Cd^{2+}$  ions, initially positioned near to the centre of the single 8-ring (S8R), to the S6R-site. Due to the very slow structural changes, diffraction patterns show two coexisting phases, one acentric and the other centric. In our case, the observations for the nanosized RHO zeolites are different. Indeed, the diffraction pattern collected of sample RHO-1 at room temperature, despite the high peak broadening due to the nanosized crystals dimension, shows slight peak splits and appearance of shoulders originated by a second phase which are identified even at room temperature thanks to the high-resolution data obtained using synchrotron radiation (Figure 5). The two phases, named (*a*) and (*b*), show very similar, but distinct, cell parameters: 15.0813(2) Å and 15.0742(4) Å (see Table 1).





**Figure 5.** (a) XRD patterns of nanosized RHO-1 zeolite at room temperature (arrows indicate the peak splits due to the presence of a second phase, and (b) the refinement of XRD patterns RHO-1 at room temperature (black cross represents the observed pattern, red line the calculated pattern and cyan line is the differences between the two; green and pink markers are related to the reflections belonging to phase (a) and (b).

No structural refinements can be performed due to the biphasic nature of the sample. We may suppose the presence of two different phases, coexisting at room temperature, also for sample RHO-2, but here the smaller nanosized crystals domains strongly affects the peak broadening, thus no signal of a second phase is clearly recognized. RHO-2 sample present at room temperature an “average” cell parameter of 14.8005(2) Å. Overall, the presence of two different phases is more clearly observed in dehydrated condition. Each sample consists of two phases (a) and (b) characterized by two different cell parameters (Table 1). The two phases depend on the chemical composition of the RHO zeolite, and phases (a) has always the larger cell parameter which is probably due to the larger Al content and higher concentration of extra framework cations (Na and Cs). For sample RHO-1, the dehydration induces a cell parameter decrease for the phase with higher cation contents (a) and a cell parameter increase for the phase with less cations content (b). This different behavior is linked to the different water content in the two phases: in phase (a), where more cations are present (higher Al content in the RHO structure) thus water molecules are hosted, and the thermal behaviour is mostly influenced by water release (i.e. contraction of the cell parameter), while in phase (b) is mostly influenced by the thermal expansion (i.e. expansion of the cell parameter). This is applicable for the RHO-2 sample, but due to the smaller differences between the cell parameter of phase (a) and (b) at dehydrated condition and to the smaller nanosized crystals domains, it is not possible to identify the presence of the two phases at ambient

conditions (RT), since their peaks appear superimposed revealing only an “average” cell parameter.

Table 1. Cell parameters obtained after refinement for RHO-1 and RHO-2 samples.

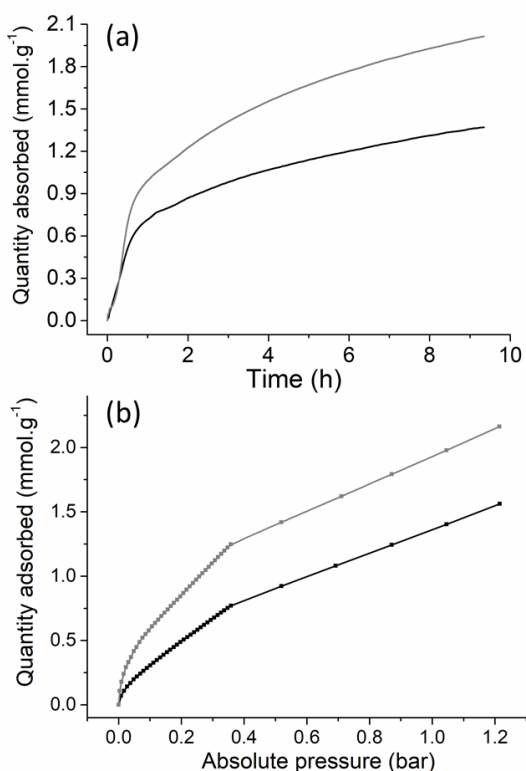
	<b>RHO-1</b>		<b>RHO-2</b>	
	<b>Phase (a) (Å)</b>	<b>Phase (b) (Å)</b>	<b>Phase (a) (Å)</b>	<b>Phase (b) (Å)</b>
<b>r.t.</b>	15.0813(2)	15.0742(4)	14.8005(2)	
<b>350 °C</b>	14.526(1)	15.1460(4)	14.620(2)	15.0839(7)
<b>1 bar</b>	14.3590(6)	14.551(1)	14.505(2)	14.6690(8)
<b>5 bar</b>	14.3706(8)	14.549(1)	14.502(1)	14.7031(8)

Besides the different amount of water molecules in the two hydrated phases at r.t., other factor could be co-responsible of the variations of the unit cell such as: i ) possible phase transition of one of the two phases [24], ii) different cations contents with different cesium displacement, and iii) a combination of the previous two hypotheses.

### 3.3. CO<sub>2</sub> adsorption on dehydrated nanosized RHO zeolite samples

#### *BET and TGA analyses*

The CO<sub>2</sub> adsorption on dehydrated RHO-1 and RHO-2 samples was followed by BET and TGA methods (Figure 6). Each of the two zeolites is consisting of two slightly different phases, as indicated by XRPD analysis (see section above), however, the BET and TGA results represent the average behavior of samples.



**Figure 6.** CO<sub>2</sub> adsorption monitored on nanosized RHO-1 (black) and RHO-2 (grey) zeolite samples by (a) TGA and (b) BET at 0 °C (details are presented in the Experimental section).

The same trend on both samples at the initial stages of CO<sub>2</sub> adsorption at 1 bar is observed (Figure 6a). The total adsorption of CO<sub>2</sub> on RHO-1 and RHO-2 after 9 h reached is 1.3 and 2 mmol g<sup>-1</sup>, respectively as measured by TGA. The isotherms collected at 0 °C confirmed this tendency that the RHO-2 sample has a higher capacity for CO<sub>2</sub> than the RHO-1, but the trend in the adsorption is similar (Figure 6b). The different CO<sub>2</sub> capacity of the two samples is probably due to the different cation contents in the RHO framework. The more Na<sup>+</sup> cations are present in the RHO type framework, the lower the capacity of the RHO zeolite towards CO<sub>2</sub> is measured. As the Cs<sup>+</sup> cation contents in both samples are similar, the trends of adsorption observed in TGA and BET isotherms are rather similar. Cs<sup>+</sup> cations are responsible for the selective adsorption of CO<sub>2</sub> and possible rejection of bulky molecules such as CH<sub>4</sub> [25].

*In situ FTIR analysis.*

In order to understand the type of CO<sub>2</sub> species adsorbed in the samples, *in situ* FTIR study on both nanosized RHO-1 and RHO-2 zeolite samples was carried out. CO<sub>2</sub> gas with small doses from 1 to 760 T was delivered to the activated self-supported zeolite pellet (Figure S3 and S4). As shown in both sets of the IR spectra, water was present confirmed by the peak at 1610 cm<sup>-1</sup>. The intensity of this peak corresponding to water is gradually increased with an increase of CO<sub>2</sub> concentration. The CO<sub>2</sub> absorption in the RHO zeolite is confirmed by the presence of a band at 2250 cm<sup>-1</sup> corresponding to physisorbed CO<sub>2</sub> as well several bands around 1650 cm<sup>-1</sup> due to the chemisorbed CO<sub>2</sub> species. The chemisorbed CO<sub>2</sub> is originated from the formation of carbonates in the presence of water. The *in situ* IR results show that RHO-2 has higher CO<sub>2</sub> capacity, which is due to the lower concentration of Na cations in the sample (Figure S5). These results are in a good accordance with the BET and TGA data shown in the previous section. The high content of Na in the RHO-1 sample leads to a reduced CO<sub>2</sub> capacity.

*- In situ X-Ray Powder Diffraction Analysis.*

The presence of two distinct phases (*a*) and (*b*) in both nanosized RHO-1 and RHO-2 zeolite samples persists after restoring the room temperature conditions and CO<sub>2</sub> pumping. Figure 7 shows the evolution of cell parameters before and during CO<sub>2</sub> adsorption in both zeolite samples (absolute values are reported in Table 1). In both samples phases (*a*) and (*b*) experience a reduction of the cell parameters due to the penetration of CO<sub>2</sub> molecules at 1 bar in the RHO framework. This behavior was already observed by Polisi et al. [20] where the penetration of molecules into the zeolite induced a decrease of the cell volume due to the strong interaction occurring between the framework and the gas molecules. In our case it is not possible to propose further hypothesis to explain this behavior due to the lack of structural information. Nevertheless, we can confirm the CO<sub>2</sub> molecules intrusion in the nanosized RHO-2 zeolite on the basis of the changes in the intensity ratio of diffraction peaks before and after the CO<sub>2</sub> pumping (Figure 8). Under delivering of CO<sub>2</sub> at 5 bars, very little changes in the cell parameters of RHO-1 and 2RHO-2 are observed with respect to that at 1 bar. This indicates the complete saturation of both zeolite sample under CO<sub>2</sub> even at 1 bar.

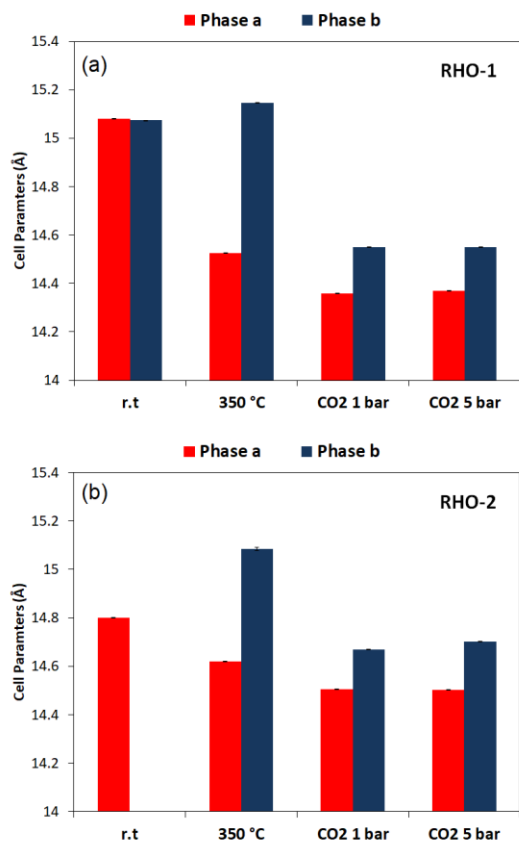


Figure 7. Change of the cell parameters of nanosized RHO-1 and RHO-2 zeolite samples at room temperature (r.t.), after dehydration at 350 °C (a) and under CO<sub>2</sub> adsorption at 1 bar and 5 bars (b).

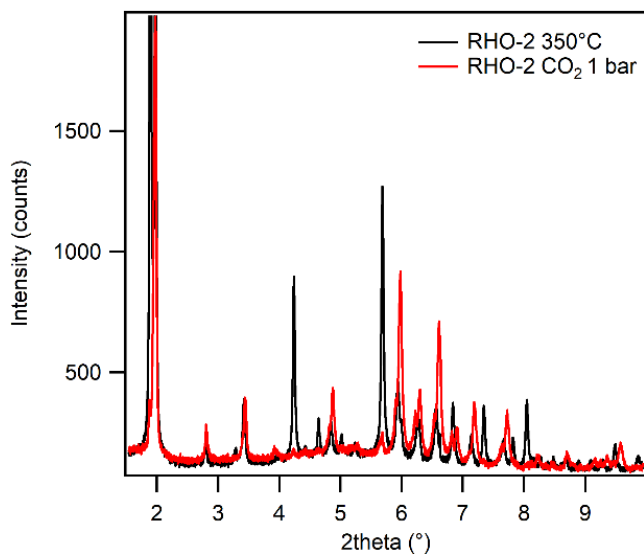


Figure 8. XRD patterns of nanosized RHO-2 zeolite after dehydration at 350 °C and CO<sub>2</sub> adsorption at 1 bar.

#### 4. Conclusions

In this work two different nanosized RHO zeolite samples were synthesized and tested for CO<sub>2</sub> adsorption. Initial materials were fully characterized providing information about chemical composition, morphology and porosity. The two RHO zeolite samples were proved to be highly crystalline, presenting individual grain size of 80 nm for sample RHO-1 and aggregates of 200 nm for sample RHO-2. Upon dehydration, the splitting of the diffraction peaks indicates the presence of two phases with different cell parameters in both samples. Differently from previous works, which report a slow phase transition leading to a biphasic sample, here we observed for the first time, thanks to high resolution XRPD data, the presence of a second phase even at room temperature, probably due to chemical gradients in the samples.

The CO<sub>2</sub> adsorption capacity of the RHO zeolite is controlled by the sodium content in the nanosized crystals with different Si/Al ratios. The Na content can be tuned by modifying the synthesis conditions and this will influence the particle sizes and CO<sub>2</sub> capacity of the RHO materials. Higher Na content in the initial gel is required in order to synthesize pure highly crystalline discrete RHO zeolite by omitting completely the organic structural directing agent.

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#### References

- [1] U. Siegenthaler, H. Oeschger, *Tellus B*, 39B (1987) 140-154.
- [2] C.D. Keeling, T.P. Whorf, M. Wahlen, J. van der Plicht, *Nature*, 375 (1995) 666-670.
- [3] T.R. Anderson, E. Hawkins, P.D. Jones, *Endavour*, 40 (2016) 178-187.
- [4] J.E. Szulejko, P. Kumar, A. Deep, K.H. Kim, *Atmos. Pollut. Res.*, 8 (2017) 136-140.
- [5] R.E. Morris, P.S. Wheatley, *Angew. Chem. Int. Ed.*, 47 (2008) 4966-4981.
- [6] S. Choi, J.H. Drese, C.W. Jones, *ChemSuschem*, 2 (2009) 796-854.
- [7] A. Zukal, J. Mayerova, M. Kubu, *Top. Catal.*, 53 (2010) 1361-1366.
- [8] C. Baerlocher, L.B. McCusker, D.H. Olson, *Atlas of zeolite framework types*, 6th ed., Elsevier, Amsterdam, The Netherlands, 2007.
- [9] J.-S. Lee, J.-H. Kim, J.-T. Kim, J.-K. Suh, J.-M. Lee, C.-H. Lee, *J. Chem. Eng. Data*, 47 (2002) 1237-1242.

- [10] C.Y. Lu, H.L. Bai, B.L. Wu, F.S. Su, J. Fen-Hwang, *Energy & Fuels*, 22 (2008) 3050-3056.
- [11] R.V. Siriwardane, M.S. Shen, E.P. Fisher, *Energ. Fuels*, 19 (2005) 1153-1159.
- [12] G. Maurin, P.L. Llewellyn, R.G. Bell, *J. Phys. Chem. B*, 109 (2005) 16084-16091.
- [13] D.F. Plant, G. Maurin, I. Deroche, P.L. Llewellyn, *Microporous and Mesoporous Mater.*, 99 (2007) 70-78.
- [14] W. Wong-Ng, J.A. Kaduk, Q. Huang, L. Espinal, L. Li, J.W. Burrell, *Microporous and Mesoporous Mater.*, 172 (2013) 95-104.
- [15] R. Arletti, L. Gigli, F. di Renzo, S. Quartieri, *Microporous and Mesoporous Mater.*, 228 (2016) 248-255.
- [16] B. Ilic, S.G. Wettstein, *Microporous and Mesoporous Mater.*, 239 (2017) 221-234.
- [17] P. Rzepka, Z. Bacsik, S. Smeets, T.C. Hansen, N. Hedin, D. Wardecki, *J. Phys. Chem. C*, 122 (2018) 27005-27015.
- [18] T.D. Pham, M.R. Hudson, C.M. Brown, R.F. Lobo, *Chemsuschem*, 7 (2014) 3031-3038.
- [19] T.D. Pham, M.R. Hudson, C.M. Brown, R.F. Lobo, *Chemsuschem*, 10 (2017) 946-957.
- [20] M. Polisi, J. Grand, R. Arletti, N. Barrier, S. Komaty, M. Zaarour, S. Mintova, G. Vezzalini, *J. Phys. Chem. C*, 123 (2019) 2361-2369.
- [21] T. De Baerdemaeker, D. De Vos, *Nature Chemistry*, 5 (2013) 89-90.
- [22] B.H. Toby, R.B. Von Dreele, *J. Appl. Crystallogr.*, 46 (2013) 544-549.
- [23] J.B. Parise, T.E. Gier, D.R. Corbin, *J. Phys. Chem.*, 88 (1984) 1635-1640.
- [24] J.B. Parise, L. Xing, D.R. Corbin, *J. Chem. Soc. Chem. Comm.*, (1991) 162-163.
- [25] F.X. Coudert, D. Kohen, *Chem. Mater.*, 29 (2017) 2724-2730.



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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: