

## Optimized cesium and potassium ion-exchanged zeolites A and X granules for biogas upgrading

Kritika Narang<sup>a</sup>, Kristina Fodor<sup>a</sup>, Andreas Kaiser<sup>b</sup>, Farid Akhtar<sup>a\*</sup>

<sup>a</sup>Division of Materials Science, Luleå University of Technology, Luleå 97187, Sweden

<sup>b</sup>Department of Energy Conversion, Technical University of Denmark, Roskilde 4000, Denmark

\*-Corresponding author's email address: farid.akhtar@ltu.se

### Supplementary information

#### S1: Ion exchange procedure

The ion-exchange process was optimized in two steps.

**First step – Ion exchange with K<sup>+</sup> cations:** The zeolite powders/granules were mixed with the potassium chloride in distilled water and stirred at room temperature. The samples were washed three times with distilled water and dried at 110 °C. The degree of the partial ion-exchange was evaluated with the energy dispersive spectroscopy analysis, CO<sub>2</sub> and CH<sub>4</sub> adsorption and BET surface area. The ion-exchanged compositions demonstrating the high CO<sub>2</sub> adsorption capacity and CO<sub>2</sub>/CH<sub>4</sub> selectivity were used for further ion-exchange with Cs<sup>+</sup> cations in the second step.

**Second step - Ion exchange with Cs<sup>+</sup> cations:** The optimum K<sup>+</sup> ion exchanged zeolites powders/granules obtained in the first step were mixed with cesium chloride in distilled water and stirred at room temperature. The samples were washed three times with distilled water and dried at 110 °C. The degree of the partial ion-exchange was evaluated with the energy dispersive spectroscopy analysis, CO<sub>2</sub> and CH<sub>4</sub> adsorption and BET surface area.

The detailed amount is described in Table 1S for NaX powder as well as NaX binderless granules whereas Table 2S shows the detailed description of the ion exchange process for the CaA powders and CaA granules.

Table 1S: Ion exchange process description for NaX powder

NaX Powder							
Starting zeolite	Amount of zeolite (g)	Amount of KCl (g)	Amount of CsCl (g)	Amount of water (ml)	Stirring time (min)	Final zeolite Composition*	Selectivity K <sub>H</sub> (CO <sub>2</sub> )/K <sub>H</sub> (CH <sub>4</sub> )
NaX	1.003	0.203	-	100	30	NaK <sub>5.9</sub> X	143
NaX	5	1.001	-	500	30	NaK <sub>3.7</sub> X	77
NaX	5.006	2.002	-	500	30	NaK <sub>5.29</sub> X	140
NaX	5.002	4.001	-	500	30	NaK <sub>6</sub> X	146
NaK <sub>3.7</sub> X	1.2023	-	0.0484	120	30	NaK <sub>3.46</sub> Cs <sub>0.38</sub> X	135
NaK <sub>3.7</sub> X	1.2018	-	0.0243	120	30	NaK <sub>3.27</sub> Cs <sub>0.19</sub> X	144
NaK <sub>3.7</sub> X	1.2034	-	0.0124	120	30	NaK <sub>3.42</sub> Cs <sub>0.17</sub> X	143
NaK <sub>5.29</sub> X	1.2011	-	0.0486	120	30	NaK <sub>4.75</sub> Cs <sub>0.45</sub> X	132
NaK <sub>5.29</sub> X	1.2004	-	0.0251	120	30	NaK <sub>4.57</sub> Cs <sub>0.20</sub> X	146

\*The final composition of the zeolite after ion-exchange was determined by EDS analysis.

Table 2S: Ion exchange process description for CaA powder

<b>CaA Powder</b>							
Starting zeolite	Amount of zeolite (g)	Amount of KCl (g)	Amount of CsCl (g)	Amount of water (ml)	Stirring time (min)	Final zeolite Composition*	Selectivity $K_H(\text{CO}_2)/K_H(\text{CH}_4)$
CaA	1.003	0.051	-	100	30	CaK <sub>0.94</sub> A	138
CaA	1.0167	0.1016	-	100	30	CaK <sub>1.54</sub> A	66
CaA	1	0.203	-	100	30	CaK <sub>1.94</sub> A	38
CaA	1.003	0.403	-	100	30	CaK <sub>2.68</sub> A	175
CaA	1.003	0.8	-	100	30	CaK <sub>3.40</sub> A	288
CaA	1.015	1.608	-	100	60	CaK <sub>4.26</sub> A	127
CaA	1.003	3.199	-	100	60	CaK <sub>4.57</sub> A	48
CaA	5.006	2	-	500	30	CaK <sub>2.77</sub> A	139
CaA	5.009	4.004	-	500	30	CaK <sub>3.08</sub> A	179
CaA	5	8	-	500	30	CaK <sub>3.11</sub> A	223
CaK <sub>2.77</sub> A	1.8010	-	0.144	180	30	CaK <sub>1.55</sub> Cs <sub>0.80</sub> A	144
CaK <sub>2.77</sub> A	1.8011	-	0.0723	180	30	CaK <sub>1.88</sub> Cs <sub>0.42</sub> A	128
CaK <sub>2.77</sub> A	1.8018	-	0.0359	180	30	CaK <sub>1.74</sub> Cs <sub>0.17</sub> A	168
CaK <sub>3.08</sub> A	1.8011	-	0.1446	180	30	CaK <sub>1.91</sub> Cs <sub>0.8</sub> A	152
CaK <sub>3.08</sub> A	1.8006	-	0.0728	180	30	CaK <sub>2.21</sub> Cs <sub>0.43</sub> A	152
CaK <sub>3.08</sub> A	1.8012	-	0.0362	180	30	CaK <sub>2.5</sub> Cs <sub>0.21</sub> A	160
CaK <sub>3.08</sub> A	1.8012	-	0.0610	180	30	CaK <sub>2.5</sub> Cs <sub>0.45</sub> A	220
CaK <sub>3.11</sub> A	1.802	-	0.1450	180	30	CaK <sub>2.51</sub> Cs <sub>0.79</sub> A	50
CaK <sub>3.11</sub> A	1.8012	-	0.0728	180	30	CaK <sub>2.63</sub> Cs <sub>0.40</sub> A	77
CaK <sub>3.11</sub> A	1.8008	-	0.0369	180	30	CaK <sub>2.76</sub> Cs <sub>0.19</sub> A	100

\*The final composition of the zeolite after ion-exchange was determined by EDS analysis.

## S2: Electron Dispersive Spectroscopy (EDS)

EDS analysis was done on the powdered zeolite NaX, CaA and its ion exchange derivatives in order to confirm the ion exchange. The result of few selected zeolites is shown in table 3S.

Table 3S: Elemental analysis of zeolite NaX, CaA powder and its ion exchange derivatives

Zeolite powder	Ca (at%)	Na (at %)	O ( at%)	Al ( at%)	Si ( at%)	Cl ( at%)	K (at%)	Cs (at %)
CaA	3.94±0.52	--	70.52±2.04	12.18±1.20	10.71±0.78	--	--	--
CaK <sub>3.08</sub> A	3.12±0.57	--	69.54±1.34	11.43±0.88	9.65±1.10	1.83±0.99	3.11±0.51	--
CaK <sub>2.5</sub> Cs <sub>0.79</sub> A	4.1±0.46	--	68.84±1.31	12.66±0.46	11.03±0.38	0.06±0.03	2.5±0.27	0.21±0.03
NaX	--	11.85±0.39	62.35±3.11	12.21±1.78	13.31±1.68	--	--	--
NaK <sub>5.88</sub> X	--	5.63±0.45	62.06±0.95	11.65±0.70	13.38±0.62	1.31±0.43	5.88±0.51	--
NaK <sub>5.97</sub> Cs <sub>0.10</sub> X	--	4.95±0.50	64.27±2.90	11.73±0.82	12.88±0.68	0.05±0.04	5.97±1.96	0.10±0.09

## S3: SEM and XRD data

Scanning electron micrographs of the CaA, NaX powders and some chosen ion exchange derivatives of these zeolite powders are shown in Fig. 1S. The analysis showed that the size and shape of the crystals are similar before and after the partial ion exchange. The average size of the polyhedral crystal was found to be 3µm.

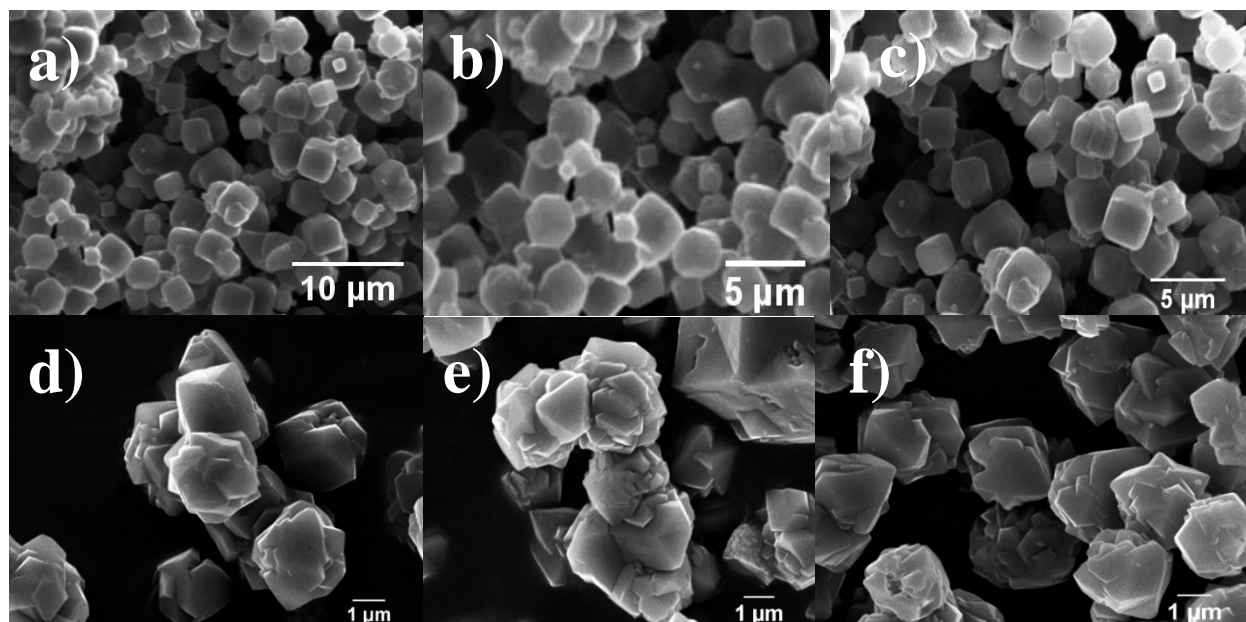


Fig. 1S: SEM images of a) zeolite CaA powder b)  $\text{CaK}_{3.08}\text{A}$  c)  $\text{CaK}_{2.5}\text{Cs}_{0.2}\text{A}$  d) zeolite NaX powder e)  $\text{NaK}_{5.9}\text{X}$  f)  $\text{NaK}_{6.83}\text{Cs}_{0.61}\text{X}$ .

The PXRD pattern of the as-received zeolite NaX and CaA powder is shown in Fig. 2S. Randomly, ion exchange samples are chosen to compare the XRD of as received and ion exchange derivatives. The structure of zeolite NaX and CaA powder does not change by partial ion exchange with potassium and the same is observed when next to potassium a small amount of cesium was introduced. However, the added quantities were very small; therefore, no changes in the crystallinity were expected.

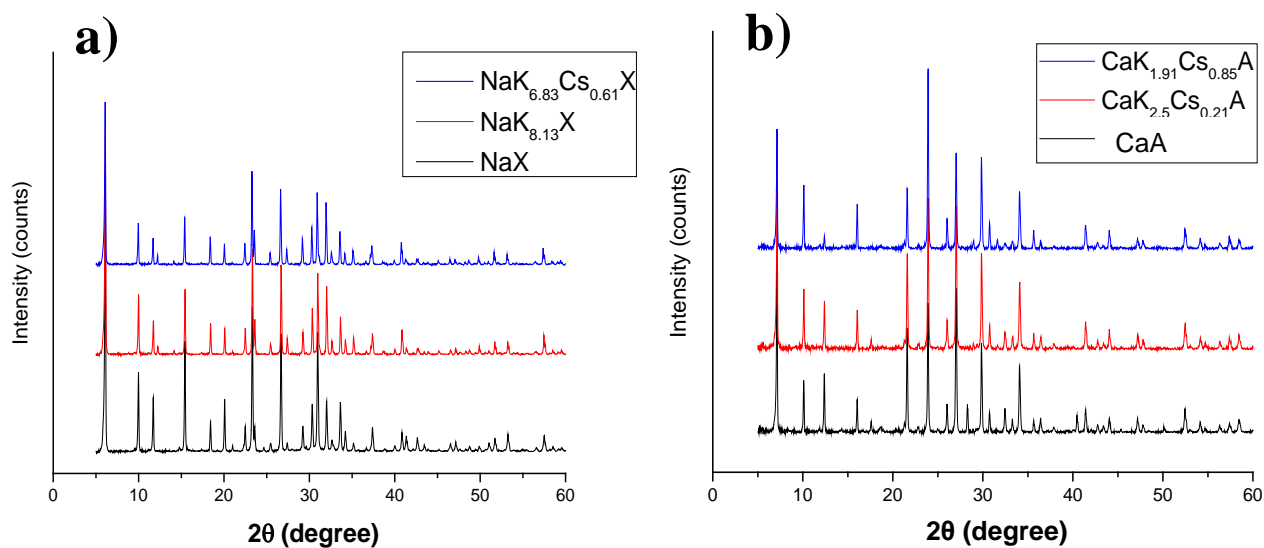


Fig. 2S: Powder XRD pattern of a) NaX (black) and  $\text{NaK}_{8.13}\text{X}$  (red),  $\text{NaK}_{6.83}\text{Cs}_{0.61}\text{X}$  (blue); b) CaA (black) and  $\text{CaK}_{2.5}\text{A}$  (red),  $\text{CaK}_{1.91}\text{Cs}_{0.85}\text{A}$  (blue)

## S4: Adsorption Isotherm

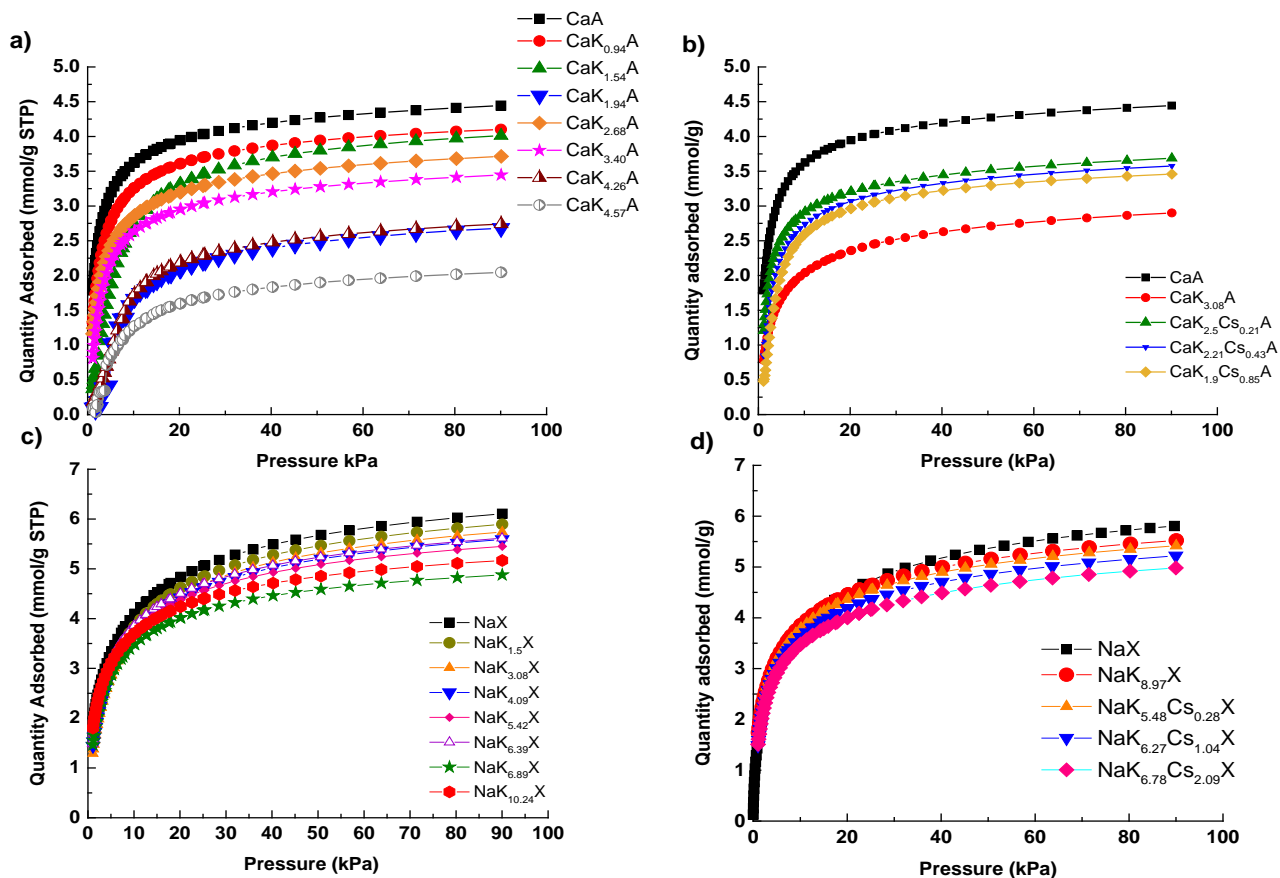


Fig. 3S: a) CO<sub>2</sub> uptake isotherms of CaA powder (as-received powder, whole optimization with K cations) b) CO<sub>2</sub> uptake isotherms of CaA powder (optimized with K cations followed by whole optimization with Cs cations) c) CO<sub>2</sub> uptake isotherms of NaX powder (as-received powder, whole optimization with K cations) d) CO<sub>2</sub> uptake isotherms of NaX powder (optimized with K cations followed by whole optimization with Cs cations).

Fig. 3S shows the CO<sub>2</sub> adsorption isotherms of zeolite CaA and NaX powder with the follow-up potassium ion exchange and cesium ion exchange derivatives. The CH<sub>4</sub> adsorption isotherms for both powder zeolites and its follow up potassium and cesium exchange derivatives is given in Fig. 4S.

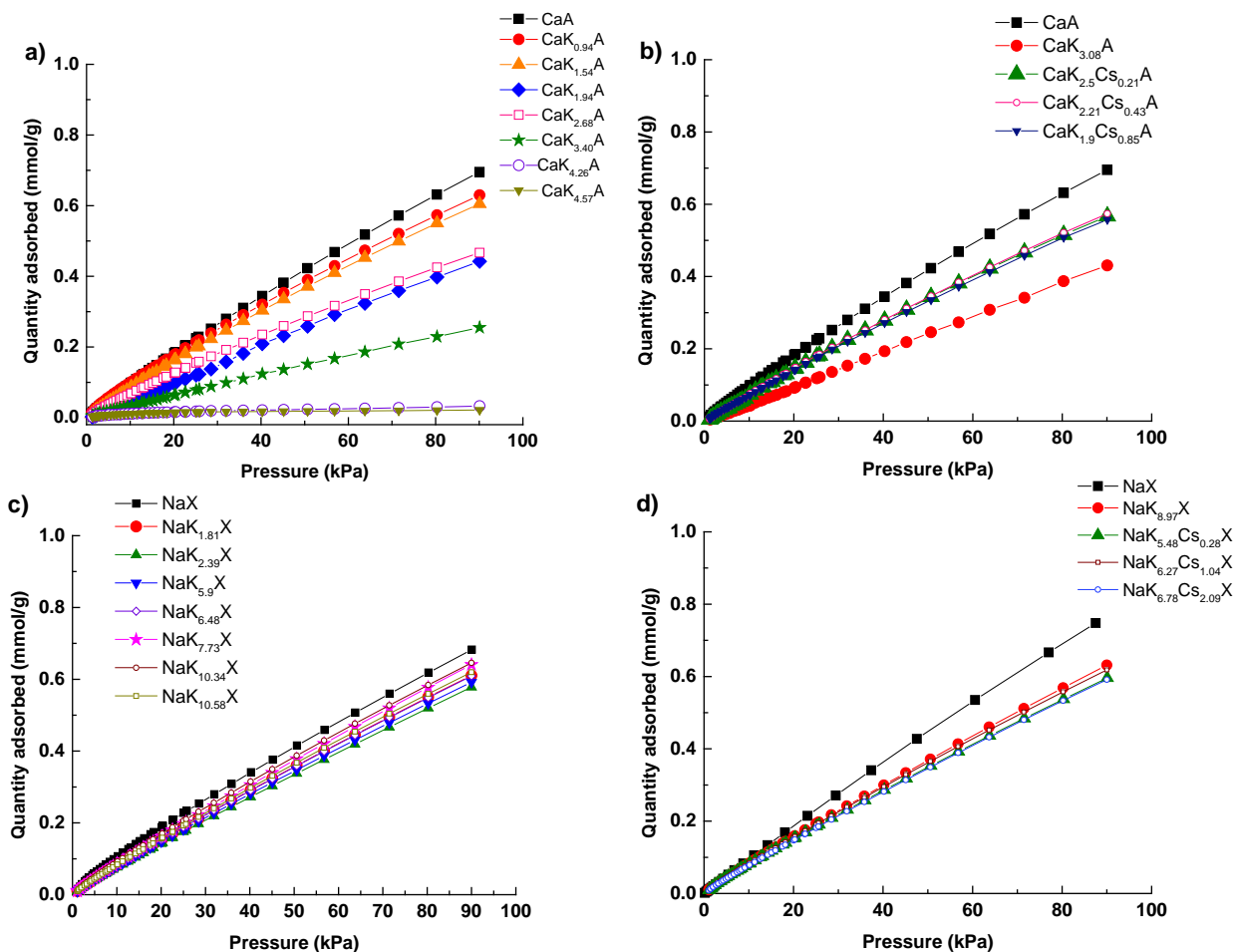


Fig. 4S: a) CH<sub>4</sub> uptake isotherms of CaA powder (as-received powder, whole optimization with K cations) b) CH<sub>4</sub> uptake isotherms of CaA powder (optimized with K cations followed by whole optimization with Cs cations) c) CH<sub>4</sub> uptake isotherms of NaX powder (as-received powder, whole optimization with K cations) d) CH<sub>4</sub> uptake isotherms of NaX powder (optimized with K cations followed by whole optimization with Cs cations).

The CO<sub>2</sub> and CH<sub>4</sub> maximum adsorption  $q_m$ , Langmuir constant  $b$  parameter and Henry's constant are obtained from the adsorption isotherm at 298K and 100 kPa fitted by the Langmuir model for zeolite NaX, CaA and its ion exchanged derivatives for both granules and powders and is represented in Table 4S.

## S5: Langmuir parameters and Henry's constant

Table 4S: Langmuir parameters and Henry's constant for the powders and granules as well as their optimum ion exchange derivative for both CaA and NaX zeolites.

Powder	CO <sub>2</sub>			CH <sub>4</sub>		
	q <sub>m</sub> (mmol/g)	b (1/kPa)	K <sub>H</sub>	q <sub>m</sub> (mmol/g)	b (1/kPa)	K <sub>H</sub>
NaX	6.07	0.2306	1.4	1.12	0.0107	0.012
NaK <sub>5.88</sub> X	5.47	0.2473	1.35	1.064	0.0068	0.0072
NaK <sub>5.97</sub> CS <sub>0.10</sub> X	5.08	0.2464	1.25	1.1036	0.0068	0.0075
CaA	4.42	0.4714	2.08	1.86	0.0056	0.0104
CaK <sub>3.08</sub> A	2.88	0.2554	0.735	1.276	0.0032	0.0041
CaK <sub>2.5</sub> CS <sub>0.79</sub> A	6.46	0.0248	0.16021	0.019	0.1655	0.0031
<b>Granules</b>						
NaX	5.19	0.4105	2.130	4.60	0.0019	0.0087
NaK <sub>3.9</sub> X	5.03	0.2063	1.038	3.49	0.0017	0.006
NaK <sub>4.5</sub> CS <sub>0.3</sub> X	4.84	0.2121	1.026	3.00	0.0020	0.006
CaA	4.43	0.6265	2.775	3.142	0.0056	0.018
CaK <sub>2.6</sub> A	4.425	0.4864	2.152	2.154	0.005	0.011
CaK <sub>2.5</sub> CS <sub>0.2</sub> A	4.4237	0.5233	2.315	2.541	0.00408	0.0103

## S6: Zeolite X and A structure

There are 88 cations in the unit cell of zeolite X, and these charge-balancing cations have different locations within the framework, as it can be seen in Fig. 5Sa). These sites are: Site I- near the center of the double six-member ring, site I' is within the sodalite cavity nearly symmetrically positioned with the site I. Site II can be found at the center of the single six-member ring or into the supercage, while site II' is inside the sodalite cavity around the single six-member ring. Site III and III' are found in the supercage, from which site III' is on the inner surface of the supercage<sup>1</sup>. In order to exchange the cations present in the super cage, the ion has to diffuse through the 12 ring pore opening (free diameter around 7-9 Å), while to exchange the ions, in the small cages they need to diffuse through the 6 ring opening (free diameter around 2.5 Å). Fig. 5Sb) represents the framework structure of zeolite A with its cationic sites. In zeolite A, eight sodalite cages (β cages) are located at the corners connected together via four-membered oxygen rings. This arrangement gives rise to α cage with a free diameter of about 11.4 Å. In the zeolite A, the cations are located at the center of the six rings on the threefold axis (site I), in the eight ring windows (site II) and at the close proximity of the four ring (site III)<sup>2</sup>.

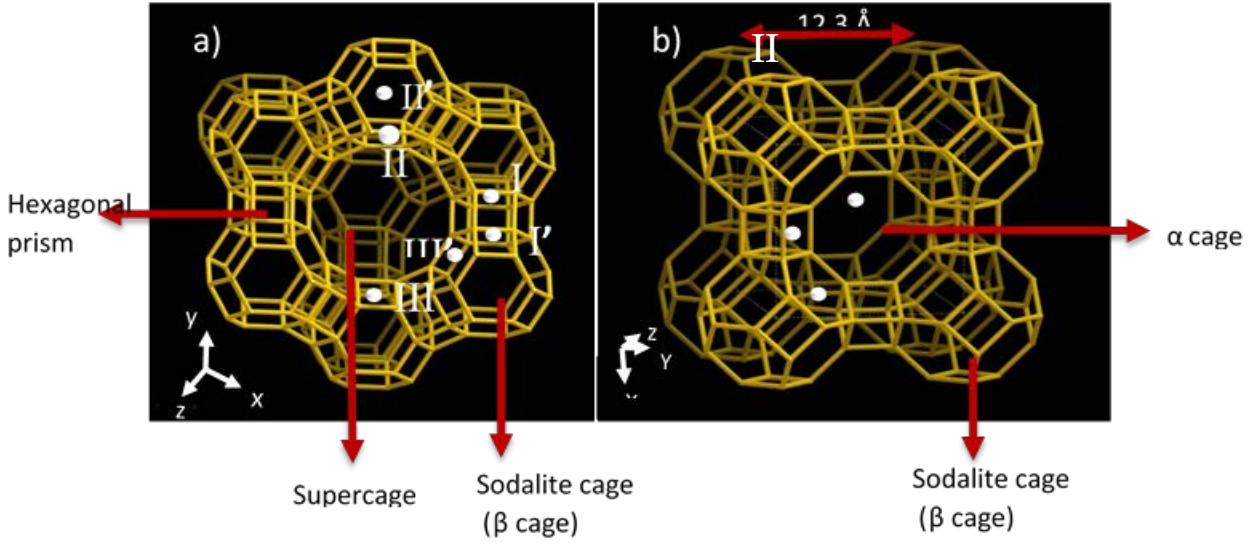


Fig. 5S: Schematic representation of a) zeolite X; b) zeolite A with their cationic sites<sup>3</sup>

## References

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