Adsorption of Carbon monoxide, Methane and Nitrogen on Alkaline Earth Metal Ion Exchanged Zeolite-X: Structure, Cation Position and Adsorption Relationship

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Supporting information

Structure of Zeolite-X

The Si and Al atoms occupy the vertices of these polyhedra and bridged with oxygen atoms. Si and Al atoms alternate at the tetrahedral intersections, except for Si atoms which substitutes about 8% of Al positions. The sodalite cavity or β-cages are considered as principal building unit of zeolite-X. These β-cages are connected through six member rings by bridging oxygen to give double six member rings (D6R, hexagonal prisms) along with super cage, accessible in three dimensions through 12-ring windows. Single six-member rings (S6R) are shared by sodalite and super cage, and may be viewed as the entrances to the sodalite units. A single unit cell of zeolite-X consist of 8 sodalite cages, 8 super cages, 16 D6R, 16 12-rings, and 32 S6R. The charge balancing extra-framework sodium and alkaline earth metal cations of the aluminosilicate framework are found at different sites as shown in Figure 3. The Site I is located at the centre of the D6R, Site I′ is in the sodalite cavity on the opposite side of one of the D6R, Site I, II′ are inside the sodalite cavity near a S6R, Site II at the centre of the S6R or displaced from this point into a super cage, Site III is in the super cage on a twofold axis opposite a 4-ring between two 12-rings, and Site III′ somewhat or substantially off site III (off the twofold axis) on the inner surface of the super cage.

In the crystal structure of Zeolite-NaX, 30, 32 and 26 Na^+ ions are present at site I', II and III' respectively. In a unit cell of zeolite-X there are 192 possible cation sites for 88 cations. During high temperature activation of zeolite the ions migrate to the sites of higher coordination and lower energy. The movement of cations depend on the activation condition (temperature, vacuum and duration of activation), and nature of cations. The sites with minimum energies are hidden and are not exposed to super cage. Therefore, only 40-50% of cations are found at

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exposed sites. The cations in the β-cages and the D6R (i.e. at sites I, I' and II') are sterically hidden and not available for adsorption therefore only cations present in super cage (site II, III, and III') are available for interaction with of CO, CH_4 and N_2. The electric field around the cations is partially shielded by the framework oxygen atoms. However, the dispersion forces acting on the molecules will be high as the molecule also interacts with oxygen atoms of the zeolite framework.

Adsorption Interactions and Heat of Adsorption

The total energy of adsorption for the alkaline earth metal ion exchanged zeolite samples and CO, CH_4, and N_2 gas molecules is the sum of the molecule-molecule and molecule-zeolite interaction potential (equation 1 and 2).

$$\phi = \phi_{adsorbate-adsorbate} + \phi_{adsorbate-adsorbent} \qquad (1)$$

$$\phi = \phi_D + \phi_R + \phi_{Ind} + \phi_{F\mu} + \phi_{FQ} \qquad (2)$$

Where, ϕ_D = Dispersion energy, ϕ_R = Close-range repulsion energy, ϕ_{Ind} = Induction energy (interaction between an electric field and an electric dipole), $\phi_{F\mu}$ = Interaction between an electric field (F) and permanent dipole moment (μ), ϕ_{FQ} = Interaction between field gradient (F) and quadrupole moment (Q).

The heat of adsorption can be given by equation 3.

$$\Delta H^\circ = \phi - RT + F(T) \qquad (3)$$

Where,

ΔH° = Isosteric heat of adsorption, ϕ = Adsorbate adsorbent interaction potential, $F(T)$ arises due to vibration and translational energies of the adsorbate molecule.

At ambient temperature $\Delta H^\circ = \phi$

ϕ_D and ϕ_R are non-specific (non-elecrostatic) interaction and occurs between CO, CH$_4$, and N$_2$ gas molecules and adsorbent surface, while ϕ_{Ind}, $\phi_{F\mu}$ and ϕ_{FQ} are specific (electrostatic) interactions and arises between ionic framework, alkaline earth metal cations and gas molecules. Since zeolites are ionic solids during adsorption electrostatic interactions ($\phi_{F\mu}$, ϕ_{Ind} and ϕ_{FQ}) dominates.

For CO adsorption: CO has high quadrupole moment with polarizability and dipole moment hence heat of adsorption should be high and will be given by equation 4.

$$\phi_{carbon\ monoxide} = \phi_D + \phi_R + \phi_{Ind} + \phi_{F\mu} + \phi_{FQ} \qquad (4)$$

For N$_2$ adsorption: N$_2$ has zero dipole moment and high quadrupole moment so should have zero field dipole interaction ($\phi_{F\mu}$) and high field quadrupole interaction (ϕ_{FQ}). The total heat of adsorption for nitrogen will be given by equation 5.

$$\phi_{nitrogen} = \phi_D + \phi_R + \phi_{Ind} + \phi_{FQ} \qquad (5)$$

For CH$_4$ adsorption: CH$_4$ has zero quadrupole moment and thus should have zero field quadrupole interaction ϕ_{FQ}. However, CH$_4$ has polarizability higher than N$_2$ and so induced dipole interaction ϕ_{Ind} will contribute more towards total heat of adsorption. The heat of adsorption for CH$_4$ will be given by equation 6.

$$\phi_{methane} = \phi_D + \phi_R + \phi_{Ind} \qquad (6)$$

For electrostatic interactions the following dependence holds

Field induced dipole, $(\phi_{Ind}) \propto q^2(\alpha/r^4)$ (7)

Field dipole, $(\phi_{F\mu}) \propto q(\mu/r^2)$

$\qquad (8)$

Field Gradient-Quadrupole, $(\phi_{FQ}) \propto q(Q/r^3)$

$\qquad (9)$

Where, r (equilibrium distance) = r_1 (ionic radius) + r_2 (adsorbate atom or molecule) q = electronic charge of ion, α = polarizability, F = electric field, μ = permanent dipole moment and Q = quadrupole moment.

Table S1. Molecular properties of CO, CH_4 and N_2[1-3]

Property	CO	CH_4	N_2
Molecular Weight, (amu)	28.01	16.04	28.01
Boiling point, (K)	81.5	109.0	77.2
Molecular Configuration	Linear	Tetrahedral	Linear
Pauling Molecular Dimensions, (Å)	3.7×4.2	4.2	3.0×4.1
Kinetic Diameter, (Å)	3.69	3.82	3.64
Polarizability, ($\times 10^{-25}$, cm^3)	19.5	26.0	17.6
Dipole Moment, ($\times 10^{18}$, esu cm)	0.112	0.00	0.00
Quadrupole moment, ($\times 10^{-26}$, esu cm^2)	2.5	0.00	1.52

Table S2. Polarizability, ionic radie and polarizing power of different alkaline earth metal ions[1-3]

Alkaline earth metal atom/ion	Polarizability (α) 10^{-24} cm^3	Ionic radius of cation (pm)	Polarizing power of cation (q/r) $\times 10^{-10}$ C m^{-1}
Na$^+$	0.180	97	16.5
Mg^{2+}	0.072	66	48.5
Ca^{2+}	0.471	99	32.3
Sr^{2+}	0.863	112	28.6
Ba^{2+}	1.560	134	23.9
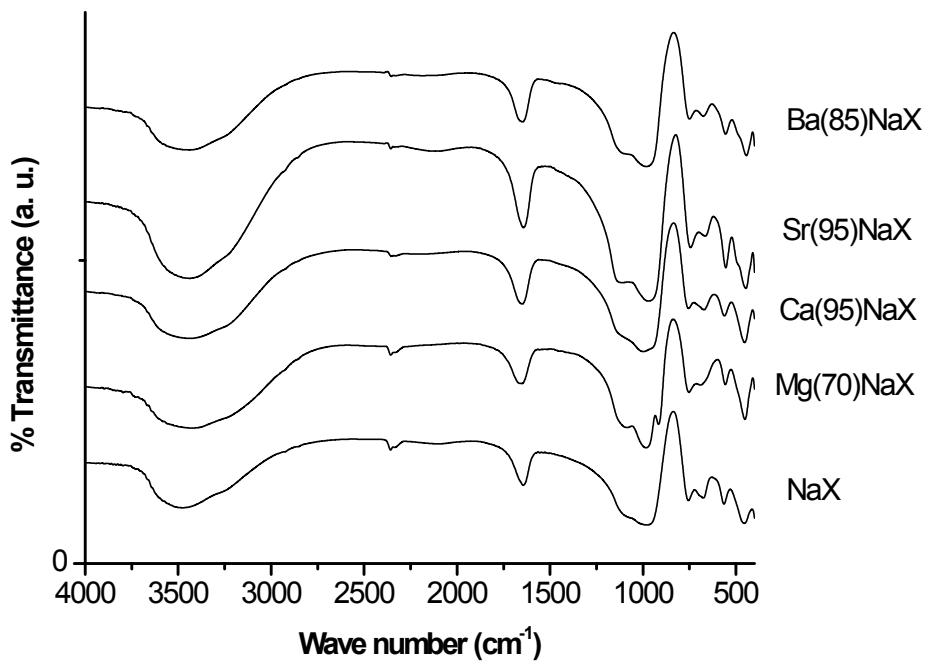
Fig. S1 FT-IR spectra of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ion exchanged zeolite-X.
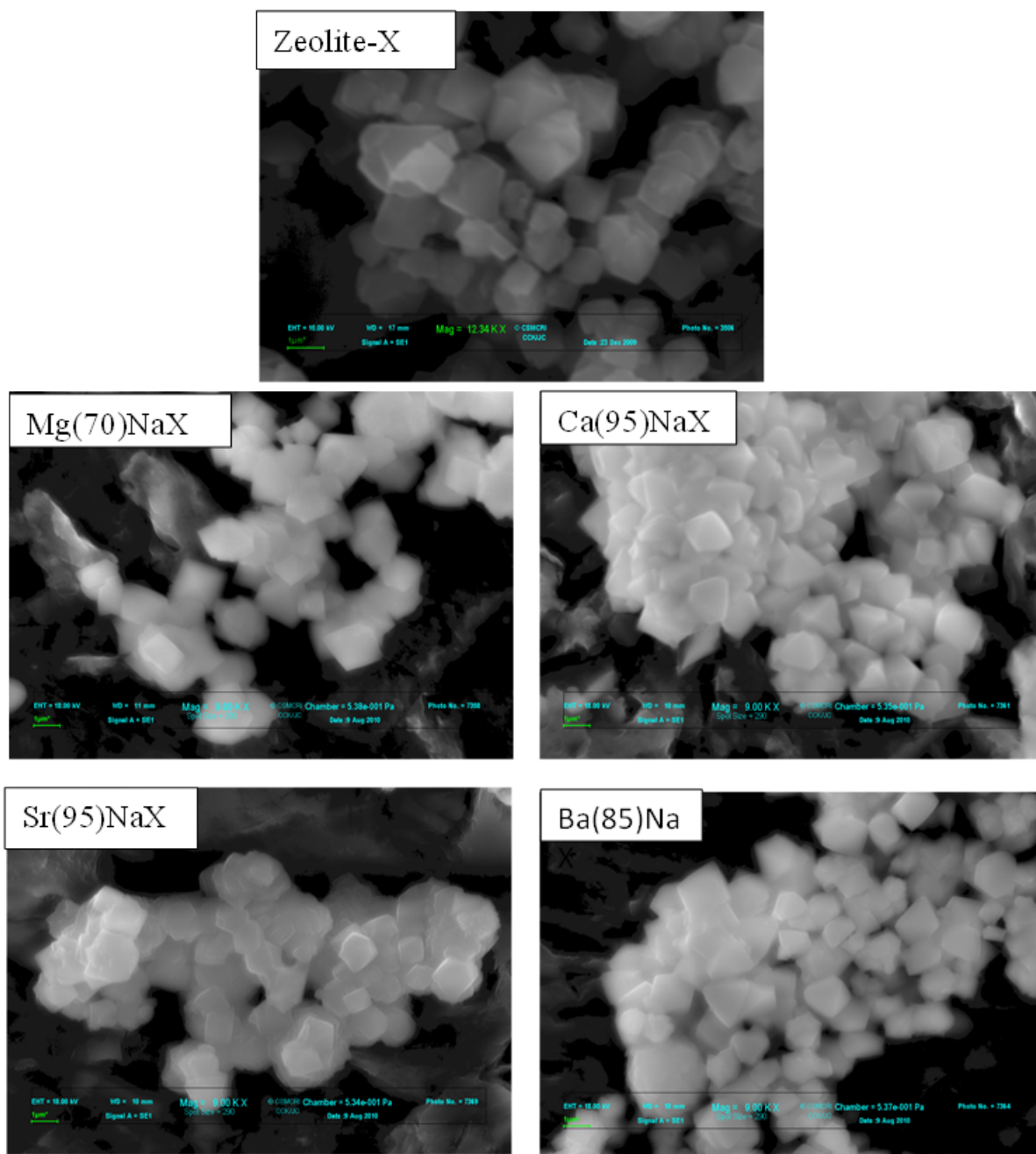
Fig. S2 SEM images of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ion exchanged zeolite-X.
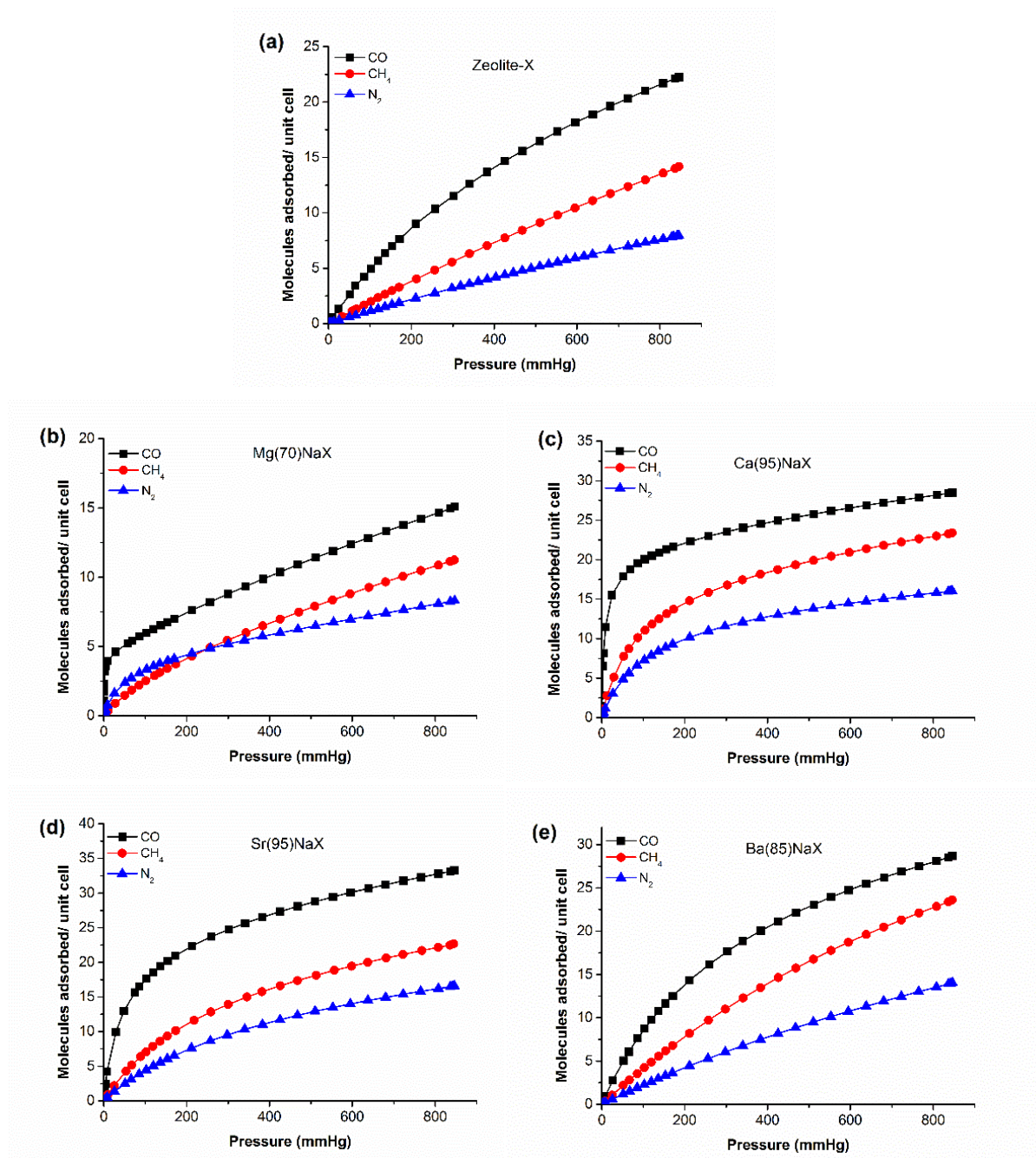
Fig. S3(a-e) Adsorption isotherms of CO, CH$_4$, and N$_2$ at 288 K and 760 mmHg pressure (a) Zeolite-X, (b) Mg(70)NaX, (c) Ca(95)NaX, (d) Sr(95)NaX and (e) Ba(85)NaX.

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Table and Figure Captions:

Table S1. Molecular properties of CO, CH$_4$ and N$_2$[1-3]

Table S2. Polarizability, ionic radii and polarizing power of different alkaline earth metal ions[1]

Fig. S1 FT-IR spectra of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ion exchanged zeolite-X.

Fig. S2 SEM images of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ion exchanged zeolite-X.

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