

Confirmation of the Nanopore Inner-Sphere Enhancement (NISE) Theory Using Flow Calorimetry and EPR

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Introduction

Recent research into the adsorption of cations on zeolite minerals shows that nanopore channels ≤ 0.5 nm can enhance the adsorption of ions, especially weakly hydrated ones.^{1,2} This occurs due to the removal of hydrating water molecules inside the small nanopore channel. A new adsorption theory, called the nanopore inner-sphere enhancement (NISE) theory explains this unusual adsorption mechanism. The NISE theory has been confirmed for Na adsorption on various zeolites using NMR spectroscopy.³

NISE Theory: The ability of an ion to adsorb on an adsorption site located inside a nanopore channel will significantly increase if the ion's ability to dehydrate is enhanced by the physical environment of the adsorption site.

Monovalent ions will generally adsorb weakly due to the weak electrostatic attraction to the adsorption sites. The NISE theory predicts that monovalent ions will adsorb strongly if the adsorption site is located inside nanopore channels with channel dimensions small enough to weaken the ion's ability to stay hydrated. The hydration energies of monovalent ions are generally already quite weak to begin with.

Divalent ions generally adsorb strongly on due to their strong electrostatic attraction. The nanopore channels will not easily stabilize the dehydrated divalent cation unless the channel dimensions are very small. This is because the hydration energies of divalent ions are generally quite strong. In very small nanopore channels, the divalent ions will dehydrate and their adsorption strength will increase significantly.

Accordingly, the NISE theory explains why the adsorption of monovalent cations outperforms the adsorption of divalent cations on adsorption sites located in medium-sized nanopore channels.

Objectives:

- 1) Monitor the heat of reaction of Na-Ca ion exchange reactions, and
- 2) Confirm the predictions made by the NISE theory concerning inner-sphere and outer-sphere adsorption mechanisms by divalent cations as a function of pore channel dimensions.

Citations:

- 1: Schulthess, C.P., R.W. Taylor, and D.R. Ferreira. 2011. The nanopore inner sphere enhancement effect on cation adsorption: Sodium and nickel. *Soil Sci. Soc. Am. J.* 75:378-388.
- 2: Ferreira, D.R., and C.P. Schulthess. 2011. The nanopore inner sphere enhancement effect on cation adsorption: Sodium, potassium, and calcium. *Soil Sci. Soc. Am. J.* 75:389-396.
- 3: Ferreira, D.R., C.P. Schulthess, and M.V. Giotto. 2012. An investigation of strong sodium retention mechanisms in nanopore environments using nuclear magnetic resonance spectroscopy. *Environ. Sci. Technol.* 46:300-306.



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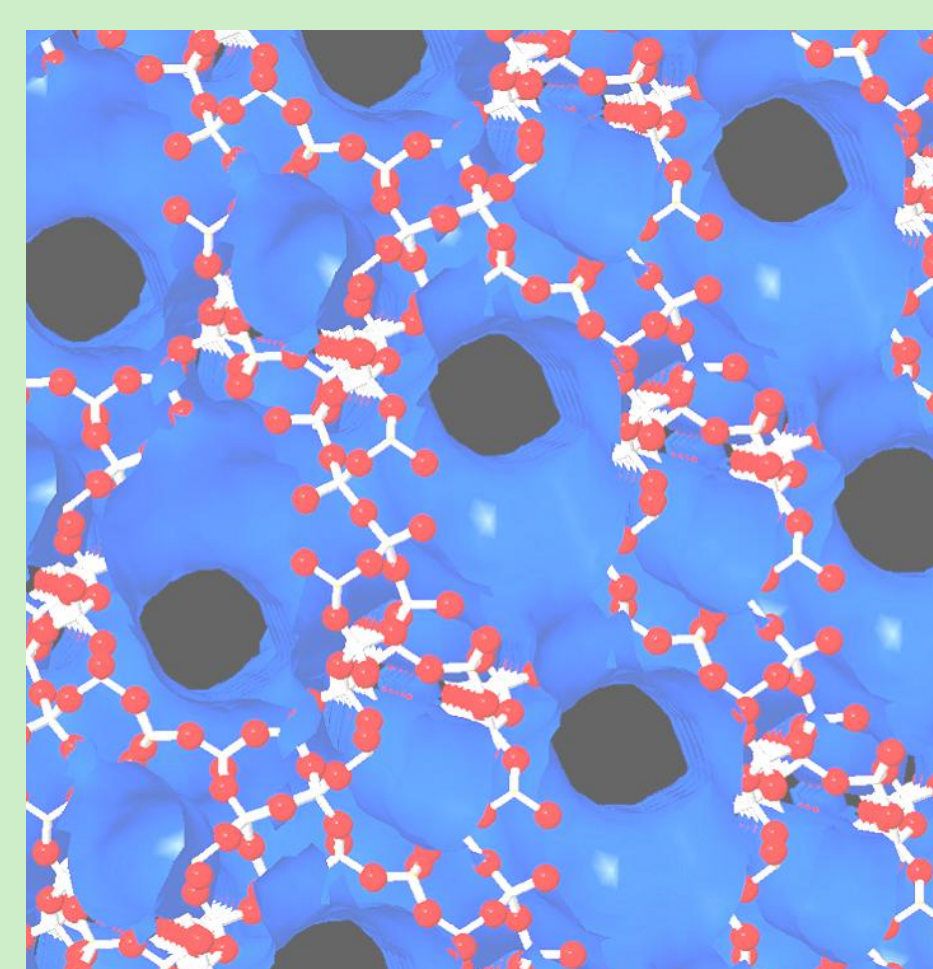
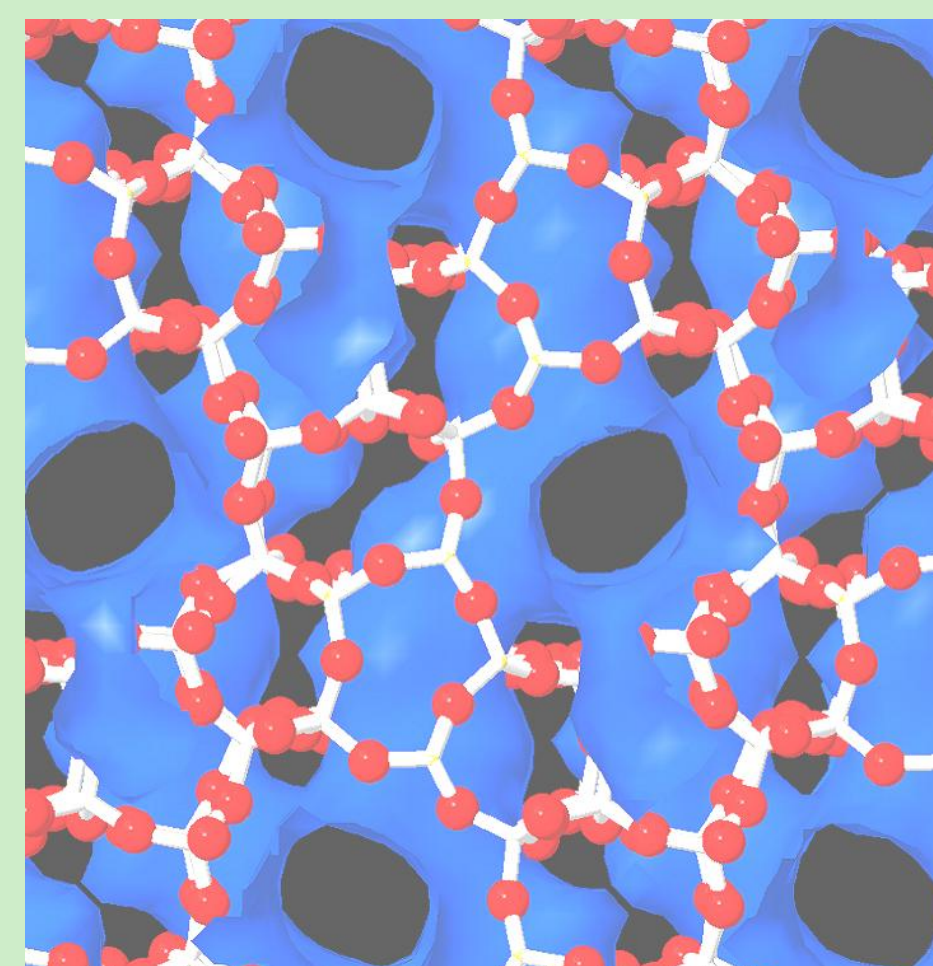
Materials & Methods

Zeolite Y (FAU)

Pore dimensions:
0.74 nm x 0.74 nm

Surface area: 700 m² g⁻¹

SiO₂:Al₂O₃ Ratio: 80:1

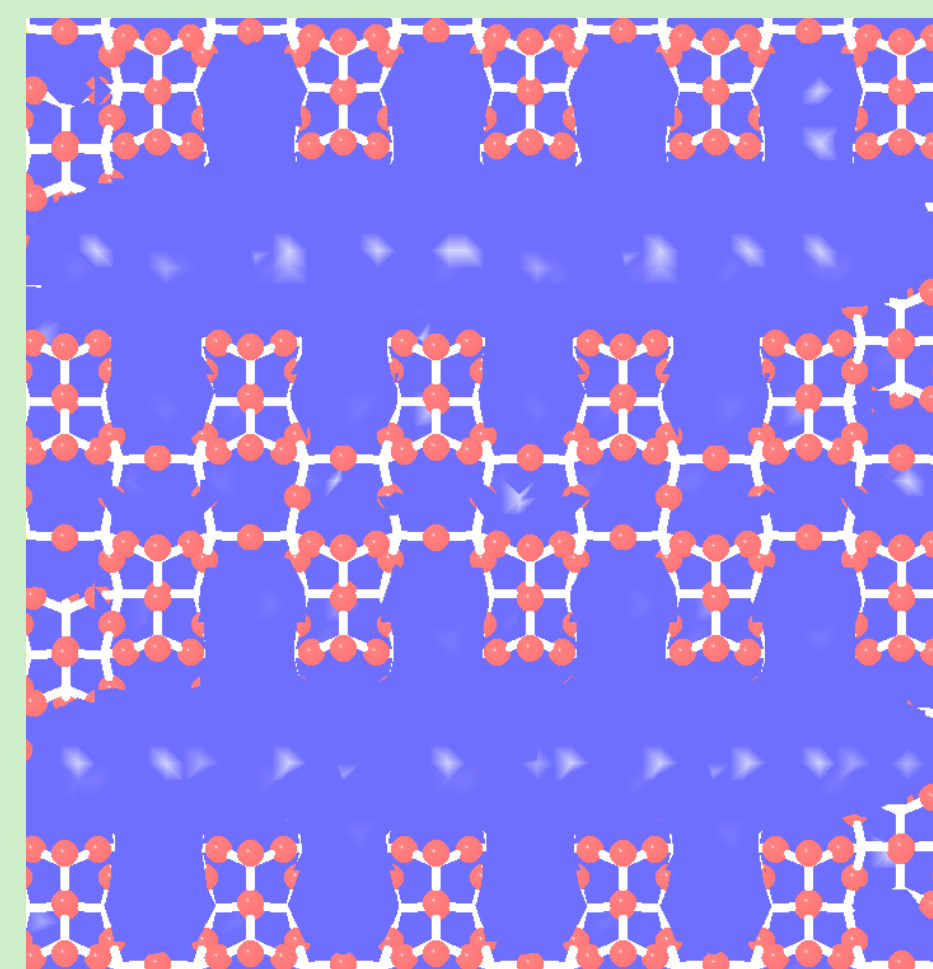


ZSM-5 (MFI)

Pore dimensions:
0.51 nm x 0.55 nm
0.53 nm x 0.56 nm

Surface area: 425 m² g⁻¹

SiO₂:Al₂O₃ Ratio: 80:1

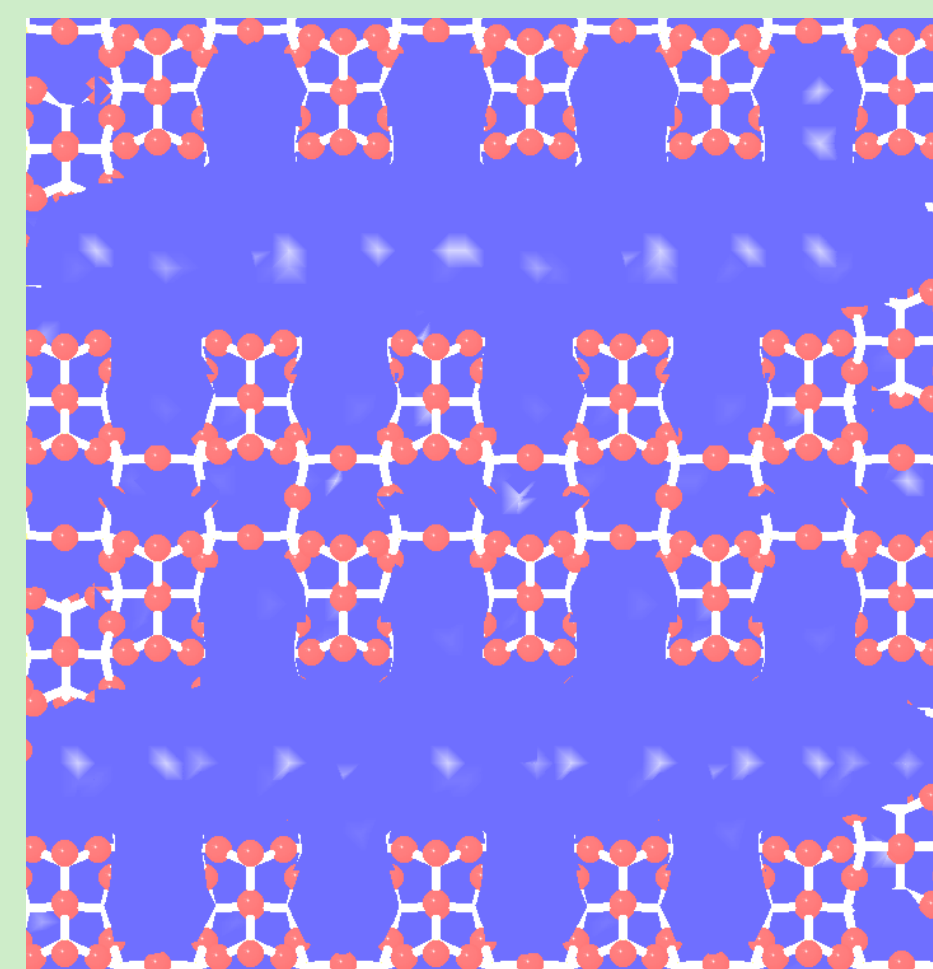


Mordenite (MOR)

Pore dimensions:
0.70 nm x 0.65 nm
0.26 nm x 0.57 nm

Surface area: 500 m² g⁻¹

SiO₂:Al₂O₃ Ratio: 90:1



NOTE: Zeolite nanopores are interconnected and ions can move freely between different pore channels.

Flow Adsorption Calorimetry (FAC) Study

Room temperature. Used 45 to 100 mg of solid saturated with 10 mM Ca(AcO)₂ at pH=5.35 carrier solution. Injection of 20 mM NaAcO at pH = 5.40.

Electron Paramagnetic Resonance (EPR) Study

Samples: Zeolite slurry with 20 mM Na plus 20 mM of Cu²⁺ at pH 2.5 or Mn²⁺ at pH 5.3. Solids concentration was 0.5 g, equilibrated overnight, centrifuged, liquid decanted and water washed once. The solids were analyzed on a Bruker 380E X-band EPR spectrometer at 9.779 GHz.

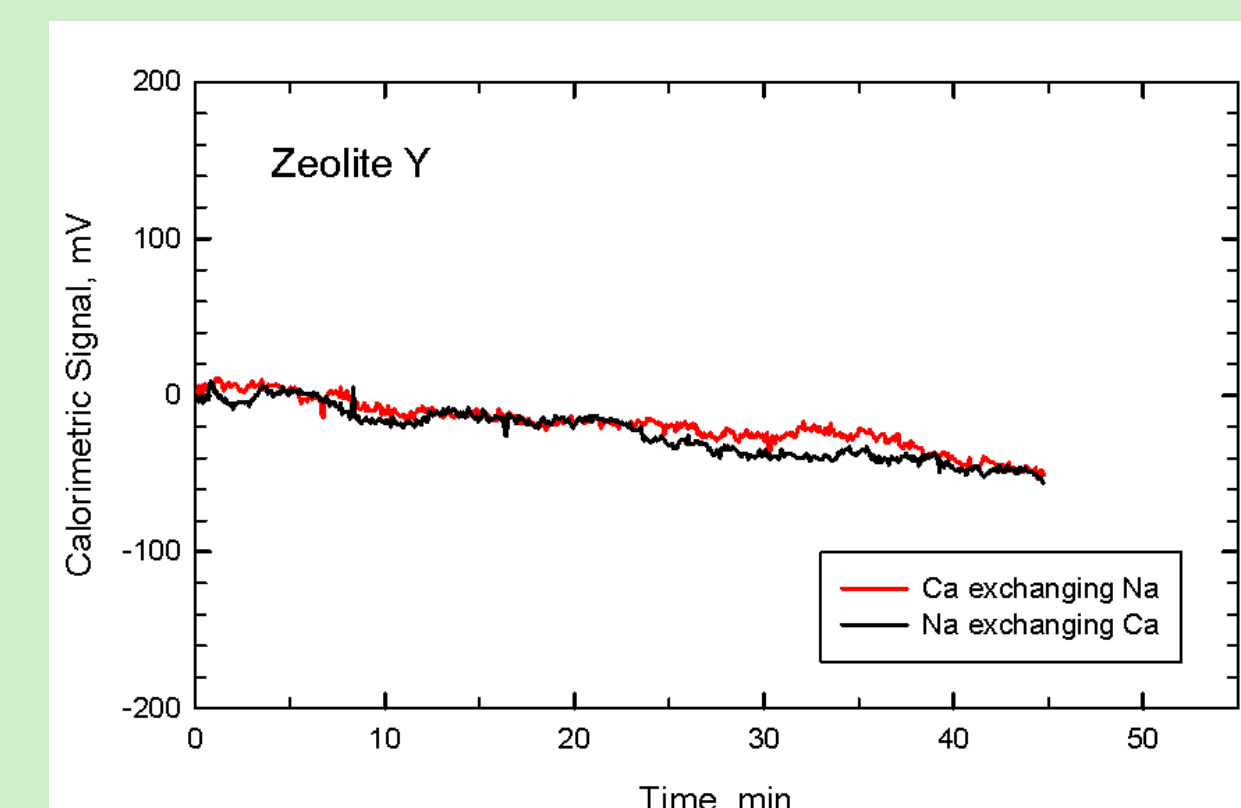
Flow Calorimetry

Heat of exchange of Ca by Na (red) followed by heat of exchange of Na by Ca (black) on various zeolites.

Zeolite Y

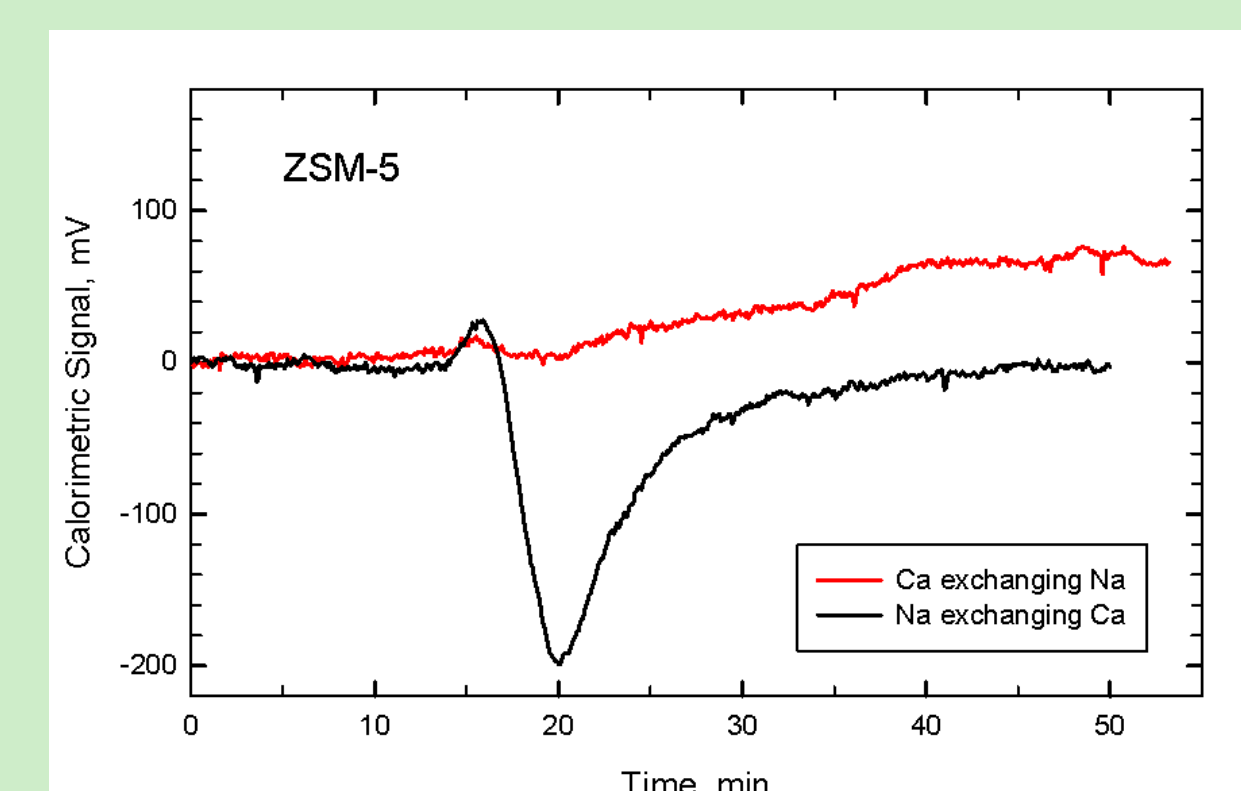
Weak reaction.
No heat detected.

Adsorption of Na & Ca is weak.



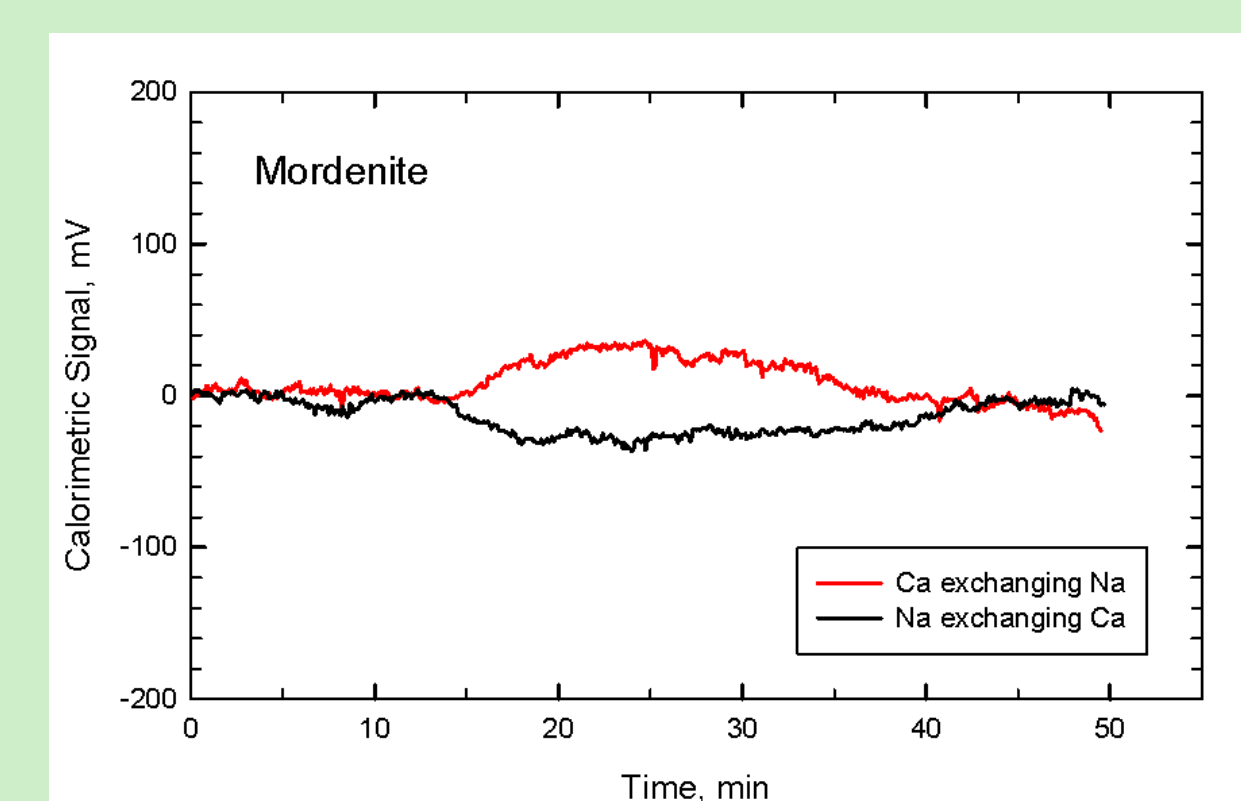
ZSM-5

Na ads. is strong & endothermic.
Ca ads. is weak & exothermic.
Notice exotherm at 15 min; this is a unique feature of this size range.



Mordenite

Strong Na & Ca adsorption.
Similar strength & pattern for both.



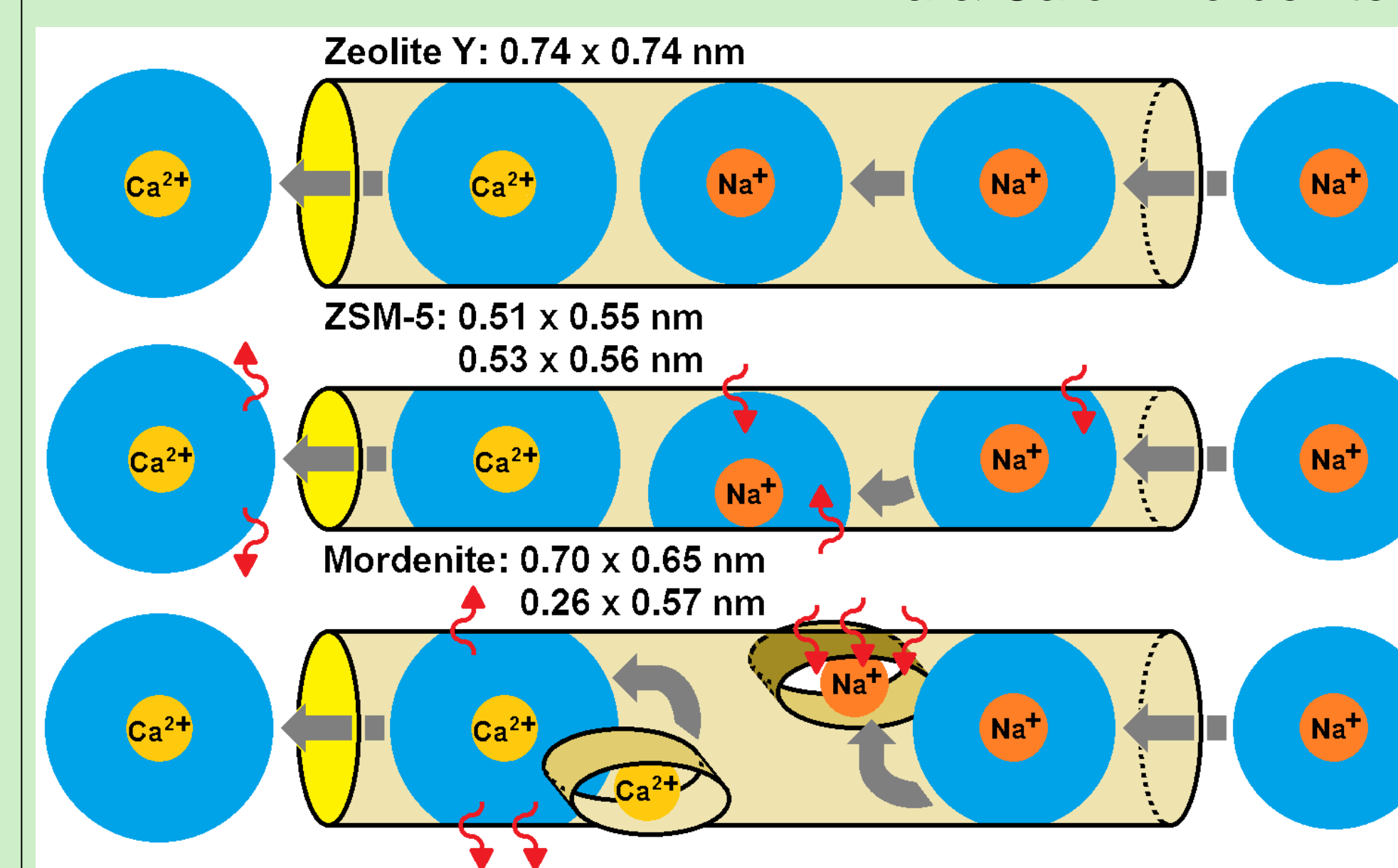
Explanation:

Adsorption and dehydration are endothermic.
Na/Ca exchange is entropy (ΔS) driven.

Desorption and hydration are exothermic.
Ca/Na exchange is enthalpy (ΔH) driven.

Outer sphere adsorption is weak: Na & Ca on zeolite Y
Ca on ZSM-5

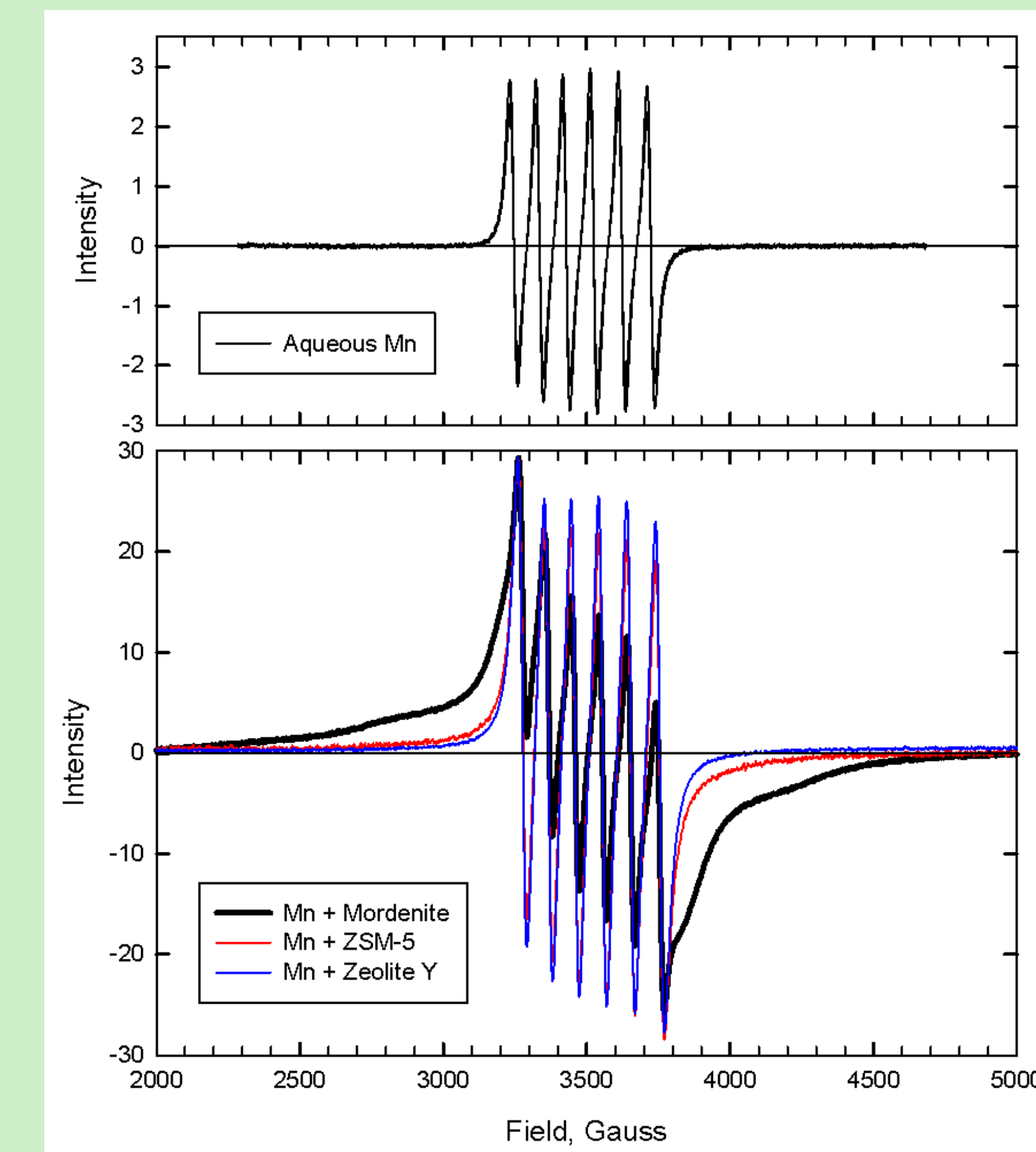
Inner sphere adsorption is strong: Na on ZSM-5
Na & Ca on mordenite



EPR

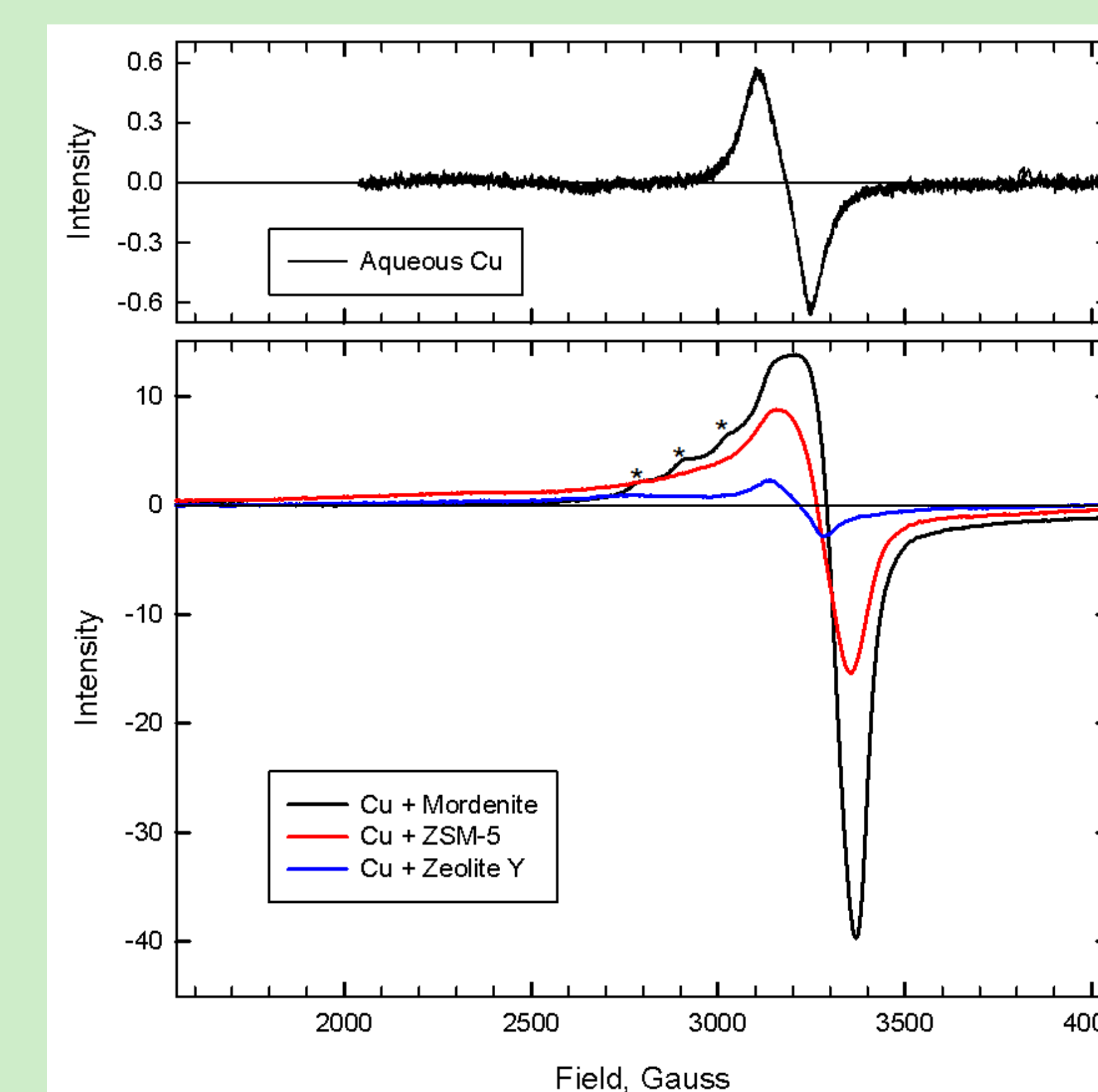
EPR spectra of Mn on zeolite Y and ZSM-5 are similar to spectra of aqueous Mn. This indicates adsorption is outer sphere.

Spectrum broadening of Mn on mordenite is asymmetrical. This indicates a strong surface inner sphere interaction.



EPR spectra of Cu on zeolite Y is similar to spectra of aqueous Cu. This indicates adsorption is outer sphere.

Spectrum broadening of Cu on ZSM-5 and mordenite are both asymmetrical. Hyperfine features are observed with mordenite. This indicates a strong surface inner sphere interaction on ZSM-5 and a very strong inner sphere interaction on mordenite.



Conclusions

- NISE theory is consistent with flow calorimetry for Na⁺-Ca²⁺ ion exchange and EPR spectra for Mn²⁺ and Cu²⁺.
- Flow calorimetry also captures a small exotherm that was reproduced on all ZSM-5 samples. This may be a signature heat exchange feature in medium sized pore channels for inner-sphere outer-sphere exchange.
- EPR spectra of Cu²⁺ on ZSM-5 suggests that the hydration energy of divalent cations is not a perfect predictor of the ease of dehydration of ions in constrained environments. Cu ions are subject to the Jahn-Teller effect, which causes a distortion in the coordination of its hydration sphere.