The NISE Effect on Sodium, Potassium and Cesium Adsorption onto ZSM-5

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Introduction

Recent research by Schulthess et al. (2010) and Ferreira and Schulthess (2010) has shown that Nanopore Inner-Sphere Enhancement (NISE) can significantly affect the adsorption strength of cations on zeolites with nanopore channels having a diameter of ≤0.5 nm. The number of adsorption sites is presumably controlled by Si/Al ratio in zeolite.

NISE occurs due to the removal of hydrating water molecules inside the small nanopore channel. This NISE effect can create cation selectivity scenarios in minerals. Sodium, potassium and cesium (Na^+, K^+, Cs^+) ions have different hydrated radius.

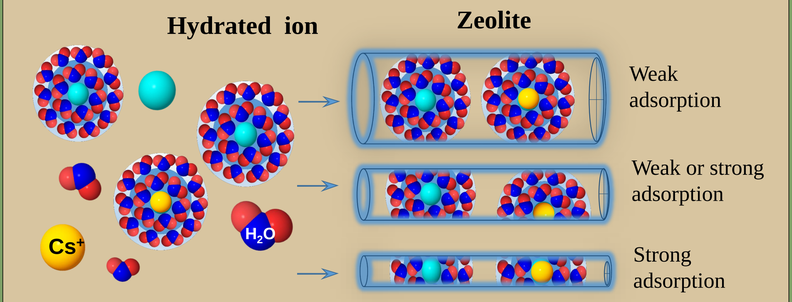


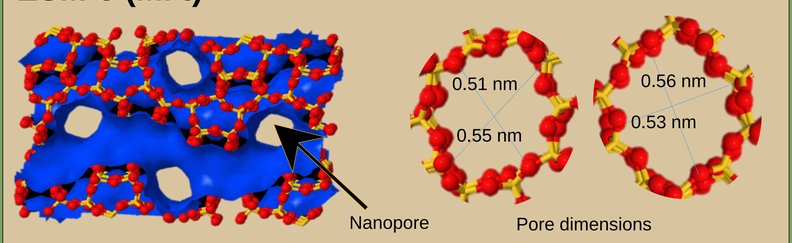
Figure 1. Illustration of the impact of hydration on inner-sphere verses outer-sphere retention

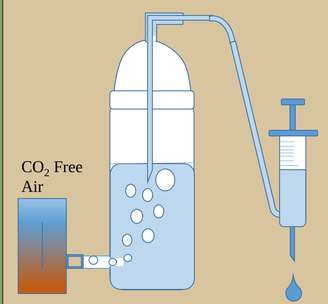
Objectives

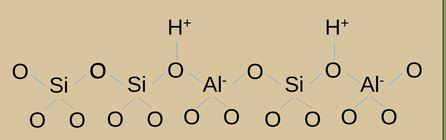
- Confirm that the number of adsorption sites is controlled by the Si/Al ratio on ZSM-5.
- Confirm that the adsorption strength correlates with published hydration energy values for sodium, potassium and cesium (Na^+, K^+, Cs^+) ions.

Materials & Methods

ZSM-5 (MFI)



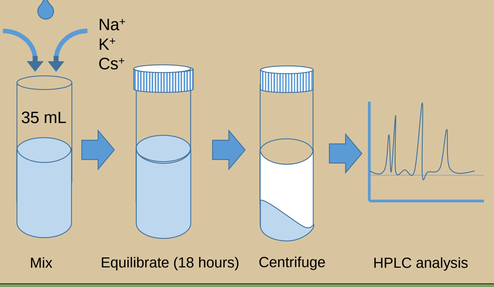




SiO_2:Al_2O_3 Ratio = 23:1 or 80:1
Surface area = 425 m^2 g^{-1}
Zeolite concentration = 13.1 g L^{-1}

Solution	Final conc.
NaOH	20 mM
KOH	20 mM
CsOH	20 mM

pH adjustment	
HCl	2.5 M



Results & Discussion

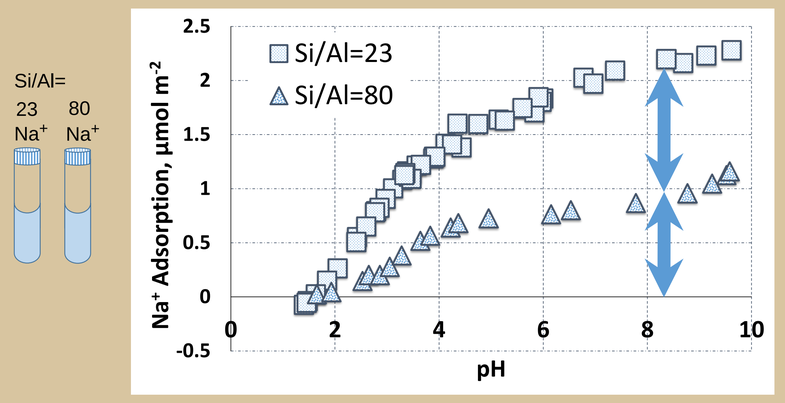


Figure 2. Adsorption of Na^+ onto ZSM-5. Initial [NaOH]=20 m*M*.

Si/Al=23 doubled the amount of Na^+ adsorbed onto ZSM-5

Magnification of Figure 3:

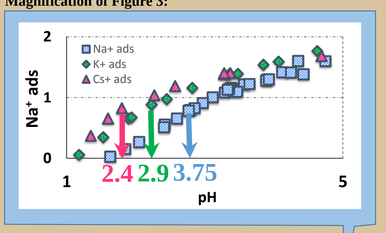


Table 1. Hydration enthalpies of ions and equilibrium constant (p*K*) edge. Δ*H* source: Smith, 1977.

Cations		ΔH° kJ mol-1	pK
Sodium	Na^+	-406	2.79
Potassium	K^+	-320	2.13
Cesium	Cs^+	-264	1.78

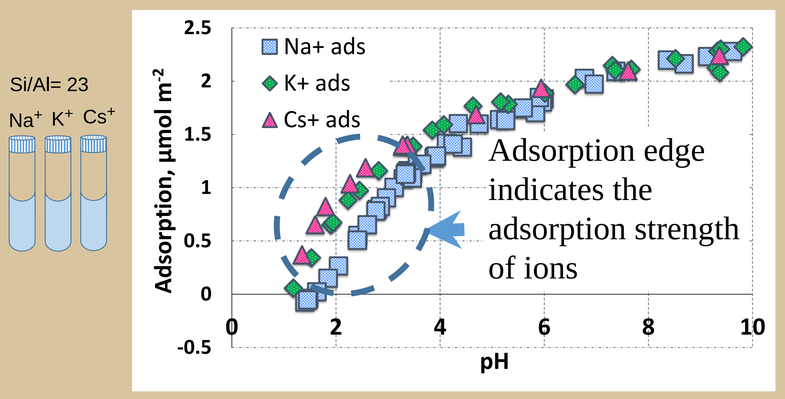


Figure 3. Adsorption of Na^+, K^+ or Cs^+ onto ZSM-5. Initial [NaOH]=[KOH]=[CsOH]=20 m*M*.

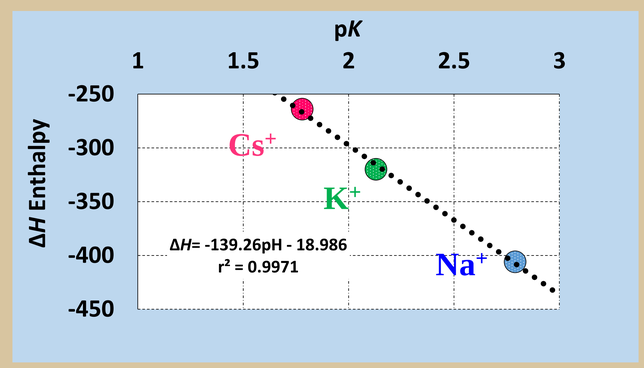


Figure 5. Correlation of hydration energy and equilibrium constant p*K* edge.

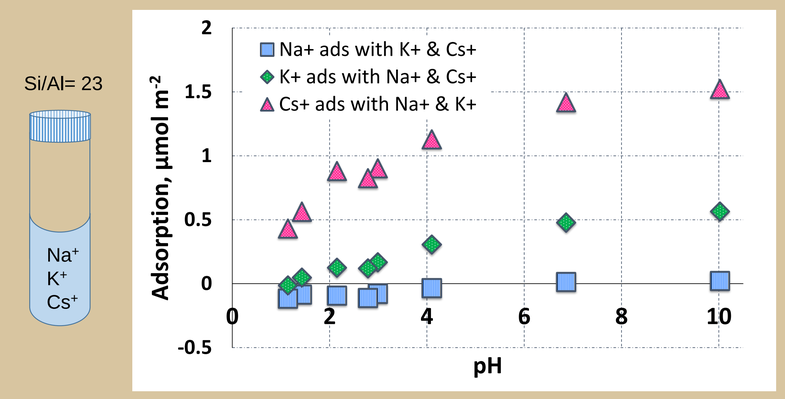
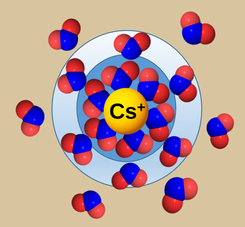
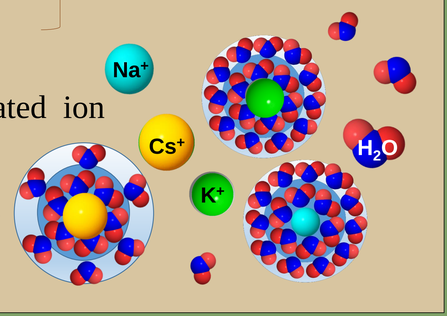


Figure 4. Competitive adsorption between Na^+, K^+ & Cs^+ onto ZSM-5. Initial [NaOH]=[KOH]=[CsOH]=20 m*M*.

Cesium absorbs strongly. Cs^+>K^+>Na^+



Large ionc radius.
Weak hydration.



Zeolite channel: ZSM-5

Conclusions

- Adsorption of Na^+ onto ZSM-5 with a Si/Al ratio=23 increased compared with the Si/Al=80. This indicates that the number of adsorption site is controlled by Al content. The function of hydration energy affects the adsorption strength of the cation as follows: Cs^+>K^+>Na^+.
- Cesium is a toxic element at elevated concentration. ZSM-5 has a potential to immobilize Cs and reduce the amount of Cs in the soil.

Citations

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.
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.
Smith, D.W. 1977. Ionic hydration enthalpies. J. Chem. Educ. 54:540-542.

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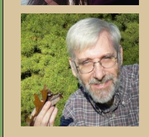

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