

Gas adsorption on zeolites: The role of multiple-cation sites



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Cation exchanged zeolites find practical usage in a number of technological processes which often rely on specific interactions between the zeolite and adsorbed gases; examples can be found in the fields of gas separation and purification (e.g. oxygen from air or CO from a variety of industrial feedstocks), atmosphere pollution control, heterogeneous catalysis, and gas storage and transport. Developments in these practical applications of zeolites can substantially benefit from improved knowledge on the interaction between adsorbed gas molecules and the zeolite adsorbing centres. Single (isolated) metal cations are usually considered to constitute such gas-adsorbing centres. However, recent studies [1-3] have shown that zeolites can also contain adsorbing centres formed by two or more metal cations. Interaction of adsorbed molecules with these multiple-cation sites can be stronger than interaction with single-cation sites; hence, the interest of studying multiple-cation sites. We report studies on CO adsorbed on Na⁺ and K⁺-exchanged ferrierite (FER), zeolite-A (LTA) and ZSM-5 (MFI); such studies included experimental determination of adsorption enthalpy and theoretical calculations using periodic DFT.

[1] E. Garrone et al., *J. Phys. Chem. B* **2006**, *110*, 22542-22550. C. O. Areán et al., *Phys. Chem. Chem. Phys.* **2007**, *9*, 1421-1436.

[2] C. O. Areán et al., *Phys. Chem. Chem. Phys.* **2007**, *9*, 4657-4661.

[3] C. O. Areán et al., *J. Phys. Chem. C*, DOI: 10.1021/jp7109934.

Adsorption thermodynamics:

Variable-temperature IR (VTIR) spectroscopy

$$S_{(s)} + M_{(g)} \rightleftharpoons S \cdot M_{(ads)} \quad \text{Adsorption equilibrium}$$

Coverage = θ , at T and p (equilibrium)

$$\theta = N_{(a)}/N_{(max)} = k(T)p/[1 + k(T)p] \quad \text{Langmuir}$$

$$k(T) = \exp(\Delta S^{\circ}/R) \exp(-\Delta H^{\circ}/RT) \quad \text{Van't Hoff}$$

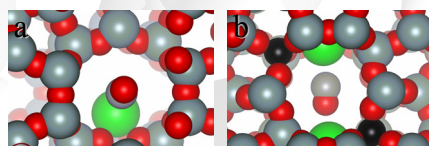
IR absorbance, A, proportional to θ

$$\theta/(1 - \theta) = p \exp(\Delta S^{\circ}/R) \exp(-\Delta H^{\circ}/RT)$$

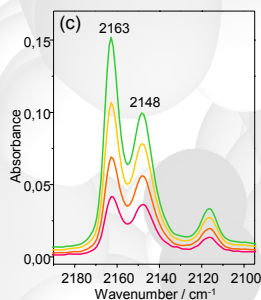
$$\ln \{\theta/[(1 - \theta)p]\} = (\Delta S^{\circ}/R) - (\Delta H^{\circ}/RT)$$

$$\ln \{A/[A_M - A]\} = (\Delta S^{\circ}/R) - (\Delta H^{\circ}/RT)$$

CO / M-FER (M = Na, K)

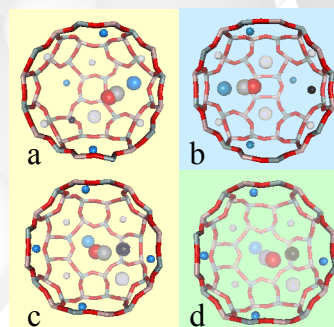


CO adsorbed on K-FER (Si:Al = 27.5:1): (a) Monocarbonyl on an isolated K⁺ site. (b) Bridged CO complex on a dual-cation site. O, Si, Al, K, and C depicted in red, black, green, and grey, respectively. (c) VTIR spectra. T = 176-223 K, p = 0.12-0.64 Torr (from top to bottom).

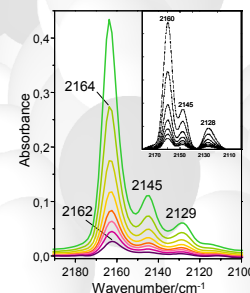


K-FER: Single sites, K⁺...CO, $\nu_{CO} = 2163$ (2164–2165) cm⁻¹
 $\Delta H^{\circ} = -25$ (-18.1 a -20.4) kJ mol⁻¹
 Dual sites, K⁺...CO...K⁺, $\nu_{CO} = 2148$ (2141–2157) cm⁻¹
 $\Delta H^{\circ} = (-20.9$ a -25.1) kJ mol⁻¹

CO / Na-A



Zeolite Na-A (LTA): CO on dual-cation sites (a), and on multiple-cation sites (b, c, d).



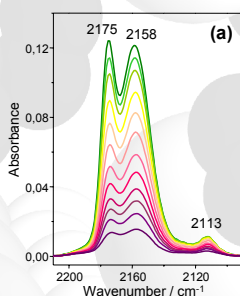
VTIR spectra. T = 222-274 K, p = 1.7-3.1 Torr (from top to bottom). Inset (white) shows the corresponding simulated spectra.

Na-A: 2164 (2160) cm⁻¹, $\Delta H^{\circ} = -28.4$ (-28.5 a -30.2) kJ mol⁻¹

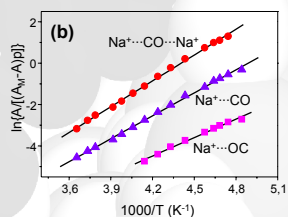
2145 (2148) cm⁻¹, $\Delta H^{\circ} = -28.1$ (-32.5) kJ mol⁻¹

2129 (2128) cm⁻¹, $\Delta H^{\circ} = -24.6$ (-31.3) kJ mol⁻¹

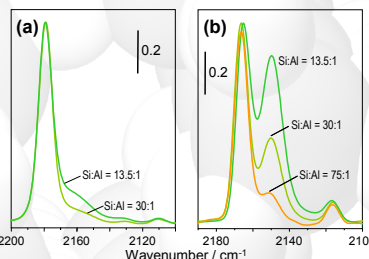
CO / M-ZSM-5 (M = Na, K)



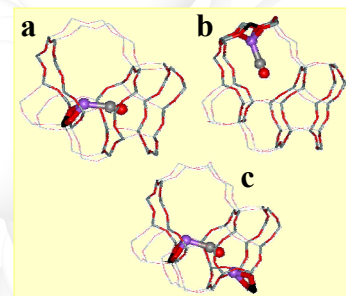
CO adsorbed on Na-FER (Si:Al=8:1): (a) VTIR spectra. T = 207-274 K, p = 0.14-1.01 Torr (from top to bottom). (b) Van't Hoff plot for spectra on (a).



Na-FER: Single sites, Na⁺...CO, $\nu_{CO} = 2175$ (2174–2178) cm⁻¹
 $\Delta H^{\circ} = -30.5$ (-25.3 a -29.4) kJ mol⁻¹
 Dual sites, Na⁺...CO...Na⁺, $\nu_{CO} = 2158$ (2138–2167) cm⁻¹
 $\Delta H^{\circ} = -34.6$ (-32.8 a -35.4) kJ mol⁻¹



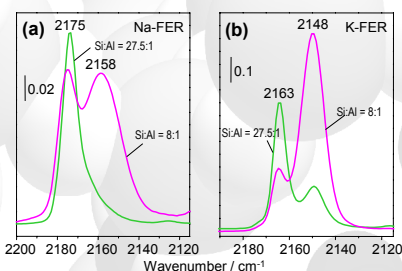
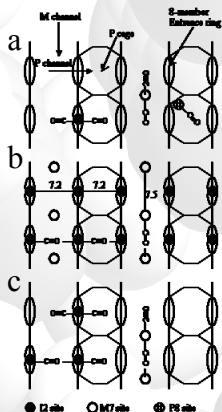
FTIR spectra of CO adsorbed (at 77K) on (a) Na-ZSM-5 and (b) K-ZSM-5 having different Si:Al ratios.



Zeolite Na-ZSM-5: CO on single-cation sites (a), and on dual-cation sites (b).

Na-ZSM-5: Single sites, $\nu_{CO} = 2179$ (2177–2184) cm⁻¹
 $\Delta H^{\circ} = -33.5$ (-28.9 a -36.6) kJ mol⁻¹
 Dual sites, $\nu_{CO} = 2155$ (2152–2162) cm⁻¹
 $\Delta H^{\circ} = -35.8$ (-35.2 a -36.2) kJ mol⁻¹

K-ZSM-5: Single sites, $\nu_{CO} = 2164$ cm⁻¹
 $\Delta H^{\circ} = -28.2$ kJ mol⁻¹
 Dual sites, $\nu_{CO} = 2150$ cm⁻¹
 $\Delta H^{\circ} = -31.6$ kJ mol⁻¹



FTIR spectra of CO adsorbed (at 77K) on (a) Na-FER and (b) K-FER having different Si:Al ratios.

Sketch of possible CO adsorption complexes in K-FER for: (a) high-silica, (b) low-silica, and (c) intermediate Si:Al ratio cases.

The above studies, strongly suggest that multiple-cation sites are likely to be present in many zeolites, and their relative proportion is expected to increase when Si:Al ratio decreases. Adsorbed molecules can show an interaction energy with multiple-cation sites significantly different from that on single sites, which would affect practical uses of zeolites in processes involving gas adsorption.