Site Selectivity of Thallium in Ion Exchange in Zeolite A

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Summary The site selectivity of Tl^+ in ion exchange of Linde 4A is the same as that of K^+ and different from that of Ag^+; Tl^{ex}-A is thermally more stable than Linde 3A.

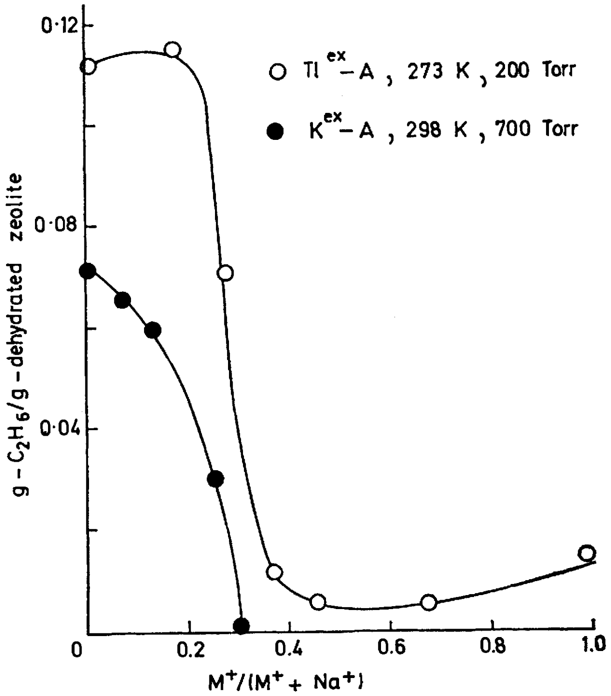
Breck[1] and Barrer[2] report that Na^+ in zeolite A exchanges easily with Tl^+. The crystal structure[3] of $Tl^{ex}_{1\cdot 00}$-A shows that 8 Tl^+ ions occupy site I (6-oxygen ring site) and 4 Tl^+ ions occupy site II (8-oxygen ring), although it is not known which site Tl^+ occupies first.

(Tl^{ex}, Na)-A was prepared from Linde 4A (Na-A). All the samples had good crystallinity. The Figure shows isobaric adsorption curves of ethane on (Tl^{ex}, Na)-A and (K^{ex}, Na)-A[1] as a function of the degree of exchange. Ethane adsorption fall drastically at an exchange level of *ca.* 30% (4/12) on Tl^{ex}-A. This indicates strongly that Tl^+ first enters site II, because the curve is the same as that of K^{ex}-A and K^+ is known to prefer site II to site I.[1] The previous investigation[4] demonstrated that Ag^+ prefers site I to site II. Although the reason for this site selectivity of the cation is not clear, it may be related to the size of exchangeable cations.

Table. Results of DTA

Sample	Endothermal peaks (due to dehydration) T/K	Exothermal peak (due to loss of structure) T/K
Linde 3A	527	1172, 1263
$Tl^{ex}_{0\cdot 68}$ $Na_{0\cdot 32}$-A ..	387—449	1248, 1275

Linde 3A is an important sorbent for dehydrating petroleum-cracked gases and organic solvents, and is thermally less stable than (Ca^{ex}, Na)-A, possibly because potassium has a lower b.p. (1033 K) than calcium (1513 K). The thermal stability of Tl^{ex}-A should be higher than that of K^{ex}-A, because of the high b.p. (1730 K) of thallium. This was supported by DTA results (see Table). Exotherms for Tl^{ex}-A due to loss of crystal structure appeared at higher temperatures than those of Linde 3A, suggesting that Tl^{ex}-A is much more stable towards heat-treatment and would therefore be a useful sorbent. The number of water molecules per unit cell of hydrated Tl^{ex}-A was nearly equal to that of hydrated K^{ex}-A.



Figure

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