

Aluminium-independent Cation Exchange of Internal Siloxy Groups in ZSM-5 and ZSM-11

Arthur W. Chester,^{*a} Yung F. Chu,^a Ralph M. Dessau,^b George T. Kerr,^b and Charles T. Kresge^a

^a Mobil Research and Development Corporation, Paulsboro Research Laboratory, Paulsboro, NJ 08066, U.S.A.

^b Central Research Laboratory, Princeton, NJ 08540, U.S.A.

The highly siliceous zeolites ZSM-5 and ZSM-11 exhibit intracrystalline cation exchange capacity under basic conditions in excess of the framework tetrahedral aluminium content.

Recently Fegan and Lowe¹ suggested that highly siliceous zeolites may be ion exchangers to an extent greater than the amount of aluminium in the tetrahedral framework. We now report data demonstrating this phenomenon for ZSM-5 and ZSM-11 over a wide range of tetrahedral framework Al content. Our investigation was the result of observations, similar to those of Fegan and Lowe,¹ that as-synthesized, highly siliceous (low Al) ZSM-5 contains cations (quaternary ammonium and Na⁺) well in excess of that required by the tetrahedral framework aluminium content. Furthermore, the total cation content of the as-synthesized zeolites is relatively independent of the SiO₂/Al₂O₃ ratio.

Experiments were performed with ZSM-5 with SiO₂/Al₂O₃ ratios from 39 to 32 307; the as-synthesized zeolites were calcined to remove the tetrapropylammonium ion, which owing to its size limits the observable exchange. A ZSM-11 sample with SiO₂/Al₂O₃ of 2 044 was included in the series. Exchange experiments were conducted at ambient conditions with the chloride salts of tetrammineplatinum(II) and tetra-

methylammonium ions (TMA), both of which are known to be stable (to hydrolysis) under highly alkaline conditions. The exchange products were washed to remove chloride ions and analysed to confirm the absence of both Cl and Na.

The results of the exchange with the Pt(NH₃)₄²⁺ ion are shown in Table 1. For all zeolite samples with SiO₂/Al₂O₃ in excess of 70, the Pt content was well in excess of that required as counterions for the tetrahedral framework Al content. The presence of Pt as the complex ion in the zeolite structure was verified by quantitative measurement of the ammonia evolved during thermal decomposition.² The ratio of equiv. Pt(NH₃)₄²⁺/equiv. Al increases with increasing SiO₂/Al₂O₃ ratio, clearly demonstrating that its exchange is independent of tetrahedral Al content. However, when based on cation content per 96 Si+Al atoms, a reasonably constant stoichiometry of 1–1.5 Pt(NH₃)₄²⁺ is observed for all zeolites with SiO₂/Al₂O₃ greater than 39.

When the calcined Na forms of ZSM-5 with SiO₂/Al₂O₃ ratios of 39, 64, and 635 were exchanged with ammonium ions,

Table 1. Tetrammineplatinum(II) ion exchange of ZSM-5 and ZSM-11.^a

Zeolite SiO ₂ /Al ₂ O ₃	Initial Na		Equiv. Pt(NH ₃) ₄ ²⁺ /equiv. Al ^c	Mol Pt(NH ₃) ₄ ²⁺ /96(Si+Al)
	% wt	Mol Na/ 96(Si+Al)		
39	0.71	2.0	0.69	1.65
64	0.79	2.1	0.76	1.1
137	0.78	2.1	1.57	1.1
220	1.1	2.9	3.04	1.3
329	1.6	4.2	4.9	1.45
635	0.92	2.4	5.0	0.75
2 044 ^d	0.88	2.3	23.5	1.1
32 307	0.94	2.5	504	1.5

^a Zeolites precalcined at 538°C to remove organic material. ^b 0.01 M [Pt(NH₃)₄]Cl₂ solution. 50 ml Pt solution/g zeolite at ambient temperature for 16 h. ^c Na <0.03%, Cl <0.01% in all exchanged products. ^d ZSM-11; all other samples are ZSM-5.

Table 2. Tetramethylammonium ion exchange of highly siliceous ZSM-5.^a

Treatment	TMA content/mequiv. g ⁻¹	TMA/Al
TMACl ^b	0.33	6
Acidification to pH 5–6, TMACl exchange	0.08	1.3
Acidification to pH 5–6, TMAOH exchange (pH 12)	0.54	10

^a Al = 0.054 mmol/g⁻¹ (SiO₂/Al₂O₃ 635), Na = 0.410 mequiv. g⁻¹, calcined 538°C to remove organic material. ^b 1 g zeolite, 2.5 g TMACl, 50 ml H₂O at ambient temperature for 4 h.

the products all had NH₄/Al ratios of 1. When these products were then exchanged with the Pt(NH₃)₄²⁺ cation at pH 7, the observed ratios of equiv. Pt(NH₃)₄²⁺/equiv. Al were 0.68, 0.78, and 0.77. This result suggests that the acidic ammonium exchange destroys the Al-independent exchange sites, allowing only the expected aluminium-dependent exchange.

The results for exchange of the 635 SiO₂/Al₂O₃ ZSM-5 with the TMA ion are shown in Table 2; again, the high exchange capacity with TMA indicates an Al-independent mechanism. Acidification appeared to destroy these exchange sites; however, exchange with TMAOH under alkaline conditions resulted in restoration of the exchange sites. The stoichiometry after the alkaline exchange corresponds to 3 TMA/96 Si+Al atoms.

The above data clearly demonstrate that ZSM-5 and ZSM-11 have ion exchange capacity that is in excess of the framework Al content. Several possibilities exist as to the nature of the anionic sites, including occluded silicate ions, trapped OH⁻ ions or SiOH (or SiO⁻) groups that are part of the framework but not associated with Al atoms. The results of Fegan and Lowe¹ suggest that there are 6–8 anionic sites per 96 Si+Al atoms. Further, Boxhoorn, *et al.*³ have identified a substantial number of SiOH groups in similarly prepared ZSM-5 by ²⁹Si n.m.r. spectroscopy; they estimate that as many as 18% of the framework Si atoms have associated OH. The existence of 6–8 occluded silicate ions per 96 Si+Al would certainly limit both exchange and sorption capacities (which is not observed); further, trapped hydroxy ions would become labile under calcination and ion exchange conditions. Thus the aluminium-independent exchange phenomenon may well be the result of framework SiO⁻ groups formed during synthesis as counterions for the quarternary cations.

The pH effects described above are also revealing. The calcined zeolites, which contain Na well in excess of that required by the tetrahedral Al content, all produce considerable basicity (pH 10) when slurried with water.

However, both the as-synthesized and Na-free ammonium exchanged forms produce neutral slurries, so that subsequent exchange of the ammonium form with Pt(NH₃)₄²⁺ or TMA results in only the tetrahedral aluminium-dependent exchange. These observations are consistent with the Al-independent exchange sites being very weakly acidic silanol groups that are transformed to silicate anions at high pH. Hexane cracking activities measured on the zeolites used in this study correlate with the tetrahedral Al content.⁴ The silanol groups themselves contribute no catalytic acidity.

The data in Table 1 clearly show that the degree of aluminium-independent exchange is dependent on the SiO₂/Al₂O₃ ratio. As the Al content increases, normal exchange replaces that based on SiOH groups. Thus, at 39 SiO₂/Al₂O₃, only normal exchange appears to occur, while at 137 SiO₂/Al₂O₃, Al-independent exchange is clearly contributing substantial additional exchange capacity. Given the lower selectivity of ZSM-5 for divalent ions,⁵ the Al-independent mechanism is likely to be contributing some exchange capacity even at 64 SiO₂/Al₂O₃. The effect of the SiO₂/Al₂O₃ ratio is readily understood if Al occupies the same sites as the SiO⁻ groups that give rise to Al-independent exchange. Further, the stoichiometries determined above can be limited by the steric constraints of the zeolite lattice, which would limit the capacity for exchange by large ions such as Pt(NH₃)₄²⁺ and TMA to, at most, 4 per 96 Si+Al atoms in ZSM-5 and ZSM-11. Exchange would be further limited by diffusion and insufficient Al to maintain a balance of charges when silanol groups are largely absent (*e.g.* at SiO₂/Al₂O₃ <100).

Received, 9th October 1984; Com. 1433

References

- 1 S. G. Fegan and B. M. Lowe, *J. Chem. Soc., Chem. Commun.*, 1984, 437.
- 2 W. J. Reagan, A. W. Chester, and G. T. Kerr, *J. Catal.*, 1981, **69**, 89.
- 3 G. Boxhoorn, A. G. T. G. Kortbeeck, G. R. Hays, and N. C. M. Alma, *Zeolites*, 1984, **4**, 15.
- 4 W. O. Haag, R. M. Lago, and P. B. Weisz, *Nature*, 1984, **307**, 589.
- 5 P. Chu and F. G. Dwyer, *Am. Chem. Soc., Symp. Ser.*, 1983, **218**, 59.