

Co-ZSM-5 and Mn-ZSM-5 synthesised directly from aqueous fluoride gels

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Isomorphously substituted zeolite ZSM-5 is synthesised using an aqueous, slightly acidic, fluoride medium incorporating tetrahalometallate compounds of cobalt and manganese; final products were characterised using XRD, SEM, XRF, FTIR, TG-DTA, and evidence of metal incorporation into the zeolite framework is given.

Zeolite ZSM-5 is a catalyst of great industrial importance owing to its reactant, product and transition-state selectivity.¹ Modification to acid site strengths and density by isomorphous substitution of transition-metal elements can enhance catalytic activity, stability and selectivity. For example methane is generally regarded as a non-selective reducing agent, yet a cobalt or manganese exchanged HZSM-5 has proved to be an effective catalysts for the selective catalytic reduction of NO_x by methane, with excess oxygen.²⁻⁴

Zeolite gels are normally prepared from solutions of silicates and aluminates at high pH. The as-synthesised material is then calcined and ion-exchanged with acid or ammonium salts to produce the Brønsted- and Lewis-acid sites necessary for catalytic activity. Metals are exchanged into the zeolite matrix by such complex secondary synthesis methods as cation exchange using metal nitrate solutions⁵ and impregnation by metal carbonyl vapour.⁶ The metal either inserts into lattice defect sites, or it acts as a charge balancing species which can then migrate and agglomerate at the external surface.^{7,8}

This work reports the synthesis of Co-ZSM-5 and Mn-ZSM-5 by primary synthesis methods, employing a non-alkaline aqueous fluoride medium. Synthesis in a fluoride medium, replacing OH⁻ with F⁻ as a mineralising agent has been extensively studied in recent years.^{9,10} It allows controlled nucleation and slower growth rates resulting in larger crystals with fewer lattice defects.¹⁰

Pure silica ZSM-5 was synthesised from a gel with molar composition 0.25HF : 0.75NaF : 0.25NaCl : 1.25TPABr : 10SiO₂ : 330H₂O.¹¹ CAB-O-SIL M5 fumed silica (BDH 98%) was dispersed in deionised water, NaF (Fluka Chemika 99%) and HF (Fluka Chemika, puriss 40%) were added to the silica slurry, NaCl (General purpose reagent) and TPABr (Aldrich 98+) added last and stirred by hand to homogeneity. Gels were heated to 170 °C in Teflon-lined reaction vessels. Samples were removed at regular intervals, quenched, filtered and dried at 40 °C. X-Ray powder diffraction (XRD) analysis confirmed highly crystalline ZSM-5 had been synthesised (Fig. 1). Scanning electron microscopy (SEM) analysis showed elongated prismatic crystals, typical of ZSM-5¹² 490–570 μm long.

[NEt₄]₂[CoCl₄] and [NPr₄]₂[MnBr₄] were crystallised as salts of large organic cations.¹³ These tetrahedral tetrahalometallates have been used successfully in the synthesis of a number of highly substituted aluminophosphate zeotypes¹⁴ but are unstable in basic conditions. The reaction gels for the metal substituted zeolites had a molar composition of 0.25HF : 0.75NaF : 0.25NaCl : 1.25 (1 - x) TPABr : x[NR₄]₂[MX₄] : 10SiO₂ : 330H₂O where x is in the range 0–0.5, and [NR₄]₂[MX₄] represents [NEt₄]₂[CoCl₄] or [NPr₄]₂[MnBr₄]. Molar compositions of the various reaction gels, and the products formed are listed in Table 1.

XRD analysis showed the products to be crystalline with the orthorhombic space group *Pnma* (Fig. 1). The volume of the unit cell, given in Table 2, increases with the levels of gel substitution.

SEMs of the substituted systems showed a change in crystal morphology. The 0.1 mole fraction cobalt system produced smaller crystals *ca.* 80–100 μm in length with irregular facets. This system showed a decreasing level of crystallinity inversely proportional to the level of substitution, which could be attributed to the increasing mole fraction of the associated TEA⁺. The manganese system at 0.1 mole fraction showed an average crystal length of *ca.* 165 μm with the appearance of raised faces along the crystallographic *c* axis. The 0.2 Mn

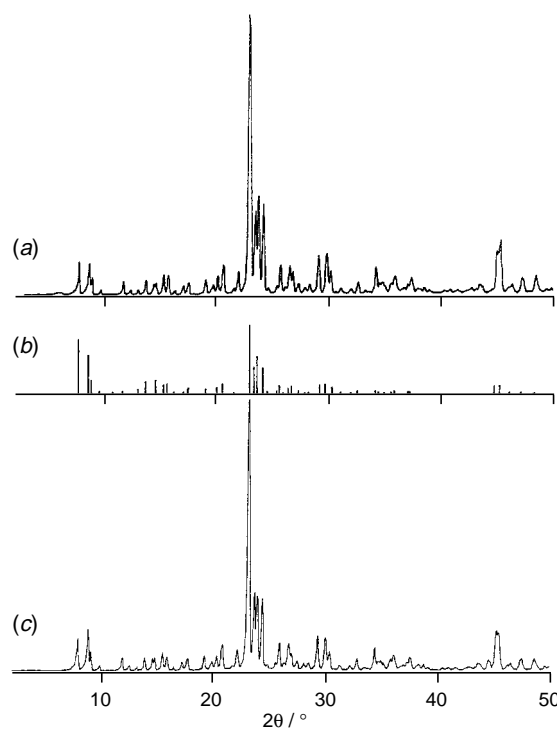


Fig. 1 (a) XRD pattern of protonated pure silica ZSM-5, (b) JCPDS pattern 37-359 and (c) XRD pattern of Mn:Si substituted at 0.2 mole fraction

Table 1 Molar compositions of reaction gels

TPABr	TEA ₂ CoCl ₄	TPA ₂ MnBr ₄	Start pH	Final pH	Product ^a
1.25			6.3	5.5	37-359 ZSM-5
1.05	0.1		6.0	4.5	37-359
0.85	0.2		6.2	5.3	37-359
0.65	0.3		5.4	3.5	37-359 ^b
1.05		0.1	5.9	5.3	37-359
0.85		0.2	6.1	5.4	37-359
0.65		0.3	5.5	5.2	37-359
0.25		0.5	5.0	4.8	Amorphous

^a With reference to XRD (JCPDS) on-line analysis standard reference patterns. ^b Poorly crystalline material.

Table 2 Chemical analysis and unit-cell parameters

M mol	Chemical formulation ^a	LOI ^b (%)	U ^c /Å ³
— ^d —	Si _{95.2} Zn _{0.7} Na _{0.1} O ₁₉₂ ·12.3H ₂ O	11.8	5306 ^e
Co 0.05	Si _{95.6} Co _{0.18} Zn _{0.2} Na _{0.12} O ₁₉₂ ·12H ₂ O	13.2	5310
Co 0.1	Si _{95.2} Co _{0.7} Zn _{0.1} Na _{0.2} O ₁₉₂ ·11.8H ₂ O	11.2	5354
Co 0.15	Si _{94.9} Co _{0.7} Zn _{0.4} O ₁₉₂ ·12.4H ₂ O	10.4	5370
Co 0.2	Si _{94.5} Co _{1.2} Zn _{0.3} O ₁₉₂ ·12.6H ₂ O	11.2	5455
Co 0.3	Si _{92.9} Co _{2.9} Zn _{0.1} O ₁₉₂ ·12H ₂ O	6.87	5071
Mn 0.05	Si _{95.5} Mn _{0.1} Zn _{0.3} Na _{0.2} O ₁₉₂ ·12H ₂ O	12.2	5371
Mn 0.1	Si _{95.3} Mn _{0.3} Zn _{0.3} Na _{0.1} O ₁₉₂ ·10.9H ₂ O	12.1	5110
Mn 0.15	Si _{95.3} Mn _{0.5} Zn _{0.1} Na _{0.2} O ₁₉₂ ·11.4H ₂ O	14.1	5305
Mn 0.2	Si _{94.9} Mn _{0.7} Zn _{0.4} Na _{0.1} O ₁₉₂ ·12.3H ₂ O	12.1	5360
Mn 0.3	Si _{95.2} Mn _{0.6} Zn _{0.3} Na _{0.1} O ₁₉₂ ·12.2H ₂ O	10.7	5381
Mn 0.5	— ^f —	11.4	— ^g —

^a X-Ray fluorescence. ^b Loss on ignition determined by TG. ^c Unit-cell volume. ^d Pure Si form. ^e Lit. value for ZSM-5 = 5332 Å.¹⁶ ^f Not obtained, poorly crystalline. ^g Not obtained.

system had smaller crystals, *ca.* 60 μm and there was crystal twinning along both *b* and *c* crystallographic axes with raised faces still evident (see graphical abstract). The reduction in crystal sizes is similar to that observed by Dwyer *et al.*,¹⁵ and the raised faces indicates that crystallisation has occurred in a less supersaturated medium.¹⁰

TG losses on ignition (LOI) for the most crystalline samples compare well with the literature value¹¹ of 12%. The manganese substituted series has one type of templating species, TPA⁺, and shows a two stage mass loss above 300 °C. The DTA trace shows a regular increase in the second stage mass loss, at the higher temperature, with increasing levels of substitution. The small mass losses, below 300 °C, in both the cobalt and the manganese systems are attributed to the water content, or to the two types of template cations either on the crystal surface or associated to anionic surface species (F⁻ or CoO₂²⁻).

The DTA trace in the cobalt system, also shows a two-stage mass loss above 300 °C. This system contains two types of

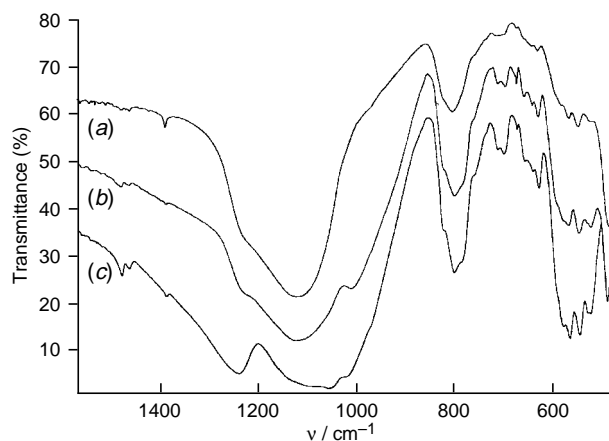


Fig. 2 FTIR transmission spectra of (a) pure silica ZSM-5, (b) cobalt 1.5 mole fraction and (c) manganese 1.5 mole fraction

templating species, TPA⁺ and TEA⁺ as the levels of substitution are increased. However, according to Szostak,¹⁶ a two-stage mass loss is due to two types of TPA⁺ species. The first type is occluded in the zeolite channels, it is less strongly bound and is lost at a lower temperature. The second type is a more strongly bound counter ion species and is lost at a higher temperature. The counter ions could be associated with an occluded fluoride anion or to a negatively charged MO₄²⁻ coordinated into the silica framework. The fluoride in the gel has remained constant at 1 mole fraction, the increase in the template loss therefore could be due to those cations associated with the increased mole fraction of heteroatoms.

FTIR transmission spectra of the pure silica ZSM-5 closely matched literature spectra.¹⁷ Substitution of cobalt and manganese into ZSM-5 resulted in a broadening in the T–O–T asymmetric stretching region, ranging from 1230 to 1085 cm⁻¹ (Fig. 2), which indicates heteroatom substitution.

It is clear from the analytical data that there are changes in the substituted materials compared with the pure silica form. This work represents levels of substitution comparable to levels currently reported but with the advantage of using a simple primary synthesis procedure. The materials produced in a fluoride medium do not require complex ion-exchange procedures to obtain the protonated form necessary for catalytic activity.

Footnote and References

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