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THERMOGRAVIMETRIC EVIDENCE OF NICKEL OR COPPER ISOMORPHOUSLY SUBSTITUTED INTO A ZEOLITE

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Abstract

The synthesis of pure silica ZSM-5 has been modified to produce highly crystalline material in the protonated form, necessary for catalytic activity, directly from a low water fluoride gel. Tetrahedrally co-ordinated divalent species of nickel and copper have been synthesised as salts of large organic cations and increasing mole fractions incorporated into the zeolite gels. The products have been analysed and characterised using simultaneous thermogravimetric and derivative thermogravimetric analysis (TG-DTG). The thermal decomposition under nitrogen of the metal associated cations, tetraethylammonium (TEA^+), occluded within the zeolite channels is indicative and characteristic of the incorporation of heteroatoms into the zeolite framework. Anomalous losses in the systems can be explained by Jahn–Teller distortions. The mass losses increased with increased metal loading and were consistent with those reported in full water system, analysis also confirmed that the material was hydrophobic and thermally stable.

Analysis by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR) and Atomic Absorption Spectroscopy (AAS) has confirmed the reliability of TG-DTG as a diagnostic tool. The maximum levels of substitution achieved were (mass%) Ni 3.93 and Cu 4.38.

Keywords: copper, fluoride, isomorphous substitution, nickel, ZSM-5

Introduction

Zeolite H-ZSM-5 is an important industrial catalyst and isomorphous substitution of specific transition metals into the framework can modify the catalytic application by changing the strength and density of the active acid sites [1]. Synthesis in a slightly acidic fluoride medium produces the protonated form required for catalytic activity

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and encourages relatively slow crystallisation and therefore defect-free crystal structure [2–4]. Earlier work reported the synthesis of Co-ZSM-5 and Mn-ZSM-5 and demonstrated the importance of TG-DTG analysis [5, 6]. Following associated research [7] the original stoichiometric formula for the synthesis of H-ZSM-5 was modified to reduce the water content, to minimise synthesis waste [2].

Nickel is less active than cobalt for the selective catalytic reduction (SCR) of NO with methane but it has been shown to facilitate hydrodesulphurisation in combined Co^{2+} and Ni^{2+} zeolite catalysts [8]. Kucherov *et al.* [9] investigated the stability of square planar Cu^{2+} sites in ZSM-5 prepared by secondary synthesis methods, and concluded that acidic pretreatment increased the thermal stability of the catalyst. Torre-Abreu *et al.* [10] concluded that the catalytic behaviour of ZSM-5 for the SCR of NO by propene, in the presence of oxygen and of isolated Cu^{2+} species, is enhanced by the structure.

Experimental

The gels were synthesised according to the procedures, and using reagent sources, described in an associated paper [2]. The molar composition of the metal substituted synthesis gels is given in formula 1.

Formula 1

$0.25HF:0.75NaF:0.25NaCl:1.25\ (1–x)\ TPABr:x[NR_4]_2[MX_4]:10SiO_2:82.5H_2O$, where x has values of 0–0.5, and $[NR_4]_2[MX_4]$ represents $[TEA]_2[NiCl_4]$ or $[TEA]_2[CuCl_4]$.

Table 1 Metals and templates in gel, product molar compositions, unit cell sizes and metal content

TPABr	$[TEA]_2$ $[NiCl_4]$	$[TEA]_2$ $[CuCl_4]$	Product composition	u.c./Å	M% conc.
1.25			$SiO_{95.3}:Zn_{0.7}:O_{192}$	5352* OC#	0.00
1.15	0.05		$SiO_{94.83}:Ni_{1.06}:Zn_{0.12}:O_{192}$	5309 OP	1.11
1.05	0.10		$SiO_{93.91}:Ni_{2.02}:Zn_{0.07}:O_{192}$	5329 OP	2.11
0.95	0.15		$SiO_{92.44}:Ni_{3.56}:O_{192}$	5336 OC	3.71
0.85	0.20		$SiO_{92.16}:Ni_{3.77}:Zn_{0.07}:O_{192}$	5429 OC	3.93
1.15		0.05	$SiO_{95.26}:Cu_{0.60}:Zn_{0.14}:O_{192}$	5327 OC	0.63
1.05		0.10	$SiO_{94.06}:Cu_{1.76}:Zn_{0.18}:O_{192}$	5359 OC	1.84
0.95		0.15	$SiO_{93.01}:Cu_{2.72}:Zn_{0.26}:O_{192}$	5366 OC	2.84
0.85		0.20	$SiO_{92.09}:Cu_{3.63}:Zn_{0.28}:O_{192}$	5385 OC	3.79
0.65		0.30	$SiO_{90.03}:Cu_{4.12}:Zn_{1.57}:O_{192}$	5382 OP	4.38

*Literature Value ZSM-5, 5334 Å, OP [11]; Fluoride Silicalite 5354 Å, OP, [12]
#OP=orthorhombic primitive, OC=orthorhombic face centered

The molar compositions of the reaction gels, the chemical formula of the calcined material, the unit cell sizes (Å) and the metal concentration (mass%) in the products are given in Table 1 [11, 12]. The products contained a small amount of zinc found as an impurity in the silica reagent source.

Simultaneous TG-DTG analysis was carried out using a Mettler TG50 thermobalance and a Mettler TA3000 processor, under nitrogen, with a flow rate of 20 ml min^{-1}, at a heating rate of 20°C min^{-1} from 40–800°C, and using ~20 mg of sample. The samples were ground to uniform particle size [13] and the same alumina crucible was used for each analysis. The total percentage losses on ignition (LOI) compared well with the literature values of 12% [11, 14].

Results and discussion

Thermal analysis of the pure silica sample shows a single, well-defined asymmetric reaction interval commencing at 388°C and ending at 626°C (Fig. 1). As previously reported, in the systems synthesised with $330H_2O$ in the synthesis gel [5, 6], DTG analysis showed very little water loss and no drift in the DTG base line indicative of hydrophobic material. Mass losses can be attributed to the degradation of four types of TPA^+ cations [15]. The first type are those cations ion-paired to crystal surface defects and the second type are those cations occluded in the zeolite channels, these are the least strongly bound and are lost most easily. The third types are those cation species that neutralise internal framework defects. Losses above ~475°C causing the asymmetric reaction interval are due to the fourth type of TPA^+ cations which neutralise the framework negative metal centres, or are ion-paired to occluded fluoride

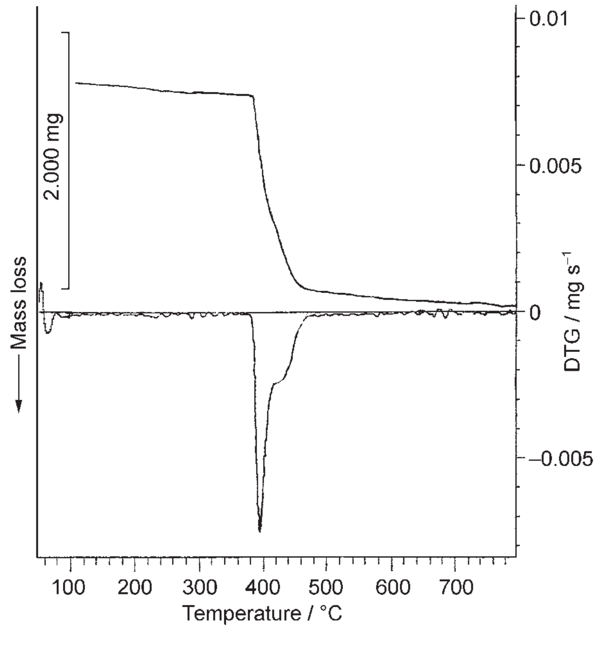

Fig. 1 TG-DTG analysis of pure silica ZSM-5

anions. This is illustrated by the DTG trace for pure silica system, the asymmetry of the single stage loss being due to $TPA^+ F^-$ associations.

The optimum template for the synthesis of ZSM-5 is tetrapropylammonium (TPA^+), but the tetrahedral metals complexes would only precipitate as salts of TEA cations. A series of experiments was conducted to establish the effect on product crystallinity of substituting TEA for TPA in the synthesis gel. Results showed that it was possible to substitute 80% of the TPA, and earlier work [16] also concluded that crystallisation stopped only when the TPA was exhausted from the gel. Figure 2 shows the DTG trace of the template loss from pure silica ZSM-5 synthesised with 60% TEA and 40% TPA; this is equivalent to 3% metal substitution in the gel. The temperature ranges for the two-stage mass losses are given in Table 2. As the level of substitution increases, the onset loss temperature decreases, this is due to the smaller TEA ion being less sterically hindered and lost more easily. The second stage of template loss is introduced due to a propyl group being replaced by an ethyl group and the associated increased charge to size ratio in ion-paired losses. In the previously reported cobalt and manganese systems, the degradation of these ion-paired losses show a classical continuous change as a function of, and relative to, increasing mole fractions of metal incorporated into the zeolite framework [6]. In general, the DTG traces for the nickel and copper systems show anomalous behaviour (Figs 3 and 4). The DTG traces of the reaction intervals are visibly different when compared to the definite asymmetrical single-stage mass loss characteristic of the pure silica material

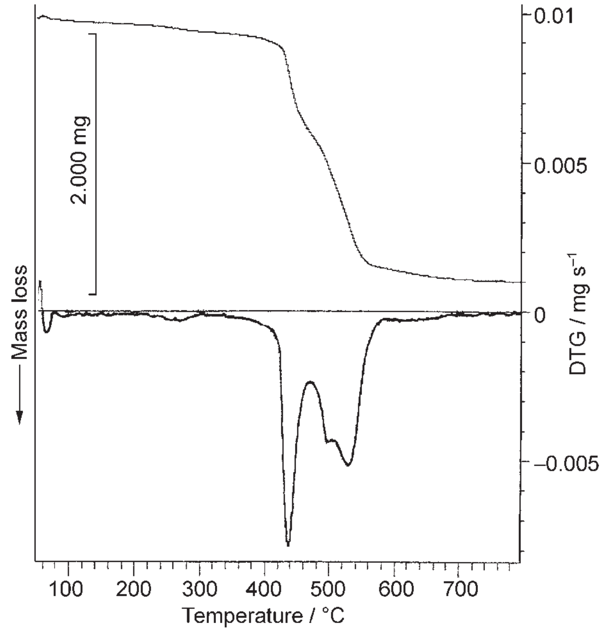

Fig. 2 TG-DTG analysis of pure silica ZSM-5 synthesised with 60%TEA^+ and 40% TPA^+ as templates

(Fig. 1), and the two-stage mass loss characteristic of the same material synthesised with 60%TEA (Fig. 2).

Table 2 Thermogravimetric behaviour of the nickel and copper substituted ZSM-5 series

M^{2+} mol in gel	Temperature range/°C	LOI %	Temperature range/°C	LOI %	Total LOI%
Ni 0.05	200–469	5.59	469–646	6.90	12.49
Ni 0.10	148–461	7.72	461–649	6.69	14.41
Ni 0.15	123–470	6.32	470–717	8.13	14.45
Ni 0.20	154–478	7.55	478–730	8.44	15.99
Cu 0.05	149–457	6.10	457–683	7.67	13.77
Cu 0.10	156–461	7.17	461–706	8.71	15.88
Cu 0.15	242–466	5.74	466–706	9.11	14.85
Cu 0.20	249–462	7.30	462–580	10.4	17.74
Cu 0.30	234–464	7.00	464–578	9.43	16.43
Pure silica ZSM-5	388–626	11.80			11.80
ZSM-5 60%TEA	336–470	4.93	470–684	7.20	12.13

Typical DTG traces for the nickel system (Fig. 3) shows a maximum temperature increase with increased metal loading. This is in agreement with a study of iron distribution in ZSM-5 type zeolites, synthesised in a fluoride medium. Patarin *et al.* [17] observed a peak temperature increase when compared to the pure silica form and concluded that TG-DTG curves can be used as a standard to determine the amount of iron incorporated into the lattice. The first loss interval in the nickel system commenced at ~120°C and is particular to the nickel substituted series. Generally the peak temperature changed by ±20°C in different samples and the peak intensity changed without any obvious trend. As previously discussed, these losses are assigned to surface and occluded template species and the anomalous behaviour could result from Jahn–Teller distortion of the nickel complexes causing some flexibility in the framework. Framework flexibility and the effect on zeolite pore openings have been well documented [18, 19] and this flexibility would allow the template species to be lost more easily. The nickel complexes as incorporated in the gel have four halide ligands and thus can be considered as having tetrahedral configuration [20]. For most four co-ordinated Ni(II) complexes a square planar geometry is preferred but simple crystal field theory predicts a distortion of tetrahedrally co-ordinated Ni(II) complexes in the form of an elongated tetrahedron [21]. It has been shown however, that spin-orbit forces can remove the degeneracy, and as the nickel is surrounded by four identical ligands, any distortion due to asymmetric ligand fields is eliminated. The bond angles of $[NiBr_4]^{2-}$ are only slightly distorted at 106.83 and 110.81° [22]. Incorporating Ni(II) into the zeolite framework means the loss of large bromide lig-

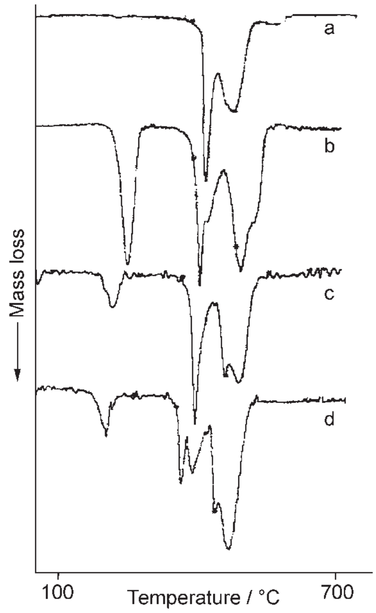

Fig. 3 Typical decomposition patterns of the nickel substituted system at a – 0.05 mol, b – 0.10 mol, c – 0.15 mol and d – 0.2 mol in the gel

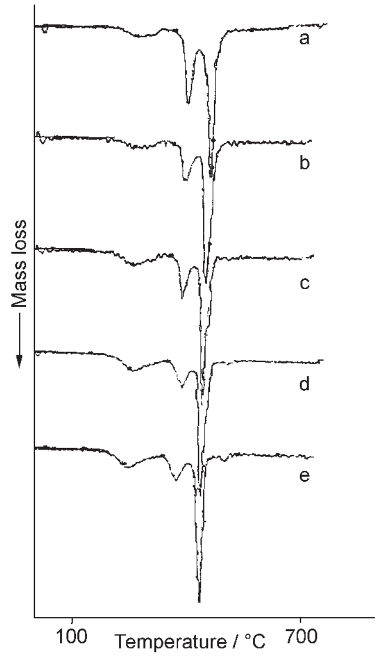

Fig. 4 Typical decomposition patterns of the copper substituted system at a – 0.05 mol, b – 0.10 mol, c – 0.15 mol, d – 0.2 mol and e – 0.25 mol in the gel

ands to become oxygen-bridge co-ordinated, during which the nickel would distort and tend towards the ground state square planar configuration leading to irregular flexing of the framework on metal substitution. The second loss interval due to the loss of occluded and ion-paired template species shows a change of symmetry. The changes may be due to the change of template species as TPA^+ is replaced by TEA^+ with the increase in metal loadings, but this behaviour was not as apparent in the comparison system without metal. The broadening of the second stage high temperature loss indicates increased losses of template cations ion-paired to metal centres substituted in the framework. The irregular distortion of the Ni^{2+} species on framework substitution would lead to anomalous and irregular template losses compared to an unsubstituted pure silica system and this change is shown in the DTG traces.

The TG-DTG traces in the copper substituted series (Fig. 4), are well defined and regular and very different to the nickel series. The procedural decomposition temperature is higher with irregular variation in the maximum temperature, which is generally higher than the pure silica system at 626°C and the 60%-TEA system at 684°C. There is a noticeable drift in the low temperature base-line indicating increasing hydrophilicity with increased metal loadings. The temperature onset of the second stage ion-paired losses remains consistent throughout all levels of copper substitution at ~460°C, generally 10°C lower than the 60%-TEA system, whereas in the nickel system the onset temperature increases with increased metal loadings. The change in the template species with increased copper loading does not affect the trace for the second stage loss which remains the same as the comparison system without metal substitution. The higher temperature losses, which are due to template cations ion-paired to negative copper centres in the framework, increase from 7.6 to 10.4% over the series (0.05 to 0.2 mol in the gel). The change in the thermal behaviour at the 0.3Cu fraction may be due to deterioration in crystal quality as confirmed by XRF and SEM analysis. Crystal Field theory predicts Jahn–Teller distortion for tetrahedral Cu(II) complexes in the form of a flattened tetrahedron, it is rarely seen in a cubic environment [20]. The copper complex is less flexible than the nickel complex. It has been shown [23] that while the degeneracy of Ni(II) complexes is removed by spin-orbit coupling, distortion of the $[CuCl_4]^{2-}$ leads to a more stable configuration. Substitution of Cu ions into the framework requires the loss of smaller chloride ligands to form the framework oxygen bridge links. So while the framework would be distorted when compared to the pure silica material, the copper substituted system would produce a regular distortion of the channels allowing the regular template loss shown by the DTG traces, and the increases in percentage losses at the higher temperatures can be attributed to increased Cu(II) substituted in the zeolite framework.

Other techniques were used to analyse and characterise the products formed to establish product purity and crystallinity, and isomorphous heteroatom substitution. XRD analysis was carried out between 5 and 40°2θ on an automated Philips 1710 diffractometer using CuK_α radiation. This was interfaced to a DEC MicroVAX computer with Philips APD software including a search and match facility using the International Committee Diffraction Data standards (ICDD) database. In the nickel system the products remained crystalline up to the 0.2 mol level of substitution and were

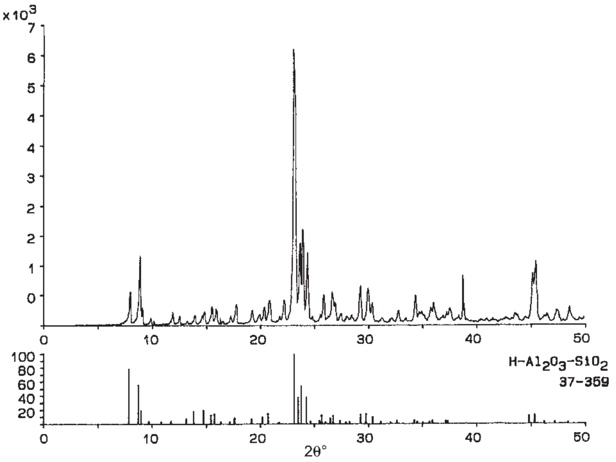

Fig. 5 XRD pattern of Ni-ZSM-5 at 0.2 mol level of gel substitution

identified as a ZSM-5 type material, ICDD reference pattern 37-357 (H–Al_2O_3–SiO_2) (Fig. 5). The material was indexed as orthorhombic-primitive at the lower levels of substitution (0.05 and 0.1 mol) and as orthorhombic-face centred at the 0.15 and 0.2 mol levels of substitution. The unit cell dimensions were comparable to literature values for ZSM-5 and increased in volume with increasing levels of substitution (Table 1). XRD analysis of the copper substituted series showed crystalline material for all samples taken. The unit cells parameters were generally higher than the literature value for ZSM-5 and increased with increasing levels of substitution (Table 1). The material was indexed as orthorhombic face centred at the lower levels of substitution and as orthorhombic, primitive at the 0.2 and 0.3 mol levels of substitution. The changes in the unit cell volumes when compared to the literature values and to the as-synthesised pure silica samples provides persuasive evidence for heteroatom substitution.

XRF bulk chemical analysis of both systems showed levels of substitution to be comparable to levels achieved by ion-exchange methods, and the molar ratio of metal in the products increased regularly with a corresponding decrease in the molar ratio of silica.

The thermal stability of the material was investigated by calcining the most crystalline sample to 780°C in air, to remove all water and template species. The samples were rehydrated and XRD analysis confirmed the presence of highly crystalline material that was stable to 780°C to 0.2 mol levels of substitution in the nickel system and to 0.25 mol levels of substitution in the copper system.

Changes in the crystal morphology were investigated using a Cam Scan Series 2 scanning electron microscope (SEM). Photomicrographs of dried samples of the most crystalline material were taken and compared with the unsubstituted material. Changes in the crystal sizes, and crystal aspect ratio (i.e. the relative proportions of the crystallographic *a*, *b*, and *c*, axes), which are indicative of changing growth patterns, were studied. In general the substituted gels produced smaller crystals ~80–100 μm (compared to ~470–570 μm in the pure silica samples) with irregular facets and evidence of crystal twinning in the higher metal substituted material. The 0.3Ni system showed deterioration to amorphous material consistent with XRD analysis. The reduction in crystal sizes, consistent with previous work [5, 6] and crystal twinning has previously been cited as evidence of heteroatom substitution in ZSM-5 type zeolites [4].

Analysis of the material by FTIR spectroscopy showed broadening of the spectral bands, in both the copper and nickel series similar to those reported for cobalt and manganese. The nickel-substituted series shows a distortion of the spectra between 1250–900 cm^{-1}. This is the area of the spectra assigned to T–O–T asymmetric stretching and indicates heteroatom substitution [24].

AAS analysis of the filtrate from the EDTA-exchanged material showed that there are tetrahedrally co-ordinated M^{2+} species in the material and relatively small amounts were removed by EDTA extraction.

Conclusions

TG-DTG analysis of the Ni-ZSM-5 and the Cu-ZSM-5 compared to the pure silica ZSM-5 indicated interesting peak temperature losses relative to the levels of the metals substituted. Also, anomalous reaction intervals and percentage mass losses which could be explained by the Jahn–Teller distortion of the tetrahedral Ni(II) and Cu(II) species. The degradation of occluded and ion-paired tetralkylammonium species show changes relative to, and as a function of, the mole fraction of divalent heteroatoms in the synthesis gel and incorporated into the framework.

The supporting analytical data shows that there are changes in the characteristics of the material. XRD analysis established the presence of highly crystalline and thermally stable material, and increasing unit cell dimensions with increasing levels of heteroatom substitution. XRF analysis showed increasing levels of heteroatoms in the material with a corresponding decrease in the mole fraction of silica. Changes in patterns of crystal growth and deterioration of crystal morphology were shown by SEM analysis. AAS analysis showed that there are tetrahedrally co-ordinated M^{2+} species in the material and FTIR analysis showed distortion in significant regions of the spectra indicative of heteroatom substitution.

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