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THERMOGRAVIMETRIC EVIDENCE OF COBALT OR MANGANESE ISOMORPHOUSLY SUBSTITUTED INTO A ZEOLITE

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Abstract

Pure silica zeolite ZSM-5 has been synthesised in a slightly acidic aqueous fluoride medium which produces the protonated form of the zeolite ZSM-5 [1]. Tetrahalometallate [2] species of cobalt and manganese have been synthesised and increasing mole fractions incorporated into the zeolite synthesis gel. The products have been analysed and characterised using simultaneous thermogravimetric-derivative thermogravimetric analysis (TG-DTG). The thermal decomposition, under nitrogen of the associated tetraethylammonium (TEA^+) and tetrapropylammonium (TPA^+) cations occluded within the zeolite channels is indicative and characteristic of the incorporation of the heteroatoms into the zeolitic framework. Analysis by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence (XRF), and Fourier transform infrared spectroscopy (FTIR) has confirmed the reliability of thermogravimetric (TG) and derived thermogravimetric analysis (DTG) as a diagnostic tool.

Keywords: cobalt, isomorphous substitution, manganese, tetraalkylammonium cations

Introduction

The catalytic reduction of NO_x emissions with hydrocarbons, in an oxidising atmosphere is the subject of intense research [3]. Zeolite HZSM-5 is an important industrial catalyst, and isomorphous substitution of transition metals into the zeolitic framework of ZSM-5 can change the strength and density of the active acid sites. This can enhance and 'fine tune' the performance in the catalyst's activity, selectivity and stability. Methane is generally regarded as a non-selective reducing agent, yet a cobalt or manganese exchanged HZSM-5 has proved to be an effective catalyst for the novel selective catalytic reduction of NO_x by methane in the presence of excess oxygen [4, 5]. Zeolite ZSM-5 is a hydrophobic

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pentasil type zeolite normally synthesised in alkaline hydrothermal conditions, with the degree of hydrophobicity depending upon the of negative charges associated with heteroatoms in the framework [6].

Structure analysis, water content, and configuration of the occluded tetraalkylammonium template enclosed at the channel intersections, is well documented [7]. Synthesis using a fluoride containing medium obtained by replacing the hydroxide anion with F^- as a mineralising agent, produces zeolites at lower pH values, but with the same morphology as the alkaline route [1]. In the milder slightly acidic fluoride medium, the protonated form of the zeolite can be obtained directly. The thermoanalytical characterisation of pentasil type zeolites synthesised in a fluoride medium has also been studied [8], and the molar ratio of silica to substituted trivalent heteroatoms (Al or B) in the framework was derived from the thermoanalytical data. Recent reports also confirm that TG-DTG give strong evidence for the framework incorporation and the redox activity of transition metals [9, 10]. This work concerns the use of TG-DTG to determine increasing mole fractions of divalent cobalt or manganese incorporated into the framework of a pure silica protonated ZSM-5 zeolite.

Experimental

The gels were synthesised according to the procedures and using reagents sources to be described in an associated paper [11]. The metal substituted synthesis gels had a molar composition of $0.25HF:0.75NaF:0.25NaCl:1.25_{(1-x)}TPABr:x[NR4]_2[MX_4]:10SiO_2:330H_2O$ where x has values from 0–0.5, and $[NR_4]_2[MX_4]$ represents $[TEA]_2[CoCl_4]$ or $[TPA]_2[MnBr_4]$. Molar compositions of the various reaction gels, and the products formed are listed in Table 1. The products contain a small amount of zinc as an impurity contained in the reagents.

Simultaneous TG-DTG analysis was carried out using a Mettler TG50 thermobalance and 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 to 800°C and using ~ 20 mg of sample.

The samples had been ground to uniform particle size and the same alumina crucible was used for each analysis. The total percentage losses on ignition (L.o.i.) compared well with the literature values of 12% [8, 12] (Table 1).

Results and discussion

In the pure silica sample (Fig. 1) the DTG trace shows an asymmetric, well defined single reaction interval commencing at 388°C, ending at 626°C. There is very little water loss, and no drift in the DTG base line, indicating the presence of hydrophobic material. Mass losses up to ~475°C can be attributed to the degradation of three types of TPA^+ cations occluded in the framework as identified

Table 1 Metals and templates in gel molar compcsitions, products formed and TG losses

TPABr	$[TEA]_2[CoCl_4]$	$[TPA]_2[MnBr_4]$	Product composition		LOI% (total)	Reaction intervals/°C for template species	
1.25			$Si_{95.2}Zn_{0.7}Na_{0.1}O_{192}$	$12.3H_2O$	11.8	388–626	
1.15	0.05		$Si_{95.6}Cc_{0.18}Zn_{0.2}Na_{0.12}O_{192}$	$12H_2O$	13.2	413–556	
1.05	0.1		$Si_{95.2}Cc_{0.7}Zn_{0.1}Na_{0.2}O_{192}$	$11.8H_2O$	11.2	331–655	
0.95	0.15		$Si_{94.9}Cc_{0.7}Zn_{0.4}O_{192}$	$12.4H_2O$	10.4	361–464	464–566
0.85	0.2		$Si_{94.5}Cc_{1.2}Zn_{0.3}O_{192}$	$12.6H_2O$	11.2	376–432	432–617
0.65	0.3		$Si_{92.9}Cc_{2.9}Zn_{0.1}O_{192}$	$12H_2O$	10.4[a]		
1.15		0.05	$Si_{95.5}Mn_{0.1}Zn_{0.3}Na_{0.2}O_{192}$	$12H_2O$	12.2	383–553	
1.05		0.1	$Si_{95.3}Mn_{0.3}Zn_{0.3}Na_{0.1}O_{192}$	$10.9H_2O$	12.1	407–553	
0.95		0.15	$Si_{95.3}Mn_{0.5}Zn_{0.1}Na_{0.2}O_{192}$	$11.4H_2O$	14.1	408–579	
0.85		0.2	$Si_{94.9}Mn_{0.7}Zn_{0.4}Na_{0.1}O_{192}$	$12.3H_2O$	12.1	351–436	436–607
0.65		0.3	$Si_{95.2}Mn_{0.6}Zn_{0.3}Na_{0.1}O_{192}$	$12.2H_2O$	10.7	298–438	438–624
0.25		0.5	not obtained-poorly crystalline		11.4		

[a] poorly crystalline material

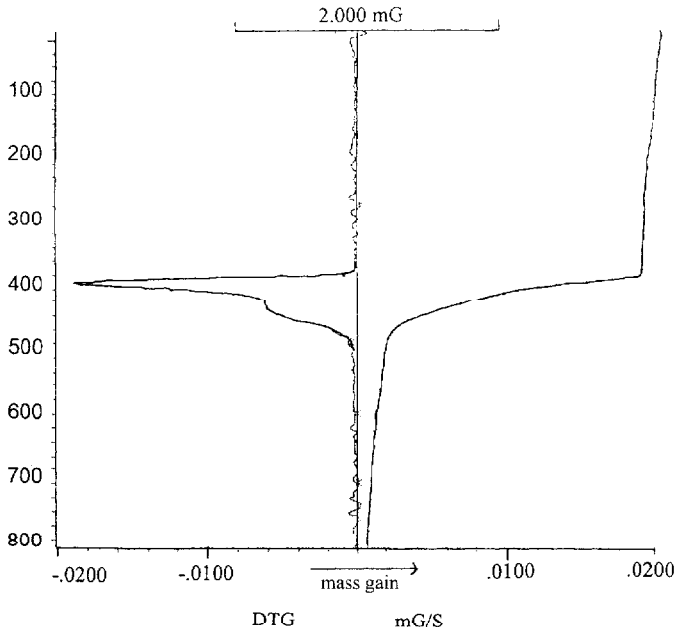

Fig. 1 TG-DTG curves of pure silica H-ZSM-5

by El Hage-Al Asswad [13] and co-workers. Losses above ~475°C, causing the asymmetrical reaction interval, are due to those TPA^+cations which are ion-paired to occluded fluoride anions. The DTG traces of the cobalt substituted gel compositions of 0.05, 0.1 and 0.2 mole fractions (Figs 2, 3 and 4) all show a well defined procedural decomposition temperature. The reaction intervals increase with the increasing mole fractions, and there are extended intermediate plateaux, which are due to the overlap of occluded and ion-paired losses, producing a DTG trace displaying two stages of weight loss. There is also broadening of the second mass loss interval with increasing levels of substitution (Table 1). These changes are due to the increasing negative charges introduced into the previously uncharged pure silica framework being counterbalanced by the cationic species. The traces of the cobalt 0.15 and 0.2 mole fraction, (Fig. 4) show a small additional mass loss (~1.5%) below ~300°C, attributed to water loss. This is due to the increasing hydrophilicity of the zeolites with increasing negative framework charges as a result of the divalent framework cobalt. In all of the syntheses, the volume of fluoride in the synthesis gel remains constant at one mole fraction. The changes in thermogravimetric behaviour can therefore be attributed to losses of alkylammonium cations associated to the increased mole fraction of cobalt, isomorphously substituted into the zeolite framework.

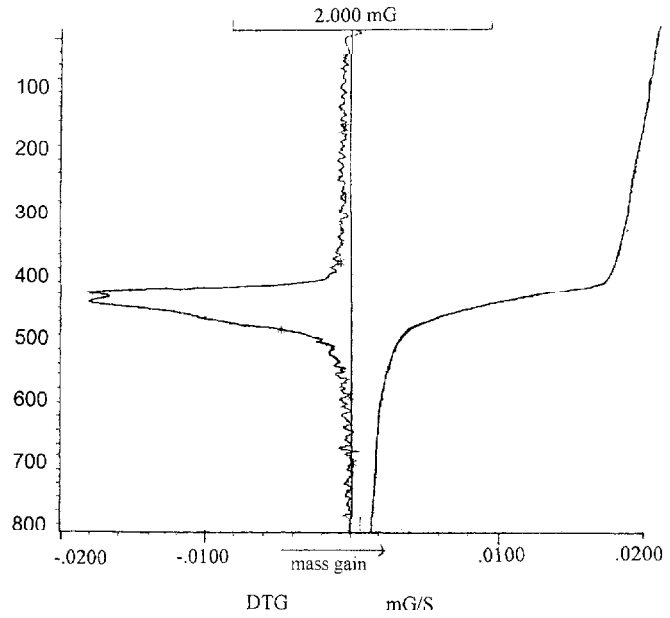

Fig. 2 TG-DTG curves of product from gel containing 0.05 mole fraction of cobalt

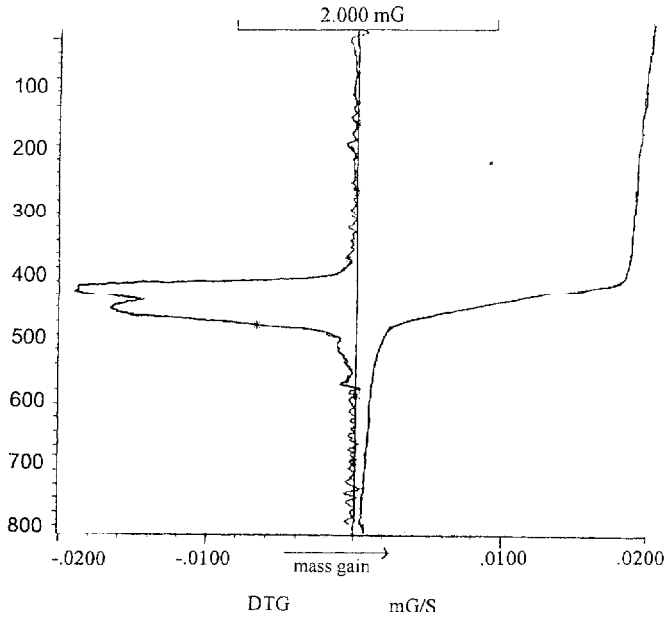

Fig. 3 TG-DTG curves of product from gel containing 0.1 mole fraction of cobalt

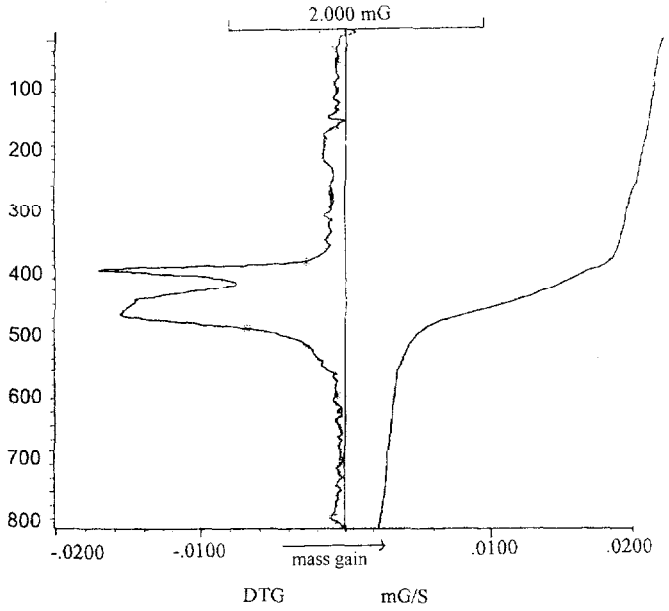

Fig. 4 TG-DTG curves of product from gel containing 0.2 mole fraction of cobalt

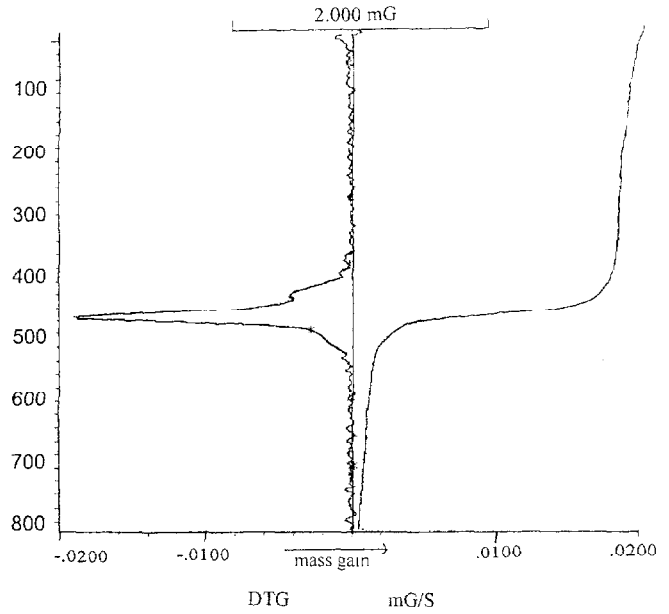

Fig. 5 TG-DTG curves of product from gel containing 0.05 mole fraction of manganese

The systems with isomorphously substituted divalent manganese (Figs 5–8) show similar thermogravimetric behaviour; namely broadening of the reaction intervals, extended overlap of occluded and ion pair losses, a change from a single stage to a two-stage weight loss, an increase in the second stage of weight loss and an increasing tendency to hydrophilicity commensurate with increasing levels of substitution. The cobalt and manganese systems show a continual change in thermogravimetric behaviour corresponding to the changing proportions of the two types of TPA^+ and TEA^+, i.e. occluded and ion-paired, as a function of the change in framework metal substitution.

Other techniques were used to analyse and characterise the products formed to establish isomorphous substitution [11]. XRD characterisation of the dried zeolite material was carried out between 5 and 40° 2θ on an automated Phillips 1710 X-ray diffractometer, using CuK_α radiation. This was interfaced to a DEC MicroVAX computer with Phillips APD software including a search and match facility using the Joint Committee on Powder Diffraction Standards (JCPDS) database. The crystal composition of each sample was determined and, in each synthesis, only pure phases of protonated ZSM-5 were identified (Fig. 9). Increases in the unit cell parameters, which can indicate other elements being incorporated into the framework, were noted. The changes were compared to the unit cell volume of the as-synthesised pure silica ZSM-5, and to the literature value for silicalite [12].

Changes in morphology were investigated by Scanning Electron Microscopy (SEM) with increasing substitution levels of the different metals substituted. The crystal sizes, uniformity of crystal sizes, crystal aspect ratios (i.e. the relative proportions of the crystallographic *a*, *b* and *c* axes) and changes in aspects indicative of changing growth patterns were also studied. The dried sample material was viewed using a CamScan Series 2 scanning electron microscope. Photomicrographs were taken of the most crystalline samples in both systems to compare with the unsubstituted ZSM-5

The 0.1 mol fraction cobalt system produced smaller crystals of ~80–100 μm (compared to ~490–570 μm in the pure silica system) with irregular facets and an aspect ratio of 5. The 0.3 mol fraction substituted systems showed deterioration to amorphous material consistent with the XRD analysis. The manganese system at 0.1 mol fraction showed an average crystal length of ~165 μm with the appearance of raised faces along the crystallographic *c* axis, and an aspect ratio of 4.7. The 0.2 mol fraction system had smaller crystals ~60 μm long. The aspect ratio of 15 was larger and there was twinning of crystals along both *b* and *c* axes, but the raised faces were still evident. The reduction in the crystal sizes is in agreement with the results of Dwyer and co-workers [14] who reported a reduced crystal size when synthesised in a fluoride medium, inversely proportional to the sizes of the metal substituted. The crystallographic *c* axis in ZSM-5 corresponds to the length direction and growth is restricted in the presence of fluoride anions

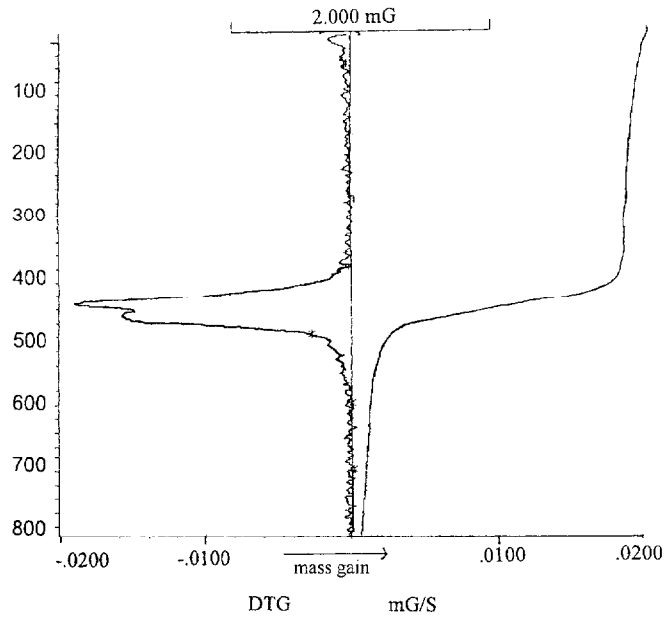

Fig. 6 TG-DTG curves of product from gel containing 0.1 mole fraction of manganese

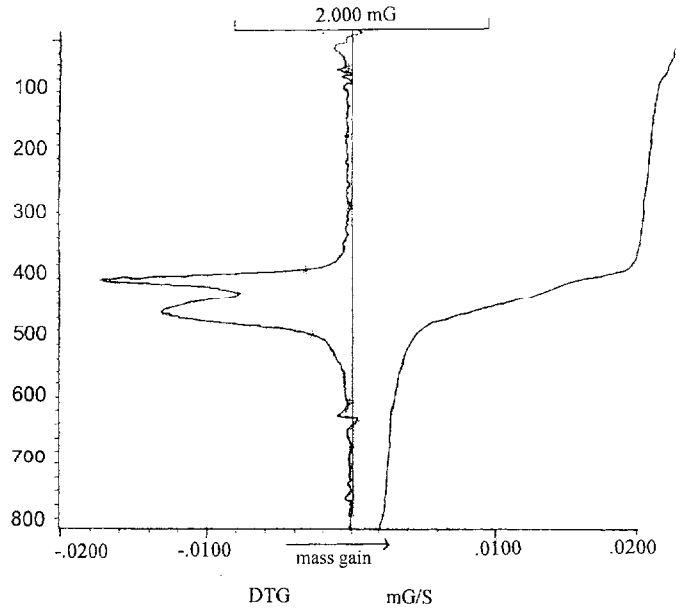

Fig. 7 TG-DTG curves of product from gel containing 0.2 mole fraction of manganese

as the radius of the substituting heteroatom is increased. Kessler and co-workers [1] observed large twinned crystals in MFI [15] type zeolites partly substituted with T^{3+} elements (T=B, Al, Fe). They also reported a decrease in the length to width ratio of crystals with increasing levels of silica substitution. Metal substitution in MFI type zeolites synthesised in fluoride media generally leads to less flat faces [1] which indicates that crystalllisation has occurred in a less supersaturated medium.

Analysis of the material by FTIR spectroscopy indicated structural change in the materials by showing broadening of the spectral bands in significant regions of the spectra [12]. The spectra were obtained using a Nicolet Impact 404 spectrophotometer interfaced with a 486DX-microprocessor and FTIR software OMNIC version 2.

Compared with the pure silica material, the samples substituted with cobalt at the 0.1 mol fraction level of substitution showed the development of a shoulder at ~1221 cm^{-1}. At 0.2 mol there was an enhanced development of the shoulder at ~1229 cm^{-1} and the appearance of a second shoulder at ~1009 cm^{-1}. In the manganese system at the 0.1 mol substitution level shoulders had developed at ~1227 cm^{-1} and ~893 cm^{-1}. At the 2% substitution level the shoulder at ~1227 cm^{-1} remained and a second shoulder at ~1009 cm^{-1} had developed. These are assigned to asymmetrical T–O–T stretching [13] and could indicate an increasing level of heteroatom substitution per unit cell.

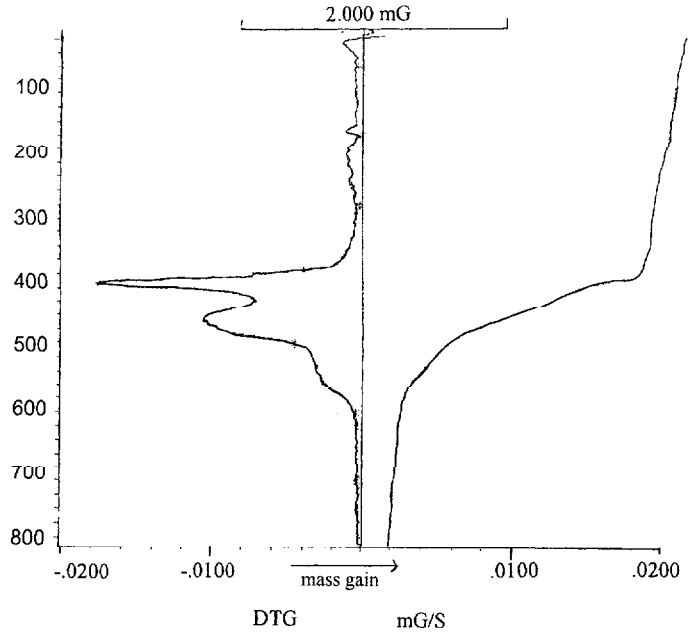

Fig. 8 TG-DTG curves of product from gel containing 0.3 mole fraction of manganese

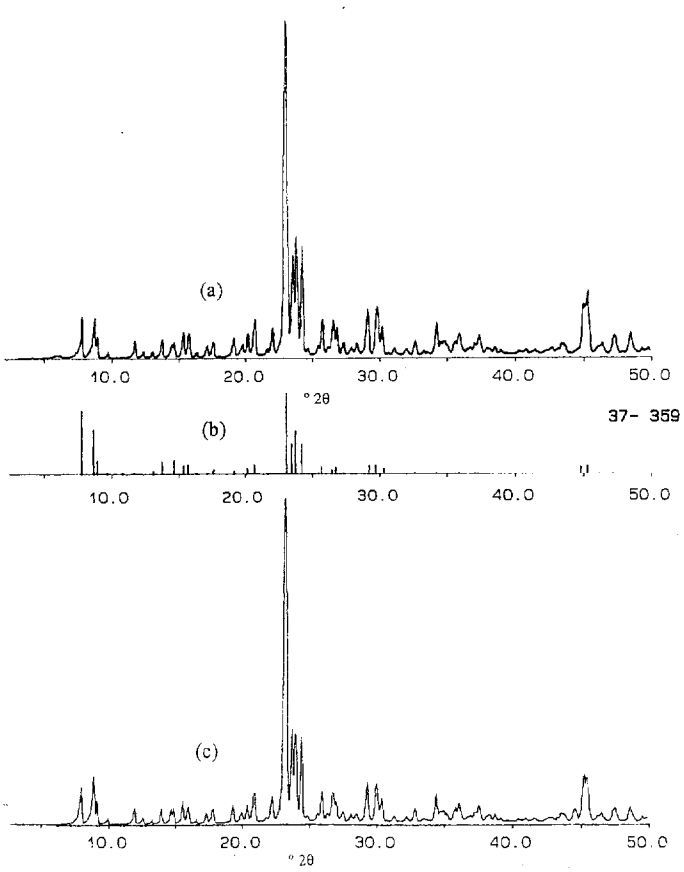

Fig. 9 XRD pattern of (a) H-ZSM-5, (b) JCPDS pattern 37-359, (c) XRD pattern of system containing 0.2 mole fraction of manganese

XRF bulk chemical analysis of the product shows a regular increase in the mole fraction of hetematoms and a corresponding decrease in the mole fraction of silica.

Conclusions

The systems investigated varied only by the mole fraction of cobalt or manganese introduced into the synthesis gels (Table 1). TG-DTG plots demonstrate that this method of analysis can be used qualitatively for the systematic study of the properties of zeolitic material relative to their incremental incorporation of divalent heteroatoms.

The degradation of the occluded and ion paired tetralkylammonium species display a continuous change relative to, and as a function of, the mole fraction of

divalent heteroatoms in the synthesis gel and incorporated into the framework. This is supported by XRD, XRF, FTIR and SEM analysis. The synthesis series can be expanded to produce a quantitative statement equating the DTG analysis results with the number of heteroatoms per unit cell.

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