# Ni-ZSM-5 and Cu-ZSM-5 Synthesized Directly from Aqueous Fluoride Gels

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Ni-ZSM-5 and Cu-ZSM-5 have been synthesized in a slightly acidic fluoride medium. A low water H-ZSM-5 formula was used to synthesize the metal-substituted systems using bis(tetraethylammonium) tetrachloronickelate(II) $[N(CH_2CH_3)_4]_2[NiCl_4]$ and bis(tetraethylammonium) tetrachlorocuprate(II) $[N(CH_2CH_3)_4]_2[CuCl_4]$ as the tetrahedrally coordinated metal species. X-ray diffraction analysis established the presence of highly crystalline and thermally stable material. Unit cell dimensions increased with increasing levels of metal substitution. X-ray fluorescence (XRF) bulk analysis showed increasing levels of metals in the material and corresponding decreases in the moles of silica. The maximum levels of substitution achieved were Ni 3.93 and Cu 4.38 (in wt %). Analysis by scanning electron microscopy (SEM) showed a crystal morphology similar to that of H−ZSM-5 but with smaller crystals having an increasing aspect ratio in the substituted materials. There was evidence of twinned crystals and the appearance of raised faces in all substituted samples. Thermogravimetric and derivative thermogravimetric analysis showed anomalous losses, which could be explained by Jahn−Teller distortions. Fourier transform infrared analysis of the materials showed an increasing level of distortion in significant regions of the spectra. Analysis of the filtrate, from EDTA-exchanged material, by atomic absorbance spectroscopy (AAS) showed that there were tetrahedrally coordinated $M^{2+}$ species in the material and relatively small amounts were removed by ion exchange.

## Introduction

Modifying zeolite catalysts by isomorphous substitution of heteroatoms effectively changes the catalytic application and is the subject of much research.[1−3] Synthesis of ZSM-5 in a slightly acidic fluoride medium produces the protonated form required for catalytic activity.[4] Following the successful synthesis of H−ZSM-5 substituted with cobalt and manganese,[5,6] the series has been modified to minimize waste. The mole fraction of water used in the synthesis gel was reduced[7,8] and the metal-substituted series was extended to introduce copper and nickel into pure silica H−ZSM-5 framework.

Nickel is less active than cobalt for the selective catalytic reduction of NO with methane[1] but has been shown to facilitate hydrodesulfurization in combined $Co^{2+}$ and $Ni^{2+}$ zeolite catalysts.[9] Trout et al.[10] reported that copper-loaded ZSM-5 is the most active catalyst known for $NO_x$ decomposition. The structure and catalytic activity of both Ni−ZSM-5 and Cu−ZSM-5 produced by secondary synthesis methods [11,12] have been extensively studied in recent years.[13−15]

We report here the synthesis of crystalline MFI zeolite catalytic material isomorphously substituted with tetrahedrally coordinated bivalent nickel and copper. This is a simple primary synthesis process using a slightly acidic aqueous fluoride medium.

## Experimental Section

**Synthesis of Pure Silica ZSM-5 with a Low Water Gel Composition.** A series of experiments were conducted to investigate the effect of reducing the molar ratio of water in the synthesis gel to minimize synthesis waste.[7] The original molar composition[5] was modified as given in formula 1.

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**Table 1. Molar Composition of Products, Losses on Ignition, Unit Cell Sizes and Metal Content of Samples**

| $M^{2+}$ mol In gel | chem. formulation of calcined material | gel pH | prod. pH | LOI % as synthesized | LOI % after rehydration | u.c.$^a$/Å | M/M + Si | M% conc. |
|---|---|---|---|---|---|---|---|---|
| Ni 0.05 | $Si_{94.83}Ni_{1.06}Zn_{0.12}O_{192}$ | 6.6 | 6.3 | 12.5 | 0.93 | 5309 *OP** | 0.011 | 1.11 |
| Ni 0.1 | $Si_{93.91}Ni_{2.02}Zn_{0.07}O_{192}$ | 6.7 | 6.5 | 14.4 | 0.87 | 5329 *OP* | 0.021 | 2.11 |
| Ni 0.15 | $Si_{92.44}Ni_{3.56}Zn_0O_{192}$ | 6.8 | 5.5 | 14.3 | 1.16 | 5336 *OC* | 0.037 | 3.71 |
| Ni 0.2 | $Si_{92.16}Ni_{3.77}Zn_{0.07}O_{192}$ | 5.8 | 5.8 | 14.4 | 0.94 | 5429 *OC* | 0.039 | 3.93 |
| Cu 0.05 | $Si_{95.26}Cu_{0.60}Zn_{0.14}O_{192}$ | 7.0 | 8.6 | 12.9 | 0.71 | 5327 *OC* | 0.006 | 0.63 |
| Cu 0.1 | $Si_{94.06}Cu_{1.76}Zn_{0.18}O_{192}$ | 7.0 | 6.6 | 16.1 | 0.70 | 5359 *OC* | 0.018 | 1.84 |
| Cu 0.15 | $Si_{93.01}Cu_{2.72}Zn_{0.26}O_{192}$ | 6.5 | 5.3 | 15.2 | 1.80 | 5366 *OC* | 0.028 | 2.84 |
| Cu 0.2 | $Si_{92.09}Cu_{3.63}Zn_{0.28}O_{192}$ | 5.6 | 5.6 | 17.8 | 1.15 | 5385 *OP* | 0.038 | 3.79 |
| Cu 0.3 | $Si_{90.03}Cu_{4.12}Zn_{1.57}O_{192}$ | 5.6 | 5.5 | 16.4 | 0.80 | 5382 *OP* | 0.044 | 4.38 |
| pure silica | $Si_{95.3}Zn_{0.7}O_{192}$ | 5.6 | 5.5 | 12.6 | 0.65 | 5352$^\#$ *OC* | | |

$^a$ OP = orthorhombic primitive; OC = orthorhombic face centered. $^b$ Literature value ZSM-5, 5334 Å, *OP*.[17] Fluoride silicalite 5345 Å, *OP*.[27]

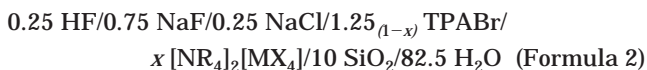$$0.25\ HF/0.75\ NaF/0.25\ NaCl/1.25\ TPABr/10\ SiO_2/x\ H_2O$$

$$\text{(Formula 1)}$$
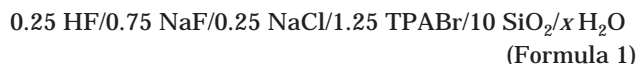
where $x$ = 330, 165, 82.5, 50, 33, and 22 mol.

In a typical gel, 37.5 g of Ludox HS 40 wt % suspension in water (Aldrich) was used as the silica source. Added to this was 0.78 g of NaF (Fluka Chemika 99%), 0.125 g of HF (Fluka Chemika puriss 40%), 0.368 g of NaCl (general-purpose reagent), 8.33 g of TPABr (Aldrich 98+%), and 14.58 g of deionized water. Between each addition, the gel was stirred to homogeneity; the pH was favorable at pH 6.3. There was no aging period, and the gel (~60 g) was divided into five sample portions in Teflon-lined, steel reaction vessels and incubated at 170 °C for 2−5 days. Samples were quenched, filtered, washed, and dried at 40 °C. All products were analyzed using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), thermogravimetric and derivative thermogravimetric (TGDTG), and Fourier transform infrared (FTIR) analysis. Most crystalline samples were calcined to 780 °C, rehydrated, and X-rayed to establish thermal stability.

**Synthesis of $[N(CH_2CH_3)_4]_2[NiCl_4]$ and $[N(CH_2CH_3)_4]_2$-$[CuCl_4]$.** The synthesis of tetrahedral tetrahalometalates of the types $[R_4N]_2[MX_4]$, where R = tetraalkylammonium species, M = divalent transition metals, and X = Cl, Br, or I have been described by Gill and Taylor.[5] They are crystallized as salts of large organic cations from a solution of hot ethanol. The reagents used were copper(II) chloride, dihydrate, 99+% (Sigma Aldrich); nickel(II) bromide trihydrate, purum >98%, (Fluka Chemika); tetraethylammonium bromide, (TEABr) 98+%, (Lancaster Chemical Co.); tetraethylammonium chloride monohydrate, (TEACl·H_2O) 95+%, (Lancaster Chemical Co.); and ethyl alcohol, $C_2H_5OH$, (general laboratory reagent).

**Synthesis of Ni-ZSM-5 and Cu-ZSM-5.** A series of gels were produced according to formula 2.

$$0.25\ HF/0.75\ NaF/0.25\ NaCl/1.25_{(1-x)}\ TPABr/$$

$$x\ [NR_4]_2[MX_4]/10\ SiO_2/82.5\ H_2O \quad \text{(Formula 2)}$$

where $x$ is in the range 0−0.3, and $[NR_4]_2[MX_4]$ represents $[NEt_4]_2[NiBr_4]$ or $[NEt_4]_2[CuCl_4]$.

The gels were prepared as previously described with the templating species and the metal halide species ground together to homogeneity and added last. There was no aging period and a typical synthesis produced ~60 g of gel which was incubated at 170 °C, and samples taken from 2 to 5 days. The pH of the gels and the product solutions are given in Table 1.

## Results

### Synthesis of Pure Silica ZSM-5 with a Low Water Gel Composition.

The material was analyzed using a Philips 1710 X-ray diffractometer using Cu Kα radiation. The samples were compared by computerized on-line isotypical search which confirmed that highly crystalline pure silica ZSM-5 was produced in all systems. The data plots matched ICDD reference patterns 44-2 ($Al_2O_3$ 54 $SiO_2$) and 45-737 ($C_{48}H_{112}F_4O_{192}$-$Si_{96}$). The average unit cell ranged from 5279 to 5428 Å$^3$. The systems using 82.5 mol of water had averaged unit cells of 5352 Å$^3$ and were similar to literature values of 5334 Å$^3$.[16]

The crystal morphology was investigated using a Philips 515 scanning electron microscope. The samples were mounted on aluminum stubs and coated with gold-evaporated film. Single elongated prismatic "boat-shaped" crystals, typical of ZSM-5 morphology[17] were produced. The crystal sizes ranged between 40 and 100 $\mu$m with increased twinning as the gel water was reduced. SEMs for the 22 mol water system showed irregularly shaped material. This agrees with the SEMs published by Dou et al.,[18] for the synthesis of pure silica ZSM-5 from a dry powder system.

TG analysis showed that losses on ignition (LOI) averaged 12%, attributable to the thermal decomposition of TPA$^+$ and consistent with literature values.[5,6] There was little evidence of water loss below 300 °C, confirming hydrophobicity. FTIR spectra matched literature spectra for Silicalite.[16] XRF analysis confirmed that the amount of water remained consistent at ~12 $H_2O$ per unit cell of the material as synthesized. For metal substitution, the system using 82.5 mol $H_2O$ was preferred for optimum crystallinity and ease of preparation.

Synthesis of the metal species all used tetraethylammonium (TEA) cations as the coordinating organic species, the optimum organic template species used in the synthesis of ZSM-5 is tetrapropylammonium (TPA) cations. Attempts to precipitate the nickel and copper complexes using [TPA]$^+$ as the countercation failed due to the solutions being subject to superheating as the ethanol was evaporated. A series of experiments were conducted to synthesize pure silica ZSM-5 replacing [TPA] with [TEA] to investigate the effects on the product crystallinity. The results showed that it was possible to substitute 80% of the TPA. Earlier work[9] also concluded that crystallization stopped only when the TPA was exhausted from the gel.

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**Synthesis of $[N(CH_2CH_3)_4]_2[NiCl_4]$ and $[N(CH_2CH_3)_4]_2[CuCl_4]$.** XRD, FTIR, and TGDTG established the purity of the tetrahalometalates. $[TEA]_2[NiBr]_4$, was determined as space group $P4_2/nmc$ with unit cell constants of $a = b = 9.00$ Å and $c = 14.97$ Å. By use of space group and unit cell data, the chloro and bromo complexes have been shown to be isostructural.[20] In a similar study of nickel complexes, Weisner et al.[21] described possible space groups as $Pn2_1a$ or $Pnma$. The nickel complexes that can be considered as having tetrahedral configurations are those that have four halide ligands,[22] and for most four-coordinated nickel-(II) complexes, a square-planar geometry is preferred. Simple crystal field theory predicts a distortion of tetrahedrally coordinated nickel(II) in the form of an elongated tetrahedron.[21] This can be explained by the Jahn−Teller theorem. It has been shown, however, that spin−orbit forces can remove the degeneracy of the ground state and leave a species that is not subject to Jahn−Teller distortion.[21] The nickel is surrounded by four identical ligands, eliminating any distortion due to asymmetric ligand fields and asymmetric crystal packing. The bond angles are described as only slightly distorted at 106.83° and 110.81°,[20] and the deliquescent aggregated crystals are described as "aqua" blue in color. Square-planar Ni(II) complexes are usually red, yellow, or brown.[22]

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 regular cubic environment.[22] It has been shown[23] that while the degeneracy of Ni(II) complexes is removed by spin−orbit coupling, distortion of the $[CuCl_4]^{2-}$ ion leads to a more stable configuration. Most copper compounds are blue-green; exceptions caused by strong UV charge-transfer bands have a red-brown color. The $[TEA]_2 [CuCl]_4$ as synthesized, were deep yellow; this is consistent with published data.[24]

FTIR analysis identified the main spectral bands of the complexes, and the results agreed with previous work.[24] The infrared spectra for all complexes show characteristic vibration frequencies for the stretching, bending, and deformation of saturated C−H and C−C bonds. The strong bands at 2960−2850 cm$^{-1}$, indicative of C−H stretching, are broadened by the overtone bands of the N−C groups (2820−2780 cm$^{-1}$).[25]

From the thermal analysis data, the trend in the onset of peak temperature loss was consistent with the charge-to-size ratio of the metals in the +2 oxidation state.[26] The losses in the copper complex commenced at a lower temperature due to the distorted configura-
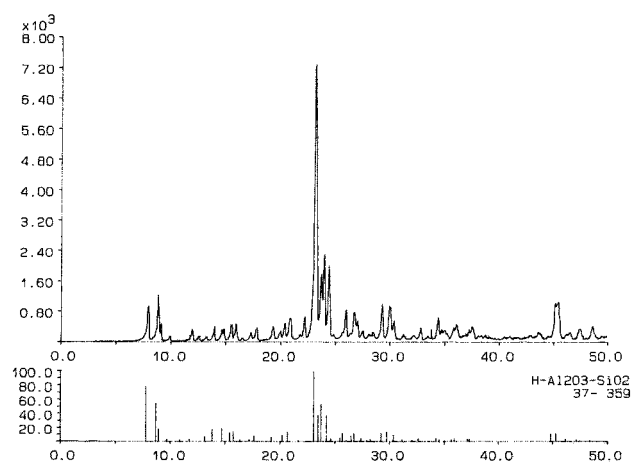


**Figure 1.** XRD plot of Ni-ZSM-5 synthesized with 0.2 Ni$^{2+}$ in the gel.

tion. The nickel complexes showed a third stage loss possibly due to the higher density of the bromide anions. These stable tetrahedrally coordinated metal species were shown to be compatible with the low water ambient pH zeolite synthesis gel.

**Synthesis of Ni-ZSM-5 and Cu-ZSM-5.** XRD analysis of the nickel system showed that the products stayed crystalline up to the 0.2 mol level of substitution and were identified as a ZSM-5 type material, ICDD reference pattern 37−357 ($H-Al_2O_3-SiO_2$) (Figure 1). The material was indexed as orthorhombic−primitive at the lower levels of substitution (0.05 and 0.10 mol) and as orthorhombic−face centered 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).[27]

The syntheses attempted at substitution levels of 0.25 mol fraction and above remained amorphous. This could be due to Jahn−Teller distortions of tetrahedral d$^8$ and d$^9$ configurations generally observed as changes in the bond angle from 109.5°. This would cause strain in the lattice.

XRD analysis of the copper-substituted series showed crystalline material for all samples taken over a period of 2−5 days. The unit cells parameters were generally higher than the literature value for ZSM-5 and increase with increasing levels of substitution (Table 1). This may indicate framework-heteroatom incorporation. The material was indexed as orthorhombic−face centered at the lower levels of substitution and as orthorhombic−primitive at the 0.2 and 0.3 mol levels of substitution.

XRF bulk chemical analysis of both systems showed levels of substitution to be comparable with levels achieved by ion-exchange methods: e.g., 1.8 wt % Ni−ZSM-5[28] and 2.73 wt % Cu−ZSM-5.[29] There were consistent small quantities of zinc in the material shown to have been introduced as an impurity in the silica source.[26]

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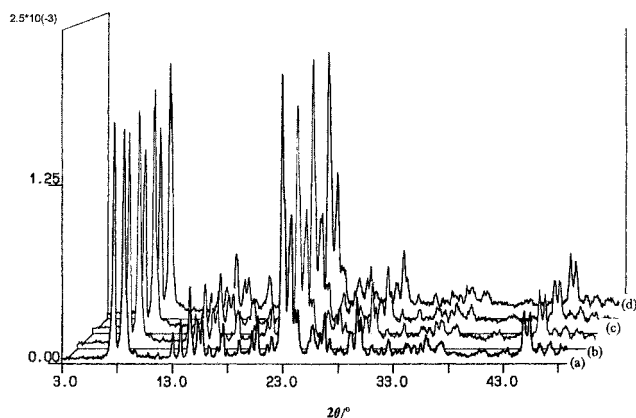
**Figure 2.** XRD plot of Cu-ZSM-5 with $Cu^{2+}$ in the gel at (a) 0.05, (b) 0.1, (c) 0.15, and (d) 0.2 mol.
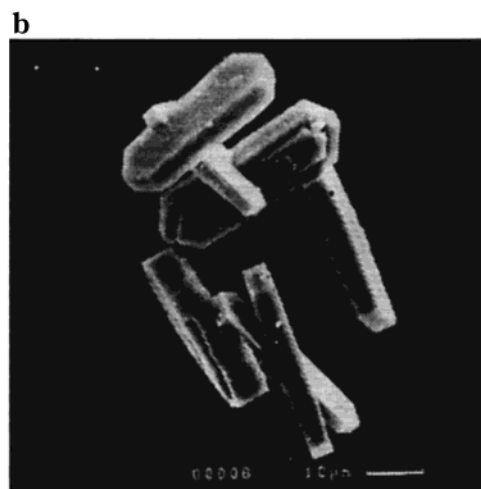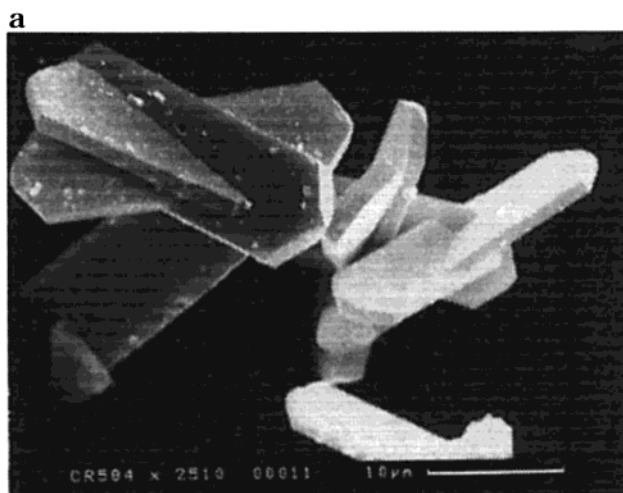
The thermal stability of the material was investigated by calcining the most crystalline sample to 780 °C in air, to remove all water and template species. The samples were rehydrated in a controlled atmosphere over a saturated salt solution of 0.7 relative humidity for 7 days. XRD analysis confirmed the presence of highly crystalline material that was stable to 780 °C to 0.20 mol levels of substitution in the nickel system and to 0.25 mol levels of substitution in the copper system. Figure 2 shows the XRD plots of the copper series (0.05–0.2 mol) after calcination and rehydration.

SEM analysis showed changes in morphology when compared to the crystals in the pure silica system, with increasing levels of substitution. In the nickel-substituted material, the 0.1 mol fraction produced small crystals (30–40 $\mu$m) as shown in Figure 3a,b. The 0.2 mol fraction showed deterioration in crystal quality that was consistent with XRD analysis.

The copper-substituted series produced similarly sized crystals, but with less deterioration in crystal quality. Both systems showed evidence of decreasing crystal size, increasing aspect ratios, evidence of twinned crystals, and the appearance of raised faces. These features are consistent with isomorphous heteroatom substitution.[5]

TGDTG analysis was carried out on the most crystalline samples at all levels of substitution between 40 and 800 °C. The losses on ignition are summarized in Table 1. The total losses, compared to the literature value of 12% for pure silica ZSM-5,[4] increase irregularly with increased metal loading, and there is a noticeable difference of the thermal behavior between these systems. The anomalous reaction intervals and percentage weight losses could be explained by the Jahn–Teller distortion of the tetrahedral Ni(II) and Cu(II) complexes. The degradation of occluded and ion-paired tetralkyl-ammonium species show changes relative to, and as a function of, the mole fraction of divalent heteroatoms in the synthesis gel. The thermal analysis of the material is reported fully elsewhere.[30]

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 (Figure 4) shows a distortion of the spectra between 1250 and 900 $\nu$ cm$^{-1}$; this is the region of the spectrum assigned to

(30) Round, C. I.; Williams, C. D.; Latham, K.; Duke, C. V. A. *J. Therm. Anal.* accepted for publication.



**Figure 3.** SEM of (a) Ni-ZSM-5 with 0.2 $Ni^{2+}$ in the gel and (b) Cu-ZSM-5 with 0.2 $Cu^{2+}$ in the gel.

asymmetrical T–O–T stretching and is indicative of heteroatom substitution.[16]

These traces are typical of the material analyzed but were not consistent with increasing levels of substitution. For example, in Figure 4, the trace for the 0.05 mol fraction shows considerable distortion, whereas the 0.1 mole fraction shows little or no distortion and is very similar to the trace of an unsubstituted sample.

Increasing the levels of $M^{2+}$ substitution should increase the acidity of the framework, but there was no obvious trend in the absorption bands assigned to terminal hydroxyl groups (3740 cm$^{-1}$), or to the absorption bands assigned to bridging OH groups associated with a Brønsted site (3600–3650 cm$^{-1}$).[31] A spectroscopic study of H–ZSM-5 [31], found that the stretching vibrations of the hydroxyl groups varied with aluminum content. A previous study[32] concluded that low-intensity hydroxyl vibrations were due to defect-free crystals. These theories could explain the inconclusive trends in these absorption bands due to the low metal content and defect-free crystals synthesized in a fluoride medium.

From the atomic absorbance data and the XRF bulk analysis, the concentration of metal in the samples was calculated, and the results are given in Table 1. From

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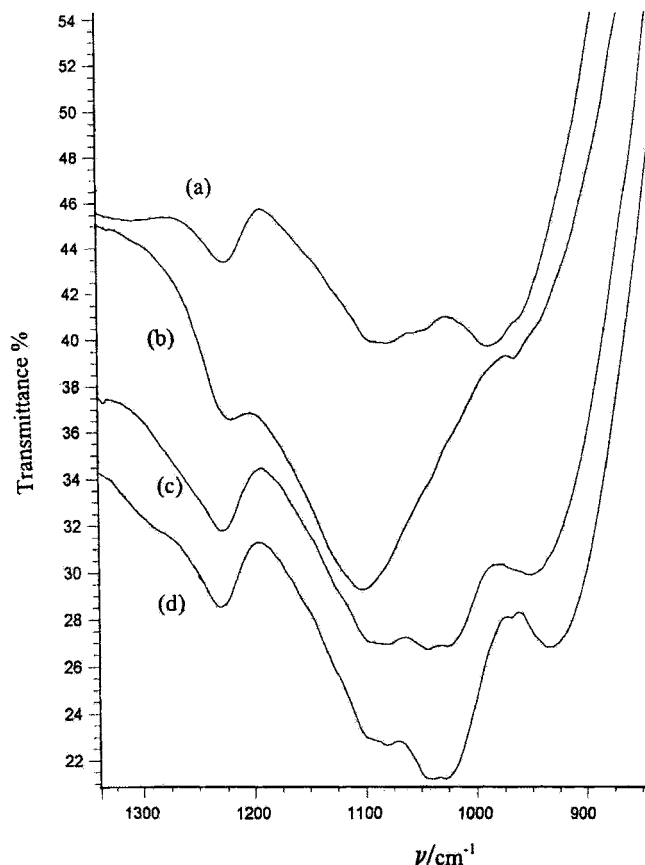
**Figure 4.** FTIR spectra of the Ni-substituted series.

the XRF bulk analysis, the quantity of $M^{2+}$ in the copper-substituted samples is similar to that in the nickel-substituted samples. However, the volume of extraframework $Cu^{2+}$ removed by ion exchange was consistently higher: 15−32.8% (wt) in the Cu system compared to 0.42−1.49% (wt) in the Ni system. This is possibly due to the large ionic radius of the $Cu^{2+}$ ion at 0.7 Å. This size increase would increase the strain on the zeolite framework, which would make the isomorphous substitution less efficient. Cu(II) complexes are subject to Jahn−Teller distortion and are in the form of a flattened tetrahedron. They are rarely seen in a

regular cubic environment, and this distortion could decrease the framework stability. In the nickel-substituted material, the volume of extraframework $Ni^{2+}$ removed by ion-exchange is very small. The ionic radius of $Ni^{2+}$ is similar at 0.69 Å (0.63 Å in square-planar geometry). The stability of the Ni systems could be due to the flexibility of the bond angles, described as slightly distorted,[20] which would increase the metal's stability in the framework.

## Conclusions

The Ni- and Cu-substituted ZSM-5 zeolites have been synthesized in a one-step reaction, using a low water fluoride medium. This system has been demonstrated to be a relatively defect-free material. The analytical data shows that there are changes in the characteristics of the Ni−ZSM-5 and the Cu−ZSM-5 compared to those of the pure silica form. XRD analysis established the presence of highly crystalline and thermally stable material, with increasing unit cell dimensions and increased 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 of the filtrate from the EDTA-exchanged material showed that there are tetrahedrally coordinated $M^{2+}$ species in the material and that relatively small amounts was removed by ion exchange.

TGDTG analysis indicated interesting peak temperature losses relative to the levels of the metals substituted. Also, the anomalous reaction intervals and percentage losses, which could be explained by the Jahn−Teller distortion of the tetrahedral Ni(II) and Cu-(II) species, provide persuasive evidence for heteroatom substitution.

FTIR spectroscopy showed distortion of the spectra, when compared to unsubstituted material, between 1250 and 900 $\nu$ cm$^{-1}$, assigned to T−O−T asymmetric stretching which also supports heteroatom substitution