

Abstract

The benzene methylation with methane over zeolite catalysts was previously shown in our laboratory to require the presence of oxygen. Thus, a two-step mechanism involving the intermediate formation of methanol by partial oxidation of methane followed by the methylation of benzene with methanol in the second step, was postulated. This paper now reports the results of the characterisation of the zeolite catalysts used for the oxidative benzene methylation reaction in order to provide some information about their composition, structure, properties and their behaviour before and after the reaction. The catalysts were characterised by XRD, ICP-AES, XRF, FTIR and solid state NMR. XRD results indicate that the crystalline structures of all the ZSM-5 and H-beta catalysts remained unchanged after batch reaction of benzene with methane over the catalysts in agreement with the observation that the catalysts recovered from the reactor could be reused without loss of activity. Elemental analyses and FTIR data show that as the level of metal ion exchange increases, the Brönsted acid concentration decreases but this metal ion exchange does not totally remove Brönsted acidity. FTIR results further show that only a small amount of acid sites is actually necessary for a catalyst to be active since used catalysts containing highly reduced Brönsted acidity are found to be reusable without any loss of their activity. ^{29}Si and ^{27}Al MAS NMR together with FTIR spectra also show that all the active zeolites catalysts contain some extra-framework octahedral aluminium in addition to the normal tetrahedral framework aluminium. The presence of this extra-lattice aluminium does not, however, have any adverse effect on the crystallinity of the catalysts both before and after oxidative benzene methylation reaction. There appears also to be no significant dealumination of the zeolite catalysts during reaction since their catalytic performance was retained after use.

Keywords: Catalysts characterisation, oxidative benzene methylation, spectroscopic techniques, X-ray diffraction, zeolites

1. Introduction

In our recent investigations [1, 2] on the methylation of benzene with methane at 400 °C over zeolite catalysts in a high pressure batch reactor, we demonstrated clearly that the presence of oxygen was required for the reaction to proceed to yield methylated products. It was also observed that when the batch reactor was flushed with oxygen in absence of catalyst prior to adding methane, methanol was obtained as the major product (about 86% selectivity). On the other hand, methanol was not detected in the presence of zeolite catalysts when oxygen was introduced into the reactor indicating that all the methanol, being more reactive than the initial methane reactant, was consumed in the reaction to form methylated products over the catalysts. Thus, a two-step mechanism involving the intermediate formation of methanol by partial oxidation of methane followed by the methylation of benzene with methanol, was postulated. Further support to this mechanism has also been reported in our later investigation [3] which showed excellent correlation between the activity of the catalysts used for both the benzene methylation with methanol in a low pressure flow reactor and benzene methylation with methane in the presence of oxygen in high pressure batch reactor.

In this paper, we report the results of characterisation of the metal-exchanged zeolite catalysts that were used for the oxidative benzene methylation reaction. The characterisation of the materials using a series of physical techniques was undertaken in order to provide some information about their composition, structure, properties and their behaviour before and after the benzene methylation reaction. Such information will be quite useful for further development of the catalysts for the optimisation of their activity and product selectivity in the oxidative benzene methylation reaction.

2. Experimental

2.1 Catalyst Preparation and Catalytic Experiments

The zeolite catalysts used in this study were commercial samples of HZSM-5 (PQ Corporation, SiO₂/Al₂O₃ = 35) and H-beta (PQ Corporation, SiO₂/Al₂O₃ = 28). The Na-exchanged catalyst which was also used was prepared by conventional ion exchange into the HZSM-5 sample with aqueous sodium nitrate. The Co-, Mn- and Cu-exchanged zeolites were then prepared from the NaZSM-5 produced by ion

exchange with appropriate metal salts. A detailed description of the preparation of these metal-exchanged ZSM-5 catalysts has been reported elsewhere [2]. The details of the experimental procedures for the catalytic experiments are similar to those published recently [1, 4]. The used catalyst residues were filtered out of the chloroform or dichloromethane solutions of the reaction products, dried first in the air and finally in a desiccator before reuse in some experiments.

2.2 Characterisation of the catalysts

2.2.1 Chemical Analysis by ICP-AES and XRF

The elemental compositions of ZSM-5 and H-beta samples were determined using PLASMALAB Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) instrument purchased from Labtam International, Melbourne, Australia. The polychromator of the instrument was utilised to perform simultaneous multi-elemental analyses of the zeolite samples. Blank and standard solutions were used to measure the polychromator background and response factors for each element prior to and following the measurement of the sample solutions.

The results of the measurement of elemental silicon present in the samples using ICP-AES were unstable and thus, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the H-beta catalyst which was unknown was determined using X-ray Fluorescence (XRF). The XRF instrument used was SIEMENS SRS 300 XRF with Rh end-window tube and “SPECTRA-AT” software. CuZSM-5 with a known $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35 was used as standard.

2.2.2 Powder X-Ray Diffraction

The powder X-ray diffraction patterns of the zeolite samples were recorded on a Siemens D-500 X-ray powder diffractometer over 2Θ range of 5° to 55° at a scanning speed of 2° (2Θ) per minute and a step size of 0.05° . The diffractometer was equipped with Ni-filtered Cu K- α radiation source (8978 eV or $\lambda = 1.5418 \text{ \AA}$). The X-ray source was operated at 30 mA and 40 kV. Sample preparation for the X-ray analysis involved gentle grinding of the solid into a fine powder and packing of approximately 0.3-0.5 g of the sample into an aluminium sample holder with light compression to make it flat and tight. The X-ray diffraction patterns of the sample were then recorded

on a PC computer with SIE 122D software and saved in CPI text format for further manipulation and processing on a Macintosh computer using the Igor® program.

2.2.3 Solid State MAS NMR Spectroscopy

The solid state magic angle spinning (MAS) ^{29}Si and ^{27}Al NMR spectra of the H-beta catalyst were recorded on a Bruker MSL-300 NMR spectrometer operating at a magnetic field strength of 7.2 Tesla. Kaolin was used as the reference for the chemical shift for both ^{29}Si and ^{27}Al MAS NMR spectra. A QUADCUCCL.PC pulse program was used to measure single bloch decay in the ^{27}Al NMR while a HPDEC.PC program was used to apply high proton decoupling during acquisition for the ^{29}Si NMR.

2.2.4 FTIR Spectroscopy

The measurement of zeolite catalyst acidities using FTIR of adsorbed pyridine are similar to those described elsewhere [2, 3].

3. Results and Discussion

3.1 X-ray Diffraction

The X-ray diffraction (XRD) patterns of all the fresh metal exchanged ZSM-5 zeolites were found to be similar to the fresh commercial HZSM-5 sample as illustrated in Figure 1. The X-ray patterns were obtained for the major catalysts not only before batch reaction of benzene with methane but also after reaction. The X-ray patterns of the catalysts remained unchanged after the reaction except that the relative intensities of the peaks decreased as shown in Figure 2 for H-beta. This lowering of peak intensities might be due to X-ray shielding caused by absorption of carbonaceous material during reaction by the zeolite samples. A similar observation has been reported by Breck et al. [5] on hydration of zeolites and more recently by Long et al. [6] for the methylation of naphthalene by methane over substituted aluminophosphate molecular sieves. The fact that the X-ray patterns of the zeolite samples remained unchanged after reaction with methane, except for the intensity change, indicates that their crystalline structure remained intact after the reaction. This is interesting since

these zeolite catalysts were also observed to remain active for the reaction (with similar product selectivities) after each use (Table 1).

3.2 Chemical Analysis using ICP-AES and XRF

Table 2 summarises the results of the elemental analyses of the zeolite catalysts obtained from ICP-AES and XRF techniques. Table 2 indicates that many acid sites were still present in the NaZSM-5 (obtained by exchanging only once) used for the catalytic experiments since the sodium exchange level was only 41.2%. This is actually in agreement with the results of acidity measurement (presented in the next section) which indicate a relatively high concentration of Brønsted acidity when compared with other metal exchanged ZSM-5 catalysts. This low sodium exchange level in NaZSM-5 resulting in high concentration of acid sites might therefore be responsible for the high catalytic activity reported earlier for the batch reaction of methane with benzene [2] and with toluene [2, 7] in comparison with other transition metal exchanged ZSM-5 and H-beta catalysts. Table 2 also shows that the cobalt exchange level in CoZSM-5 is comparable to the manganese exchange level in MnZSM-5 and that might be why these two catalysts were found by acidity measurements using FTIR (as reported in the next section) to have comparable Brønsted acid site concentration. It should be noted that CuZSM-5 is shown to have more than 100% copper exchange level and lowest Na/Al ratio among the metal-exchanged catalysts. Similar observations have also been previously reported for CuZSM-5 [8] and Cu-Mordenite [9], and this excessive exchange of copper has been attributed to the hydrolysis of copper ions leading to the formation of polynuclear complexes of the type $[\text{Cu}_x(\text{OH})_y]^{(2x-y)+}$ species during the ion exchange process [10, 11].

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the H-beta catalyst was also determined by XRF to be 28.0 as shown in Table 2. Table 2 also shows that $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 38.9 obtained using XRF for CuZSM-5 which was used as the standard is quite close to the known value of 35, thus indicating the accuracy of the technique.

3.3 Characterisation of Acidity using FTIR Spectroscopy

3.3.1 The Hydroxyl Region

The hydroxyl stretching vibration region of the infra-red spectra of fresh ZSM-5 samples before and after adsorption of 2 μL pyridine is illustrated in Figure 3 for HZSM-5, CoZSM-5 and CuZSM-5. The catalysts showed the two well-known main peaks at 3606 and 3740 cm^{-1} attributed to bridging hydroxyl group affiliated with the tetrahedrally coordinated aluminium and non-acidic terminal silanol stretching vibrations [12, 13], respectively. A broad absorption band at about 3660 cm^{-1} which has previously been described [14] and assigned to hydroxyl groups associated with extra-lattice aluminium [15] was also observed. Figure 3 shows that, on adsorption of pyridine, the infra-red band at 3606 cm^{-1} was lost and bands due to adsorbed pyridine appeared in the region 1400 to 1700 cm^{-1} . In the case of H-beta, it took more than 2 μL pyridine to remove all the 3606 cm^{-1} band (Figure 4) suggesting that H-beta contains a higher total concentration of acid sites than the ZSM-5 catalysts. After reaction, coking caused some of the ZSM-5 samples to become opaque to infra-red radiation in the hydroxyl region leading to the disappearance of both the 3606 and 3740 cm^{-1} peaks. The hydroxyl region was therefore not used for quantification in this work.

3.3.2 The region 1400 - 1700 cm^{-1} after Pyridine Adsorption for Characterisation of Acidity

Figure 5 shows the FTIR spectra in the region 1400 - 1700 cm^{-1} after pyridine adsorption on fresh ZSM-5 samples at 100 $^{\circ}\text{C}$. Figure 5 shows well resolved bands at about 1544, 1490 and 1453 cm^{-1} . The bands at 1544 and 1453 cm^{-1} are assigned to pyridine adsorbed to Brönsted (protonic) acid sites and to Lewis acid sites (coordinatively unsaturated Al^{3+}), respectively, while the band at 1490 cm^{-1} is attributed to the adsorbed pyridine species on both Brönsted and Lewis acid sites. Figure 5 also indicates a shift in the coordinately bound pyridine band from 1453 cm^{-1} to lower wavenumbers at about 1443 and 1449 cm^{-1} for NaZSM-5 and MnZSM-5, respectively. This may be attributed to the weaker interaction of the Na^{+} and Mn^{2+} cations in agreement with an earlier report [16] that, for a given coordination, the

strength of interaction of cations which also function as Lewis acid sites increases with increase in the formal charge/radius ratio of the cation.

Figure 5 shows further that the exchange of the metal ions into the parent ZSM-5 causes an increase in the Lewis acid sites and a decrease in the Brönsted acid sites. In their study of cobalt and iron impregnated in MFI zeolites, Rhee et al. [17] explained that the increase in the number of Lewis acid sites was due to the function of the electron acceptors of transition metal cations as additional Lewis acid sites in a general sense. The reduction in the Brönsted acid sites is reasonable as these sites are replaced by metal ions. However, the metal ions did not totally remove Brönsted acidity. It is interesting to note that CuZSM-5 showed the greatest reduction in the Brönsted acid sites in agreement with the results of elemental analysis by ICP-AES which showed more than 100% copper exchange level in CuZSM-5. Figure 5 also shows quantitatively that MnZSM-5 and CoZSM-5 have comparable concentrations of Brönsted acid sites consistent with the ICP-AES results which indicated comparable metal exchange levels.

Table 2 shows the calculated Brönsted and Lewis acid concentrations of all the ZSM-5 and the H-beta catalysts per unit cell for both the fresh samples before reaction and for the samples after batch reaction of methane with benzene in the presence of oxygen. These Brönsted and Lewis acid concentrations were determined by measurement of the peaks areas of the 1544 and 1453 cm^{-1} , respectively. Correction for wafer thickness was made by dividing the peak areas of these bands by the areas of the zeolite framework overtone bands at about 2000 cm^{-1} . Corrections for differences in absorptivity values [18] were applied and it was assumed that the total acid site concentration of the parent HZSM-5 (or the H-beta) sample was equal to the aluminium content of the zeolite. Table 2 shows quantitatively the decrease in Brönsted acid sites and increase in Lewis acid sites when metal ions are exchanged into the parent HZSM-5 catalyst. Table 2 also shows clearly that the higher the metal exchange level, the lower the Brönsted acid concentration of the fresh catalysts. The order of Brönsted acidity for the ZSM-5 catalysts was found to be HZSM-5 > NaZSM-5 (exchanged only once) > CoZSM-5 \approx MnZSM-5 > NaZSM-5 (exchanged 3 times) > CuZSM-5. The total acid concentration was also observed to decrease gradually with increase in metal exchange levels.

It is clearly shown too in Table 2 and Figure 6 that after the batch reaction of methane with benzene in the presence of oxygen, the Brönsted acid site concentration decreased to a much greater extent than Lewis acid site concentration. However, only a small amount of Brönsted acid sites is actually necessary for a catalyst to be active for this reaction since used catalysts containing this highly reduced Brönsted acidity were observed to be reusable without loss of activity (Table 1). It is very unlikely that any part of the procedure adopted for preparing the catalysts for reuse as described in section 2.1 led to a regeneration of acid sites. It should, however, be noted that CuZSM-5 showed no decrease in concentration of Brönsted acid sites and its Lewis acid concentration almost doubled after reaction. This behaviour on CuZSM-5 is not clear but may be due to its autoreduction into Cu^+ and Cu^{2+}O^- species which has been previously observed to occur on pre-treatment at 673 - 773 K under vacuum or flowing helium [19]. Table 2 also demonstrates that the total acid concentration was reduced to a much greater extent in the more acidic HZSM-5 and H-beta than in the metal exchanged ZSM-5 catalysts. This behaviour may be attributed to more extensive coking on these more acidic catalysts since acidity generally promotes cracking and coking of hydrocarbons.

3.4 Solid State NMR Spectroscopy

The ^{29}Si and ^{27}Al MAS NMR spectra obtained for both H-beta and HZSM-5 catalysts are similar and showed that the zeolites contained some low level of extra-framework octahedral aluminium in the addition to the normal tetrahedral framework aluminium except that the proportion of this extra-framework aluminium in HZSM-5 is even much lower in HZSM-5 than in H-beta. Thus, only the NMR spectra of the H-beta are presented in this section to illustrate the results of the characterisation using NMR spectroscopy.

3.4.1 ^{29}Si MAS NMR of H-beta

The ^{29}Si MAS NMR spectrum of the H-beta catalyst is shown in Figure 7. The broad asymmetrical peak at about -111 ppm together with a shoulder at about -115 ppm has been attributed to a silicon atom with no aluminium in the next nearest neighbours [i.e. Si(0Al)] [20] while the shoulder at about -103 ppm has been assigned to a silicon atom with one aluminium in the next nearest neighbours [i.e. Si(1Al)] [20]. It has

been reported [21] that the framework tetrahedral Si/Al ratio can be quantitatively determined from the Si(nAl) peak intensities, $I_{\text{Si}(n\text{Al})}$, according to the equation

$$(\text{Si}/\text{Al}) = \frac{\sum_{n=0}^4 I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^4 \frac{n}{4} I_{\text{Si}(n\text{Al})}} \quad (1)$$

provided that the ^{29}Si NMR spectrum is correctly interpreted in terms of Si(nAl) units and no AlOAl linkages are present in the zeolite sample (i.e. Loewenstein's rule applies). It should be noted that the Si/Al ratio determined by equation (1) includes only the aluminium that is substitutionally incorporated into the tetrahedral framework and excludes any non-framework aluminium present. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of H-beta was determined to be 33.5 using equation (1). This value is slightly higher than the value of 28 obtained from XRF (section 3.2) for the total $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite. This difference may be due to the presence of some non-framework aluminium in the zeolite as confirmed by the results of ^{27}Al NMR presented in the next section.

3.4.2 ^{27}Al MAS NMR of H-beta

Figure 8 shows the ^{27}Al MAS NMR spectrum of the fresh H-beta catalyst. The spectrum exhibited two well resolved signals at about 54 and -1.5 ppm assigned to tetrahedral and non-framework octahedral aluminium, respectively. The presence of non-framework aluminium is therefore confirmed by the spectrum. This is in agreement with the FTIR spectra which show a broad absorption band at about 3660 cm^{-1} due to hydroxyl groups associated with extra-lattice aluminium (Figure 3). It has been established that if all the aluminium is visible in the spectrum (i.e. no signal intensity is lost as a result of very strong quadrupolar line broadening), the relative proportions of framework and non-framework Al in a zeolite can be directly determined from the peak intensities of the well separated tetrahedral aluminium, $I_{\text{Al}(\text{tet})}$, and the octahedral aluminium, $I_{\text{Al}(\text{oct})}$ signals [21]. If the total Si/Al ratio,

$(\text{Si}/\text{Al})_{\text{tot}}$, of the sample is known from chemical analysis, the Si/Al ratio of the tetrahedral framework, $(\text{Si}/\text{Al})_{\text{fr}}$, can be calculated using the equation (2):

$$(\text{Si}/\text{Al})_{\text{fr}} = (\text{Si}/\text{Al})_{\text{tot}}(I_{\text{Al}(\text{tet})} + I_{\text{Al}(\text{oct})})/I_{\text{Al}(\text{tet})} \quad (2)$$

The $(\text{SiO}_2/\text{Al}_2\text{O}_3)_{\text{fr}}$ of the tetrahedral framework was calculated using equation 2 to be 36.1 which is close to the value of 33.5 obtained from ^{29}Si NMR but higher than the value of 28 obtained from chemical analysis by XRF. The difference between the NMR results and the chemical analysis result represents the contribution from non-framework octahedral aluminium in the sample on the assumption that all the aluminium is visible in the NMR spectrum. However, the presence of this non-framework aluminium has no significant effect on the crystallinity of the zeolite catalysts either before or after reaction of benzene with methane in the presence of oxygen as shown by XRD patterns (Figures 1 and 2). A previous report by Barrage et al. [22] showed, on the basis of ^{29}Si NMR spectra of both fresh and used HZSM-5 samples, that dealumination of the zeolite lattice occurs following catalyst use in the methanol to gasoline (MTG) conversion reaction. These workers observed that the catalytic behaviour of both fresh and used catalysts was nearly identical. In other words, the loss of aluminium from the zeolite lattice did not appear to have any detrimental effect on the catalytic activity of the zeolite for methanol conversion. In agreement with this finding, any further dealumination of the zeolites that might occur during the oxidative benzene methylation which also involves significant contribution from methanol-to-aromatics reaction [23], did not also significantly affect the performance of the catalysts for the reaction as shown by the results presented in Table 1. However, it has also been previously reported [24] that extensive dealumination of ZSM-5 zeolites caused by water produced during the reaction when used as catalysts for extended periods during repeated conversion-regeneration MTG cycles resulted in enhanced performance in terms of the total quantity of methanol converted before deactivation. It therefore follows that since no such enhanced performance was observed in this work, there appeared to be little or no dealumination of the zeolite catalysts during the reaction.

3.4.3 Conclusion

In conclusion, the crystalline structures of all the ZSM-5 and H-beta catalysts used for the methylation of benzene with methane in the presence of oxygen in a batch reactor are shown by XRD data to remain intact after the reaction in agreement with the observation that the catalysts recovered from the reactor could be reused without loss of activity. FTIR data together with chemical analysis results indicate that the Brønsted acid concentration decreases with increase in the metal ion exchange level. However, this metal ion exchange does not totally remove Brønsted acidity and only a small amount of acid sites is actually necessary for a catalyst to be active since used catalysts containing highly reduced Brønsted acidity are observed to be reusable without loss of their catalytic performance. ^{29}Si and ^{27}Al MAS NMR spectra showed the presence of some low levels of extra-framework octahedral aluminium in addition to the normal tetrahedral framework aluminium in all the active ZSM-5 and H-beta catalysts. This is in support of the 3660 cm^{-1} broad band observed in the FTIR spectra assigned to hydroxyl groups associated with extra-lattice aluminium. The presence of this non-framework aluminium does not appear to have any significant effect on the crystallinity of the zeolites both before and after oxidative methylation of benzene with methane. There appears also to be little or no dealumination of the zeolite catalysts during reaction since the catalytic performance of used catalysts remains unchanged.

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Figure Captions

Figure 1. XRD patterns of fresh ZSM-5 catalysts.

Figure 2. XRD patterns of H-beta before and after reaction.

Figure 3. FTIR spectra of the hydroxyl region of fresh HZSM-5, CoZSM-5 and CuZSM-5 samples: (1) before and (2) after pyridine adsorption.

Figure 4. FTIR spectra of the hydroxyl region of fresh H-beta catalyst: (1) before addition of pyridine and after addition of: (2) 2 μL ; (3) 3 μL and (4) 4 μL pyridine.

Figure 5. FTIR spectra of pyridine adsorption on fresh ZSM-5 catalysts in the region 1400 - 1700 cm^{-1} .

Figure 6. FTIR spectra in the region 1400 - 1700 cm^{-1} of both fresh HZSM-5 and HZSM-5 used for the batch methane/benzene reaction after pyridine addition.

Figure 7. ^{29}Si MAS NMR spectrum of fresh H-beta.

Figure 8 ^{27}Al MAS NMR spectrum of fresh H-beta.

Table 1. Comparison of fresh with used ZSM-5 catalysts for methane reaction with benzene in the presence of residual air at 400 °C and 6.9 MPa pressure

Reaction Time/Catalyst	Benzene Conversion (%)	Selectivity to products (%)		
		Toluene	Ethylbenzene	Xylenes
<u>2 Hours</u>				
Fresh HZSM-5	4.19	92.9	4.25	2.86
Used HZSM-5	4.01	91.7	4.34	3.98
<u>4 Hours</u>				
Fresh CoZSM-5	4.36	91.4	3.85	4.75
Used CoZSM-5	3.39	94.1	2.65	3.30

Table 2. Characterisation of ZSM-5 catalysts using ICP-AES, XRF and FTIR

A. Results obtained from fresh samples before reaction							
Catalysts	SiO ₂ /Al ₂ O ₃	Na/Al	M ^a /Al	Metal exchange level (%)	Acid sites from FTIR of pyridine		
					Bronsted sites, B (uc) ⁻¹	Lewis sites, L (uc) ⁻¹	Total (B + L) (uc) ⁻¹
HZSM-5		0.011			4.2	1.0	5.2
H-beta	28.0 ^d	0.011			3.0	1.3	4.3
NaZSM-5 ^b		0.41		41.2	2.5	2.3	4.8
CoZSM-5		0.080	0.28	56.7	1.5	2.2	3.7
MnZSM-5		0.21	0.28	55.2	1.4	2.4	3.8
NaZSM-5 ^c			0.71		0.7	2.8	3.5
CuZSM-5	38.9 ^d	0.034		141.0	0.6	1.5	2.1
B. Results obtained after batch reaction of methane with benzene							
CoZSM-5					1.1	2.0	3.1
HZSM-5					0.7	0.2	0.9
CuZSM-5					0.6	2.9	3.5
H-beta					0.4	1.0	1.4

^a M = transition metal exchanged into HZSM-5 (i.e. Mn, Co and Cu).

^b This NaZSM-5 sample was prepared by performing sodium ion exchange only once on HZSM-5.

^c This NaZSM-5 sample was prepared by performing Na ion exchange three times on HZSM-5.

^d These SiO₂/Al₂O₃ ratios were determined by XRF

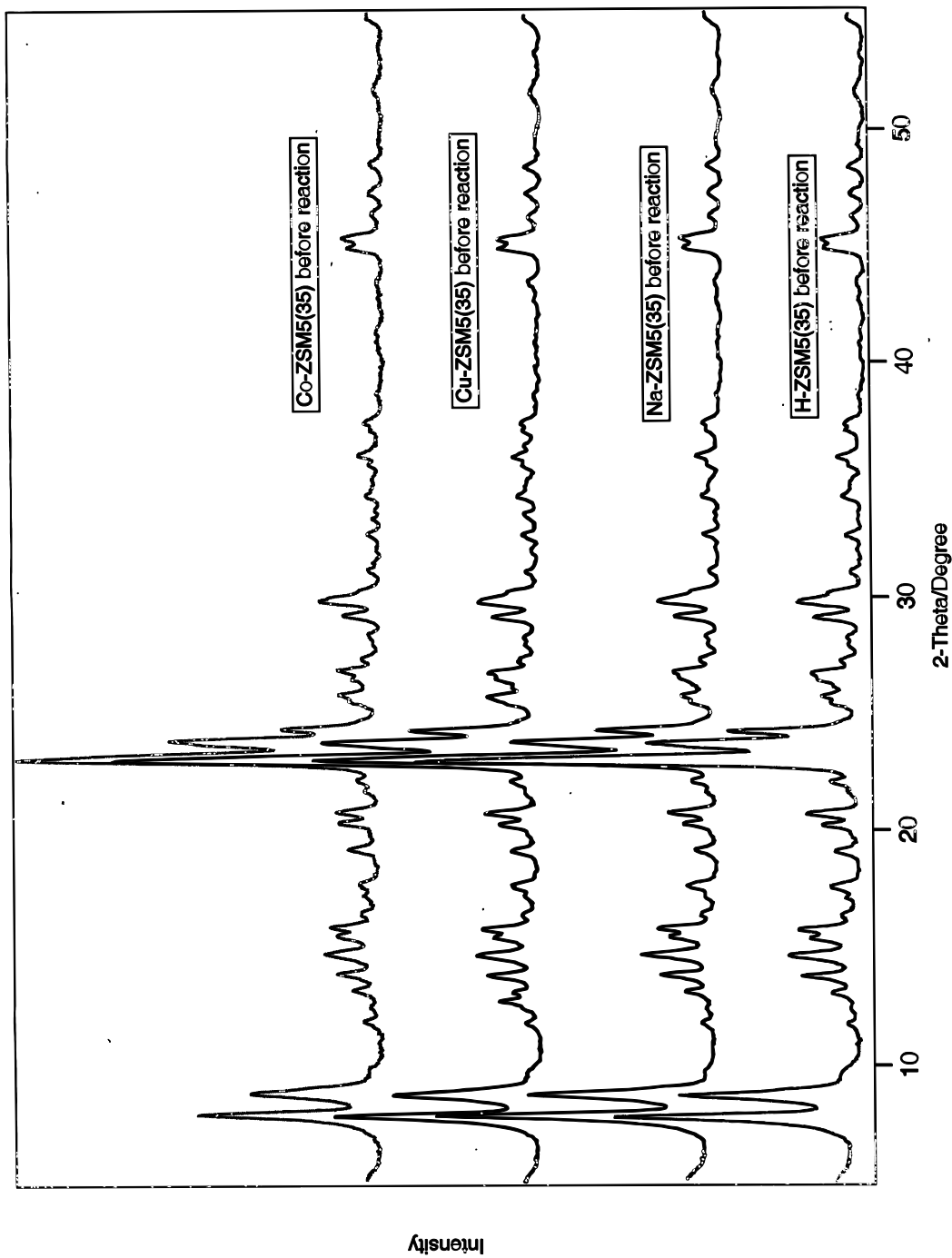


Figure 1

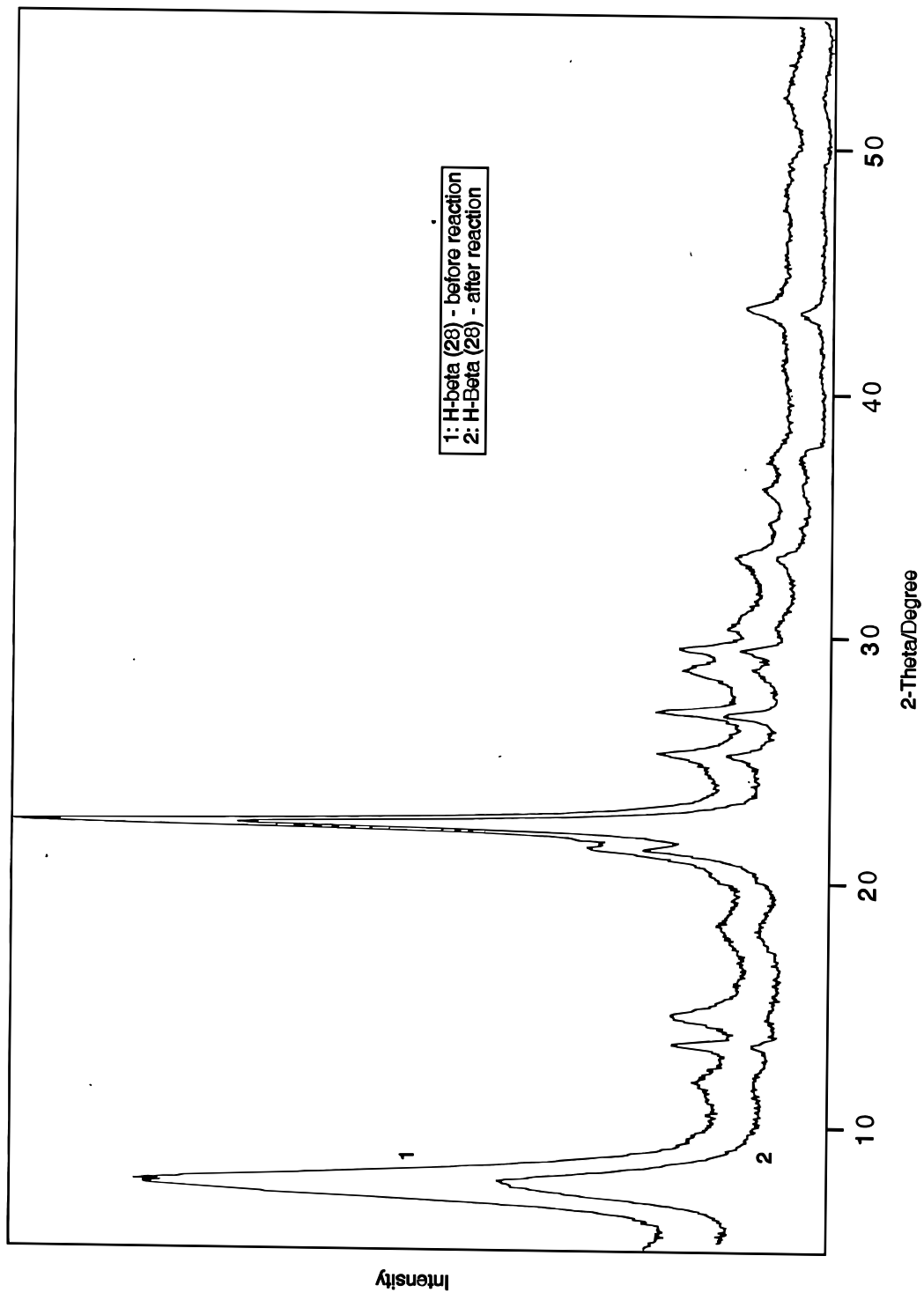


Figure 2

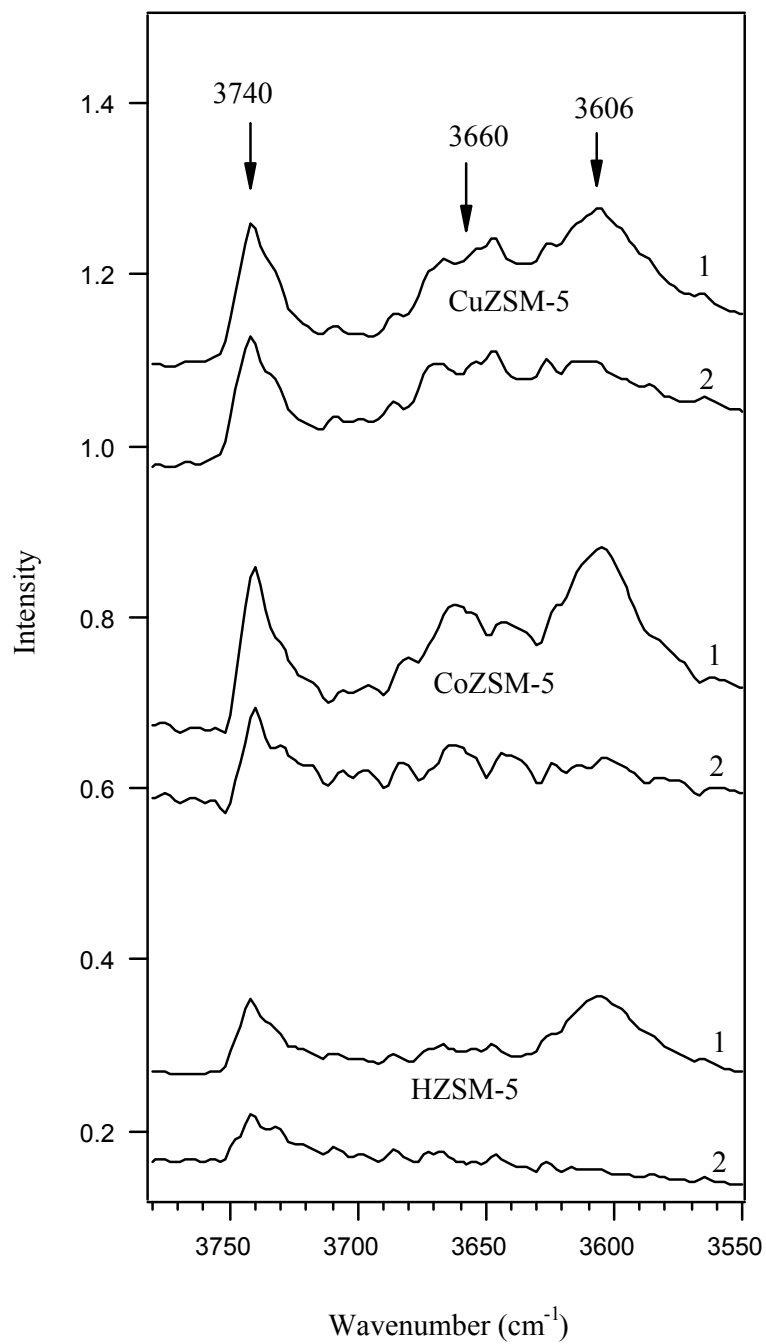


Figure 3

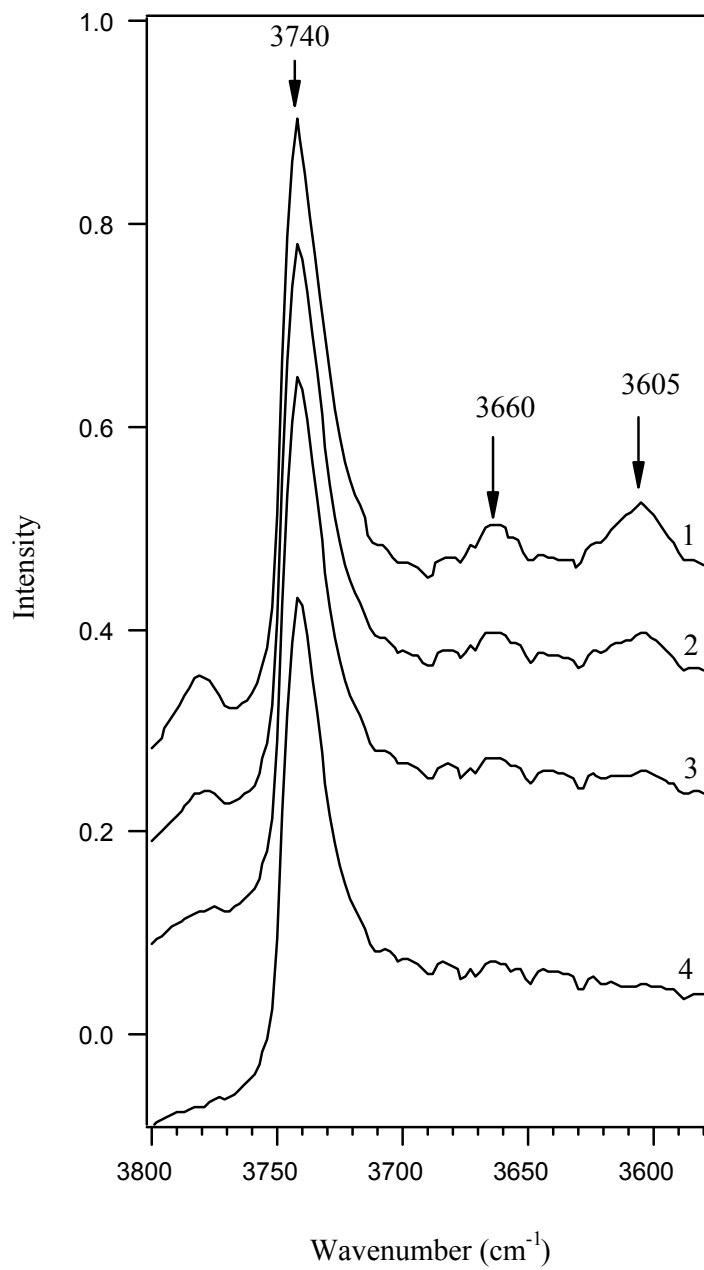


Figure 4

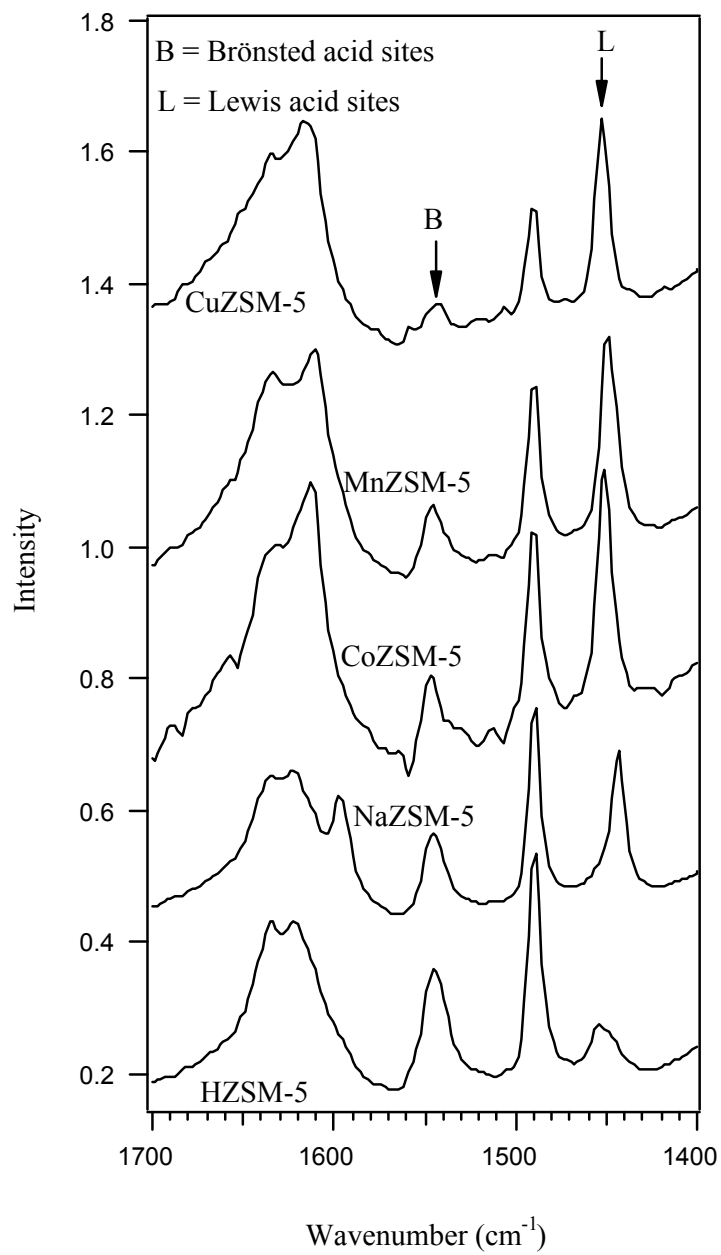


Figure 5

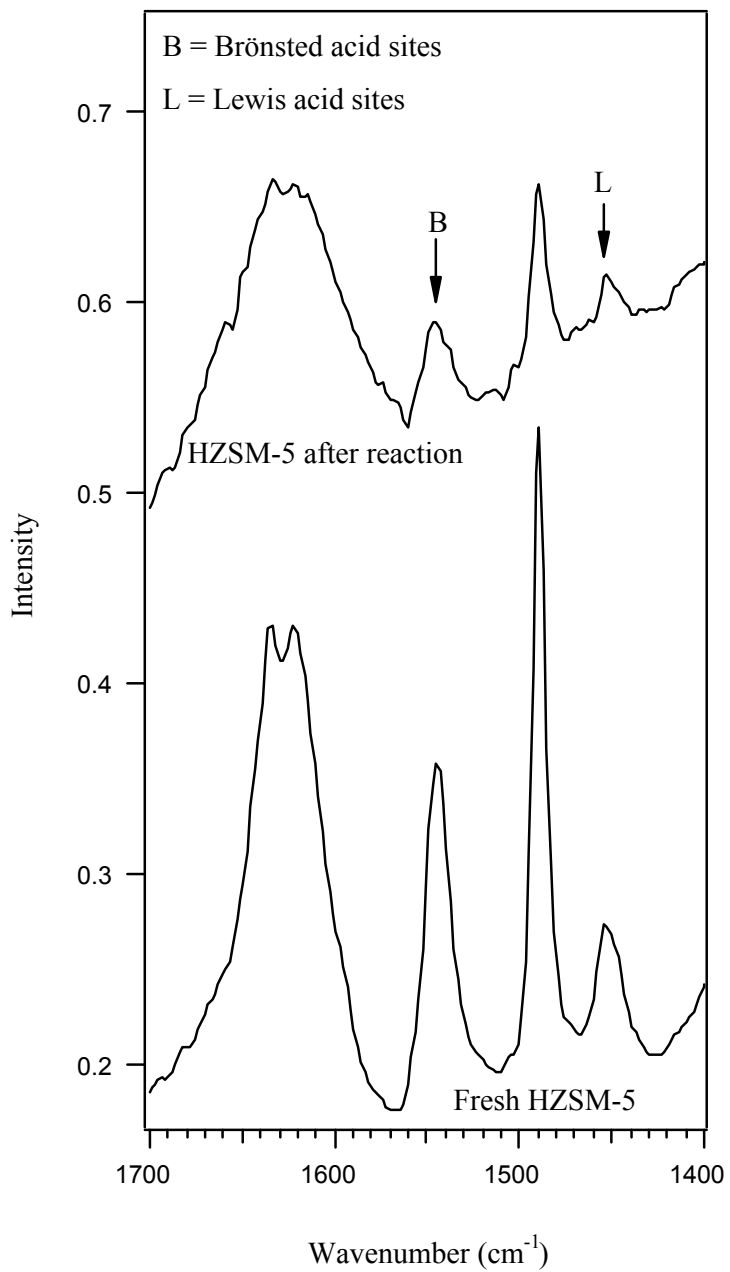


Figure 6

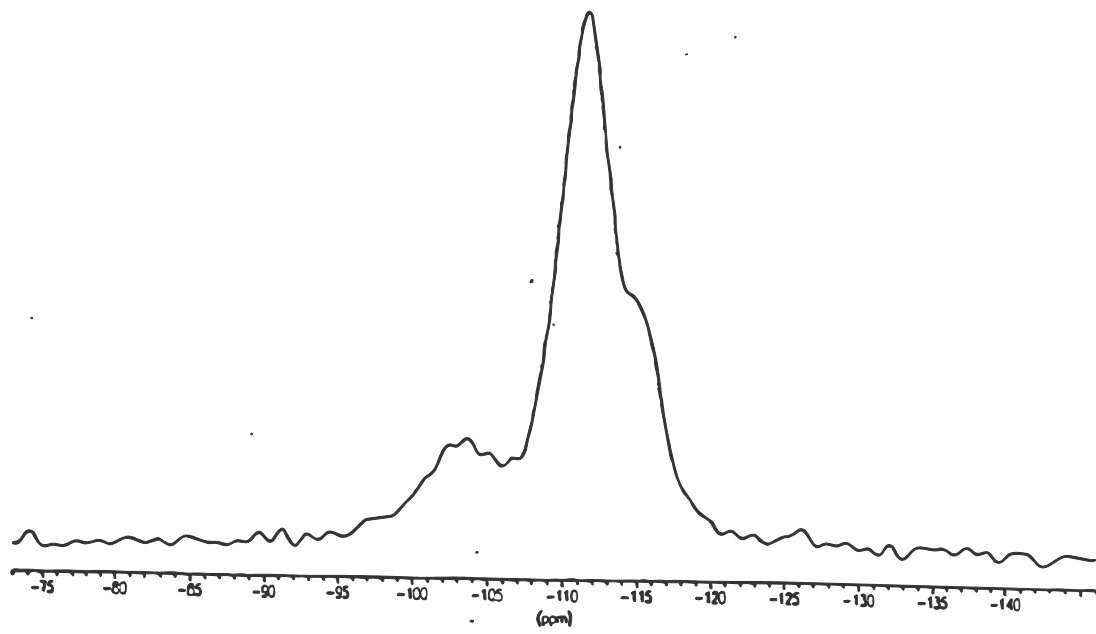


Figure 7

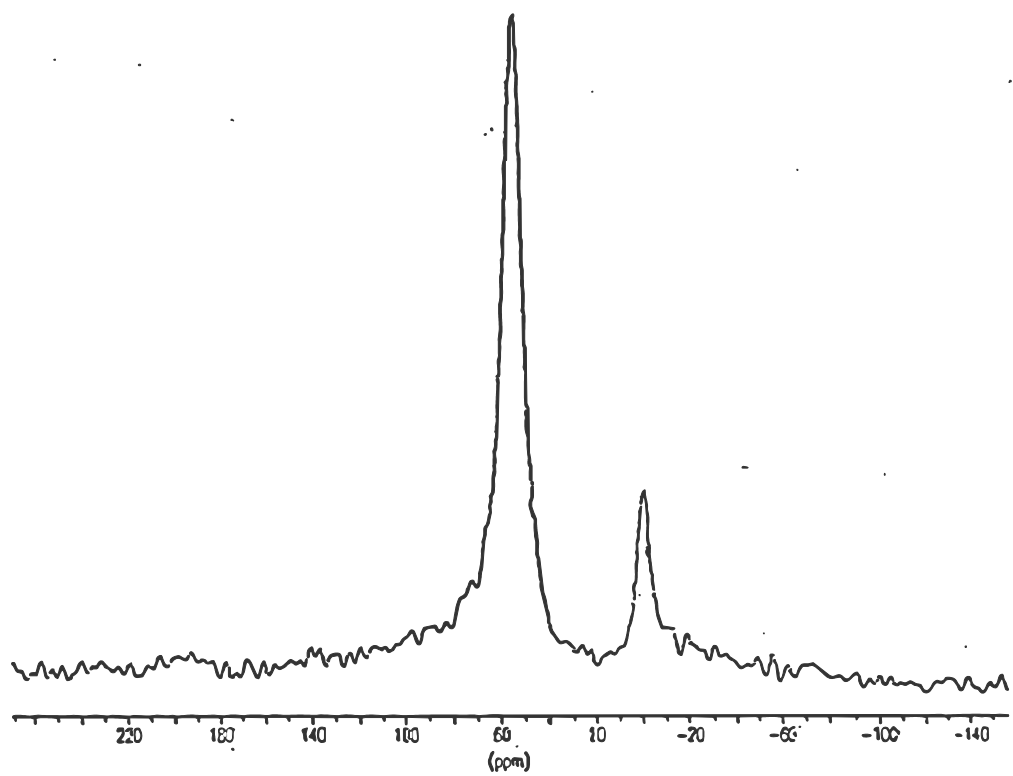


Figure 8