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Simultaneous $S0_2/N0_x$ Abatement Using Zeolite-Supported Copper

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INTRODUCTION

Several catalysts for NO decomposition have been reported in the literature to include the following: Cu/ZSM-5; [1-3] Cu/Zeolite-Y [3]; Cu/mordenite [3]; Cu/β zeolite [3]; Cu/alumina [4]; and Cu/silica [5] which have been studied less than Cu/ ZSM-5. The catalytic properties for NO conversion are found to be different on these samples [3] with the ZSM-5 supported catalysts showing the highest activity in a dry environment free from sulfur oxides. One of the goals of this study is to have a better fundamental understanding on the different roles of Cu and the support in the catalytic reaction.

The source of Cu ion in the previous studies is the aqueous salt which permits dynamic and facile equilibrium between aqueous species having different charges and copper ion nuclearity. For example, copper acetate in aqueous solutions shows the neutral, hydrated dimer along with hydroxy Cu(I) cations and hydrated divalent Cu cations [6]. Therefore, the catalyst synthesized from this solution will show these Cu complexes in contact with the surface.

We use stable, cationic metal complexes in non-aqueous solvents as sources of the Cu ions for these and other catalysts [6]. For example, Kenvin showed that $Cu(acac)_2$ can be prepared on silica as a single layer which produces a stable, high dispersion of Cu/silica when the ligands are removed [7]. Choksi, *et al.*, produced a similar robust catalyst beginning with the dimer of Cu(bipy) cation on silica [8]. Bruce, *et al.*, showed, how $Cu(en)_2^{2+}$ could be affixed to silica using acetonitrile as the solvent [9]. Very stable complexes, such as the $Cu(en)_2^{2+}$, appear to resist dissociation even when contacted with strong acids [10]. Thus, we use a set of stable metal complexes as the sources of Cu in producing model catalysts for which the fate of the source molecule is known and is controlled during the ion exchange/impregnation. Molecular models of these systems can be used to identify the possible configurations of the metal complexes within the zeolite support. We compare the performance of the model catalysts to one prepared by aqueous impregnation of ZSM-5 zeolite. The performance of the dinuclear metal complex on silica is compared to the same complex in ZSM-5 and Y-zeolites.

EXPERIMENTAL

Chemicals

$Cu[ClO_4]_2$ and ethylenediamine were obtained from Alfa Inorganics and used without further purification. 2,2'-bipyridine was purchased from Aldrich Chemicals. The NO/He gas mixture (4 vol % NO) was purchased from Matheson. High purity He was obtained from Matheson. The gases were passed through a Matheson Gas Purifier to remove water prior to use.

Metal complexes

The complexes $Cu(en)_2[ClO_4]$, where (en) is the ethylenediamine ligand, and the dimer of $Cu(bipy)[ClO_4]$, where (bipy) is the bipyridil ligand, were synthesized by the standard preparations [9, 10, 12]. Elemental analyses and single crystal XRD confirmed the structure of the complexes as shown in Figures 1 and 2.

Supports

The zeolites ZSM-5 and Y were obtained in the sodium forms from Dr. P. S. Dai of Texaco Research and Development Co. (Port Arthur, TX). Elemental analyses of the zeolites are shown in Table 1 to include the bulk Si/Al ratio. Cab-O-Sil (M-5 grade) silica was obtained from Cabot Corporation.

Table 1 Elemental Analyses

Element	HZSM-5	Y
Silicon, wt%	41.5	26.54
Aluminum, wt%	1.14	7.67
Sodium, wt%	0.76	0.08
Si/Al, molar (bulk)	36.40	3.32
Si/Al, molar (framework)	55	
Na/Al, molar	0.78	0.01

The framework Si/Al ratio was determined using the reactive probe, isopropyl amine described by Kofke, et *al.* [11]

Preparation methods

We prepared state-of-the-art catalysts according to the method of Li and Hall as described in reference [3] using the acetate salt of Cu(II). These catalysts are designated as CuLH4. The model catalysts derived from copper ethylenediamine were prepared by dissolving the required mol of $Cu(en)_2^{2+}$ in acetonitrile at room temperature under constant stirring. The zeolite was added and the system allowed to stir for 24 hours. The supernatant solution was removed by filtering and the catalyst was washed 2 times with fresh acetonitrile so as to remove metal complexes not ion exchanged with the zeolite which were identified as CUZ5EN21. To show the effect of changing the zeolite, we used the same procedure to prepare the $Cu(en)_2^{2+}$ on Y zeolite (CUZYEN). Additional catalysts were prepared to show the effect of copper ensemble size using stable Cu complexes of a known nuclearity on different supports: Cu(bipy) dimer on silica (CUSIBPD), on ZSM-5 (CUZ5BPD) and on Y-zeolite (CUZYBPD). Finally, we used the bipy monomer to build a catalyst on ZSM-5: CUZ5BPM. We report in Table 2 the metal loadings of these catalysts.

We prepared another set of catalysts by re-impregnation with $Cu(en)_2^{2+}$ of a Cu/ZSM-5 which was prepared from the same metal complex cation and was calcined prior to the second impregnation (CUZ5EN22). The purpose of this preparation was to increase the copper loading and hopefully increase the average Cu ensemble size.

Elemental analyses

Samples were sent to Galbraith Laboratories, Inc. (Knoxville, TN) for analysis of metals (Na, Cu, Si, and Al) plus non-metals (C, N, and H.)

Vibrational spectroscopies

Selected solids were examined by vibrational spectroscopy. The mid-IR spectra were obtained on a Nicolet Magna 750 FT-IR spectrometer with a narrow-band MCT/A detector. The spectra were recorded using the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Harrick Scientific Controlled Atmosphere Cell (HVC-DR2, Harrick Scientific). The sample was diluted in KBr (6% sample by weight, balance KBr) and KBr was used as the reference material. The far-IR range was examined on a using the transmission IR technique. Solid samples were diluted (5% by weight) using polyethylene powder obtained from Spectra Tech.

Reaction studies

A tubular flow reactor was constructed of stainless steel tubing (12 mm OD) serviced by two mass flowmeter/ controllers (Matheson model 8274 control electronics, Matheson 8172 flowmeter and Matheson 8242 control valve) in a gas-metering manifold fabricated from stainless steel tubing (6 mm OD). The gases were mixed after metering and sent to the reactor. The desired mass of catalyst (2-4 g) was confined in the reactor by filamentous alumina (Safil). Thermocouples were installed up- and down-stream of the catalyst bed and the heater (Linberg Furnace) was controlled by an Omega Engineering controller, model #CN 8600. The product gases were sent to a HP 5780 Series II+ gas chromatograph equipped with a HP 5972A mass selective detector with ChemStation and an air operated gas sampling valve. The partitioning agent was a zeolite column by Alltech Associates (Deerfield, IL 60015; GS-MOL, P/ N 115-3632; 0.53 mm x 30 m long) operated at 100°C for a He carrier gas flowrate of 2 STP cm^3/min.

MOLECULAR MODELING

The nature of the catalyst synthesis suggest that molecular modeling of the Cu metal complexes may be possible which could help in the understanding of the results for the calcined catalysts. We used the BIOSYM Catalysis software. The approach was to examine the steric hindrances to ion exchange/impregnation for the metal complexes inside the channels of the zeolite. We used 50% of the van der Waals radii to represent the exclusion volume of the atoms/molecules in the systems.

Figures 1 and 2 show representations of the two copper precursor complexes used in the current investigation, $Cu(en)_2^{2+}$ and $[Cu(bipy)(OH)]_2^{2+}$, respectively. Figure 3 shows an assembly of $Cu(en)_2^{2+}$ cations in the channels of ZSM-5 which is intended to model the first impregnation. No attempt is made in this first model to locate the ion exchange sites nor to model the same. We wish to examine the filling of the channels by the cation to identify the maximum loading of metal complex and to identify if multi-nuclear Cu ensembles will result upon thermolysis. This model suggests that each metal complex fills the channel so that another metal complex cannot pass it during impregnation. Moreover, we see that two complexes approach at the intersection of two channels so that the Cu ions are within 4 Å, suggesting that a water molecule could bridge the two ions to form a dimeric species during thermolysis.

We reported the NO chemisorption properties of a catalyst synthesized from a monolayer film of the dimer of Cu(bipy)/silica [9]. This catalyst chemisorbed NO with the stoichiometry of 1 NO/Cu ion to leave 1 O/Cu. We speculated that that this material would release N_2 initially, but would not catalyze a continuous decomposition. It was of interest to determine if the dimer would fit into the channels of ZSM-5 and zeolite Y. Figure 4 shows that the dimer cannot fit in ZSM-5 even when assembled from the monomer which is accommodated in the channels. Figure 5 illustrates how the dimer fits in cages of Y after assembling from the monomer which passes easily through the apertures to the cage.

RESULTS

Elemental analysis

The catalysts were analyzed for C, N, H, and Cu analyses before the samples were calcined to determine the apparent C/N/Cu stoichiometry of the supported metal complexes (Table 2). Shown in the same table is the predicted C, N, and H analyses assuming that the Cu analyses was correct and using the stoichiometry of the parent Cu complex in predicting the analyses. We assumed the following stoichiometries for these predictions: CUZ5EN21 and EN22 -- $Cu(N_2C_2H_6)_2$; CUZ5BPM -- $Cu(N_2C_{10}H_8)$; CUZ5BPD and CUSIBPD -- $[Cu(N_2C_{10}H_8]_2$; CuLH4 -- $Cu_2(O_2CCH_3)_4$. Two samples show predicted carbon and nitrogen analyses near the observed values (CUZ5BPM and CUSIBPD); whereas, all of the other catalysts show C, N, and H analyses which are higher than the theoretical. We have observed this same result in earlier studies where the solvent (acetonitrile) was strongly adsorbed by the support [12]. Notice that the incorporation of copper in the sample developed from the (bipy) monomer is greater than that derived from the dimer. In the former, we suspect that crystallites of the monomer formed in the sample without ion exchange. In the same table we show the percentage of Cu ion exchange level based on the Si/ Al ratio calculated from the bulk analyses.

Analyses: Weight Percent

Table 2 Elemental Analyses of Cu/Zeolite Catalysts

Sample ID	Carbon	Nitrogen	Hydrogen	Copper	% Cu Exchg
CUZ5BPD	7.24	1.85	1.37	2.5	
Theoretical	4.72	1.10	0.20	2.5	
CUZ5BPM	12.52	2.78	1.51	6.49	
Theoretical	12.26	2.86	0.51	6.49	
CUZ5EN21	4.19	2.3	1.47	1.44	57
Theoretical	1.09	1.27	0.18	1.44	
CUZ5EN22	2.65	1.81	1.17	1.88	75
Theoretical	1.42	1.66	0.24	1.88	
CuZ5LH4	2.10	--	1.38	1.81	72
Theoretical	1.37	--	0.26	1.81	
CUZYBP	6.16	2.96	1.81	1.7	
Theoretical	3.21	0.75	0.13	1.7	
CUSIBPD	3.99	0.87	<0.5	2.02	
Theoretical	3.81	0.89	0.16	2.02	

Note: It is assumed that Cu analysis is correct in predicting the theoretical -analyses for C, N, and H.

Vibrational spectroscopy (mid-IR).

The samples derived from the $Cu(en)_2^{2+}$ precursor were examined by mid-IR (DRIFTS) to determine if the metal complex decorated the surface intact. The ethylene diamine ligand in $Cu(en)_2^{2+}$ is expected to show vibrations in the range: 3300-3200 cm^{-1} (ν N-H); 2880-2540 cm^{-1} (ν C-H) [9]. Figures 4 and 5 shows the mid-IR spectra for the two $Cu(en)_2$/ZSM-5 catalysts, CUZ5EN21 and CUZ5EN22, respectively. The infrared spectrum for the polycrystalline $Cu(en)_2(ClO_4)_2$ is shown in Figure 6. The standard shows the expected vibrations described in the literature for the N-H (ν N-H: 3350, 3290, 3220, 3180 cm^{-1}); and C-H stretches (ν C-H: 2990, 2950, 2900, and 2890 cm^{-1}); however, these vibrations are not strong in the supported ZSM-5 samples. The peaks at 1590 and 1480 are readily apparent in the two zeolite-supported Cu samples which suggest that some of the complex remains intact on the support. These two vibrations disappear when the samples have been heated to reaction temperatures and then examined by mid-IR (Figure 7). Three additional peaks appear at frequencies of 2320, 2300, and 2285 cm^{-1} in the zeolite-supported $Cu(en)_2^{2+}$ samples before calcining which disappear upon heating.

Figure 8 shows the mid-IR spectrum of the catalyst prepared by the literature preparation using copper acetate as the precursor. In Figure 9 we show the mid-IR of the copper acetate powder used in making the catalysts. Strong absorptions in the copper acetate standard at 1450 and 1410 cm^{-1} appear also in the zeolite-supported copper catalyst at 1470 and 1450 cm^{-1}. These two vibrations are removed by calcining the catalysts. The strong peak which appears at 1600 cm^{-1} is masked by a peak at the same position in the spectrum of ZSM-5. From these data we conclude that the acetate ligand appears to be intact before calcining of the catalyst.

Reaction studies

The micro reactor results are shown in Figure 10 for the catalyst prepared from aqueous impregnation of the acetate salt into ZSM-5 (CuLH4) and the two catalysts prepared by non-aqueous impregnation of ZSM-5 with $Cu(en)_2^{2+}$ (CUZ5EN21 and CUZ5EN22). These catalysts demonstrate steady-state activities after 24 h which are only 5-10% less than the initial values. Oxygen is evolved in a proportion which is less than the stochiometric amount expected from the nitrogen production. We estimate the rate constant for this reaction by measuring the slope of the conversion versus spacetime curve at zero space-time. The spact-time is calculated by multiplying the fractional loading of copper in the catalyst (g Cu/g catalyst) by mass of catalyst in the reactor and dividing by the volumetric flowrate over the catalyst (cm^3/sec). This limiting slope has units of % conversion-cm^3/g Cu-second. The catalyst derived from the acetate salt is more active (1850 % converted-cm^3/g Cu-sec) than the two catalysts derived from the (en) salts (650 and 480 % converted-cm^3/g Cu-sec). The difference in activities cannot be attributed to Cu metal loading as the activities have been corrected for metal content by the space-time expression. The two catalysts developed from the (en) precursor show the beneficial effect of re-impregnating the catalyst with the precursor after calcining the catalyst prepared from the first impregnation 650 for two impregnations vs 480 % converted-cm^3/g Cu-sec for one impregnation).

The silica-supported catalyst (CUSIBPD) derived from the Cu(bipy) dimer complex (1.5 g) shows low initial activity (6% conversion to N_2) at a flow rate of 25 STP cm^3/min at 773 K which decreases to 1% conversion after 1.5 h . The ZSM-5 supported Cu(bipy) dimer (CUZ5BPD, 2.2 g) shows an initial activity of 16% conversion to N_2 which decreases to a steady-state conversion of 6% in 2 h at the same reaction conditions. Finally, the faujasite supported catalysts (CUZYBP, 1.88 g) developed from the Cu(bipy) dimer rapidly deactivates from 100% conversion to x% conversion in 0.5 h at the same reaction conditions. No oxygen is evolved from this last catalyst at 100% conversion to N_2.

DISCUSSION

The elemental analyses together with the vibrational analyses lead us to conclude that (en) metal complexes mount the support without wholescale destruction of the precursors. If such destruction did occur, then the observed carbon and nitrogen analyses would be lower than the predicted values. The analyses do show that the samples are contaminated with the solvent before calcination. The catalysts were prepared with Cu exchange levels lower than 100% based upon the chemical analyses of the zeolite [11].

The reaction studies suggest that catalytic activity may be developed from model catalysts derived from thermolysis of cationic, mononuclear Cu complexes on ZSM-5. The level of activity in the model catalyst is a factor of 10 smaller than the state-of-the-art catalysts developed from the aqueous acetate salt [1-3]. Molecular modeling of the $Cu(en)_2^{2+}$ suggest that the cations can assemble in ZSM-5 so as to place the Cu ions within 4 Å at the intersection of the channels. This arrangement of the precursors may enable the formation of small ensembles of Cu ions upon thermolysis. We suggest that the difference in activity between these catalysts may be the result of Cu ensemble size since the mass of Cu is similar (1.4-1.9 wt% Cu) in the CULH4, CUZ5EN21 and CUZ5EN22 catalysts.

To explore the effect of ensemble size further, we synthesized a family of catalysts using Cu(bipy) dimer on the following supports: silica, ZSM-5, and Y faujasite showing Cu loadings of 1.7-2.5 wt% . The dimer on silica showed very low activity (6% conversion) which decreased to no conversion rapidly on stream. Choksi, et al. [9] showed this catalyst will dissociate NO at room temperature to leave O atoms on the surface which cannot be removed by heating to 550°C. The dimer in the Y-zeolite showed almost total conversion, initially; however, it too deactivated rapidly to very low conversion. The Y-supported catalyst did not evolve gaseous oxygen during the test which suggest that it was sequestered by the catalyst; perhaps by the Cu species thus rendering the sites inactive. Molecular modeling of this system shows that the Y-faujasite can accommodate 2-3 Cu(bipy) dimer molecules in the supercage. During thermolysis we suggest that Cu ensembles may be formed having as many as 4-6 Cu atoms. The dimer on ZSM-5 showed modest initial activity (16% conversion) which decreased to 6% conversion to N_2 after several hours on stream. This system was modeled to reveal that the precursor cannot enter the channel network but it could reside on the external parts of the ZSM-5 crystal. The activity of this catalyst was very low compared to that observed for CUZ5EN22 and CULH4 catalysts which showed steady state conversions to N_2 of 20 and 80% at these same conditions.

We suggest that the minimum ensemble size for the catalysis is two Cu ions residing on a support such as ZSM-5. The ZSM-5 support plays an important role in the catalysis as very little conversion is observed for a dinuclear Cu ensemble residing on a neutral support such as Cab-O-Sil; whereas modest conversion is observed for ZSM-5 which has been decorated with the same metal complex before thermolysis. The maximum ensemble size for the catalysis may be as small as 4-6 Cu atoms as rapid deactivation by strong oxygen adsorption apparently occurs on the Y-supported catalysts.

ACKNOWLEDGMENTS

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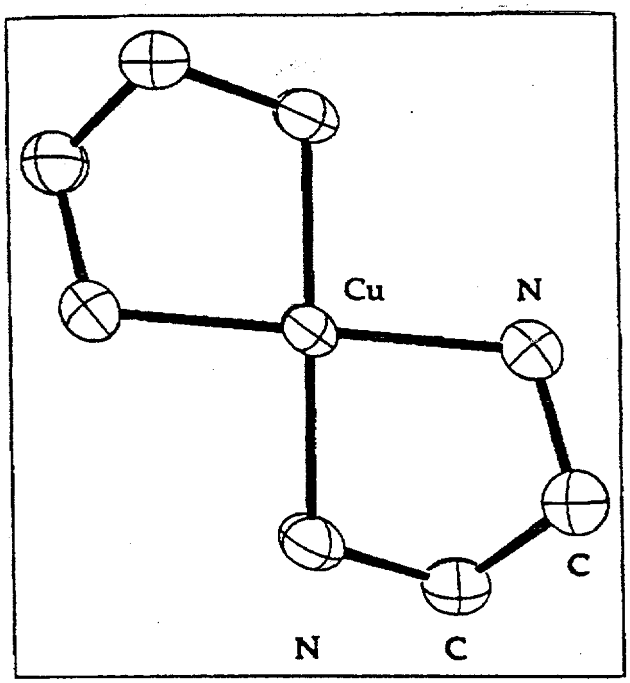
Figure 1 ORTEP Diagram of $Cu(en)_2^{2+}$ Cation



ORTEP Drawing of $[Cu(bipy)(OH)]_2{}^{2+}$

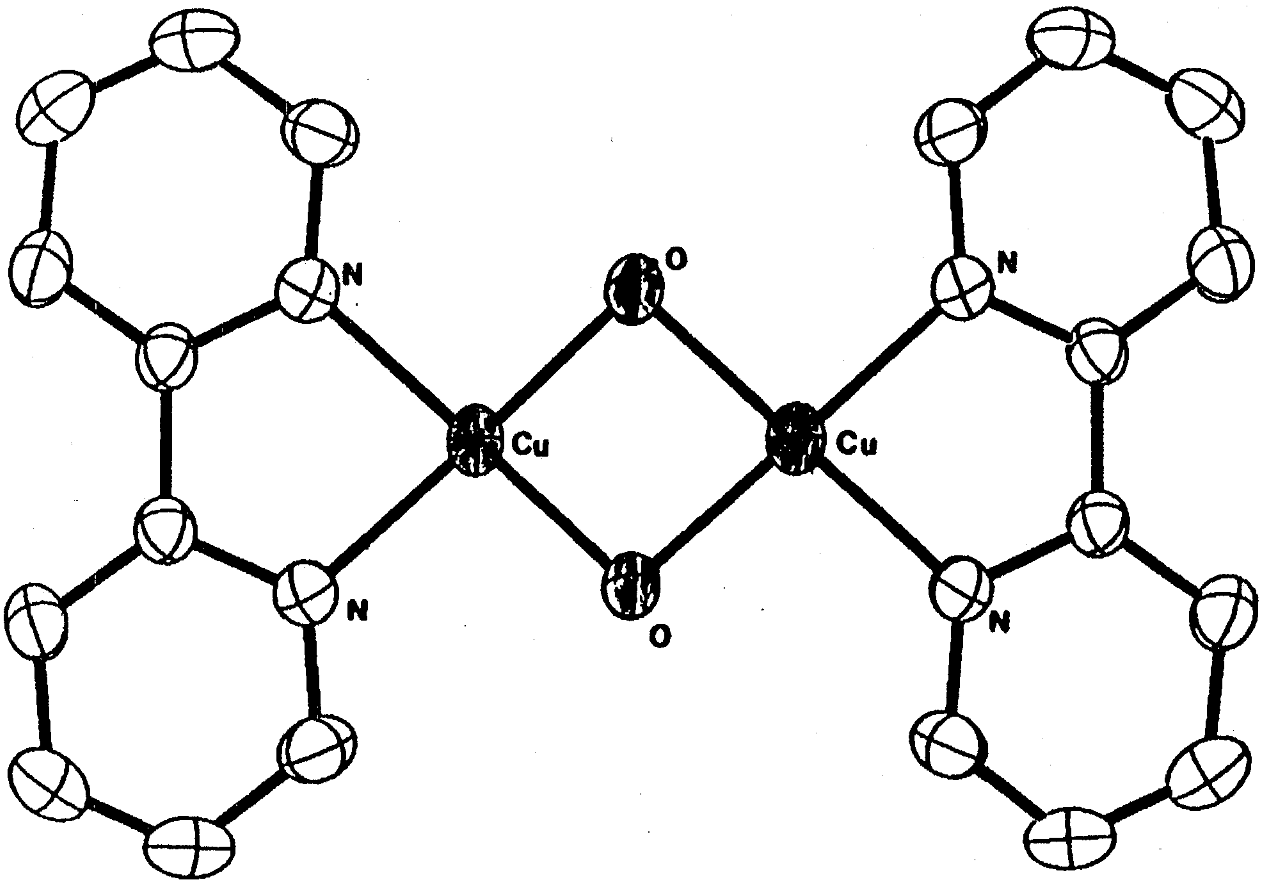
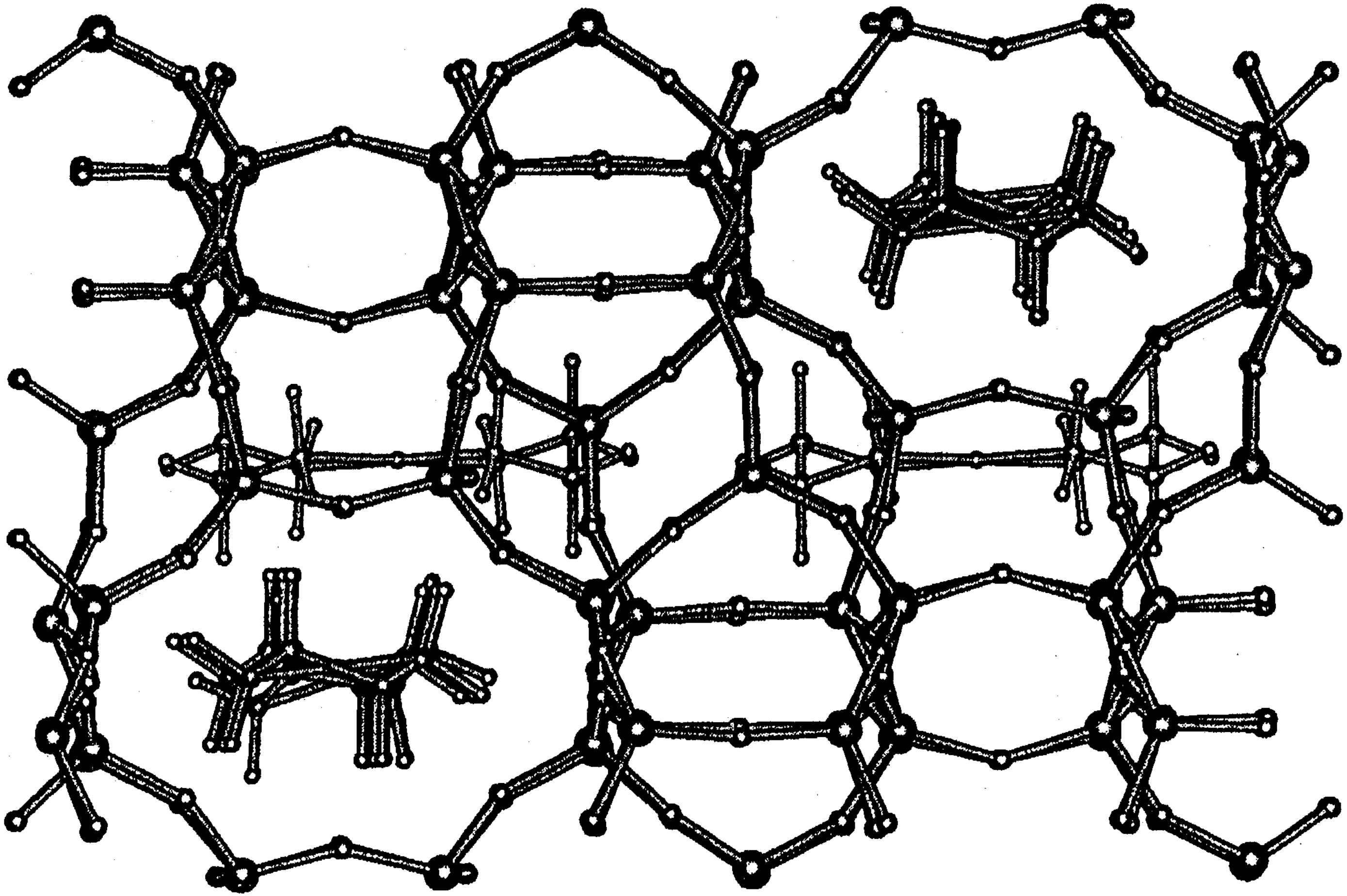


Figure 3 Simulation of Cu(en)2+ Cation Residing in Major Channels of ZSM-5



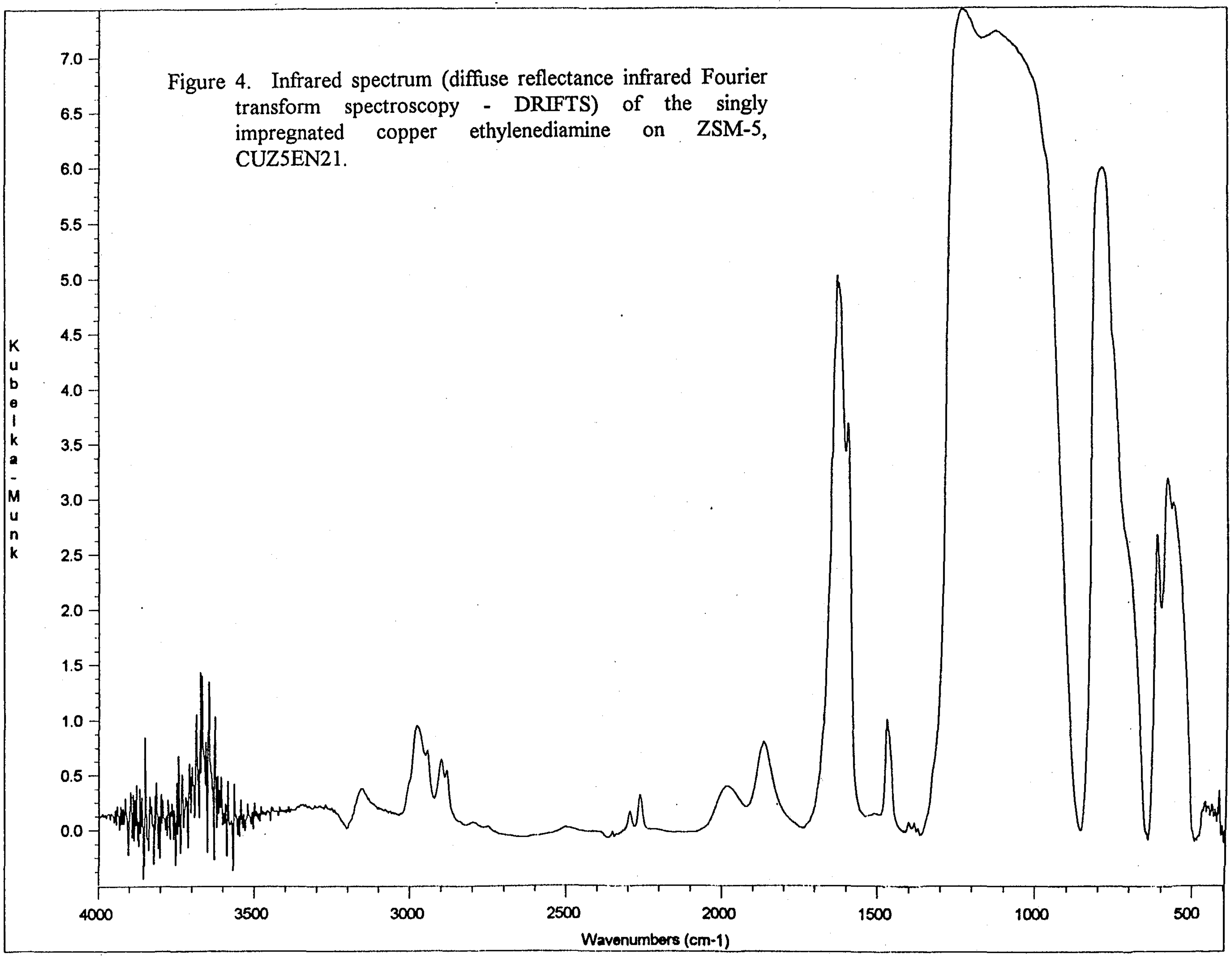


Figure 4. Infrared spectrum (diffuse reflectance infrared Fourier transform spectroscopy - DRIFTS) of the singly impregnated copper ethylenediamine on ZSM-5, CUZ5EN21.

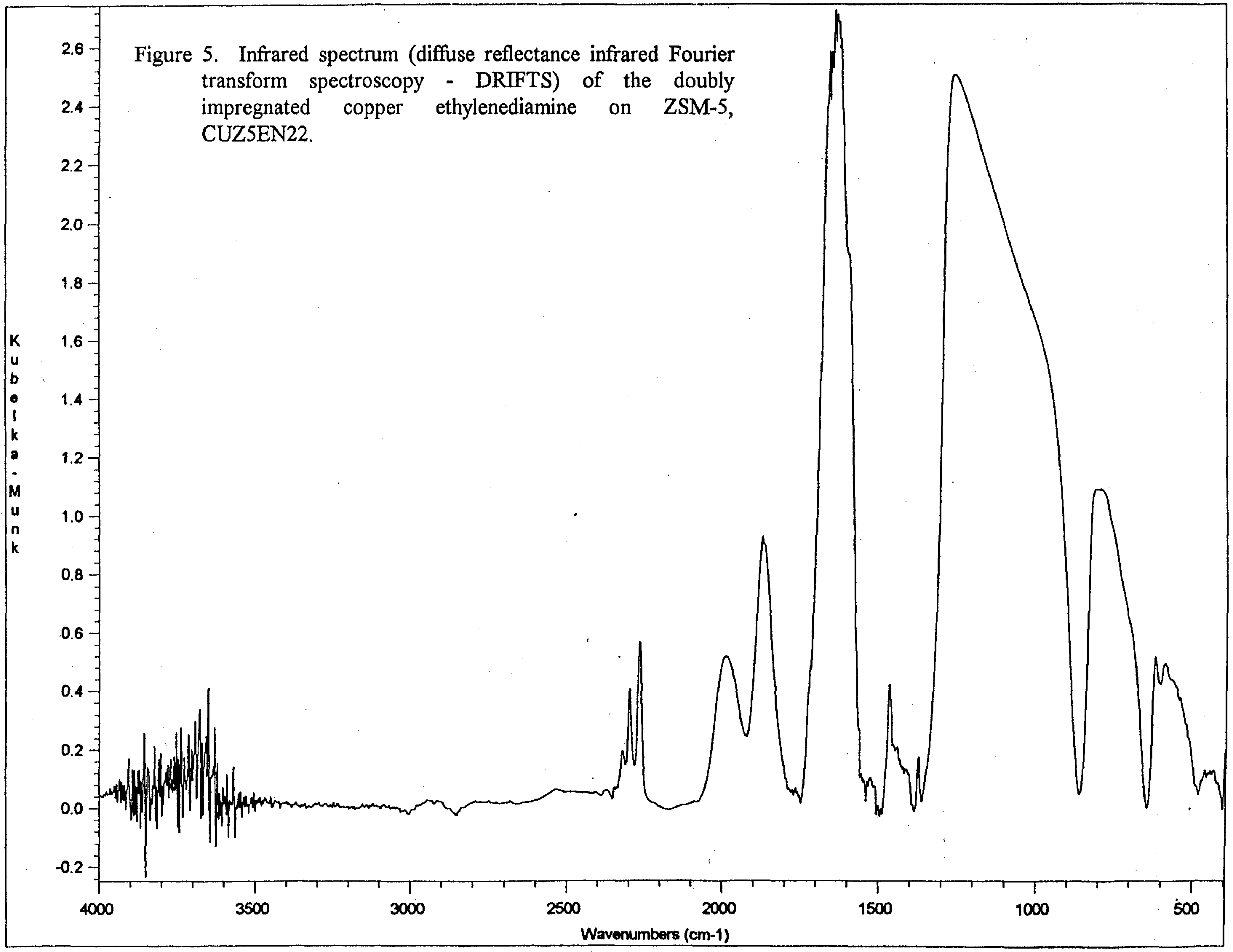


Figure 5. Infrared spectrum (diffuse reflectance infrared Fourier transform spectroscopy - DRIFTS) of the doubly impregnated copper ethylenediamine on ZSM-5, CUZ5EN22.

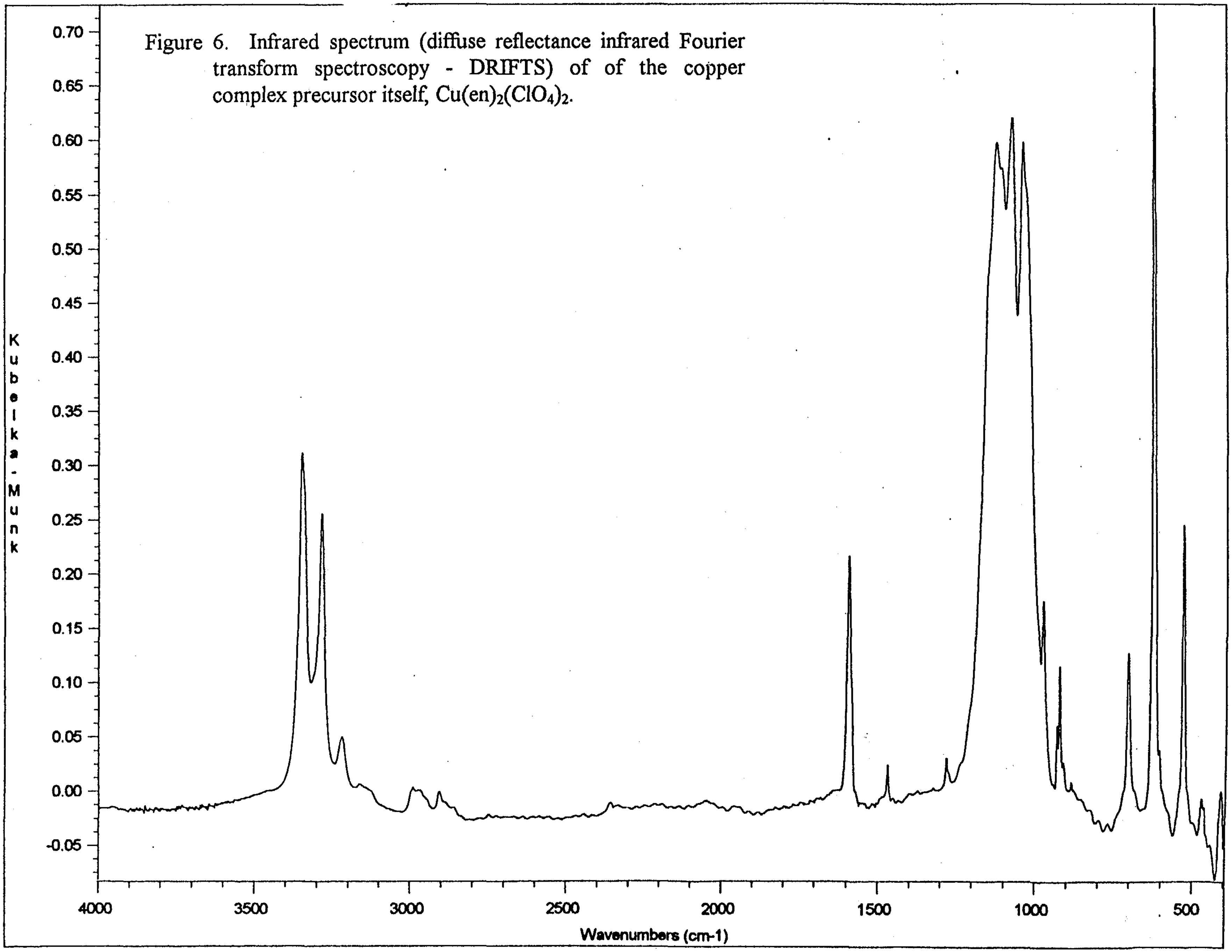


Figure 6. Infrared spectrum (diffuse reflectance infrared Fourier transform spectroscopy - DRIFTS) of of the copper complex precursor itself, $Cu(en)_2(ClO_4)_2$.

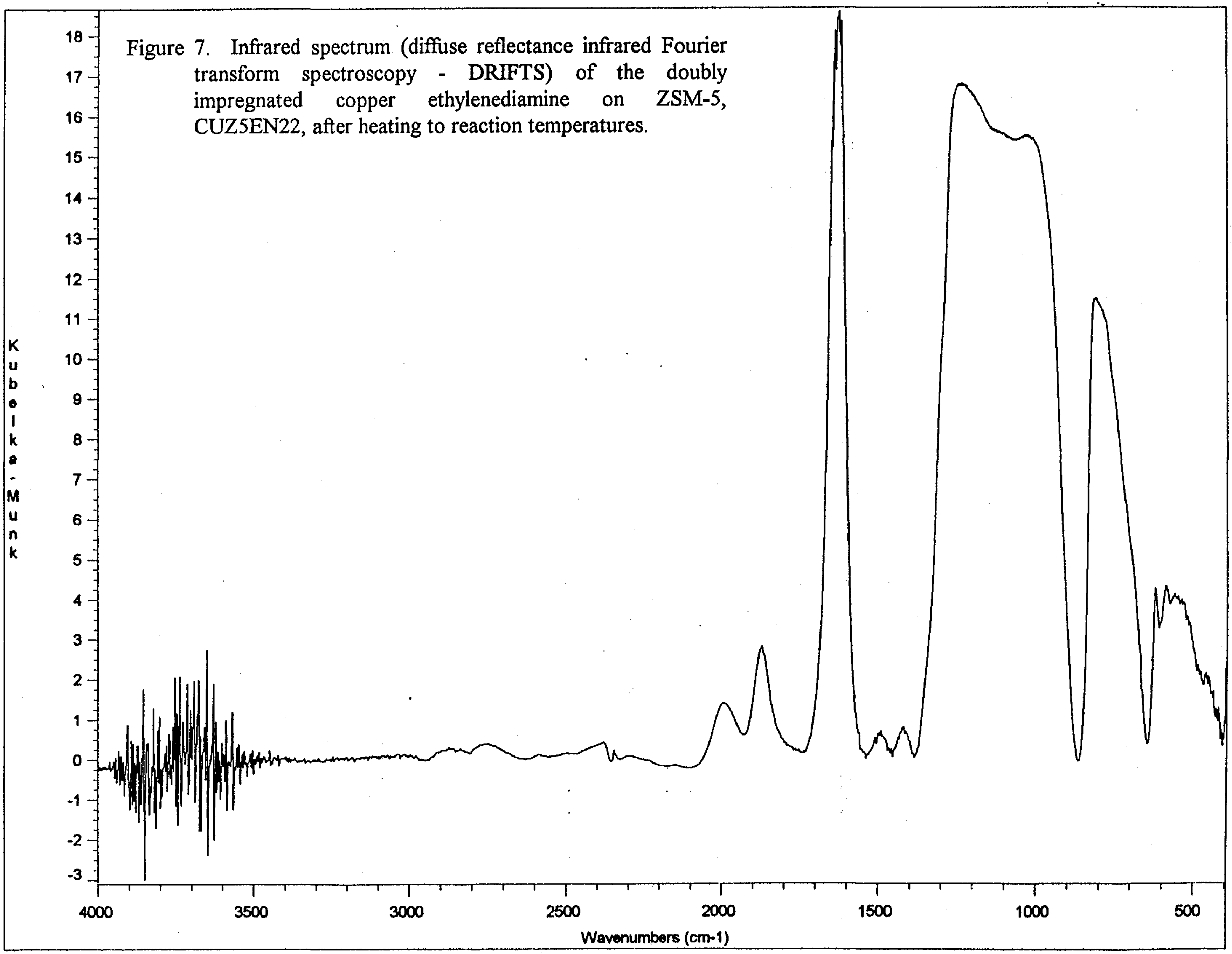


Figure 7. Infrared spectrum (diffuse reflectance infrared Fourier transform spectroscopy - DRIFTS) of the doubly impregnated copper ethylenediamine on ZSM-5, CUZ5EN22, after heating to reaction temperatures.

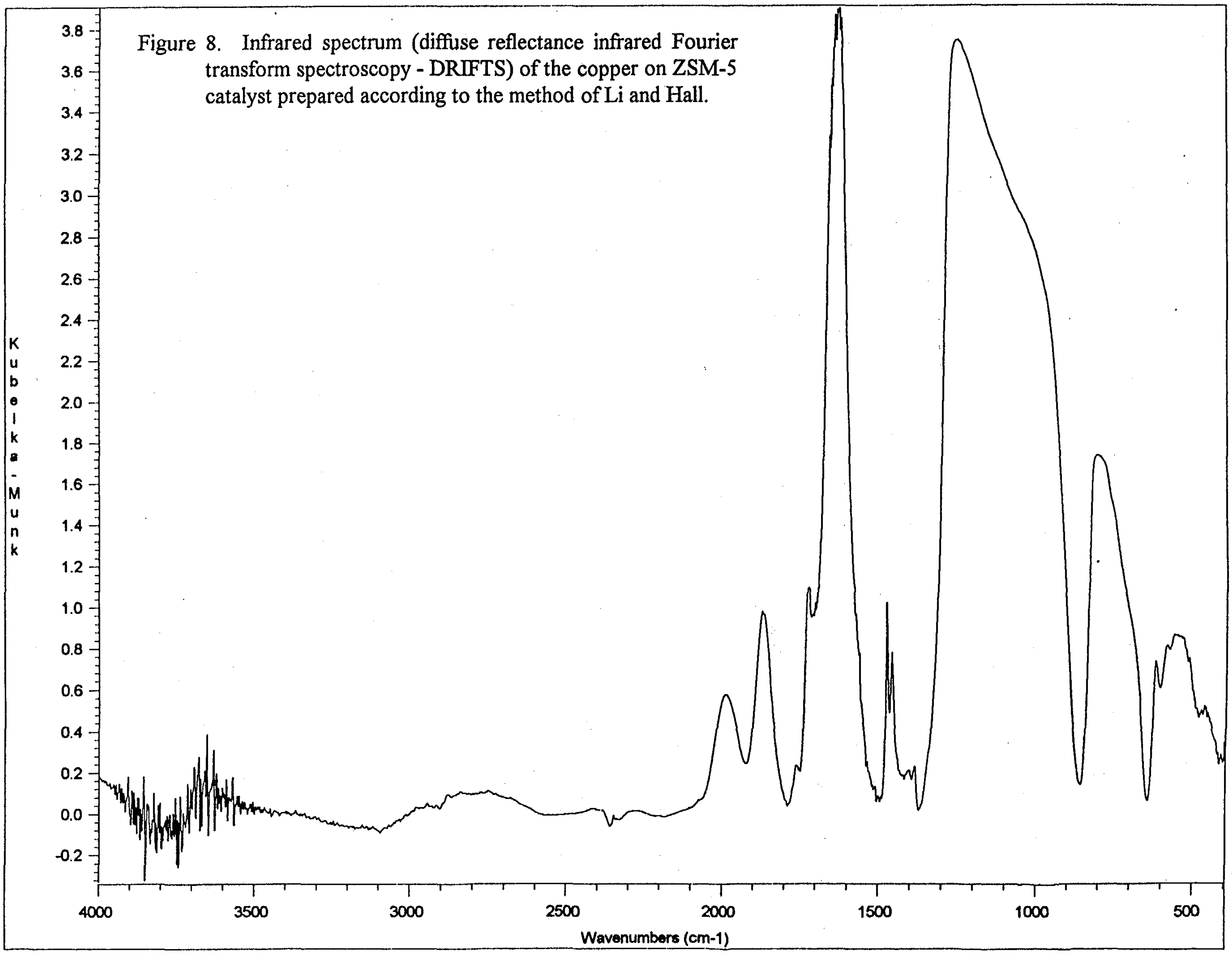


Figure 8. Infrared spectrum (diffuse reflectance infrared Fourier transform spectroscopy - DRIFTS) of the copper on ZSM-5 catalyst prepared according to the method of Li and Hall.

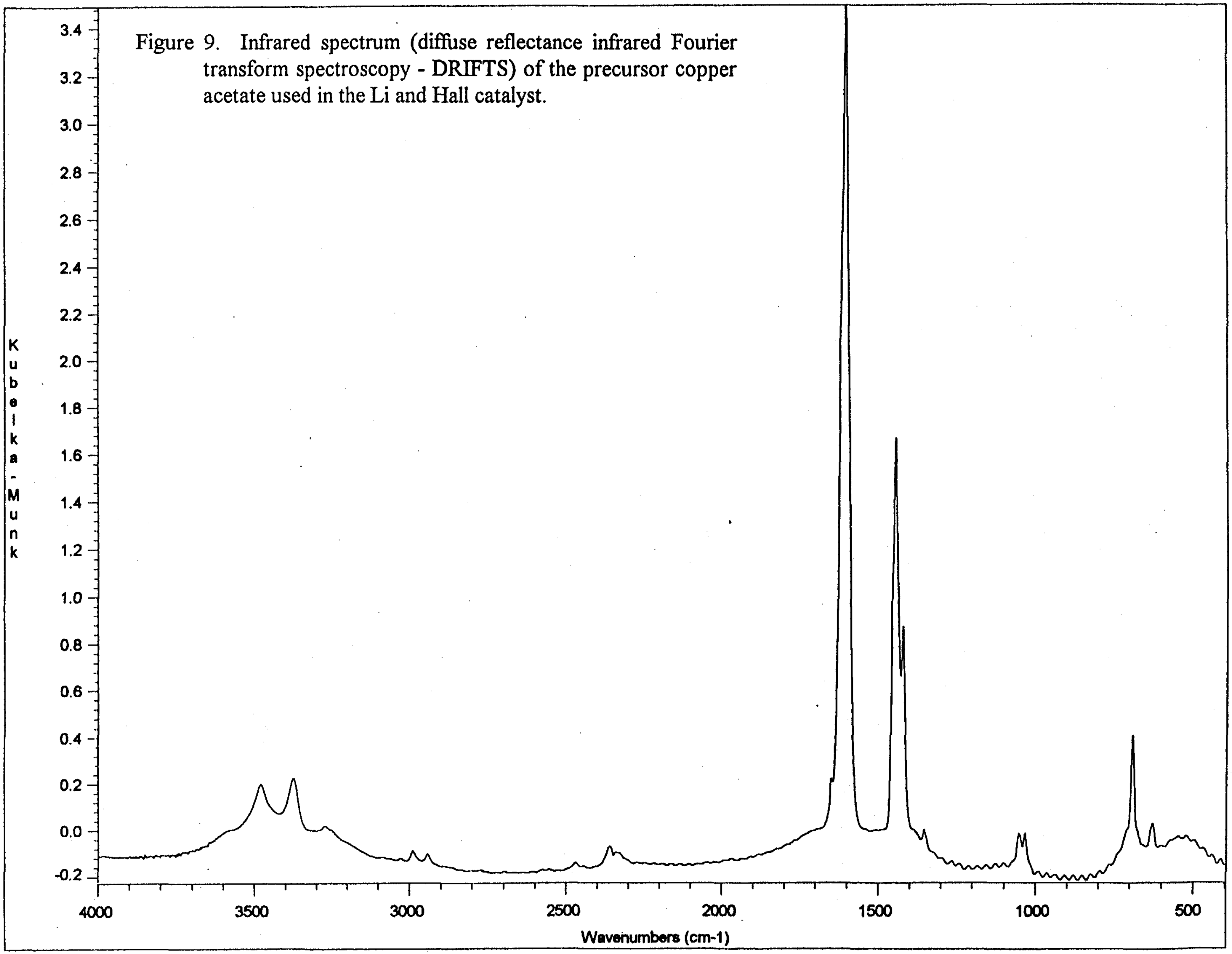


Figure 9. Infrared spectrum (diffuse reflectance infrared Fourier transform spectroscopy - DRIFTS) of the precursor copper acetate used in the Li and Hall catalyst.

Figure 10. Conversion of NO to N_2 on Cu/ZSM-5 Catalysts