# A Diamine Copper(I) Complex Stabilized in Situ within the Ferrierite Framework. Catalytic Properties

B. Gomez-Lor, M. Iglesias, C. Cascales, E. Gutierrez-Puebla,* and M. A. Monge*

*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain*

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The copper(I) complex $[Cu(NH_3)_2]^+$ has been formed in situ during the ferrierite framework constitution. The structure of the material has been determined by single-crystal X-ray diffraction. The obtained formula is $[Cu_{0.34}(NH_3)_{0.68}]^{0.34+}(Si_{35.66}\,Al_{0.34}O_{72})^{0.34-}\cdot(C_3H_9N)_2\,(NH_3)_{1.6}$. Along the 10-ring channel is housed a row of linear $[Cu(NH_3)_2]^+$ complex. The copper atom is situated in an inversion center and bonded to two $NH_3$ molecules at 2.21 Å. The compound that is white and diamagnetic as synthesized becomes blue and paramagnetic after heating to 800 °C and cooling to room temperature. The oxidation of Cu(I) to Cu(II) has been corroborated by magnetic susceptibility measurements. This material behaves as a good catalyst in the cyclopropanation of alkenes and sulfide oxidation reactions. It can be recovered and reused, retaining most of its catalytic activity.

## Introduction

Zeolites have found a number of applications in fields of commercial importance, notably as catalysts, adsorbents, and ion exchangers. The choice of zeolite catalysts is due to their well-defined porous structure, with apertures and cages of approximately the size of organic molecules. It should be also mentioned such zeolite catalysts properties as shape selectivity, thermal stability, the ease of separation from the products and the possibility of regeneration of the deactivated catalysts, as well as their advantages in decreasing environmental problems, which is one of the main objectives of green chemistry. The encapsulation of transition metal complexes in the cavities of zeolites allows the combination of the specific metal complex activity and the shape selectivity of the microporous framework. Thus, the study of the catalytic behavior of these mixed materials related to their structural features is an interesting area of research.

Metal complexes are usually formed in the zeolite by postsynthesis procedures.[1] There are some examples in which the metal complex is incorporated by adding it directly in the synthesis of the zeolite,[2−4] but to our knowledge, the only structurally characterized Cu(I) complex formed during the synthesis of a zeotype has been recently reported by us.[5] Some applications of Cu(I)−zeolites are well-known, examples being ammoxidations of toluene to benzonitrile using Cu−ZSM-5,[6,7] Diels−Alder cycloadditions using Cu(I)−Y,[8] and reduction of NO with hydrocarbon in the presence of $O_2$ with Cu(I)−ZSM-5[9] to control the emission of environmentally unacceptable products. The development of new methods for the efficient and selective preparation of cyclopropanes is of great interest in organic chemistry due to the frequent existence of these structures in biologically active compounds[10,11] and their role as valuable synthetic intermediates.[12,13] The direct transfer of carbene from diazo compounds to alkenes, which is the most straightforward route to cyclopropanes, is catalyzed by transition metals, and the use of several metal complexes has been described.[14] On the other hand, catalytic oxidation is widely used in the manufacture of bulk chemicals from hydrocarbons and, more recently, as an environmentally attractive method for the production of fine chemicals.[15,16]

Following our synthesis strategy to incorporate metal complexes during the hydrothermal synthesis of the zeotype,[5] in this paper we report the synthesis, characterization, and catalytic behavior of $[Cu(NH_3)_2]^+$ complex formed in situ during the ferrierite framework formation

## Experimental Section

**General Information.** $C_3H_9N$, $NH_4(OH)$ (30%), and HF (40%) were from Aldrich, Cab-O-Sil M-5 was from BDH

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* To whom correspondence should be addressed. E-mail: amonge@icmm.csic.es; egutierrez@icmm.csic.es.

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**Table 1. Selected Crystallographic Data for $[Cu(NH_3)_2]^+$ Intratunnel Containing Ferrierite**

| formula | $[Cu_{0.34}(NH_3)_{0.68}]^{0.34+}(Si_{35.66}\,Al_{0.34}\,O_{72})^{0.34-}$ | $N_2C_6H_{18}\,(NH_3)_{1.6}$ |
|---|---|---|
| formula weight | 2335 | |
| crystal system | orthorhombic | triclinic |
| space group | *Pmnn* (no. 58) | $P\bar{1}$ (no. 2) |
| cell dimensions, Å | | |
| a | 18.829(4) | 7.440(2), $\alpha = 69.814(4)°$ |
| b | 14.124(3) | 12.339(3), $\beta = 72.478(5)°$ |
| c | 7.440(1) | 12.342(3), $\gamma = 72.507(5)°$ |
| Z | 1 | 0.5 |
| $V$, Å$^3$ | 1978.5(7) | 989.2(4) |
| unique data | 1335 ($R_{int} = 0.13$) | 2265 ($R_{int} = 0.06$) |
| data/restraints/parameters | 1335/0/147 | 2265/0/273 |
| goodness-of-fit on $F^2$ | 0.974 | 0.928 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.084, wR$_2$ = 0.21 | R1 = 0.086, wR$_2$ = 0.21 |
| $R$ indices (all data) | R1 = 0.16, wR$_2$ = 0.26 | R1 = 0.160, wR$_2$ = 0.26 |
| largest diff. peak and hole (e Å) | 1.309 and −0.729 | 0.858 and −0.695 |
| Si−O lengths avg range (Å) | 1.593(9)−1.612(9) | 1.582(10)−1.606(9) |
| O−Si−O angles avg range (deg) | 109.4(5)−109.5(6) | 109.5(5)−109.5(5) |
| Cu−N length × 2 (Å) | 2.21(4) | 2.22(8) |
| N−Cu−N angle (deg) | 180 | 180° |

Scintran, $NO_3Cu{\cdot}3H_2O$ was from Merck, and $Al(OH)_3$ was from Probus. C, H, N analysis was carried out at the analytical department of the CNQO (CSIC) with a Heraeus apparatus. Cu content was analyzed by atomic absorption using a Perkin-Elmer 1100B spectrophotometer. Gas chromatography analysis (GC−MS) was performed using a Hewlett-Packard 5890 II with a flame ionization detector in a cross-linked methylsilicone column (mixture of methylsilicone (OV-1701) and permethylcyclodextrine as stationary phase).[17] Thermogravimetric and differential thermal analysis (TGA−DTA) was performed in a SEIKO TG/DTA 320 apparatus in air atmosphere in the temperature range between 25 and 800 °C.

**Synthesis.** The compound was synthesized from reaction mixtures containing $SiO_2$, $Al(OH)_3$, $Cu(NO_3)_2{\cdot}3H_2O$, $NH_4(OH)$, $PrNH_2$, and HF, in molar ratios 1.7:0.2:0.34:16:6:2, under hydrothermal conditions. The mixture was heated at 180 °C for 14 days. The colorless platelike crystals obtained were filtered and washed thoroughly with deionized water and acetone. Anal. Elemental analysis found: C, 4.6; H, 1.2; N, 1.9; Cu, 1.0. X-ray powder diffraction analysis showed a sole phase identified as ferrierite.

**X-ray Structure Determination.** A very small crystal of this compound with platelike habit was selected and mounted in a diffractometer equipped with CCD detector. Due to its size, the resulting spectrum was quite poor, but good enough to characterize the compound. A reduced triclinic cell was obtained from primary indexation, which is transformable to an orthorhombic I cell. There are, however, some weak reflections that violate the body-centered symmetry. Obviously, these reflections are being ignored when using either the orthorhombic I cell or the reduced triclinic one. The refinements in both cells also imply a certain degree of stiffness around some oxygen atoms situated in special positions. These facts make the orthorhombic *Pmnn* the most appropriate space group for the ferrierite framework refinement. The structure was thus refined in the orthorhombic *Pmnn* (no. 58) space group, with the reported starting model[18,19]and Cu and N atoms of the complex in the special positions (0 $^1/_2$ $^1/_2$) and (0 0.525(5) 0.21(1)), respectively. However, to improve the localization of the template, especially the diamine copper complex, the reduced triclinic cell was also used. Anisotropic refinements were carried out for the framework in both primitive cells with similar results. In regard to the template, the propylamine molecules presented the same disorder and the population factor for Cu atom led to the same composition in both cases. The solution in the triclinic cell led to a better refinement of the dyamine copper complex since the ammonia N atom is not confined to the symmetry plane constrictions allowing thus localization of the hydrogen atoms. These were located in a Fourier synthesis by using those reflections with sin $\theta/\lambda < 0.5$. A summary of the fundamental crystal and refinement data in both primitive cells is given in Table 1. Most of the calculations were carried out with SMART software, for data collection and data reduction, and SHELXTL.[20]

**Magnetic Measurements.** Direct current magnetic measurements were carried out using a SQUID (Quantum Design) magnetometer operating from 150 to 2 K at 5000 Oe. Diamagnetic corrections were taken into account.[21]

**Catalytic Reactions.** *Cyclopropanation of Alkenes.* To a stirred mixture of alkene (styrene, 1,2-dihydropyrane) (0.81 mmol) and the catalyst (0.04 mmol) was added alkyl diazoacetate (alkyl = ethyl, *tert*-butyl) (0.114 mmol) dropwise with a syringe over a period of 2 h in a $N_2$ atmosphere at 50 °C. After the evolution of $N_2$ ceased, a mixture of ethyl *cis*/*trans*-2-phenylcyclopropanecarboxylates was obtained. Chemical yields were determined by gas chromatography.

*Oxidation of Sulfides.* The catalyst (0.04 mmol), acetonitrile as the solvent (1 mL), the substrate (sulfide, 1 mmol), and 30% $H_2O_2$ (1.55 mmol) were placed in a 15 mL glass vial. The reaction vessel was heated at a constant temperature with stirring. The reaction mixtures were analyzed by GC, and the reaction products were identified by GC−MS analysis.

## Results and Discussion

The relative stabilities of copper(I) and copper(II) in aqueous solution depend very strongly on the nature of the anions and other ligands present and vary considerably with solvent or nature of the neighboring atoms in the crystal. In this synthesis procedure, the propylamine present in the reaction media reduces $Cu^{2+}$ to $Cu^+$ and the ammonia simultaneously avoids the disproportionation to $Cu^0$ and $Cu^{2+}$, stabilizing the $[Cu(NH_3)_2]^+$ cationic complex, which is incorporated into the crystal. The electrical neutrality is maintained by doping the framework with $Al^{3+}$.

The crystal structure of the ferrierite so modified indicated that its composition is $[Cu_{0.34}(NH_3)_{0.76}]^{0.34+}$-$(Si_{35.66}\,Al_{0.34}\,O_{72})^{0.34-}{\cdot}(C_3H_9N)_2\,(NH_3)_{1.6}$. Coordinates in a *Pmnn* orthorhombic cell are given elsewhere,[18,19] and Table 2 includes the atomic parameters for the triclinic cell. Elemental analysis of C, N, H, and Cu agrees with

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**Table 2. Atomic Coordinates, Equalized Temperature, and Population Factors in the Triclinic Cell**

| atom | *X* | *Y* | *Z* | $U_{eq}$ | Pp |
|---|---|---|---|---|---|
| Si(1) | 0.3823(7) | 0.5268(4) | 0.1216(4) | 23(1) | 1.00 |
| Si(2) | 0.5821(6) | 0.7153(3) | 0.1174(3) | 13(1) | 1.00 |
| Si(3) | −0.0655(6) | 0.2724(3) | 0.2726(3) | 14(1) | 1.00 |
| Si(4) | 0.5834(6) | 1.1174(3) | −0.2844(3) | 14(1) | 1.00 |
| Si(5) | 0.3834(7) | 0.1223(4) | 0.5261(4) | 25(1) | 1.00 |
| Si(6) | −0.0326(8) | 0.1225(4) | 0.5166(3) | 22(1) | 1.00 |
| Si(7) | −0.4791(6) | 0.2729(3) | 0.2721(3) | 14(1) | 1.00 |
| Si(8) | 0.6545(6) | 0.8464(3) | −0.1535(3) | 13(1) | 1.00 |
| Si(9) | −0.0309(7) | 0.5260(4) | 0.1226(4) | 25(1) | 1.00 |
| O(1) | 0.0 | 0.0 | 0.5 | 61(7) | 1.00 |
| O(2) | 0.4378(17) | 1.1385(12) | −0.3646(9) | 50(4) | 1.00 |
| O(3) | 0.5 | 0.0 | 0.5 | 72(8) | 1.00 |
| O(4) | 0.4358(18) | 0.6336 (9) | 0.1386 (11) | 43(4) | 1.00 |
| O(5) | 0.4285(15) | 0.2304 (9) | 0.4111 (8) | 33(3) | 1.00 |
| O(6) | 0.6039(18) | 0.9870(8) | −0.1944(8) | 37(4) | 1.00 |
| O(7) | −0.5278(17) | 0.2026(11) | 0.1994(10) | 43(4) | 1.00 |
| O(8) | 0.1271(17) | 0.2016(11) | 0.2017(10) | 50(4) | 1.00 |
| O(9) | 0.1562(17) | 0.5601(9) | 0.1270(9) | 32(3) | 1.00 |
| O(10) | −0.0720(18) | 0.2287(9) | 0.4117(8) | 35(3) | 1.00 |
| O(11) | −0.0693(17) | 0.4112(8) | 0.2301(9) | 30(3) | 1.00 |
| O(12) | −0.2493(15) | 0.2490(9) | 0.2492(8) | 24(3) | 1.00 |
| O(13) | −0.5706(16) | 0.4111(8) | 0.2287(8) | 31(3) | 1.00 |
| O(14) | 0.1566(17) | 0.1263(10) | 0.5615(8) | 32(3) | 1.00 |
| O(15) | −0.2117(18) | 0.6360(10) | 0.1379(12) | 54(4) | 1.00 |
| O(16) | 0.0 | 0.5 | 0.0 | 69(7) | 1.00 |
| O(17) | −0.2092 | 0.1372 | 0.6362 | 50(0) | 1.00 |
| O(18) | 0.5050(22) | 1.2088(9) | −0.2093 | 77(5) | 1.00 |
| O(19) | 0.6030(19) | 0.8051(8) | 0.0117 | 41(4) | 1.00 |
| O(20) | 0.5 | 0.5 | 0.0 | 77(8) | 1.00 |
| N(1) | 0.204(5) | 1.498(3) | −0.499(3) | 180(17) | 0.74(8) |
| Cu | 0.5 | 0.5 | 0.5 | 148(19) | 0.17(5) |
| H1 | 0.146(5) | 1.437(5) | −0.427(5) | 160 | |
| H2 | 0.192(3) | 1.468(3) | −0.559(3) | 160 | |
| H3 | 0.109(5) | 1.563(5) | −0.498(5) | 160 | |
| N(2) | 0.101(4) | 0.302(2) | 0.698(2) | 39(7) | 0.50 |
| C(1) | 0.002(5) | 0.201(3) | 0.799(3) | 42(9) | 0.50 |
| C(2) | 0.018(9) | 0.088(6) | 0.904(6) | 133(24) | 0.50 |
| C(3) | 0.0 | 0.0 | 0.0 | 166(23) | 1.00 |

the obtained values from the refinement plus one acetone molecule per formula, from the washing procedure.

The ferrierite framework structure is based on 5-ring building units stacked along the [001] direction ([100] in the reduced triclinic cell). The connection of these rings forms 10-ring channels running along the [001] (pore size 4.2 by 5.4 Å). These channels intersect with an 8-ring channel parallel to the [010] ([01−1] in the reduced one) (pore size 3.5 by 4.8 Å).

The closeness of the Si−O distances and O−Si−O angles to the ideal value of 1.60 Å and 109° indicates the degree of accuracy in the framework determination.

Along the 10*R* channel, a row linear $[Cu(NH_3)_2]^+$ complex is hosted. The copper atom is situated at an inversion center and bonded to two $NH_3$ molecules at 2.21 Å, Figures1 and 2. The $[Cu(NH_3)_2]^+$ complexes are isolated inside the channels, the distance between the Cu atom and the nearest oxygen atom of the framework being 3.95 Å. The Cu−Cu shortest distances would be 7.44 Å in the hypothetical case of being totally occupied the copper position. This separation among metallic centers should favor the catalytic activity in the current compound. There is not even a hydrogen bond among the $NH_3$-coordinated molecules and the framework, since the shortest N1−O distance is 3.64 Å. This lack of interaction partially explains the large thermal parameters of the complex atoms. Along the 8*R* channels one disordered molecule of propylamine per formula has been found. There are hydrogen bonds between the $NH_3$ molecules and the nitrogen atoms of the propylamine molecules with the following lengths: N−H, 0.91; N···N, 2.92; N···H, 1.97, 2.55, and 2.56 Å. We found a similar environment for the $[Cu(NH_3)_2]^+$ complex in $Ge_9O_{19}[Cu(NH_3)]_2NH_4$ (ICMM2), a germanium zeotype whose framework is based on intersecting 8-ring channels. In this compound, the complex is also situated in a row along one of the 8-ring channels,[5] without any kind of interaction with the framework.

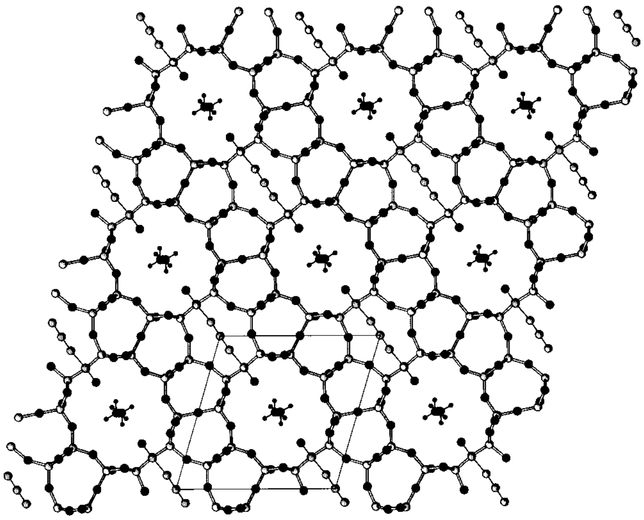


**Figure 1.** View of the ferrierite structure showing the $[Cu(NH_3)_2]^-$ complex along the 10R-channels [100] direction in the triclinic cell.

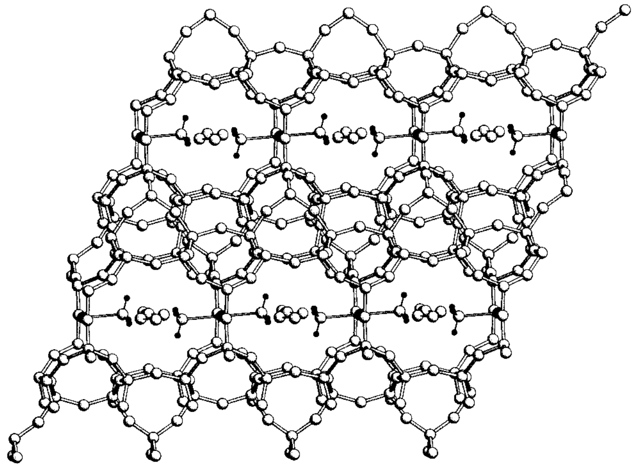


**Figure 2.** View of de cell along the [0 1 −1] directions in the triclinic cell.

Given the difficulty in the characterization of the $Cu(NH_3)_2$ complex, it is worth pointing out some facts that support its identification: (i) As for the synthesis procedure experience, a similar path led us to the stabilization of the same complex in a new germanium zeotype.[5] In that case, a diamine copper molecule per formula was required to maintain the electric neutrality, being the population factors of the atoms thus, equal to the unit. (ii) The distances and angles obtained in the structure solution, as well as the localization of the $NH_3$ hydrogen atoms are consistent with the diamine copper complex. (iii) The nonexistence of aqueous solution chemistry involving $Cu^+$ (it is known that $Cu^+$ requires soft ligands such as S, P, or N donors to form complexes) avoids the assignation of the electron density found in the $NH_3$ positions to $H_2O$ molecules. (iv) DTA, TGA, and elemental analysis are in acceptable agreement with the results of the refinement.

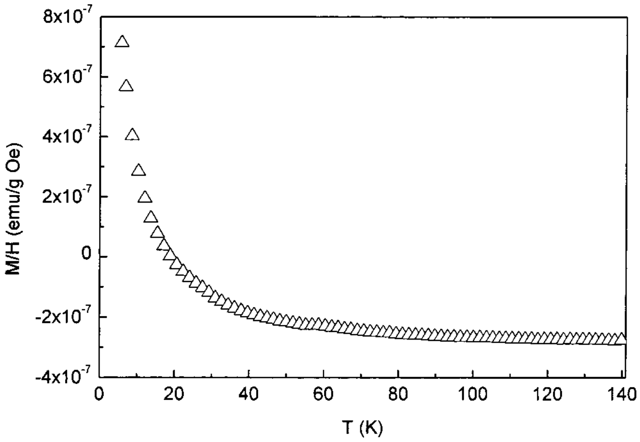


**Figure 3.** Magnetic susceptibility as a function of the temperature for fer-Cu(I).

On the other hand, the population factor of Cu atom compared with the N(1) indicates that a Cu atom is not always situated between two $NH_3$ molecules, but only 25% of these positions are occupied. This fact, which has been observed in a Cu(II) complex in siliceous ferrierite,[4] seems to indicate that the $NH_3$ molecules are held in place by their van der Waals interactions with the oxygen atoms of the framework when copper is not present.

TGA−DTA analyses show one loss of weight of about 8%, accompanied by one endothermic energy change between 375 and 700° C that corresponds to the loss of the $NH_3$ and propylamine molecules. A previous progressive loss from room temperature of about 3% attributed to the elimination of organic molecules from the washing procedure was also observed. In the cooling process a change of color from white to turquoise blue and a gain of 3% is observed. These facts are attributed to the oxidation of $Cu^+$ to $Cu^{2+}$ and subsequent incorporation of $H_2O$ and $CO_2$ molecules that could complete the coordination of the small amount of $Cu^{2+}$. X-ray powder diffraction measurements show that the structure is maintained after heating to 900 °C. The oxidation from $Cu^+$ to $Cu^{2+}$ of this material, being predictable by the change of color observed in the heating and cooling process, has been corroborated by magnetic susceptibility measurements. The material that is white and diamagnetic as synthesized, Cu(I)-fer (from now on), becomes blue and paramagnetic after heating to 800 °C and cooling to room temperature in air, Cu(II)-fer (from now on). Figure 3 shows the temperature dependence of the magnetic susceptibility with the temperature for Cu(I)-fer *white sample.* It clearly indicates the diamagnetic behavior of this material, which is consistent with the only presence of Cu(I) in it. On the other hand, Figure 4 shows the temperature dependence of the magnetic susceptibility, and its reciprocal, for the Cu(II)-fer *green sample.* The plot follows a Curie−Weiss-type law, $\chi_m^{-1} = 30.9(17) + 5.18(2)T$ mol·emu$^{-1}$ ($r$ = 0.9989), with $\theta_c = -6$ K being the calculated magnetic moment 1.2 $\mu_B$ per formula unit, which corresponds to 2.1 $\mu_B$ per $Cu^{2+}$. This value is similar to that observed for other $d^9$ $Cu^{2+}$ compounds and agrees with the expected value considering the mixing in of the excited states $^2T_{2g}$ to the $^2E_g$ ground state which results of the crystal-field splitting of the $^2D$ free ion ground term. As expected, no maxima in $\chi_m$ are observed at low temperatures, and thus, the existence of any kind of magnetic interactions between $Cu^{2+}$ ions can be discarded.

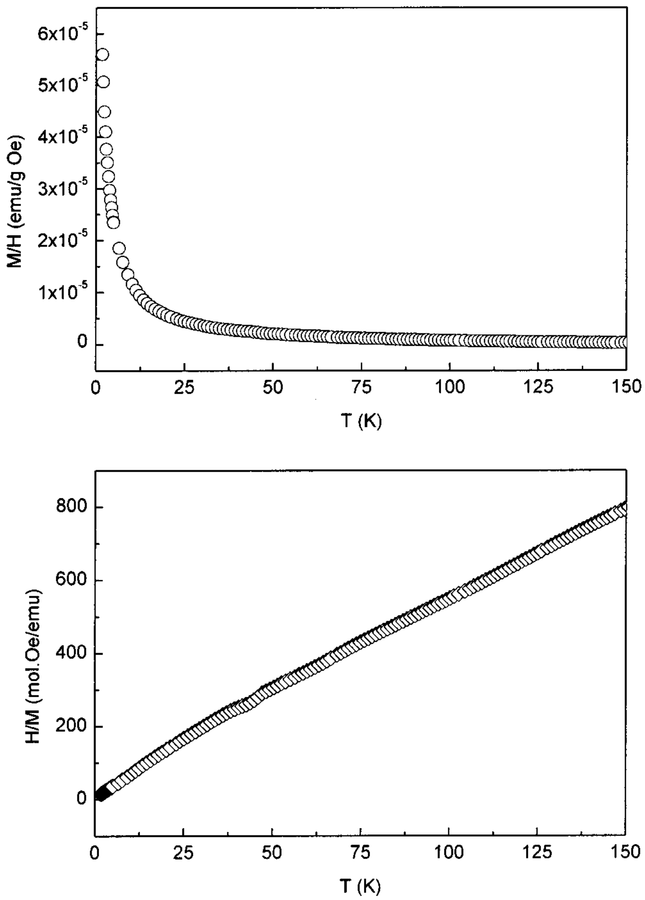
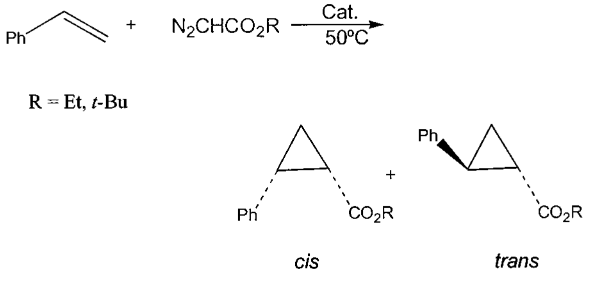


**Figure 4.** Thermal variation of the magnetic susceptibility (circles) and its reciprocal (diamonds) for fer-Cu(II).

**Catalytic Properties.** *Cyclopropanation Reactions.* To study the influence of the copper oxidation state in the catalytic reactivity, we first tested the copper-catalyzed cyclopropanation of styrene with alkyl diazoacetates (alkyl = ethyl, *tert*-butyl) (eq 1) with the catalyst in both oxidation states. The results are reported in Table 3. The reaction was carried out without solvent by slow addition of the diazoacetate to a 50 °C suspension of styrene and the copper catalyst previously prepared. In the reaction, 0.05 mol % of catalyst was used, and no differences in the chemical yield have been found when up to 2 mol % of catalyst was employed. The main product was a mixture of alkyl *cis*/*trans*-2-cyclopropanecarboxylate. The chemical yield was high (in the range 60−90%).



(1)

The selectivity in diazoacetate is high and depends on the catalyst. The active centers of the monovalent copper catalyst are selective and they do not catalyze

**Table 3. Results of the Cyclopropanation of Styrene with Alkyl Diazoacetate Using Cu(I)-fer and Cu(II)-fer Materials without Solvent at Room Temperature**

| catalyst | $N_2CHCO_2R$, R = | time (h) | convn (%) | Sel[a] (%) | trans/cis[b] |
|---|---|---|---|---|---|
| Cu(I)-fer | Et | 22 | 76 | 100 | 2.03 |
| | *t*-Bu | 23 | 79 | 100 | 1.80 |
| Cu(II)-fer | Et | 23 | 74 | 58 | 1.99 |
| | *t*-Bu | 14 | 69 | 52 | 1.86 |

[a] Cyclopropanes/conversion total. [b] Determined by gas chromatography.

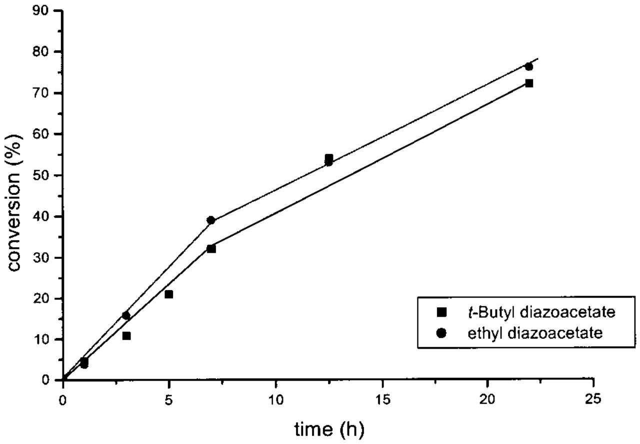


**Figure 5.** Kinetic profile for the cyclopropanation reaction catalyzed by Cu(I)-fer.

the dimerization of diazoacetate even when using it in excess, Figure 5. On the other hand, when divalent copper catalyst is used, the metallic centers are not only active for the cyclopropanation of styrene but also for the dimerization and polymerization reactions. This fact indicates lower selectivity in Cu(II)-fer. Concerning to the catalytic activity, Cu(II)-fer led to yields similar to that of Cu(I)-fer and compares well with other Cu catalysts.

The trans/cis ratio of the cyclopropanation products seems to be dependent only on the ester group of the diazoacetate, and the normal trans preference reported by others[22] was observed. A similar effect was found with ICMM2 as catalyst. In that case the trans/cis ratio was 1.98.[5]

Due to the shape selectivity of this material, only dimerization products of the diazoacetate and the unaltered catalyst are obtained when handling bulkier alkenes such as 1,2-dihydropyrane. This inoperativeness of the catalyst evidences the lack of accessibility of the reactants to the catalytic sites and, thus, the occurrence of the reaction inside the ferrierite cavities. The catalyst has been reused several times with no loss of activity or copper content.

To sum it up, this type of catalyst is a truly heterogeneous counterpart of homogeneous transition-metal complex catalysts for cyclopropanation of alkenes.

*Oxidation of Sulfides.* The performance of Cu(I)-fer as oxidation catalyst was tested in reactions with organic substrates such as methyl phenyl sulfide and (2−ethylbutyl) phenyl sulfide. The activity and selectivity attained are shown in Figure 6. The oxidations were carried out in the presence of catalytic amounts of the catalyst (0.04% based on experimental metal content). Hydrogen peroxide ($H_2O_2$) was the sacrificial oxidant in acetonitrile. This oxidant was examined due to its environmental acceptability, which depends mainly on the nature of its byproduct, water. For methyl phenyl sulfide, the reaction was performed at room temperature, since under these conditions it showed a high chemoselectivity and only sulfoxides were obtained as the main or sole product of the reaction. Higher temperatures led to a dramatic decrease in the selectivity to sulfoxide. The reaction with (2-ethylbutyl) phenyl sulfide was tested in a temperature range of 25−50 °C; however, not even at 50 °C were the oxidation products detected. This difference of reactivity depending on the size of the molecule could have been anticipated in view of the restrictions imposed on the diffusion substrate and products through the micropores of the solid, when the reaction is run at low temperatures. A series of blank experiments revealed that each component is essential for an effective catalytic reaction and the system is relatively unaffected by changing the order of mixing. To further establish the lack of Cu leaching, chemical analysis of the liquid phase after the reaction was performed. No Cu ions were detected. The catalyst could be reused four times without loss of either selectivity or activity with catalyst loading as low as 1 mol %.

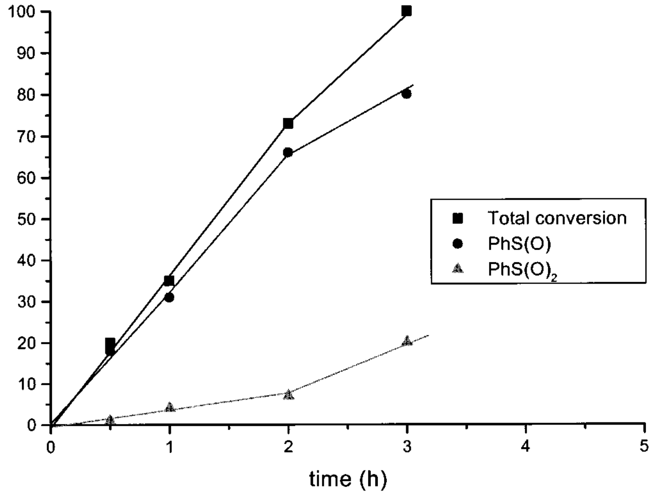


**Figure 6.** Kinetic profile for the Cu(I)-fer catalyzed oxidation of methylphenylsulfide at 293 K.

## Conclusions

A copper(I) complex $[Cu(NH_3)_2]^+$ has been formed in situ during the ferrierite framework constitution. This material exhibits the following noteworthy features: presence of isolated metal-complex molecules inside their tunnels, large separation among the active metallic centers, and unhindered accessibility of the reactants to these active sites through uniformly sized channels. It is a good catalyst in cyclopropanation of alkenes and sulfide oxidation reactions. It can be recovered and reused, retaining most of its catalytic activity.

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