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Activation of dioxygen by copper complexes incorporated in molecular sieves

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Abstract

The activation of dioxygen, at ambient conditions, by dimeric copper acetate complexes incorporated in molecular sieves Y, MCM-22 and VPI-5, in the oxidation of phenols to ortho diphenols and diphenols to *o*-quinones is reported. L-tyrosine is oxidised to L-DOPA, phenol to catechol, catechol to ortho benzoquinone and cresols to the corresponding ortho dihydroxy and *o*-quinone compounds. The incorporated copper complexes have been characterized by IR, UV and ESR spectroscopies. A linear correlation between the concentration of the copper acetate dimer in the molecular sieve (from ESR) and the conversion of L-tyrosine suggests that the dimeric copper atoms are the active sites in the activation of dioxygen. The catalytic efficiency (turnover numbers) of the copper atoms are higher in the incorporated state compared to that in 'neat' copper acetate. Our results indicate that copper acetate dimers in molecular sieves mimic both the monophenolase and diphenolase catalytic activity of the monooxygenase enzyme, tyrosinase.

Keywords: Dioxygen; Copper acetate; Tyrosinase; L-Tyrosine; L-DOPA; Hydroxylation; Phenol; Cresol; Zeozymes

1. Introduction

Selective oxidation of hydrocarbons using molecular oxygen, O_2, as the oxidant and solid catalysts at low temperatures continues to be a major goal in catalysis. The advent of titanium and vanadium silicate molecular sieves during the last decade has enabled some of the oxidative transformations to be carried out using the more expensive H_2O_2 as the oxidant. The use of H_2O_2 is, however, not economically favourable in many oxidation processes and there is still a need for solid catalyst systems capable of utilizing O_2 in selective oxidation processes. One of the various attempts to reach this goal is encapsulation of a suitable transition metal or its complex in a micro-environment (such as that in the cavities of a molecular sieve) and using such an encapsulated catalyst in selective oxidation systems using O_2 as the oxidant. It was anticipated that such a catalyst system would produce zeolite mimics of enzymes ('Zeozymes') which are known to bind and transport molecular oxygen (like hemoglobin and myoglobin) or use O_2 in the selective oxidation of inactivated alkanes to alcohols (like cytochrome P450). Workers from Du Pont were amongst the early pioneers in this approach [1]. In an attempt to prepare analogs of hemoglobin and myoglobin which can reversibly bind O_2, cobalt salen complexes were encapsulated in the supercages of zeolite Y. Such encapsulated complexes formed adducts with dioxygen which were

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more stable than those formed by the same complex in free solution [1]. Apparently, the isolation of these complexes in the zeolite cavities suppressed the dimerization reactions leading to the inactive oxo and peroxo complexes. Dimerization reactions occur to a significant extent in the case of the homogeneous complexes. In a similar attempt to prepare analogs of cytochrome P450, Fe(II)Pd(0) particles encapsulated in zeolite A exhibited remarkable substrate and regioselectivity in the oxidation of n-paraffins with O_2 [2]. Since the early work of the Du Pont workers, only a few studies have been published on the activation of O_2 by metal complexes (mostly of Fe with ligands such as porphyrins, phthalocyanines and salens) encapsulated in molecular sieves [3–5]. By contrast, extensive studies have been reported on selective oxidation of organic compounds using singlet oxygen sources such as H_2O_2, t-butyl hydroperoxide or iodosobenzene as the oxidants and as catalysts either titano-/vanadium silicate molecular sieves or transition metal complexes encapsulated in molecular sieves [6–12].

Compared to the wealth of information available on binding and activation of dioxygen by Fe-containing hemoproteins and porphyrin-containing complexes, the chemistry of copper complexes and copper proteins in such processes is known in less detail [13–15]. Tyeklar and Karlin [16] have reported extensive studies on the biomimetic binding and activation of dioxygen by various copper complexes in the homogeneous phase. Copper-containing monooxygenase enzymes, like tyrosinase, (EC 1.14.18.1) reversibly bind O_2 and catalyze two different reactions [17,18]; the hydroxylation of monophenols to O-diphenols (monophenolase activity) and the oxidation of O-diphenols to O-quinones (diphenolase activity) both using molecular oxygen. The active site contains a pair of antiferromagnetically-coupled copper ions [19]. The oxygenated form (oxytyrosinase) consists of two tetragonal Cu(II) ions each coordinated by two strong equatorial and one weaker axial N_{His} ligand. The exogenous oxygen molecule is bound as peroxide {with a side-on, (μ-η^2-η^2) rather than an end-on (*cis*-μ-1,2) geometry} and bridges the two copper centres [20]. During hydroxylation, the phenols, coordinate directly to the Cu, leading to transfer of electron density from the phenol to the Cu ions and weakening of both the O–O and Cu–O bonds. Oxygen transfer to the ortho position in phenol occurs. The resultant coordinated catecholate transfers two electrons to the binuclear cupric site, leading to the dissociative elimination of the *o*-quinone product and the formation of the deoxy site for further turnover [21].

In our search for an inorganic mimic of tyrosinase to hydroxylate aromatic compounds, we had the following points in mind: (1) the complex should contain a pair of copper atoms separated by about 2–3 Å, (2) for utilization in industrial applications, it would be preferable if during the oxidation reaction, the binuclear complex of copper remains in the solid state or can be encapsulated in the microcavities of porous solids like zeolites for easy catalyst separation and recycle, (3) the complex should be relatively easy and inexpensive to prepare and rugged to use and (4) the ligands attached to the copper ions should have coordinating properties somewhat similar to the histidine groups in tyrosinase. Neither a heterogeneous solid mimic of tyrosinase nor a molecular sieve containing an encapsulated complex of a transition metal capable of aromatic hydroxylations using O_2 as the oxidant has, so far, been reported in the literature.

In the present paper, we report a novel catalytic system consisting of dimeric complexes of copper acetate located in molecular sieves Y, MCM-22 and VPI-5 which utilize O_2 in the hydroxylation of the aromatic nucleus (in L-tyrosine, phenol and cresols) thereby mimicking, in a restricted sense, the catalytic properties of the enzyme tyrosinase.

2. Experimental

2.1. Materials

Five solid catalysts were used: (1) solid copper acetate monohydrate (Cu-Ac), and copper acetate

in (2) zeolite Na-Y (Si/Al = 2.5; 0.08% wt. Cu; designated as Cu-Na-Y) (3) zeolite H-Y (Si/Al = 2.5; 0.12% wt. Cu; designated as Cu-H-Y) (4) zeolite H-MCM-22 (Si/Al = 60; 0.05% wt. Cu; designated as Cu-MCM-22) and (5) the aluminophosphate molecular sieve VPI-5 (0.06% wt. Cu; designated as Cu-VPI-5). Cu-Na-Y was prepared by stirring 3.5 g of copper acetate and 7 g of Na-Y (PQ Corporation, USA) in distilled, deionized water for 8 h, filtering and washing with distilled water till the washings are free of copper. The above procedure was again repeated with 3.5 g of copper acetate monohydrate. The catalyst was later evacuated (10^{-3} Torr) and dried at 383 K for 24 h. Cu-H-Y was prepared by first exchanging the Na-Y (twice) with 1 M ammonium acetate for 8 h. The ammonium form was calcined at 753 K for 24 h to obtain H-Y. Cu-H-Y was prepared by the same procedure described earlier for Cu-Na-Y. Cu-MCM-22 was prepared by stirring 5.0 g of copper acetate and 9.0 g of H-MCM-22 in distilled, deionized water for 8 h, filtering, washing with distilled water till the filtrate is free from copper, evacuation (10^{-3} Torr) and drying at 383 K for 24 h. Cu-VPI-5 was prepared by stirring 4 g of copper acetate and 6.5 g VPI-5 molecular sieve in distilled, deionized water for 8 h; filtering and washing with distilled water to remove excess copper acetate. The above procedure was repeated with 4 g of copper acetate. The material was then evacuated and dried at 373 K for 36 h. After incorporation of the copper acetate, the solids were first dried in vacuum, then in nitrogen at 298 K and stored in a desiccator. The enzyme tyrosinase (from mushrooms, salt-free, lyophilized) was obtained from Koch Light Labs., England (Lot. No. 5568t).

2.2. Procedures

Catalytic reaction

In a typical oxidation reaction, the solid catalyst (20 to 40 mg) was added to the substrate in a phosphate buffer (0.05 M, pH = 6.5). The contents were stirred at 298 K in the presence of molecular oxygen. Periodically, samples were removed and centrifuged to remove the solid catalyst. Copper was not detected (by atomic absorption spectroscopy, Hitachi Model Z-8000) in the colourless filtrate when using copper acetate, Cu-Na-Y, Cu-H-Y, Cu-MCM-22 or Cu-VPI-5. The substrates chosen were monohydroxy aromatic compounds like L-tyrosine (Aldrich, USA, 2 dM), phenol (S.D. Fine Chemicals, 8% wt), *meta* and *ortho* cresols (BDH, 15% wt) in phosphate buffer. In experiments involving the enzyme, 30 μg of tyrosinase in 30 μl of 0.05 M phosphate buffer was added to a 1 ml solution of 2 mM tyrosine in 0.05 M phosphate buffer.

Product analysis

The progress of the oxidation was monitored by HPLC (for reactions of tyrosine), gas chromatography (for phenol and cresols) and UV spectroscopic techniques. In the oxidation of tyrosine, after removal of the solid catalyst, by centrifugation, the filtrate containing the reactants and products was analyzed by HPLC (Shimadzu Model LC-9A), GC (Hewlett Packard, Model 5880) and UV spectroscopy (Shimadzu Model UV-2101PC). The range 190–350 nm was scanned by UV spectrophotometry. For the quantitative assay of L-tyrosine and L-DOPA, absorption at 280 nm by the UV detector (Shimadzu Model SPD-6AV) in the HPLC was utilized. The HPLC chromatograms were calibrated using known quantities of L-tyrosine and L-DOPA (Aldrich). The HPLC column was an ODS-C_{18} column. The carrier was a 20:80 (v/v) mixture of methanol and 1% phosphate buffer solutions. The flow rate was 1 ml/min. The L-tyrosine and L-DOPA standards were prepared as 2 mM solutions in 30 ml of phosphate buffer of pH = 6.5 (prepared from 0.05 M solution of Na_2HPO_4 and NaH_2PO_4). 15 μl of sample was injected in all cases. The retention times of L-tyrosine and L-DOPA under these conditions were 3.4 and 2.6 min, respectively. The reactants and products of the phenol, *o*-cresol and *m*-cresol reactions were analyzed by gas chromatography employing a FID detector and HP1 capillary column crosslinked with methyl silicone gum (50 m × 0.25 mm). The

presence of L- and D-DOPA amongst the products was also confirmed by ^1H NMR spectroscopy (Bruker MSL-300) of the products. The samples were lyophilized twice in D_2O medium to exchange the protons for deuterium.

2.3. Catalyst characterisation

The ESR spectra of the solid catalysts were measured at room and liquid N_2 temperatures using a Bruker ESR spectrometer (200 D). The second derivative spectra were calculated from the digitised absorption spectra. X-ray diffractograms of the solid catalysts were recorded using a Rigaku D-max III, X-ray diffractometer with a CuKα target. IR and UV spectroscopy of the solid catalysts were recorded using a Perkin Elmer 1600 FTIR and Shimadzu UV-2101 UV–Vis spectrophotometers, respectively. The IR spectra of the solid catalysts were recorded in a fluorolube medium (Perkin Elmer). $BaSO_4$ was used as the reference material for recording the diffuse reflectance spectra in the 200–900 nm region. XPS of the solid catalysts was recorded with a VG Scientific ESCA III Mark (II) with MgKα (1253.6 Å) as the excitation source.

3. Results and discussion

3.1. Catalyst characterisation

The copper content and chemical composition of the catalysts are given in the Experimental section. The X-ray diffractograms of the catalysts containing the complexes did not reveal any difference from those of the pure zeolites indicating that the molecular sieves had not undergone any significant structural changes during the incorporation of the copper acetate. The XPS binding energies of copper in the molecular sieves were also similar to the values in copper acetate monohydrate. Fig. 1 shows the infra-red spectra of the copper acetate complex as well as the complex located in the molecular sieves. It is seen that the structure of the copper acetate is intact even when

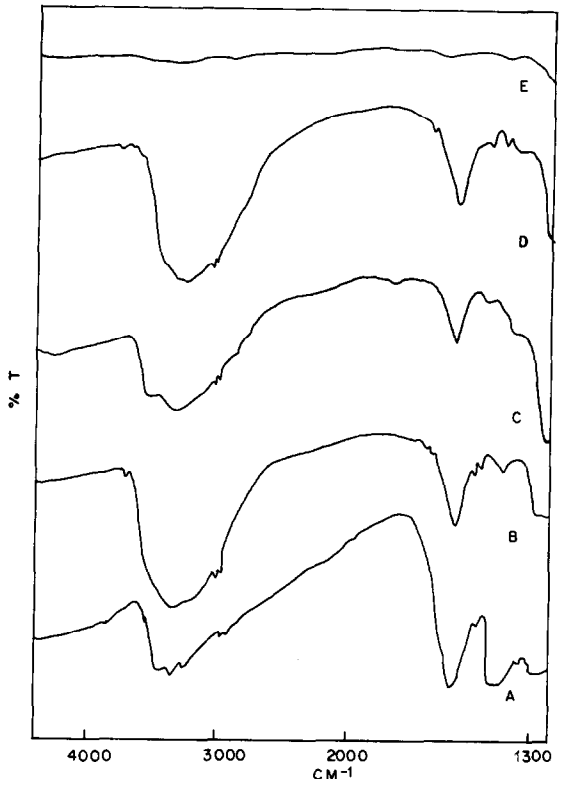

Fig. 1. IR spectra of catalysts: Copper acetate (A), Cu-H-Y (B), Cu-MCM-22 (C), Cu-VPI-5 (D) and fluorolube (E).

it is incorporated in the molecular sieve. The bands at 2960 and 2920 cm^{-1} (due to the asymmetric and symmetric stretching C–H vibrations of the $-CH_3$ group) as well as those at 1630 cm^{-1} (due to the carboxylate group) are clearly seen in the spectra of Cu-H-Y, Cu-MCM-22 and Cu-VPI-5 (curves B, C and D, respectively). The diffuse reflectance UV spectra of the molecular sieves with and without the copper complex (Fig. 2) also reveal the presence of copper acetate in the molecular sieves.

Having established the presence of copper (chemical analysis) and copper acetate (IR and UV) in the catalysts, the next question is the nuclearity (monomeric or dimeric structure) of the copper acetate complex in the molecular sieves. ESR spectroscopy was utilised to elucidate this point. It is well known [22] that copper acetate monohydrate has a dimeric structure with four carboxylate groups bridging the two Cu(II) ions (Fig. 3). The Cu–Cu distance is 2.616 Å. There

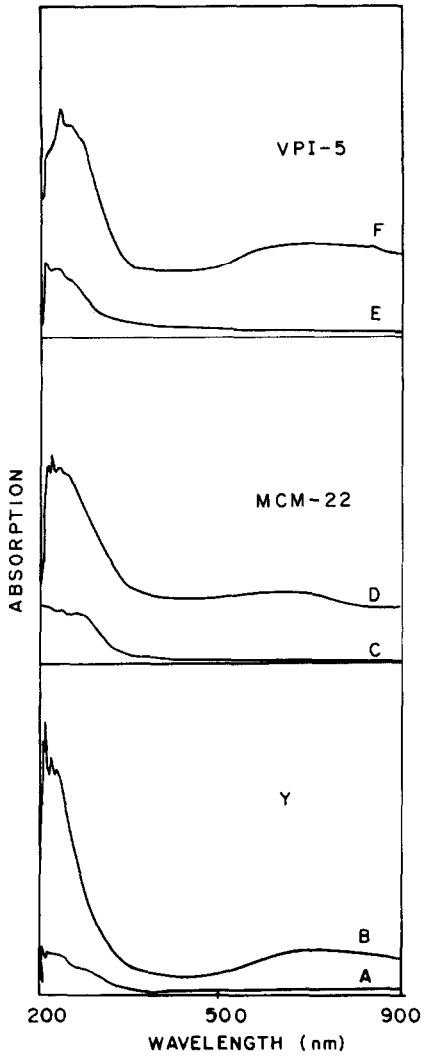

Fig. 2. Diffuse reflectance UV spectra of catalysts: Curves A–F represent H–Y, Cu-H-Y, H-MCM-22, Cu-MCM-22, VPI-5 and Cu-VPI-5, respectively.

is weak antiferromagnetic coupling of the unpaired electrons, one on each Cu(II) ion, giving rise to a singlet ground state with a triplet state lying only a few kilojoules per mole above it. At room temperature the triplet is, thus, appreciably populated leading to the paramagnetism of copper acetate. At 298 K, μ_{eff} is typically about 1.4 BM per copper atom [22]. A distinguishing characteristic of the dimeric copper acetate species is the presence of a seven line hyperfine structure in their ESR spectra [23,24]. The ESR spectra of our catalysts (Fig. 4) exhibit this seven-line pattern and, hence, indicate unequivocally the presence

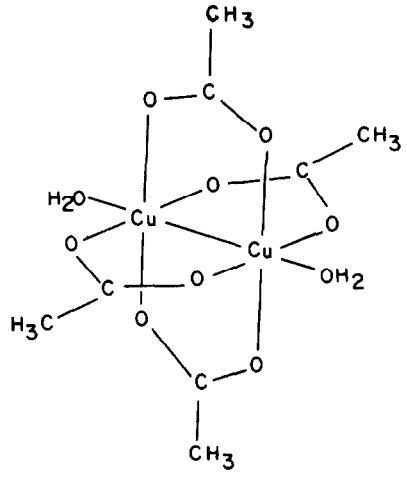

Fig. 3. Structure of copper acetate monohydrate.

of a 'dimeric' copper acetate complex similar to that present in copper acetate monohydrate. The ESR parameters for Cu-MCM-22 for example, were $g_{\perp}=2.02$, $g_{\parallel}=2.21$, $A_{\perp}=50$ and $A_{\parallel}=55$ G. The corresponding values for copper acetate monohydrate are 2.03, 2.21, 36 and 63, respectively. The latter set of values match very well with those in the literature for copper acetate monohydrate [23,24]. The ESR parameters of all our samples at 298 K are given in Table 1. The presence of a seven line pattern in the spectra of all our catalysts (Fig. 4) is a confirmatory evidence for the 'dimeric' copper structure of the incorporated complexes. The dimeric copper structure was present in the solid catalyst both before and after the catalytic reactions. A quantitative relationship between the concentration of such 'dimeric' complexes and their catalytic activity in oxidation reactions is discussed below.

3.2. Catalytic activity

Oxidation of L-*tyrosine*

Typical HPLC chromatograms of the products of the oxidation of L-tyrosine to L-DOPA with O_2 over the solid catalysts are shown in Fig. 5. along with their UV spectra. For comparison, the results for the enzyme tyrosinase are also illustrated. The reaction time, at 298 K, was 24 h in all cases. The minor (about 22%) peak (at 3.85 min) in the HPLC spectrum of L-tyrosine is due to the pres-

Table 1
ESR parameters (at 298 K) of copper acetate incorporated in molecular sieves

System	$g_\perp$	$g_\parallel$	$A_\perp$	$A_\parallel$	FWHM [a]
Cu-Ac	2.03	2.21	36	63	106
Cu-H-Y	2.00	2.22	43	58	147.15
Cu-MCM-22	2.02	2.21	50	55	141.2
Cu-VPI-5	2.03	2.22	43	66	164.8

[a] FWHM = full width at half maximum (oe).

ence of D-tyrosine formed by racemisation of the L-isomer in the phosphate buffer even in the absence of any catalyst. The separation of the L- and D-tyrosine over the C_{18} columns (used in the HPLC separation in the present study) has been reported earlier [25]. The D-isomer was also oxidised to D-DOPA (retention time = 2.85 min, Fig. 5) under our experimental conditions. The identity of L- and D-DOPA in the products was also confirmed by ^1H NMR spectroscopy of the lyophilised samples in D_2O medium. The relative proportions of L-DOPA (and D-DOPA) and quinones in the products varied with reaction conditions like catalyst quantity, reaction time, temperature, O_2 partial pressure, etc. The concentration of the quinones was negligible at low temperatures, low catalyst content or short reaction time. The catalytic activity of the various catalysts

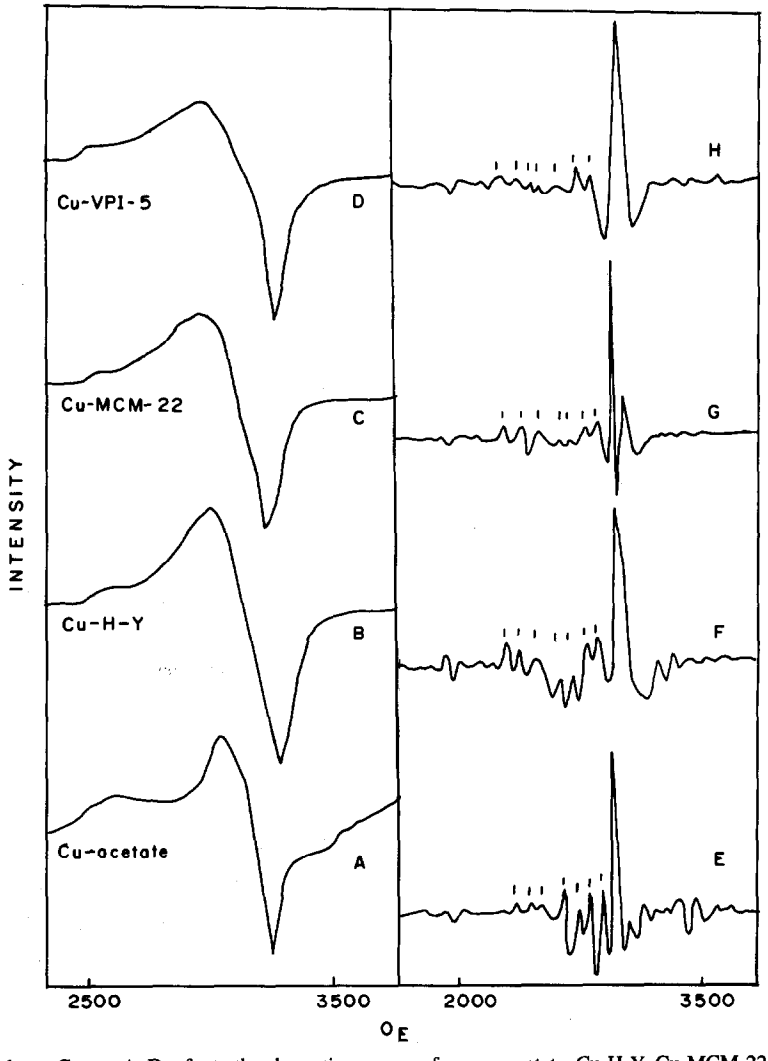

Fig. 4. ESR spectra of catalysts: Curves A–D refer to the absorption curves of copper acetate, Cu-H-Y, Cu-MCM-22 and Cu-VPI-5. Curves E–H refer to the corresponding second derivative spectra.

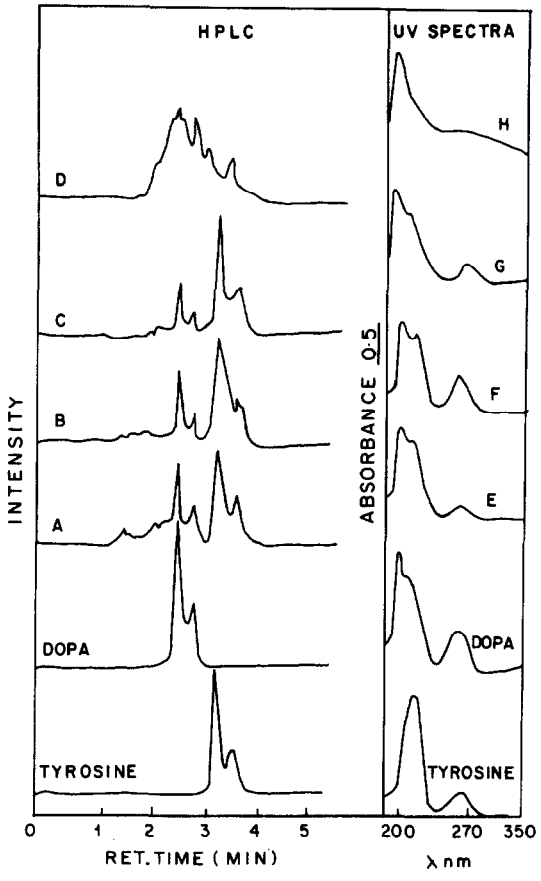

Fig. 5. HPLC chromatograms (left) and UV spectra (right) of the reactant (L-tyrosine) and products (L-DOPA and *o*-quinones). Curves A–D represent the HPLC chromatograms of the products from copper acetate monohydrate (A), Cu-MCM-22 (B), Cu-Na-Y (C) and the enzyme tyrosinase (D), respectively. Curves E–H represent the corresponding UV spectra of the products.

are compared in Table 2. All the solid catalysts exhibit both cresolase (tyrosine to L-DOPA) and catecholase (L-DOPA to *o*-quinones) activities similar to the enzyme tyrosinase [26]. There was neither any conversion of tyrosine in the absence of catalysts nor was there any product other than L-DOPA or the quinones in striking similarity to the behaviour of the enzyme. When L-DOPA, instead of L-tyrosine, was taken as the substrate, its further oxidation to the quinones was observed. The influence of catalyst concentration and temperature (Fig. 6) further confirms the catalytic nature of the reaction. The product with 0.2 g of copper acetate contained relatively more L-DOPA than *o*-quinones. The quinones were more predominant with larger quantities (0.4 g) of the catalyst. The product at 298 K (after removal of the catalyst) was colourless. At 313 and 333 K the filtrate was light blue in colour, perhaps, due to the increased solubility of copper acetate in the buffer at these temperatures. In the range of pH = 4.0 to 8.2, L-DOPA production was observed only at pH = 6.5. At this pH, copper acetate is insoluble at 298 K in the buffer (at lower pH values copper acetate dissolves in the reaction mixture) and remains a solid throughout the oxidation reaction. At the start of the reaction, the solid is pale blue in colour which turns pale green on formation of L-DOPA. Cu-Na-Y, Cu-MCM-22 and Cu-VPI-5 also behaved in a similar manner. The pH specificity (as well as the influence of temperature) of the reaction suggests that the copper acetate complex is active only in the solid state where it is present in the dimeric form. When the dimeric structure is absent {as in the dissolved state (lower pH or higher temperatures)}, the complex is inactive.

As in the case of tyrosinase, the presence of ascorbic acid, in addition to averting the initial inhibition period and enhancing tyrosine conversion, reduced the *o*-quinone formed to L-DOPA (Fig. 7) over all the four solid catalysts. In the case of tyrosinase, addition of ancillary reductants like ascorbic acid is known to suppress the induction period and reduce the *o*-quinones to L-DOPA [18]. The higher conversions obtained in the presence of ascorbic acid under otherwise identical conditions may be understood if the *o*-qui-

Table 2
Catalytic activity (TON) in the oxidation of L-tyrosine (A), phenol (B), *ortho* cresol (C) and *meta* cresol (D) at 298 K [a]

System	TON [b]			
	A	B	C	D
Cu-Ac	2.85	3.76	7.20	5.20
Cu-Na-Y	12.90	19.71		
Cu-H-Y	15.15	22.10	56.42	50.94
Cu-MCM-22	27.61	35.60	71.5	55.80
Cu-VPI-5	10.46	20.20	45.73	33.80

[a] 298 K; see Experimental for reaction conditions.
[b] TON = moles of substrate converted per mole of copper in the catalyst.

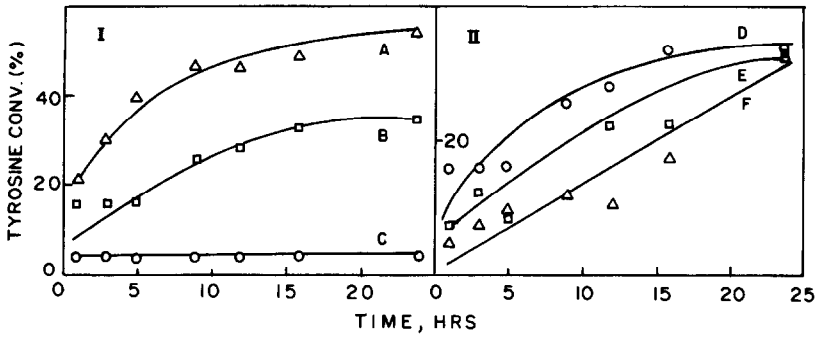

Fig. 6. Kinetic plots for L-tyrosine conversion: Curves A–C represent the influence of catalyst (copper acetate) weight (0.3, 0.2, 0.1 g, respectively) at 298 K. Curves D–F illustrate the influence of temperature (298, 313 and 333 K, respectively) with a constant catalyst weight of 0.2 g.

nones were one of the primary products whose further conversion by ascorbic acid (to L-DOPA) 'drives' the primary reaction (tyrosine conversion) to a greater extent. It may be mentioned here

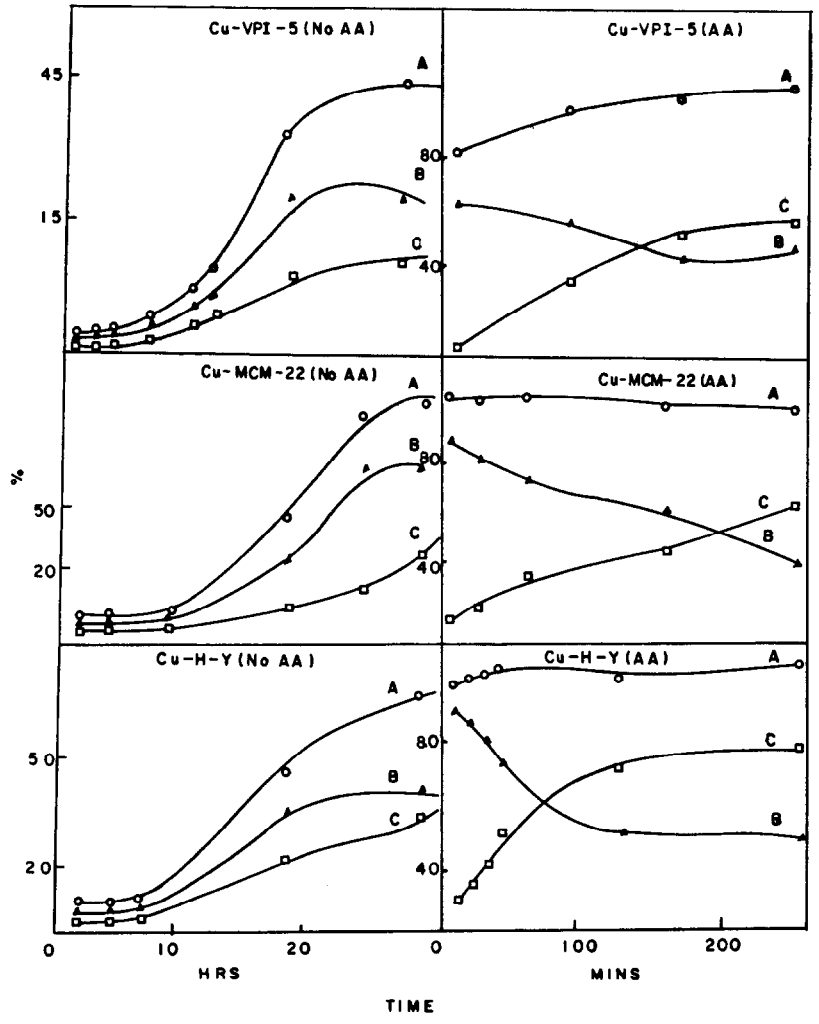

Fig. 7. Influence of ascorbic acid (AA) (0.6 mM) on tyrosine conversion, *o*-quinone and L-DOPA formation (curves A–C, respectively) at 298 K and 0.4 g of catalyst.

that there is a controversy in the recent literature [17] regarding the enzyme, tyrosinase-catalyzed oxidations, whether *o*-quinones are formed from L-tyrosine in a consecutive manner (via L-DOPA) or are also formed directly as primary products. For a given amount of catalyst, the concentration (in the range 1–4 dM) of L-tyrosine did not affect significantly the rate of hydroxylation.

Oxidation of phenols

The specific catalytic activities of the various catalysts are compared in Table 2 for the oxidation of phenol, *ortho* and *meta* cresols. In all cases, there is a very significant increase in catalytic efficiency (turnover numbers) on incorporation of the complexes in the microcavities of the molecular sieve. For example, in the oxidation of tyrosine or meta cresol over Cu-MCM-22 (columns A and D, respectively) there is a *tenfold* increase in the TON when the copper acetate complex is incorporated in the molecular sieve. This increase exemplifies the catalytic advantages arising due to the location of the transition metal complexes in an isolated state inside the cavities of the molecular sieves [6].

The molecular sieve-based catalyst also exhibited a high substrate and regio-specificity; only mono and ortho dihydroxy aromatic compounds (like phenol, catechol and cresols) underwent oxidation though at varying rates. Aromatic substrates without a phenolic OH group were not oxidised. Moreover, the monophenols were oxidised always in the ortho position. Oxidation of phenol, for example, yielded only catechol/*o*-benzoquinone; hydroquinone/*p*-benzoquinone were not observed.

3.3. Active sites

In an effort to identify the nature of the active sites responsible for the ortho oxidation reaction, we have tried to correlate the conversion of the monophenol (from kinetic experiments) with the concentration of the dimeric copper species obtained from the integrated intensity of the seven-line ESR spectra of the dimers. The results

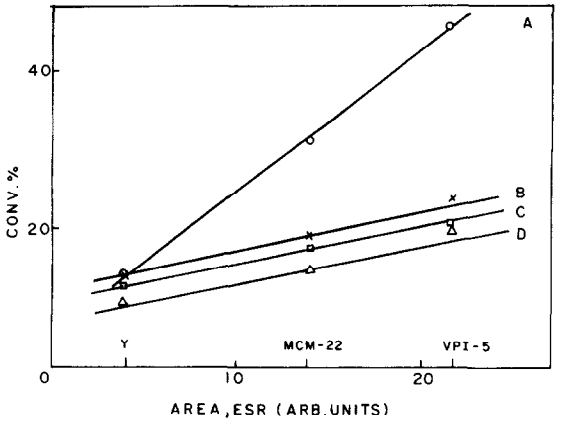

Fig. 8. Correlation between the integrated area of the seven-line ESR spectrum (of Cu-H-Y, Cu-MCM-22 and Cu-VPI-5) and conversion of L-tyrosine, phenol, *o*-cresol and *m*-cresol (Curves A–D, respectively).

(Fig. 8) show that there is, indeed, a linear correlation suggesting the involvement of the copper dimers in the oxidation reaction. It may be mentioned here that these dimers are more isolated from each other in the molecular sieve matrix than in the 'neat' solid state. For example, in Cu-Na-Y, only one in twelve of the unit cells of the Y zeolite contain a dimer of copper acetate. Similarly, in Cu-VPI-5 and Cu-MCM-22 only one in 100 and 30 unit cells, respectively, are occupied by the copper dimer. This physical isolation and dispersion in the molecular sieve matrix is, perhaps, the reason for the higher catalytic efficiency (higher TON) of the molecular sieve-based catalysts compared to the 'neat' copper acetate. While additional studies will be required to elucidate the mechanistic details of the reaction, the similarity of (1) the observed dimeric nature of the copper complex, (2) its high substrate specificity (for mono- or diphenols) and (3) high regioselectivity (oxidation only of the position ortho to the phenolic group) to the dimeric copper structure in the enzyme tyrosinase may be noted.

4. Conclusions

Dimeric copper acetate complexes incorporated in molecular sieves are catalytically active in the ortho hydroxylation of monophenols (like

L-tyrosine, phenol, *ortho* and *meta* cresols) and the oxidation of *ortho* diphenols to *ortho* quinones. There is a linear correlation between the catalytic efficiency of these materials and the concentration of the copper acetate dimeric complex obtained from their ESR spectra. The similarity in the catalytic behaviour of these novel catalysts and the enzyme tyrosinase is noted.

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