Heterogeneous Green Catalyst for Oxidation of Cyclohexene and Cyclooctene with Hydrogen Peroxide in the Presence of Host (Nanocavity of Y-zeolite)/Guest (N4-Cu(II) Schiff Base Complex) Nanocomposite Material

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Copper(II) complex of a Schiff base ligand derived from pyrrolcarbaldehyde and *o*-phenylenediamine (H_2L) has been synthesized and encapsulated in Y-zeolite matrix. The hybrid material has been characterized by elemental analysis, IR and UV-Vis spectroscopic studies as well as X-ray diffraction (XRD) pattern. The encapsulated copper(II) catalyst is an active catalyst for the oxidation of cyclooctene and cyclohexene using H_2O_2 as oxidant. Under the optimized reaction conditions 81% conversion of cyclohexene with 65% selectivity for 2-cyclohexenone formation and 87% conversion of cyclooctene with 46% selectivity for epoxide formation were obtained.

Keywords Schiff base, copper, zeolite, hydrogen peroxide, catalyst

Introduction

Schiff base transition metal complexes immobilized in zeolitic cavity are one of the subjects of current catalysis research.[1-5] Immobilization of suitable molecular species inside zeolite cavities induced a new type of functional materials.[6-9] These nanocomposite materials have been suggested as heterogeneous redox industrial catalysts,[10] photoredox,[11] photo catalysis[12] and photochemical storage of light energy.[13] Since zeolite replaces the protein mantle of the enzyme in the model compound, zeolite encapsulated metal complexes (ZEMC) have been suggested as a model compound for enzyme mimicking and often referred to as “zeozymes”.[14] Therefore, attempts have been made to encapsulate copper complexes in zeolite matrix to mimic this type of enzyme. Recently, organic dye molecules have been immobilized in a zeolite or a molecular sieve to prepare sensors.[15,16] On the other hand, copper(II) ions act as the active center in many metalloenzymes,[17-19] such as galactose oxidase, and the coordination sphere around copper center in the titled N_4-Cu(II) Schiff base complex, mimics the coordination environment of the copper(II) ion of galactose oxidase.

Development of non-heme transition metal catalysts for the oxidation of organic substrates with H_2O_2 is of interest especially during the past two decades.[20-24] Therefore, immobilization of the catalysts on the solid supports improves their recyclability of these expense catalysts and also enhances the stability of the catalysts toward oxidative degradation.

In this paper, we report the synthesis and characterization of copper complex of N_4 Schiff base ligand encapsulated within the nano pores of Y-zeolite and its catalytic efficiency in oxidation of cyclohexene and cyclooctene has been investigated.

Experimental

General

Infrared spectra were recorded as KBr pellets using Bruker Tensor 27 spectrometer. The visible spectra were determined using a Perkin Elmer, Lambda 35 UV-Vis Spectrometer. ^{1}H NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer using TMS as internal standard. The reaction products of oxidation were determined and analyzed by Agilent Series 6890. X-ray diffractograms of the catalyst were recorded using XRD, Seifect, 3003 PTS diffractometer with a Cu-Kα target. The metal contents were measured by using PU900 Philips atomic absorption spectrophotometer. Elemental analysis was performed using a CHN Perkin Elmer 2400 Sereis II.

Analytical reagents grade cyclohexene, cyclooctene, *o*-phenylenediamine, pyrrolcarbaldehyde, *tert*-butylhydroperoxide (solution 80% in di-*tert*-butylperoxide) and hydrogen peroxide were procured from Merck. Other reagents and solvents used were AR grade. NaY-zeolite was procured from Spag, Iran.

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Synthesis of ligand (H_2L)

To a stirred ethanolic solution (10 mL) of *o*-phenylenediamine (0.6 g, 5.5 mmol), pyrrolcarbaldehyde (1 g, 11 mmol) in 5 mL ethanol was added. The reaction mixture was stirred and heated to reflux for 4 h. The product was kept at ambient temperature, and the red shiny crystals were filtered, washed with cold ethanol and dried. The ligand (Scheme 1, **II**) was recrystallized from ethanol to give pure product with 67% yield and m.p. 168 ˚C. ^1H NMR (DMSO-d_6, 300 MHz) δ: 6.01—7.27 (m, 10H, ArH), 7.77 (s, 2H, HC＝N).

Preparation of copper(II) complex (CuL)

The ligand, (H_2L) (0.09 g, 0.3 mmol) was dissolved in 5 mL of ethanol. An ethanolic solution of $Cu(CH_3COO)_2•H_2O$ (0.06 g, 0.3 mmol) was added to above solution and the reaction mixture was refluxed for 3 h. After cooling down to room temperature for overnight, a reddish precipitate of copper complex was filtered off, washed with ethanol and dried in vacuum over calcium chloride to give 90% yield and decomposition point 298 ℃.[25]

Incorporation of copper(II) in NaY (metal exchanged Y-zeolite)

4 g Na-Y zeolite was suspended in 100 mL distilled water which contained copper(II) nitrate (4 mmol). The mixture was then stirrer for 24 h. The solid was filtered and washed with deionized water and dried at room temperature to give a light blue powder of Cu-NaY (Scheme 1, **I**).[26] Calcination of the prepared copper(II)-incorporated zeolite was avoided to arrest the migration of copper(II) ions from the vicinity of the supercage.[27]

Immobilization of CuL in Cu-NaY

An amount of 1.0 g Cu-NaY and acetonitrile solution of 2.5 g H_2L were mixed in a round bottom flask. The reaction mixture was heated at 100 ℃ for 5 h in an oil bath with constant stirring. The resulting material was taken out and extracted with acetonitrile using Soxhlet extractor till the complex was free from unreacted ligand. The non-complexed metal ions present in the zeolite were removed by exchanging with aqueous 0.01 mol/L NaCl solution (Scheme 1). The resulting solid was finally washed with hot distilled water till no precipitation of AgCl was observed on reacting filtrate with $AgNO_3$ solution. This was then dried at 150 ℃ for several hours till constant weight was achieved.

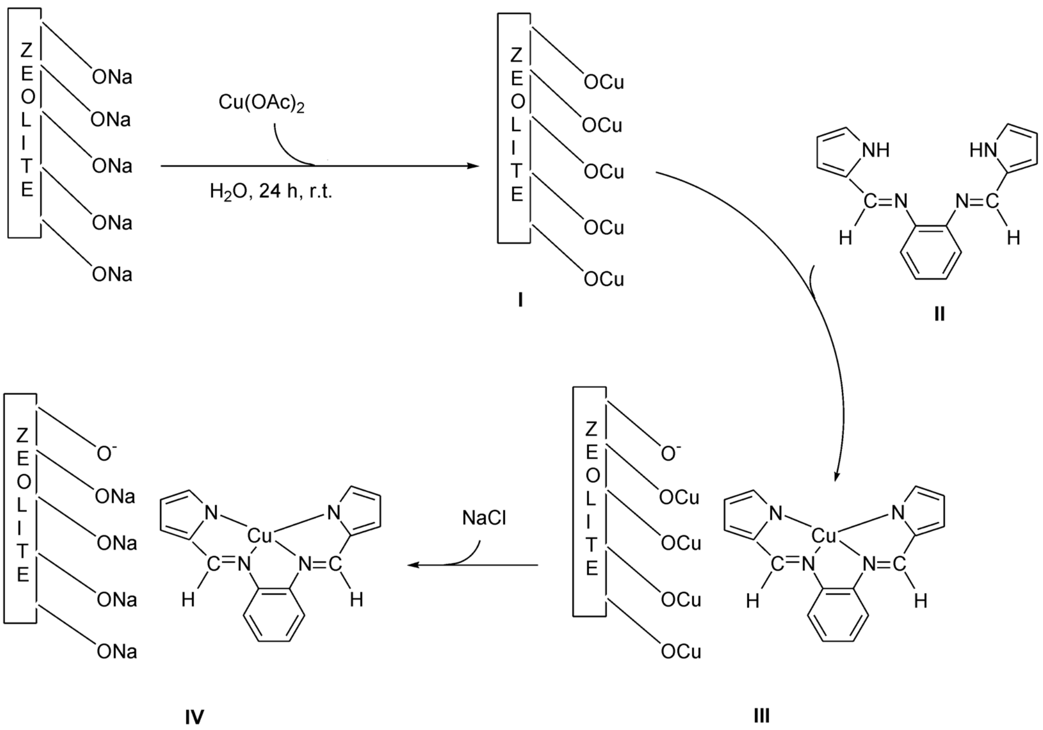
Homogeneous oxidation of cyclohexene

To a solution of cyclohexene (10 mmol) and neat copper(II) complex (0.3 mmol) in CH_3CN (10 mL), aqueous 30% H_2O_2 (25 mmol) was added. The resulting mixture was refluxed and the products were collected at different time intervals and the crude analyzed by GC and GC-MS. The concentration of products was determined using benzyl chroride as internal standard.

Heterogeneous oxidation of cyclohexene

A mixture of 0.05 g catalyst, 10 mL of CH_3CN and 10 mmol cyclohexene was stirred in a 50 mL round-bottom flask equipped with a condenser and 25 mmol of H_2O_2 (30% in water) was added. The resulting

Scheme 1



mixture was then refluxed with continuous stirring in an oil bath. After filtration and washing with solvent, the filtrate was concentrated and then subjected to GC analysis.

Results and discussion

Characterization of catalyst

Encapsulation of CuL complex in nano-cavities of zeolite was carried out by a "ship-in-bottle" synthesis technique.[28] The ligand slowly enters into the zeolite pores due to their flexible nature and forms complex with Cu. The resulting complex is being physically trapped in the supercage as well as on the surface of the Y zeolite. Since the complex is neutral, weak forces such as van der Waals interactions or electrostatic attractions are operative here to hold the complex in the cavity of the zeolite. It seems that unreacted ligand was effectively removed from the zeolite cavities via Soxhlet extraction. A sharp color change (red-gray) of complex was observed on being immobilized in Cu-NaY, such phenomena were rarely observed when metal complexes are encapsulated in zeolites.[14,29-31] The percentages of metal contents were determined before and after encapsulation (Table 1). The chemical analyses of the sample reveal the presence of organic matter with a C/N ratio roughly similar to that for neat complex.

Table 1 Elemental analysis for the neat complex, CuL-NaY and Cu-NaY

Compound	Found (calc.)				
	C%	H%	N%	C/N	Cu%
Cu-NaY	—	—	—	—	6.7
CuL	59.13 (59.22)	3.65 (3.71)	17.45 (17.29)	3.38 (3.42)	19.4
CuL-NaY	2.37	2.31	0.78	3.04	3.8

Spectral studies

The IR spectrum of the ligand (H_2L) exhibits the sharp band at 1617 cm^{-1} due to the $\nu(C{=}N)$ (azomethine), free [CuL] showed a sharp band at lower frequency in 1597 cm^{-1} attributed to the azomethine group which indicated its coordination to copper. The IR spectra of hybrid material [CuL]-NaY showed a weak band at 1583 cm^{-1} due to their low concentration in zeolite matrix. Comparison of the spectra of Cu-NaY, [CuL]-NaY with the ligand provides evidence for the coordinating mode of ligand in catalyst. IR spectra of the hybrid material showed an intense band at *ca*. 1016 cm^{-1} attributable to the asymmetric stretching of Al-O-Si chain of zeolite. The symmetric stretching and bending frequency bands of Al-O-Si framework of zeolite appear at *ca*. 725 and 457 cm^{-1}, respectively.[32]

Electronic spectral studies of H_2L, CuL and CuL-NaY have been studied. Their spectral data are also presented in Table 2. The blue shift observed for encapsulated complex may be due to stronger ligand field after immobilization of the copper complex in the zeolite cavity.[33]

Table 2 IR and electronic spectral data of the ligand, pure and encapsulated complexes

Compound	IR ν/cm^{-1}	λ/nm, (lg ε)
H_2L	3150, 1617, 1414, 738	360 (4.6), 407 (4.2)
CuL	1597, 1399, 739	340 (4.4), 437 (3.4), 501 (sh)
CuL-NaY	1583, 1403, 1016, 725, 457	312, 355 (sh), 464 (sh)

X-ray powder diffraction studies

The X-ray powder diffraction patterns of Na-Y, Cu-NaY and encapsulated copper complex was recorded at 2θ values between 11° and 80°. The XRD patterns of representative copper exchanged zeolite and zeolite encapsulated copper complex along with Na-Y are presented in Figure 1. The diffraction patterns of encapsulated copper complex, Cu-Y and Na-Y are essentially similar except a slight change in the intensity of the band in encapsulated complex. These observations indicate that the framework of the zeolite has not structurally changed during encapsulation.

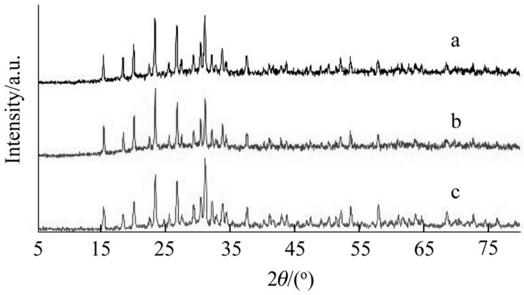


Figure 1 XRD patterns of Na-Y (a), Cu-NaY (b) and CuL-NaY (c).

Catalytic activity study

Oxidation of cyclohexene The oxidation of cyclohexene was carried out by H_2O_2 and *tert*-butylhydroperoxide (TBHP) using CuL-NaY as catalyst and two oxidation products, 2-cyclohexene-1-ol and 2-cyclohexenone along with minor amounts of other products were obtained.

In order to obtain suitable reaction conditions to achieve the maximum oxidation of cyclohexene, the effect of different reaction parameters, such as the kind of oxidant, amount of oxidant and catalyst, temperature of the reaction mixture and solvent have been studied in details using CuL-NaY as a representative catalyst.

The effect of the kind of oxidant on the oxidation of cyclohexene has been studied and the results are illustrated in Figure 2. Two different oxidants (H_2O_2 and *tert*-butylhydroperoxide) were considered while keeping the other parameters fixed as cyclohexene (10 mmol), catalyst (0.05 g) in 20 mL acetonitrile and the reaction was carried out at 80 ℃. The higher conversion (87%) and selectivity (65%) for 2-cyclohexenone formation was obtained using H_2O_2.

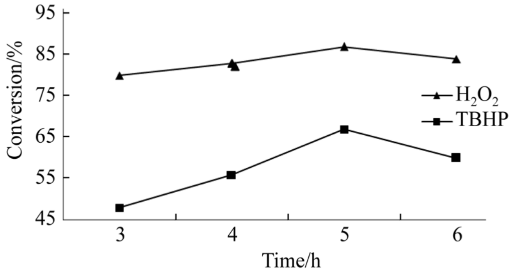


Figure 2 Effect of the kind of oxidant on the oxidation of cyclohexene.

The effect of amount of catalyst on the rate of reaction is shown in Figure 3. Four different amounts of catalyst (0.03, 0.04, 0.05 and 0.06 g) were considered and an amount of 0.05 g is sufficient to obtain almost comparable results for the fixed amount of oxidant and substrate in acetonitrile.

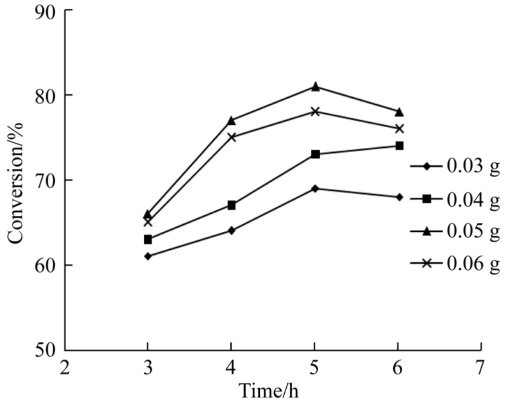


Figure 3 Effect of amount of catalyst per unit weight of cyclohexene.

In order to obtain the best reaction solvent, three different solvents *viz*. acetonitrile, ethanol and chloroform were used to see their effect on the reaction rate.

Figure 4 shows the percentage cyclohexene conversion for different solvents. Solvents have great influence on the reaction rates through competitive sorption/adsorption phenomenon in the super cages of zeolite. Polarity, hydrophilicity and size of the solvent molecule may also play some roles on the reaction rate.[34] Catalytic activity decreases in the order acetonitrile＞chloroform＞ethanol.

The influence of concentration of the oxidant, on cyclohexene conversion is given in Figure 5. The results indicate that maximum conversion was obtained at 1∶2.5 molar ratio of cyclohexene to hydrogen peroxide.

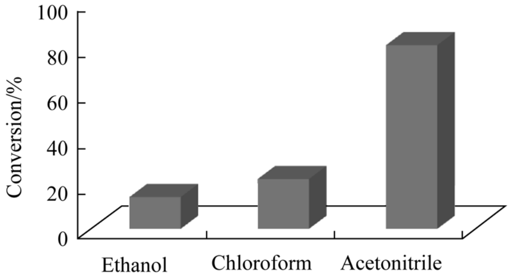


Figure 4 Effect of solvent on the oxidation of cyclohexene.

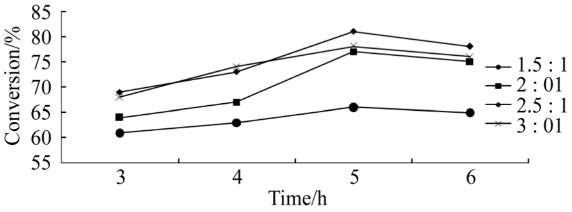


Figure 5 Effect of H_2O_2 concentration (H_2O_2∶cyclohexene) on cyclohexene oxidation.

Comparing between copper Schiff base complex encapsulated in Y-zeolite and CuL catalyst shows that the neat complex gave lower conversion of cyclohexene than their corresponding CuL-NaY (Figure 6). Homogeneous catalyst is more prone to deactivation because of two factors, the formation of Cu-O-Cu species, and the oxidative degradation of metal complex. Encapsulation of the catalyst in the walls of the nanopores of the zeolite can improve the stability of the catalyst via steric effects and also can tune the selectivity of the reaction. Selectivity of the reaction for 2-cyclohexenone formation was enhanced for CuL-NaY (Figure 7).

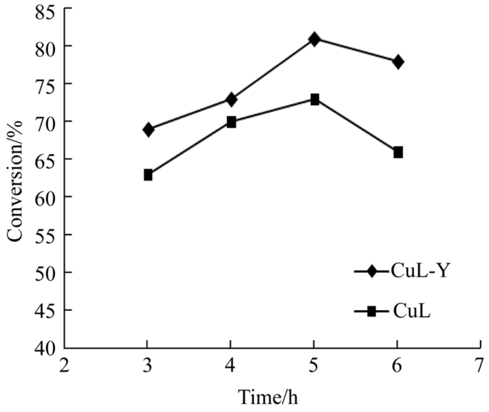


Figure 6 Effect of encapsulation of CuL in Y-zeolite on the oxidation of cyclohexene.

Oxidation of cyclooctene The oxidation of cyclooctene was carried out by H_2O_2 and *tert*-butylhydroperoxide (TBHP) (Figure 8) using CuL-NaY as catalyst and the major oxidation product was cyclooctene oxide with minor amount of alcohol product (Figure 9). Two different oxidants (H_2O_2 and TBHP) were used for oxidation of cyclooctene and the higher conversion and selectivity for epoxide formation was

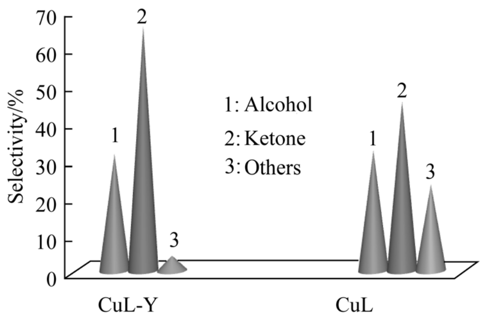


Figure7 Oxidation products distribution in acetonitrile with CuL-NaY.

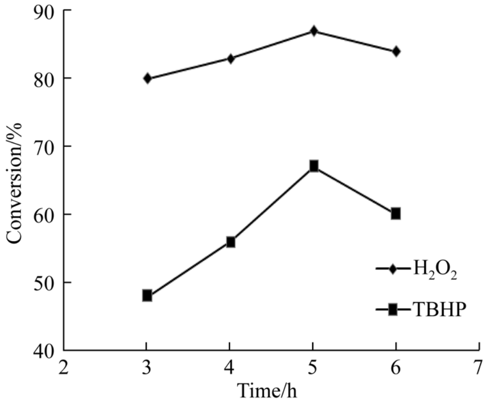


Figure 8 Effect of the kind of oxidant on the oxidation of cyclooctene.

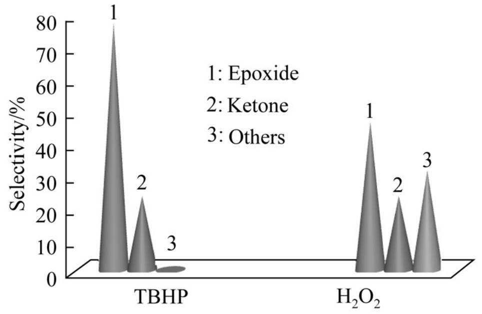


Figure 9 Oxidation products distribution in oxidation of cyclooctene in the presence of CuL-NaY.

Table 3 Comparison of the activity of Cu(II) complexes in the oxidation of cyclohexene

Olefin	Cu(II) complex	Conversion/%	Ref.	Oxidant
Cyclohexene	[Cu(sal-dach)]-Y	18.1	35	H_2O_2
Cyclohexene	PS-[Cu(ligand)$_n$]	51.0	38	H_2O_2
Cyclohexene	[Cu($H_4C_6N_6S_2$)]–NaY	40.1	33	H_2O_2
Cyclohexene	[Cu(sal-1,3-phen)]-NaY	41.4	2	TBHP
Cyclohexene	[Cu(Me$_2$salpnMe^2)]-Al_2O_3	60.1	37	TBHP
Cyclohexene	[Cu(salpnMe$_2$)]-Al_2O_3	56.9	38	TBHP
Cyclohexene	CuL-NaY	81.0	This study	H_2O_2

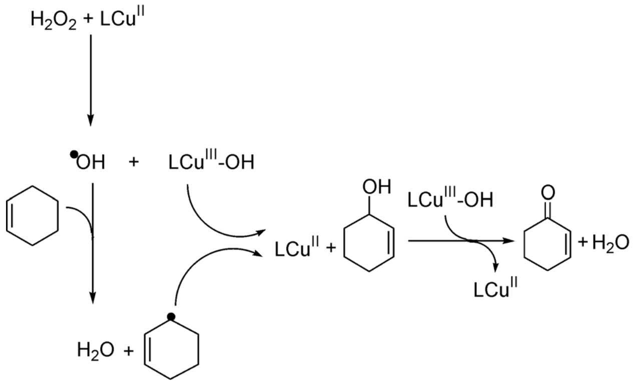
achieved with hydrogen peroxide (Figure 8).

The results of the oxidation of cyclohexene, in the presence of various Cu(II) complexes (encapsulated in Zeolite-Y or supported on alumina or polymer-anchored catalyst) with H_2O_2 or TBHP are summarized in Table 3. The conversion of cyclohexene oxidation by the CuL-NaY-H_2O_2 system is better and mostly comparable with the results of the oxidation by other catalytic systems.

Proposed mechanism

In the proposed reaction mechanism, hydrogen peroxide will be activated by coordination to CuL-NaY and generate hydroxyl radical and LCu^{III}-OH. The formed hydroxyl radical reacts with cyclohexene to yield cyclohexenyl radical that reacts with LCu^{III}-OH to yield 2-cyclohexene-1-ol. Then 2-cyclohexene-1-ol reacts with another LCu^{III}-OH to yield 2-cyclohexenone (Scheme 2).

Scheme 2



Conclusions

CuL complex has been encapsulated in the super cages of Y-zeolite by flexible ligand method and its encapsulation has been ensured by different studies. This complex has potential catalytic activity for the oxidation of cyclohexene and cyclooctene with hydrogen peroxide as oxygen source. Reaction conditions have been optimized considering different parameters to get maximum conversion. Under the optimized reaction conditions, CuL-NaY gave 81% conversion of cyclohexene with two major oxidation products, 2-cyclohexene-1-ol and 2-cyclohexenone. Also, 87% conversion was obtained using CuL-NaY as catalyst with cyclooctene oxide as major product. The catalytic activity of neat complex using similar molar concentration as that used for encapsulated complex under above reaction conditions has also been tested for comparison. It has been observed that the corresponding neat complex has shown lower catalytic activity than encapsulated one.

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