Annals of the University of Craiova
The Chemistry Series
Volume XLIX, No. 2 (2023) 23-26
homepage: chimie.ucv.ro/annals/
10.52846/AUCCHEM.2023.2.05

New oxidation catalysts based on copper complexes with salicylidene-amino acids Schiff bases onto SBA-15 support

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Received: 14.08.2023 / Accepted: 16.08.2023 / Published: 20.12.2023

Abstract:
New mononuclear Cu(II) complexes with Schiff base derived from salicylaldehyde condensed with alanine (Ala), phenylalanine (Fen), glycine (Gli) and histidine (His) amino acids were synthesized and covalently anchored onto an amino-functionalized SBA-15 mesoporous silica in order to obtain efficient heterogeneous catalysts. The elemental, structural, textural and morphological characterization confirmed the structure of the synthesized complexes and their successful immobilization into the inner pore surface of the NH_2-functionalized support without the loss of the mesoporous structure. The catalytic activity of the free or immobilized Cu(II) complexes was tested in oxidation of styrene with H_2O_2 under mild conditions with very good results.

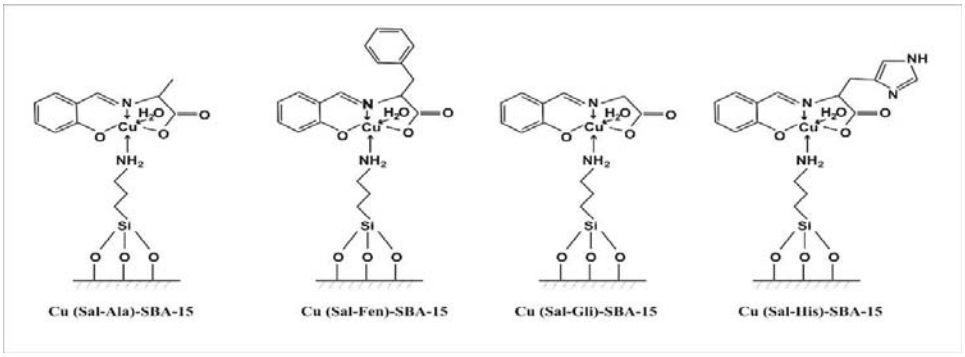
Keywords: SBA-15, Schiff bases, amino acids, Cu(II) complexes, styrene oxidation

1. INTRODUCTION

The development of sustainable methods for the catalytic oxidation of alkene and alkane substrate is of great interest in synthetic organic chemistry and chemical industry for the conversion of petroleum-based feed stocks to the more valuable chemicals such as diols, epoxides, alcohols, and carbonyl compounds.

The oxidation was carried out using a number of techniques, including the use of complexes of transition metals, with green oxidants: molecular oxygen and peroxides [1-5].

We report here the synthesis of SBA-15 mesoporous silica support to immobilize four copper complexes with Schiff base derived from salycilaldehyde condensed with alanine (Ala), phenylalanine (Fen), glycine (Gli) and histidine (His) amino acids (Scheme 1) through an organic linker, 3-(aminopropyl) triethoxysilane. This catalytic system was evaluated in styrene oxidation with H_2O_2 as the oxidant under mild conditions.



Scheme 1. Structure of Cu(II) complexes with Schiff base ligands

2. MATERIALS AND METHODS

The Schiff base ligands were firstly synthesized from salicylaldehyde and the corresponding amino acid in a methanolic basic solution followed thereafter by the complexation with Cu(II). Since the copper center in the homogeneous complexes was five-coordinate, the immobilization of the homogeneous complexes onto SBA-15 was readily achieved by the copper coordination to the amino nitrogen of NH_2-SBA-15 by simple addition [4].

Heterogeneous catalysts were characterized by XRD analysis, N_2 adsorption-desorption, SEM microscopy, IR and UV-Vis spectroscopy, TGA-DTA and elemental analysis.

3. RESULTS AND DISCUSSION

We present evidence that the properties of the Cu(II) based complexes and the specific properties of the SBA-15 mesoporous support both beneficially contributed to establish the efficiency of alkene catalytic oxidation.

Table 1. Textural and structural properties

Sample	a_0 (nm)[a]	Specific surface m^2/g	Mesopore volume (mL/g)	Pore diameter[b] (nm)	V_{BdB}[c] (nm)	Wall thickness (nm)
SBA-15	11,3	600	1,1	7,8	10	3,5
Cu(Sal-Ala)-SBA-15	10,7	213	0,3	6,1	6,8	4,6
Cu(Sal-Fen)-SBA-15	10,1	477	0,8	5,9	8,0	4,2
Cu(Sal-Gli)-SBA-15	10,7	566	1,0	6,2	8,1	4,5
Cu(Sal-His)-SBA-15	10,7	525	1,0	6,6	8,6	4,1

[a]Hexagonale: $a_0 = 2d_{100}/\sqrt{3}$; [b]$D \cong 4V/A$; [c]Mesopore volume by BdB method; [d]$E = a_0 - D$.

Table 2 Styrene oxidation

Catalyst	Conversion (%)	H_2O_2 eff.(%)	Selectivity (%)			
			I	II	III	IV
Cu(Sal-Ala)-SBA-15	66	26	69	11	4	16
Cu(Sal-Fen)-SBA-15	71	28	76	16	4	4
Cu(Sal-Gli)-SBA-15	71	28	72	12	5	11
Cu(Sal-His)-SBA-15	64	26	74	15	6	5

Reaction conditions: T = 80 °C, H_2O_2/Sty = 4:1 (mol/mol), solvent – acetonitrile (10 mL), t = 300 min.
Products: benzaldehyde (I), 1-phenyletanone (II), styrene oxide (III) and benzoic acid (IV)

4. CONCLUSION

Four immobilized amino acid Schiff base complexes were prepared and showed promising catalytic performance towards the allylic oxidation of styrene with 30% H_2O_2. The introduction of mesoporous SBA-15 resulted in the immobilized complexes giving far better catalytic performance than their homogeneous analogues. We believe that more efficient immobilized catalysts for olefin oxidation can be prepared by modifying their structures and compositions, which will result in more applications

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