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COPPER SUPPORTED ON FUNCTIONALISED MCM41 CONTAINING THIOUREA LIGAND AS AN CATALYST IN OXIDATION OF CYCLOHEXENE WITH HYDROGEN PEROXIDE

(Sokongan Kuprum kepada MCM41 Terfungsi yang Mengandungi Ligan Tiourea Sebagai Pemangkin Terhadap Tindak Balas Pengoksidaan Sikloheksena dengan Hidrogen Peroksida)

Amirah Ahmad[1*], Hamizah Md. Rasid[1] and Karimah Kassim[2]

[1]*Faculty of Applied Sciences,*
[2]*Institute of Science,*
Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia

**Corresponding author: my_silberberg@yahoo.com*

Abstract

MCM41 encapsulated with thiourea ligand and copper(II) acetate as catalyst for oxidation reaction is reported. First, MCM41 was modified using 3-aminopropyltriethoxysilane (APTES) and then was encapsulated with thiouracil and copper(II) acetate. The catalyst was characterized using X-Ray Diffraction (XRD), N_2 adsorption, single point BET, Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM) and Elemental Analyzer. The characterization results indicated that the catalyst has an ordered hexagonal structure, a narrow pore size distribution, uniform mesopores and a high surface area. Moreover, the results also revealed that thiourea ligand and copper acetate might be encapsulated onto the pores of MCM41. Catalytic activity of the catalyst was tested in the oxidation of cyclohexene using acetonitrile as solvent and hydrogen peroxide as oxidant. The CuO_2(acac)-Thio-APS-MCM41 was proven to be a good catalyst for oxidation reaction of cyclohexene with conversion up to 96.1% after 24 h reaction and providing a high selectivity to 2-cyclohexene-1-one.

Keywords: MCM41, Thiourea Ligand, Mesoporous Material, Thiouracil

Abstrak

MCM41 yang mengandungi ligan tiourea dan kuprum(II) asetat sebagai pemangkin bagi tindak balas pengoksidaan dilaporkan. Pertama, MCM41 telah diubahsuai menggunakan 3-aminopropiltrietoksisilana (APTES) dan kemudian telah ditambah dengan tiouracil dan kuprum(II) asetat. Pemangkin dicirikan dengan menggunakan kaedah pembelauan Sinar X (XRD), penjerapan N_2, penjerapan titik tunggal BET, Spektroskopi Inframerah Transformasi Fourier (FTIR), mikroskopi electron pengimbasan pancaran medan (FESEM) dan analisis unsur. Keputusan pencirian menunjukkan bahawa pemangkin mempunya struktur heksagon, taburan liang yang kecil, liang meso yang seragam dan luas permukaan yang tinggi. Selain itu, keputusan juga mendedahkan bahawa ligan tiourea dan kuprum asetat mungkin terletak pada liang-liang MCM41. Aktiviti sebagai pemangkin telah diuji dalam tindak balas pengoksidaan sikloheksana menggunakan asetonitril sebagai pelarut dan hydrogen peroksida sebagai oksida. CuO_2(acac)-Thio-APS-MCM41 terbukti manjadi pemangkin yang bagus untuk tindak balas pengoksidaan sikloheksena dengan penukaran sehingga 96.1% selepas 24 jam tindak balas dan memilih tinggi terhadap 2-sikloheksen-1-on.

Kata kunci: MCM41, Ligan Tiourea, Bahan Meso, Tiouracil

Introduction

Oxidation process is a very important in the field of catalysis due to it significant in industrial [1, 2]. One of the focus is commercial cyclohexene oxidation to produce cylohexenol and cyclohexenone which mainly used in pharmaceuticals and fragrances [3]. However, most of the oxidation processes is low in energy efficiency and generates plenty of by-products and waste. Recently, a great demand for these products causes many researchers to find more effective catalytic processes to promote high conversion of reactant and product selectivity [4, 5]. Many of these processes utilized metal complex and porous solids as a catalyst in many reaction such as transition metal

(Cr, Mn, V, Mo, Ti, Co, etc.) doped MCM41 [6,7]. Eko Adi Prasetyanto and Sang-Eon Park, 2008, was studied catalytic oxidation of cyclohexene with hydrogen peroxide over Cu(II)-Cyclam-SBA-16 catalyst and was found that the Cu(II)-Cyclam-SBA-16 was proven to be a good catalyst for oxidation reaction of cyclohexene with conversion up to 77.8% after 13 h reaction and providing a high selectivity to cyclohexenol and 3-hydroperoxycyclohexen-1-ene [8]. Among the various solid supports, the mesoporous silica materials, MCM41 has attracted greater attention from material researchers because of the ordered pore arrangements, very narrow pore diameter, uniform mesopores and high surface area. However, pure MCM41 showed very limited catalytic activity due to the hydrophilic properties and limited application. Hence, it requires modification to introduce other features into mesoporous silicates to improve their physical properties (e.g. their hydrophobicity and adsorption characteristics) and catalytic activity such as modification of surface MCM-41 with organic functionalized groups [9], introducing metal ions to increase the active sites and by grafting a suitable ligand to become as donor ligand for transition metal ions [10]. In this research, we reported the 2-thiouracil is encapsulated onto functionalized-MCM41 as potential donor ligand for transition metal to form supported metal thiourea complex and as an efficient catalyst for oxidation of cyclohexene (Fig.1).

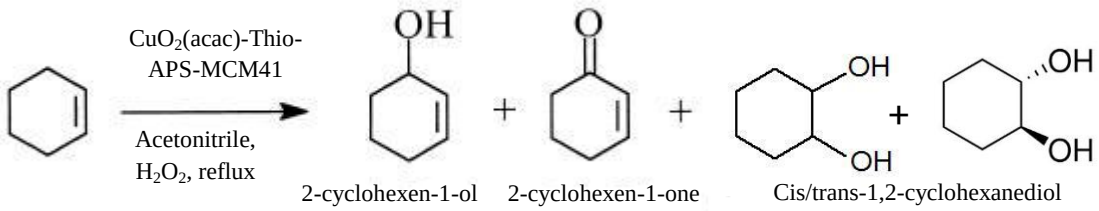


Fig. 1: Oxidation of cyclohexene

Experimental

Physical measurement

X-Ray diffraction (XRD) patterns of the samples were obtained by using Rigaku D/max-2500 powder diffractometer with Cu-Kα source (λ = 1.5418 Å, 40 kV, 40 mA). The particle size and morphology of the samples were characterized using a Zeiss Supra 35VP Field emission scanning electron microscopy (SEM). The carbon analysis of the samples was acquired by using Flash 1100 Organic Elemental Analyzer Thermo Finnigan. The FT-IR spectra were obtained on a Perkin-Elmer Spectrum One FTIR spectrometer. N_2 adsorption isotherm and BET surface area were measured at 77K on a Micromeritics ASAP 2010 Volumetric Adsorption Analyzer.

Materials

All meterials were commercial reagent grade and obtained from Merck and Sigma-Aldrich. The starting materials were used in this research were Ludox, sodium hydroxide, cetyltrimethylammonium bromide, ammonium hydroxide, 3-aminopropyltriethoxysilane, n-Hexane, thiouracil, copper acetate monohydrate, cyclohexene, acetonitrile and hydrogen peroxide.

Synthesis of purely siliceous MCM41

The MCM41 was prepared as following molar composition below:

$$6\ SiO_2 : CTABr : 1.5\ NaOH : 0.15\ (NH_4)_2O : 250\ H_2O$$

Ludox and sodium hydroxide were added in distilled water. The mixture was stirred for 2 hours as Part A. In another polypropylene bottle, cetyltrimethylammonium bromide and ammonium hydroxide were dissolved in distilled water. The mixture was heated and stirred for 1 hour as Part B. The sodium silicate solution (Part A) was added into template solution (Part B). The resulting mixture was aged overnight in an oven at 97 °C. After cooling at ambient temperature, the pH adjustment (pH = 10) of mixture was done. The precipitate was filtered, washed, dried in oven and calcined at 550°C.

Synthesis of aminopropylated MCM41

MCM41 was added to a solution of 3-aminopropyltriethoxysilane in n-Hexane and refluxed for 6 hours. The mixture was filtered, washed and dried at room temperature.

Synthesis of thiourea ligand grafted APS-MCM41

The thiourea complex grafted APS-MCM41 was prepared as following: APS-MCM41 was added to a solution of thiouracil in n-Hexane and refluxed for 24 hours. The mixture was filtered, washed and dried under vacuum overnight.

Synthesis of CuO_2(acac)-Thio-APS-MCM41

Thio-APS-MCM41 was added into a solution of $CuO_2(acac)_2$ in n-Hexane and refluxed for 24 hours. The mixture was separated by filtration, washed and dried under vacuum.

Procedure for oxidation of cyclohexene with hydrogen peroxide (H_2O_2) catalyzed by CuO_2(acac)-Thio-APS-MCM41

In 3 mL of acetonitrile, 0.5 mmol of cyclohexene, 1 mmol of H_2O_2 and 0.01 g of catalyst were added in 25 ml round bottom flask equipped with magnetic stirrer. The mixture was heated at 70 °C under stirring. The reaction progress was monitored by GC. The reaction was repeated for blank experiment in the presence of oxidant and using the same experimental conditions in the absence of catalyst.

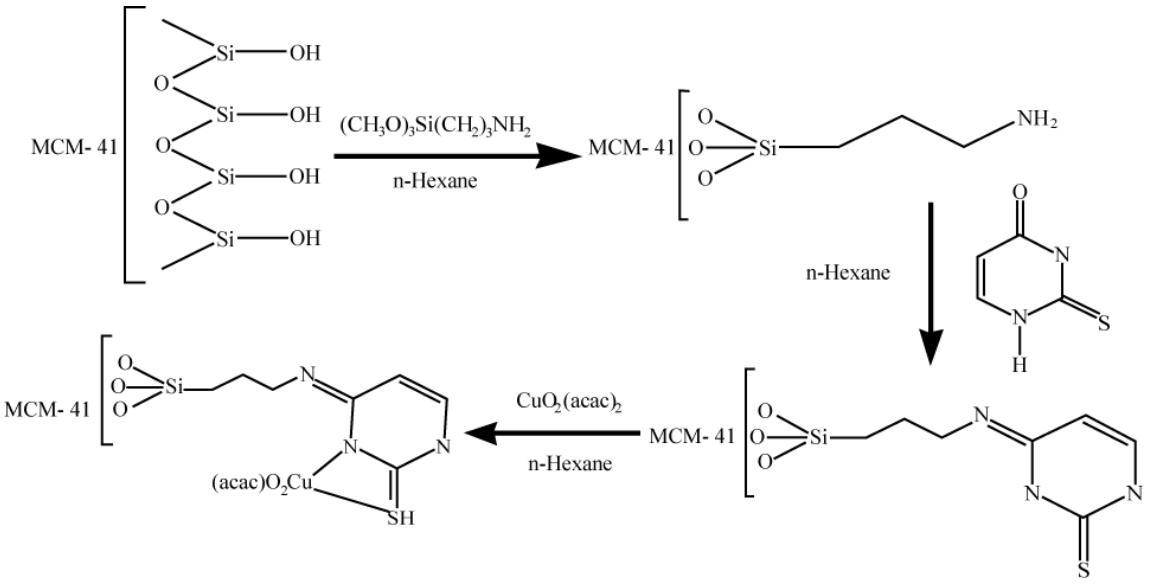


Fig. 2: Proposed structure of synthesised material

Results and Discussion

XRD Patterns

The XRD patterns of the synthesized material are shown in Figure 3A and 3B. The low angle XRD patterns show three resolved peaks that can be indexed to the (100), (110) and (200) reflections indicating the characteristics of hexagonal ordered MCM41 structure [11]. These peaks are obviously observed for the MCM41 sample (Fig. 3A (a)). High intensity of the main peak (100) shows high degree of long-range order and existence of uniform pores in the synthesized material. In the XRD pattern of CuO_2(acac)-Thio-APS-MCM41 shows the lower intensity of the (100) for the supported catalyst is attributed to filling the pore of the MCM41 due to functionalisation and

incorporation of thiourea ligand and metal. However, the mesopores structures still retain a good mesostructural order even the decreased of the long range order of the mesoporous sample. The lattice parameters, which were calculated using the d_{100} were 45.5 Å (d_{100} = 39.41 Å, 2θ = 2.24 °) and 43.9 Å (d_{100} = 38.05 Å, 2θ = 2.32) for MCM41 and CuO_2(acac)-Thio-APS-MCM41, respectively. The lattice parameter for CuO_2(acac)-Thio-APS-MCM41 decreases because of the addition of organic group, thiourea and metal results in an contraction of the hexagonal unit cell and decrease in the size of pore channels. Moreover, the addition of amino, thiourea and metal into the gel mixture will lead to some structural rearrangement. However, XRD results show that the mesopores structures still remained intact as hexagonal structure. Moreover, high angle XRD patterns shows the peak in between 2θ = 20° - 100° after addition of thiouracil and metal (Fig. 3B). The peaks at 2θ = 35.28 ° and 38.6 °, corresponding to monoclinic CuO (Fig. 3B (b)) [12].

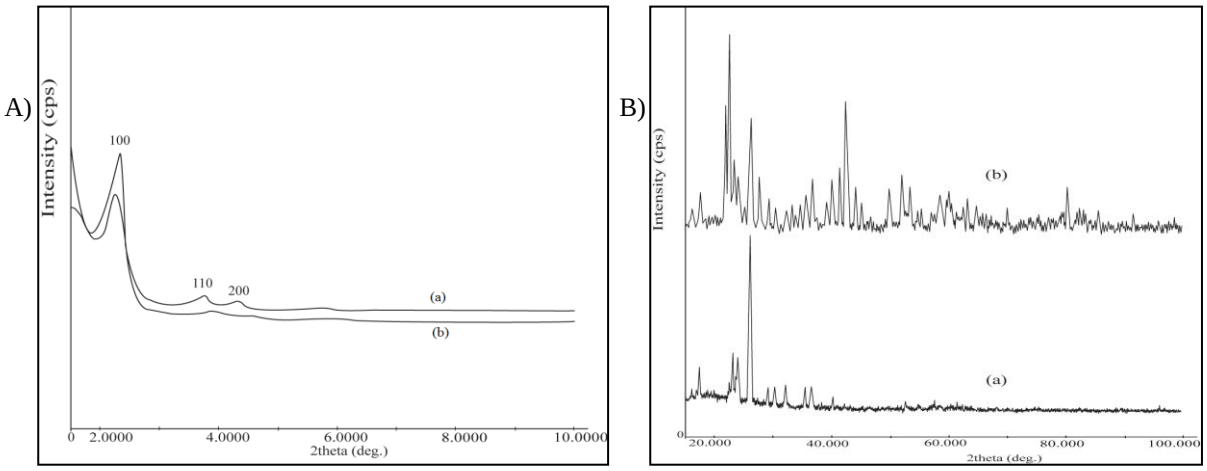


Fig. 3: (A) Low angle XRD patterns: (a) MCM41, (b) CuO_2(acac)-Thio-APS-MCM41. (B) High angle XRD patterns: (a) Thio-APS-MCM41 and (b) CuO_2(acac)-Thio-APS-MCM41.

Nitrogen adsorption

Nitrogen sorption isotherm and corresponding pore size distribution of the synthesized material is given in Figure 4. The isotherms (Fig. 3A) were of type IV which shows a typical mesoporous solid, according to IUPAC classification [13]. The MCM41 samples exhibited strong adsorption at a relative pressure in the range of $0.2 \leq P/P_0 \leq 0.5$. As the relative pressure increases ($P/P_{0>}$ 0.4), the isotherm shows inflection, where the P/P_0 position of the sharpness of the isotherm in range $0.4 \leq P/P_0 \geq 0.5$ corresponds to uniformity of mesopore size [14]. However, nitrogen uptake decreases for CuO_2(acac)-Thio-APS-MCM41 sample due to the presence of bulky materials inside the pores [15]. The narrow pore size distribution as seen from Fig. 3B revealed a uniform mesoporosity. The pore distribution become broader indicated the ordering of samples decreased as the content of heteroatoms increased.

Single Point BET

Table 1 displays the results of the synthesised material from the single-point BET analysis. Results show clearly that the BET surface area of MCM41 is 982.56 m^2/g. It has been reported that mesoporous silica materials have surface area above 600 m^2/g [16]. From the data, it can be seen that the BET surface area of APS-MCM41, Thio-APS-MCM41 and CuO_2(acac)-Thio-APS-MCM41 reduces remarkably compared to MCM41, corresponding to the various groups that were successfully grafted. The decrease in surface area suggests that mesoporous framework has turned amorphous. Once a mesoporous framework collapsed from its crystalline structure to amorphous phase, the surface area decreased significantly. Meanwhile, the pore volume of synthesized materials is significantly decreased due to the existence of high amorphous phase in Thio-APS-MCM41and CuO_2(acac)-Thio-APS-MCM41 sample that blocked the pore structure of sample to give lower pore volume.

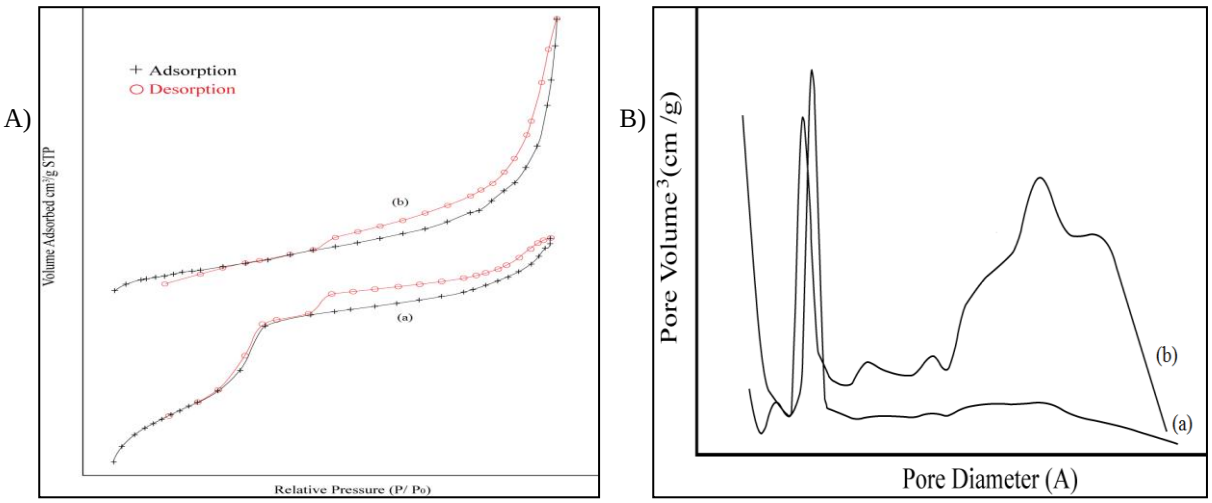


Fig. 4: (A) Nitrogen adsorption-desorption isotherms: (a) MCM41, (b) CuO_2(acac)-Thio-APS-MCM41and (B) Pore size distributions: (a) MCM41, (b) CuO_2(acac)-Thio-APS-MCM41

Table 1: Surface properties of synthesized materials.

Samples	BET surface area (m^2/g)	Average pore diameter (Å)	Average pore volume (cm^3/g)
MCM41	982.56	35.99	0.88
APS-MCM41	286.91	30.79	0.22
Thio-APS-MCM41	14.44	99.35	0.04
CuO_2(acac)-Thio-APS-MCM41	10.01	95.26	0.02

FT-IR Spectra

The FT-IR spectra of synthesized material in the region of 4000 - 400 cm^{-1} in transmission mode using pressesed KBr pellets, and shown in Fig. 5. The uncalcined MCM41 and calcined MCM41 spectra (Fig. 5A. a, b) show intense band at wavenumber 1100 and 802 cm^{-1} which accounts for the asymmetric and symmetric stretching of the Si-O-Si bonds, respectively [17]. The bands at 970 cm^{-1} and 460 cm^{-1} was assigned to the stretching and bending vibrations of surface Si-O- groups respectively [18]. For calcined MCM41, the bands at 2852 cm^{-1} and 2921 cm^{-1} corresponding to the long chain of alkyl group of the surfactant molecules were disappeared after calcination due to removal of surfactants (Fig. 5A. b). Fig. 5A.(c) show the spectra of MCM41 after being modified with APTES with $-NH_2$ symmetric bending at 1553cm^{-1} and C-N bond at 1639 cm^{-1}. Moreover, the band at 2944 cm^{-1} corresponding to asymmetric vibration of the CH_2 groups of the propyl chain of the sylilating agent at, indicates the successful grafting of organic amine onto the surface. Figure 3B shows the spectra for thiouracil (a), Thio-APS-MCM41 (b) and CuO_2(acac)-Thio-APS-MCM41 (c). The most of the bands of thiouracil was appeared after encapsulated APS-MCM41 with thiouracil while the band of Si-O-Si also retain even after incorporation of complex. It shows that thiouracil was successfully grafted onto functionalised-MCM41. The bands at 628 cm^{-1} and 691 cm^{-1} represents the Cu = O vibrations [19], indicates that the CuO_2(acac)-Thio-APS-MCM41 was successfully synthesised.

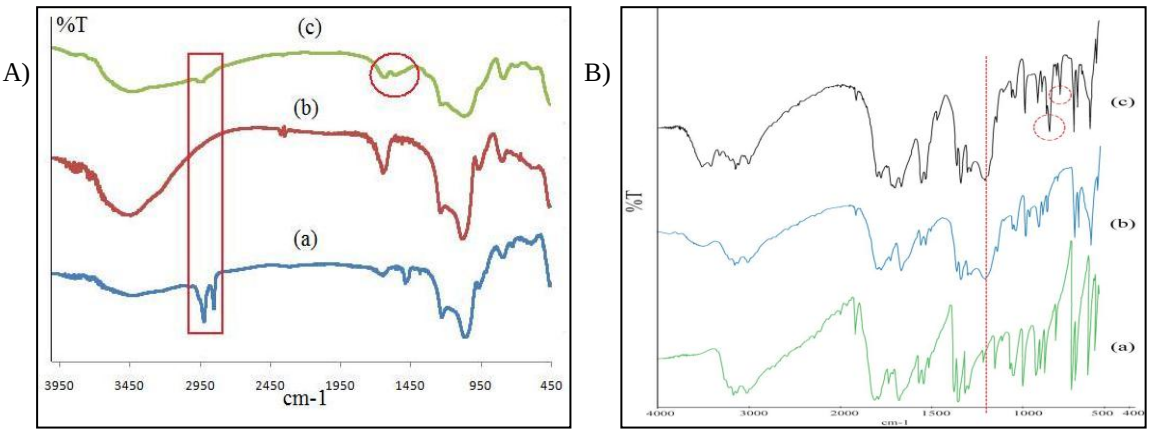


Fig. 5: (A) FT-IR spectra: (a) Uncalcined MCM41, (b) MCM41 and (c) APS-MCM41. (B) Spectra for: (a) thiouracil, (b) Thio-APS-MCM41 and (c) CuO_2(acac)-Thio-APS-MCM41.

Field Emission Scanning Electron Microscopy (FESEM)

Figure 6a and 6b display the FESEM micrograph of pure MCM41 and CuO_2(acac)-Thio-APS-MCM41, respectively. The FESEM micrograph reveals that the particle morphology of both samples consists of agglomerated particles of 1 to 3 µm in diameter. The FESEM micrograph explained the CuO_2(acac)-Thio-APS-MCM41 possess the some morphology and that the solid support were structurally unchanged upon immobilization.

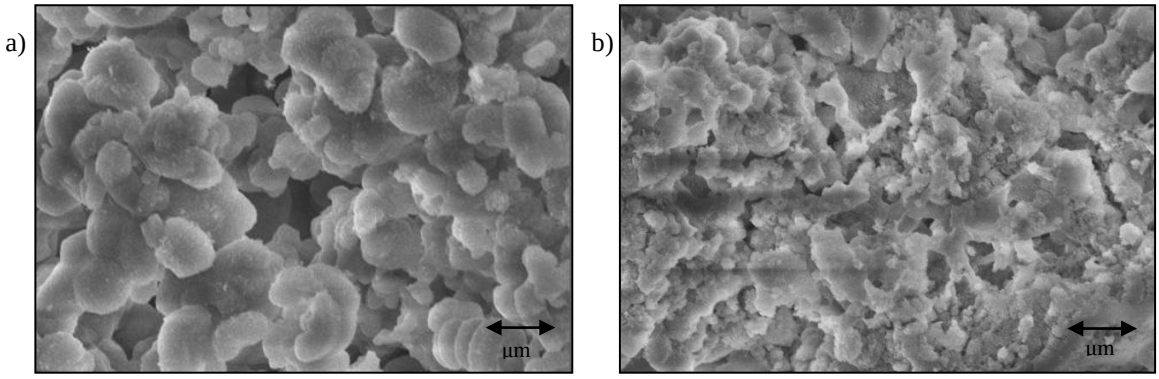


Fig. 6: Morphology of (a) MCM41 and (b) CuO_2-Thio-APS-MCM41.

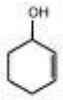
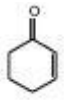
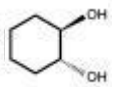
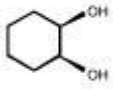
Elemental Analyzer

According to elemental analysis results, the carbon contents for the Thio-APS-MCM41 and CuO2(acac) – Thio-APS-MCM41 are determined to be 23.9 and 24.4 wt.%. respectively. Considering the theoretic carbon contents of Thio-APS-MCM41 and CuO2(acac) – Thio-APS-MCM41 are 25.6 and 23.9 wt.%, indicates the composition of prepared samples close with their molecular formula.

Catalytic Performance

The catalytic activity of CuO_2(acac) – Thio-APS-MCM41 was investigated for oxidation of cyclohexene with hydrogen peroxide as the oxidant. The selectivity and activity results of CuO_2(acac) – Thio-APS-MCM41 catalyst on the oxidation of cyclohexene with hydrogen peroxide have been given in Table 2. As shown in the Table 2, the conversion of cyclohexene reached 50 % with 66.1% selectivity to the 2-cyclohexen-1-one after 3 h of reaction time and the other products were found to be 2-cyclohexen-1-ol, trans-1,2-cyclohexanediol and cis-1,2-cyclohexanediol.

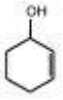
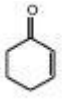
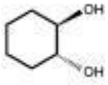
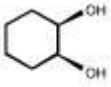
Table 2: The oxidation of cyclohexene with hydrogen peroxide.

Solvent	Oxidant	Time (h)	Conversion (%)	Product selectivity (%)			
							
Acetonitrile	H_2O_2	3	50	22.4	66.1	6.6	4.9

Effect of Reaction Time

The effect of reaction time on cyclohexene conversion and product distributions at reaction temperature of 343 K is shown in Table 3. It can be seen the cyclohexene conversion steadily increased with increasing reaction time and at time 26 h, the conversion of cyclohexene in 100%.

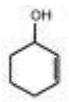
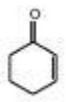
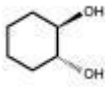
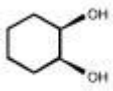
Table 3: The effect of reaction time on oxidation of cyclohexane

Reaction	Time (h)	Conversion (%)	Product Selectivity (%)			
						
1	2	52.8	16.3	73.2	6.2	4.3
2	4	64.5	18.3	69.7	6.8	5.2
3	8	80.8	15.4	72.7	6.6	5.4
4	12	92.6	11.1	76.0	5.2	7.7
5	24	96.1	7.4	80.8	5.3	6.5
6	26	100	3.3	86.0	4.7	6.0

Effect of Catalyst

The effect of catalyst was investigated by comparing the conversion and product selectivity of reaction with and without catalyst (Table 4). The results indicated that the reaction with catalyst yield more major product than without catalyst. It shows that the catalyst was increased the rate of reaction by yield more conversion and product without itself being consumed.

Table 4: The effect of catalyst on oxidation of cyclohexane

Reaction	Oxidant	Time (h)	Conversion (%)	Product Selectivity (%)			
							
With catalyst	H_2O_2	6	73.7	17.4	70.6	6.6	5.4
Without catalyst	H_2O_2	6	70.5	33.7	56.6	-	-

Conclusion

It can be concluded that $CuO_2(acac)_2$ supported on functionalised-MCM41 containing thiourea ligand was successfully synthesised and showed a high catalytic activity in the oxidation of cyclohexene with hydrogen peroxide. The reaction was found gave high selectivity to 2-cyclohexen-1-one with conversion 96.1% after 24 h reaction.

Acknowledgement

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