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RESEARCH ARTICLE

SELECTIVE OXIDATION OF CYCLOHEXENE BY MESOPOROUS MCM-41 AND SBA-15 CATALYST DERIVED FROM COAL BOTTOM ASH

Hamizah Md Rasid[1,2,*], Nurul Barakah Ab Rahman[1], Mohammad Noor Jalil[1]

[1]School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia.

[2]Multifunctional Nanoporous Material Research Group (MULNA), Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia.

Abstract. Mesoporous silica catalysts are porous materials with a highly ordered structure and a high surface area, making them ideal for various chemical reactions, particularly in heterogeneous catalysis. Conventional methods for synthesizing mesoporous silica catalysts rely on high-purity silica sources, which are expensive and environmentally damaging. This study addresses the challenge of synthesizing efficient and selective catalysts from waste-derived silica, specifically coal bottom ash, which contains a significant amount of silica. Mesoporous silica materials such as Mobil Composition of Matter No. 41 (MCM-41) and Santa Barbara Amorphous-15 (SBA-15) were produced from silica sourced from waste coal bottom ash and functionalized with 3-aminopropyltriethoxysilane (APTES) to improve hydrophobicity and catalytic efficiency. The catalytic efficiency of functionalized MCM-41 and SBA-15 was evaluated in the liquid-phase oxidation of cyclohexene under controlled experimental conditions. At the 6-hour mark, the highest cyclohexene conversion percentages were achieved with functionalized MCM-41 and SBA-15, reaching 84.05% and 62.49%, respectively. 2-cyclohexen-1-one was identified as the primary product, while 2-cyclohexen-1-ol was the minor product. The functionalized MCM-41 and SBA-15 showed 51.13% and 62.90% selectivity towards 2-cyclohexen-1-one, respectively. This study demonstrated the enhanced hydrophobicity of amine-modified mesoporous materials due to the attachment of the amine group on the silica surface, making them effective and reliable catalysts in the cyclohexene oxidation reaction.

Keywords: Mesoporous silica catalysts, coal bottom ash, MCM-41, SBA-15, cyclohexene oxidation.

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***Corresponding author: hamizah7708@uitm.edu.my**

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1. INTRODUCTION

Rapid economic growth and industrial development, coupled with a rising human population in Malaysia, have significantly increased the demand for electricity. Malaysia burns millions of tons of coal to meet this demand, generating substantial coal waste, including fly ash and bottom ash [1]. The disposal of coal bottom ash (CBA), a by-product of coal-fired power plants, has become a severe environmental concern due to its increasing accumulation. According to Alhokabi and Ing [2], coal ash production reached approximately 8.5 million tons, comprised of 6.8 million tons of fly ash and 1.7 million tons of bottom ash, highlighting the substantial volume of by-products generated from coal combustion. With ongoing urbanization, the production of these wastes is expected to escalate, potentially leading to severe environmental and health issues, such as air pollution, respiratory diseases, and groundwater contamination, if not appropriately managed [3-4].

Recycling and reutilizing waste materials, like CBA, offer a sustainable and eco-friendly approach to mitigating environmental impacts [5]. For instance, CBA has shown considerable potential as an effective adsorbent for various pollutants in wastewater treatment. Studies have shown that CBA can efficiently remove pollutants, including heavy metals like lead and cadmium, with removal efficiencies reaching up to 98.41% in some cases [6-7]. Additionally, CBA has been used to adsorb phosphorus with a removal efficiency exceeding 95%, indicating effective chemical adsorption [8]. Furthermore, CBA has proven effective in adsorbing dyes, showcasing its versatility in treating various wastewater pollutants [9].

Another promising avenue is using CBA to synthesize valuable porous silica materials like Mobil Composition of Matter No. 41 (MCM-41) and Santa Barbara Amorphous-15 (SBA-15). With a high surface area (up to 1000 m^2/g), narrow pore size distributions, and significant pore volumes, these materials are ideal as catalyst supports for various chemical processes [10]. The stable frameworks and highly ordered nanopores of MCM-41 and SBA-15 enable the diffusion of reactants and products, providing extensive contact areas for catalytic reactions while maintaining structural integrity under reaction conditions [11-12]. However, the naturally hydrophilic nature of mesoporous silica, attributed to the abundance of silanol groups, necessitates surface modification to optimize their catalytic efficiency [13].

Enhancing the hydrophobicity of MCM-41 and SBA-15 through functionalization can significantly improve their interactions with non-polar substrates and reduce moisture interference. This hydrophobicity increase is achieved by modifying the surface with various organosilanes, such as 3-aminopropyltriethoxysilane (APTES) [14], 3-aminopropyltrimethoxysilane (APTMS) [15], octyltriethoxysilane (OTES) [16], hexadecyltrimethoxysilane (HDTMS) [17], and 3-mercaptopropyltrimethoxysilane (MPTMS) [18]. These agents replace polar hydroxyl groups with non-polar alkyl groups, reducing surface energy and increasing hydrophobicity.

This study addresses the need for effective catalysts by utilizing silica derived from the CBA obtained from a power plant to synthesize modified MCM-41 and SBA-15 catalysts. The silica was extracted using an alkali-based treatment method, and the resulting mesoporous materials were functionalized to increase hydrophobicity, thus improving their catalytic properties. By employing CBA, this research not only promotes sustainable waste management but also aligns with green chemistry principles. The effectiveness of these modified catalysts was evaluated in the oxidation reaction of cyclohexene using *tert*-butylhydroperoxide (TBHP) as the oxidant. This innovative approach not only demonstrates improved catalytic activity but also highlights the potential of recycling industrial waste into valuable resources for chemical processes.

2. MATERIALS AND METHODS

The methods employed in this study were divided into two main stages: the synthesis of functionalized mesoporous silica with APTES and the evaluation of its catalytic efficiency in the oxidation of cyclohexene with TBHP.

2.1 Materials

CBA was sourced at the Tanjung Bin Energy Power Plant in Johor, Malaysia. The chemicals utilized include sodium hydroxide (NaOH, Labscan), ammonium hydroxide (NH_4OH, 28-30% ammonia basis, Sigma), hydrochloric acid (HCl, 36%, Aldrich), 3-aminopropyltriethoxysilane (APTES, $H_2N\ (CH_2)_3Si(OC_2H_5)_3$, ≥ 98%, Sigma), and n-hexane (C_6H_4, ≥ 99%, Labscan). Commercial surfactants Pluronic P123 ($EO_{20}PO_{70}EO_{20}$;M_{av}=5800, Aldrich) and cetyltrimethylammonium bromide (CTABr, $C_{19}H_{42}NBr$, ≥99%, Sigma) were used as templates for synthesizing SBA-15 and MCM-41, respectively

2.2 Synthesis of Functionalized Mesoporous Silica

The alkali-based treatment method was employed to obtain silica from CBA. Firstly, the granular CBA was pulverized to a fine powder using mortar and pestle. NaOH powder was combined with the finely ground ash in a 1.2:1 weight ratio and heated at 550 ºC for one hour. After fusion, the material was allowed to cool to room temperature and reduced to a fine powder. This powder was combined with distilled water in a 1:4 ratio and agitated for 24 hours. The mixture was subsequently subjected to centrifugation and filtration, and the supernatant obtained was utilized for synthesizing mesoporous silica.

MCM-41 was synthesized using the molar composition: $6SiO_2$: CTABr: 1.5NaOH: $0.15(NH_4)OH$: $250H_2O$, as described by Ahmad et al. [19]. SBA-15 was synthesized using the amphiphilic triblock polymer Pluronic P123. In the first step, P123 was dissolved in deionised water and 2 M HCl and agitated for 20 hours. The supernatant from the CBA was then gradually introduced while stirring vigorously. The blend was kept under fixed conditions for 24 hours. The resulting cloudy mixture was heated at 90 ˚C for another 24 hours. The solid obtained was subjected to filtration, rinsing, and drying for 72 hours, followed by calcination in air at 500 ˚C for 6 hours.

Functionalization of the amine groups on both MCM-41 and SBA-15 was achieved using APTES, following the method described by Ahmad et al. [19]. The elemental composition of the raw CBA and extracted silica was analyzed using energy-dispersive X-ray spectroscopy (EDX). The morphology of the mesoporous silica materials was analyzed using field emission scanning electron microscopy (FESEM).

2.3 Catalytic Efficiency of Functionalized Mesoporous Silica

The catalytic efficiency of the prepared mesoporous silica materials was assessed in the oxidation reaction of cyclohexene using TBHP as the oxidant. The reaction converted cyclohexene into 2-cyclohexen-1-one and 2-cyclohexen-1-ol. Activated catalysts were added to a cyclohexene solution and stirred under a nitrogen atmosphere in a round-bottom flask with a condenser at room temperature. Liquid samples were withdrawn at 1, 3, 4, and 6 hours, and the reaction mixture was refluxed at 70 ºC for 6 hours.

Reactant conversion and product selectivity were measured using gas chromatography-mass spectrometry (GC-MS) and gas chromatography with flame ionization detection (GC-FID). The GC analysis used a Hewlett-Packard 6890N model with a temperature program starting at 80 °C for 1 minute, increasing to 270 °C at 10 °C/minute, and holding at 270 °C for 2 minutes.

3. RESULTS AND DISCUSSION

The results and discussion were divided into four main stages, which are the recovery of silica from CBA, the FESEM morphological study, the conversion of cyclohexene using MCM-41 and SBA-15 catalysts, and the selectivity of 2-cyclohexen-1-one using the same catalysts.

3.1 Recovery of Silica from CBA

The chemical composition of raw CBA and the extracted silica sample was analyzed using EDX, revealing that oxygen (O), silicon (Si), carbon (C), sodium (Na), and potassium (K) were present as major components. Oxygen was found to be the most abundant element in the raw CBA sample, constituting 62.94%, followed by Si (14.37%), C (6.36%), Na (0.86%), K (0.56%), and other elements (14.91%). The additional elements detected by EDX likely originate from natural impurities associated with the mineral content of the coal used, contributing to the presence of Na, K, and trace heavy metals. The specific presence and quantities of these elements can vary based on the coal source and combustion conditions [20]. After the silica recovery process, the chemical composition of the extracted silica sample was determined to be O (61.47%), Si (3.48%), C (14.00%), Na (20.19%), K (0.46%), and other elements (0.41%). Figures 1(a) and (b) show the EDX graph of raw CBA and extracted silica, respectively. Meanwhile, the chemical composition of elements in raw CBA and extracted silica is summarized in Table 1.

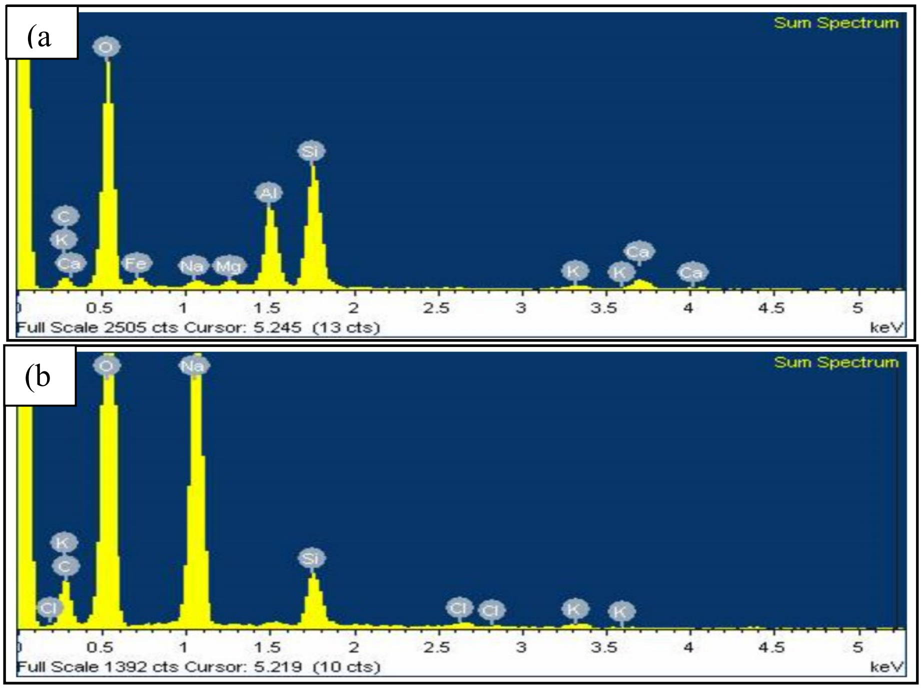

Figure 1: EDX graph of (a) raw CBA sample and (b) extracted silica sample

Table 1: Chemical composition of elements in raw CBA and extracted silica

	Chemical composition (%)					
Sample	**O**	**Si**	**C**	**Na**	**K**	**Others**
Raw CBA	62.94	14.37	6.36	0.86	0.56	14.91
Extracted silica	61.47	3.84	14.00	20.19	0.46	0.41

The percent yield of silica recovered from raw CBA was approximately 24%, calculated based on the silica content in the CBA sample and the quantity recovered in the supernatant. This yield is in close agreement with the results of Chandrasekar et al. [21], who reported a yield of approximately 28% from Korean samples. In comparison, citric acid leaching treatments have shown yields of up to 44% under specific conditions [22]. However, this study opted for NaOH alkaline treatment due to its compatibility with the synthesis objectives and overall effectiveness in silica recovery. The variation in yield across studies may also reflect differences in location, country, and the type of coal used [23]. The extracted silica was later utilized as a source for synthesizing MCM-41 and SBA-15.

3.2 FESEM Morphological Study

FESEM micrographs of raw MCM-41, calcined MCM-41, and amine-functionalized MCM 41 are presented in Figures 2(a), (b) and (c), respectively. The raw MCM-41 exhibits mixtures of amorphous spherical agglomerates of particles with sizes less than one µm. These particles appear aggregated with a rough surface texture and less-defined pores due to the presence of surfactants used during synthesis, which have not yet been removed. In contrast, the calcined MCM-41 shows similar spherical particles with smoother surfaces and well-defined pores, indicating the successful formation of the mesoporous structure. The micrograph of amine-functionalized MCM-41 reveals some changes compared to the non-functionalized samples. Introducing amine groups onto the silica surface leads to a slight aggregation of particles, creating a rougher and more compact texture. This modification can enhance the material’s interaction with various reactants, making it suitable for catalytic applications. The MCM-41 materials observed in this study agree with those reported in the literature [24].

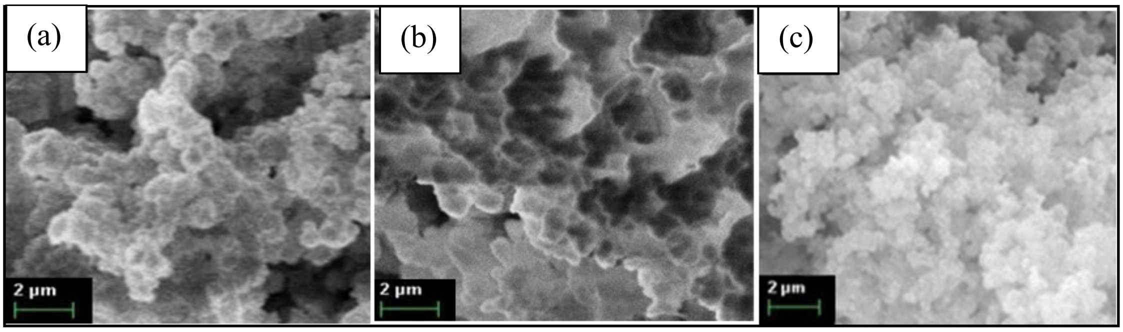

Figure 2: FESEM micrographs of (a) Raw MCM-41, (b) Calcined MCM-41 and (c) amine-functionalized MCM-41

FESEM micrographs of raw SBA-15, calcined SBA-15, and amine-functionalized SBA-15 are shown in Figures 3(a), (b) and (c), respectively. The raw SBA-15 shows agglomerates of irregularly shaped particles, indicating that the silica matrix is not fully developed yet. The surface exhibits a rough texture and an absence of mesopores. Meanwhile, the micrograph of calcined SBA-15 reveals the agglomeration of rod-like particles with a more uniform structure and well-defined mesopores. The FESEM micrograph of amine-functionalized SBA-15 shows that the morphology remains similar to that of calcined SBA-15 but with reduced particle size and a rougher surface texture due to the introduction of amine groups. The clustering observed may result from modifications in surface interactions after adding the organic functional groups, which can cause alterations in the mesopore structure, as reported in previous studies [25]. Incorporating amine functionalization is expected to enhance the catalytic efficiency of SBA-15, as it does to MCM-41.

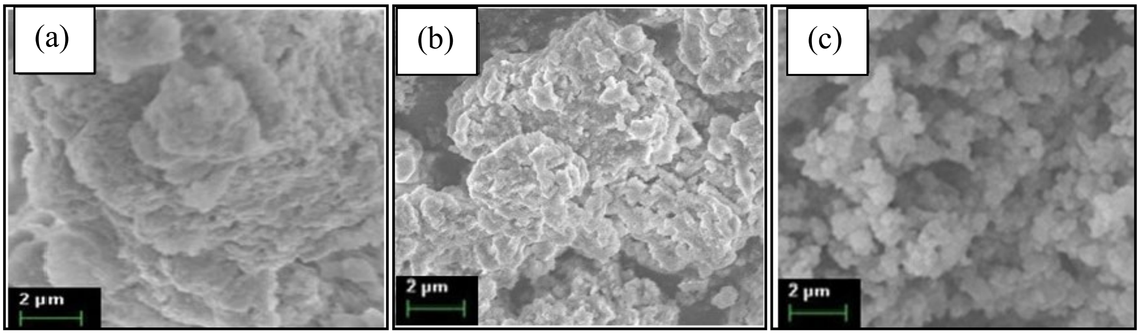

Figure 3: FESEM micrographs of (a) Raw SBA-15, (b) Calcined SBA-15 and (c) amine-functionalized SBA-15

3.3 Conversion of Cyclohexene using MCM-41 and SBA-15 Catalysts

Table 2 presents the conversion percentages of cyclohexene using different mesoporous silica catalysts over varying reaction times. The data reveals a clear trend in catalytic activity among the materials. Amine-functionalized MCM-41 exhibits the highest conversion at all time points, starting with 37.71% at 1 hour and reaching 84.05% at 6 hours. This significant enhancement in catalytic efficiency can be attributed to the amine functionalization, which increases the catalyst's hydrophobicity and surface area, promoting more significant interaction between the catalytic sites and the cyclohexene reactant. Functionalization with APTES, a silane coupling agent, enables covalent bonding to the silica surface by introducing hydrophobic alkyl groups [26-27]. This reduces the number of polar hydroxyl groups on the surface, enhancing the hydrophobic character of the catalyst and its affinity for non-polar substrates like cyclohexene while making it less attractive to water molecules. Together, these modifications optimize the catalyst's efficiency, as observed in the improved conversion rates.

In comparison, the non-functionalized MCM-41 and SBA-15 show lower conversion percentages, with MCM-41 reaching only 34.16% and SBA-15 achieving 45.61% after 6 hours of reaction. However, the amine-functionalized SBA-15 catalyst demonstrated improved efficiency than its non-functionalized counterpart, with a conversion percentage of 62.49% at 6 hours. This closely aligns with the findings of Rath et al. [28], who suggest that surface area increases and the hydrophilicity/hydrophobicity index is reduced with greater amine functionalization, leading to significantly higher catalytic activity towards cyclohexene in modified samples than unmodified ones. Overall, these results suggest that amine functionalization effectively enhances the catalytic activity of both MCM-41 and SBA-15, although the extent of improvement varies between the two mesoporous silica types.

Table 2: Cyclohexene conversion (%) using MCM-41 and SBA-15 catalysts

Reaction time (hours)	MCM-41	Amine-functionalized MCM-41	SBA-15	Amine-functionalized SBA-15
1	10.16	37.71	16.51	19.00
3	18.15	62.91	29.51	31.86
4	25.74	79.04	34.28	53.84
6	34.16	84.05	45.61	62.49

3.4 Selectivity of 2-cyclohexen-1-one using MCM-41and SBA-15 Catalysts

Table 3 provides data on the selectivity of the prepared catalysts towards 2-cyclohexen-1-one, a desired product in the oxidation reaction of cyclohexene. The selectivity percentages indicate how efficiently the catalysts favor the formation of 2-cyclohexen-1-one over other possible oxidation products. At the 1-hour mark, amine-functionalized MCM-41 exhibits a high selectivity of 87.06%, while amine-functionalized SBA-15 simultaneously achieves complete selectivity (100%). As the reaction progresses, the selectivity of amine-functionalized MCM-41 and amine-functionalized SBA-15 decreases slightly, but they still maintain higher selectivity than their non-functionalized counterparts. By the 6-hour mark, amine-functionalized MCM-41 and amine-functionalized SBA-15 exhibit selectivity percentages of 51.13% and 62.90%, respectively. These results suggest that the oxidation reaction using amine-functionalized SBA-15 is more selective towards 2-cyclohexen-1-one than amine-functionalized MCM-41, likely due to its structural advantages. The FESEM micrographs show that amine-functionalized SBA-15 features a larger pore diameter than amine-functionalized MCM-41. These structural characteristics allow for better accommodation of larger substrates and intermediates during oxidation, facilitating more selective reactions. The larger pores in SBA-15 promote a more favorable environment for forming specific products like 2-cyclohexen-1-one. In comparison, MCM-41's smaller pores may lead to a broader range of products due to steric hindrance and diffusion limitations [29].

In contrast, the non-functionalized MCM-41 starts with a selectivity of 63.64% at one hour, decreasing to 47.87% at 6 hours. This reduction in selectivity may be due to prolonged reaction times leading to side reactions that produce undesired products, thereby reducing the selectivity towards 2-cyclohexen-1-one [30]. Non-functionalized SBA-15 shows low selectivity over time, peaking at 52.80% at 6 hours. The lower selectivity observed for non-functionalized catalysts may be due to the absence of amine functional groups, which could stabilize the formation of 2-cyclohexene-1-one.

Table 3: 2-cyclohexen-1-one selectivity (%) using MCM-41 and SBA-15 catalysts

Reaction time (hours)	**MCM-41**	**Amine-functionalized MCM-41**	**SBA-15**	**Amine-functionalized SBA-15**
1	63.64	87.06	37.78	100.00
3	60.83	65.02	36.18	80.58
4	52.13	51.89	38.20	75.84
6	47.87	51.13	52.80	62.90

4. CONCLUSIONS

The functionalization of mesoporous silica materials with amine groups significantly enhances the conversion of cyclohexene and the selectivity towards 2-cyclohexen-1-one. Amine-functionalized MCM-41 emerges as the most efficient catalyst, providing the highest conversion and selectivity over the reaction duration. Amine-functionalized SBA-15, while also effective, shows slightly lower performance than amine-functionalized MCM-41. These results highlight the importance of surface modification in optimizing the catalytic properties of mesoporous silica materials for selective oxidation reactions. Furthermore, the findings suggest that mesoporous silica derived from waste CBA, when functionalized appropriately, has the potential to perform comparably to materials produced from high-purity silica sources. This opens promising avenues utilizing waste-derived silica as a sustainable and cost-effective alternative in catalytic applications, contributing to advancing green chemistry and resource recycling efforts.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work is compliant with ethical standards

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