

Silver supported on mesoporous silica combination with H₂O₂: active, recyclable, and selective oxidation component for conversion of olefins to 1, 2-diols

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ABSTRACT

The selective oxidation of olefins is a key academic and industrial research challenge. Herein, silver was supported on mesoporous silica through a facile synthesis procedure, and characterized using various technics such as FT-IR, XRD, SEM, BET, and EDX. This efficient separable agent alongside aqueous H₂O₂ was applied to the oxidation of various olefins (1-octen, 1-hexene, cyclohexene, cyclooctene, styrene, and 1, 2-diphenylmethane) to 1, 2-diol under mild reaction conditions (65 °C) with high conversion and excellent selectivity. The promoter exhibited excellent reusability and stability in the reaction medium.

Keywords: mesoporous silica; silver; selective oxidation; 1, 2-diol.

1. Introduction

One of the most important intermediates in organic chemistry is 1, 2-diols. They are applied for the pinacol rearrangement or the synthesis of α -hydroxy ketones and dioxanes [1-3]. These precursors are also used commercially for the production of a range of materials including photographic materials and lubricants [2].

Various synthesis strategies for the preparation of 1, 2-diols materials are available such as pinacol coupling reaction [4], direct alkene oxidation [5, 6], and epoxides opening [7]. In this regard, the most common method is the dihydroxylation of olefins with hydrogen peroxide using a metal catalyst [8-10]. The major disadvantages of existing approaches are low selectivity which leads to the formation of a mixture of various products containing epoxides, alcohols, ketones, and ethers. Therefore, the development of new catalytic systems that are not only efficient and steady but also possess high selectivity and reusability is very desirable.

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Hydrogen peroxide is known as one of the best oxidant candidates due to its low-cost, and efficiency [11-13]. However, the main challenge in its application is the activation of aqueous hydrogen peroxide; so, numerous efforts have been performed to find inexpensive, efficient, and environmentally friendly reaction conditions using a novel catalytic system [14,15].

Over the past decade, there has been an increased focus on the hydrogen peroxide oxidation reactions that utilize platinum group catalysts. The high cost and toxicity of these metals have stimulated the search for alternative, affordable transition metal catalysts [16-23]. However, most of these approaches applied homogeneous catalysts, harsh reaction conditions, or essentially chlorohydrocarbons or other organic solvents which make them less promising methods.

In this respect, silver has exhibited several remarkable characteristics; it is an antimicrobial active and green compound, besides its relatively low cost in comparison with platinum group metals [24-30]. Available reports on applications of Ag in various organic reactions such as the oxidation of benzyl alcohols, methanol, and carbon monoxide indicated their excellent catalytic performance [31-33]. However, they suffer from some

disadvantages such as their high tendency for aggregation, low stability, and recycling problems which can lead to debilitation of their catalytic activities and advantage [34, 35].

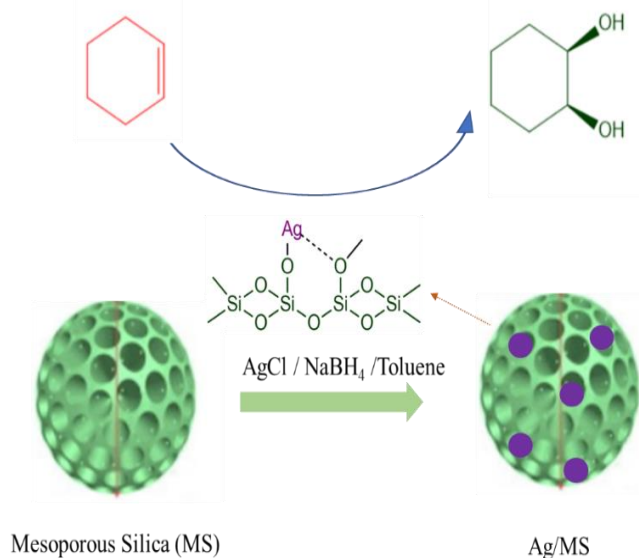
To overcome these problems, various solid supports were used to immobilize the metal nanoparticles including charcoal, inorganic silica, alumina, and synthetic polystyrene [35-39]. Available support materials have good features and some advantages; however, complex preparation process and high cost, have limited their applications. Therefore, developing suitable silica support with an easily accessible high surface area could be respected.

In this report, we introduced the facile preparation of a mesoporous silica-based Ag heterogeneous catalyst. The presented catalyst exhibited high catalytic efficiency in the oxidation of alkene to 1, 2-diol through an efficient method (**Scheme 1**). Moreover, this catalyst showed suitable reusability.

2. Experimental

Materials

In this laboratory project, all the start materials and solvents were purchased from chemical suppliers Toluene, acetonitrile, acetone, acetonitrile, ethanol, 1, 2-dichloroethane, DMF, 1-hexene, 1-octene, cyclohexene, cyclooctene, styrene, 1, 2-diphenylmethane, hydrogen peroxide 30% and 50%, NaBH₄, mesoporous silica, silver chloride, and manganese (II) oxide were purchased from Merck and Aldrich in the highest purity available and used without further purification.



Scheme 1. Synthesis procedure for the preparation of the catalyst and model reaction

Preparation of catalyst

Mesoporous silica (MS) was synthesized according to the reported method in the literature [40]. AgCl (40 mg) was added to the MS (0.2 g) in 100 mL water; after that, 80 mL of the solution of NaBH₄ (1.32 mmol, 50 mg) in toluene was added to the mixture dropwise and reacted for 2 h, at room temperature. The Ag supported on mesoporous, silica was separated from the reaction mixture, washed with ethanol several times, and dried under vacuum at 70 °C.

General procedure for the oxidation of 1-olefin to alkyl-1, 2-diol

In a round-bottom flask, a mixture of olefin (2.0 mmol) and acetonitrile was added to 10.0 mg of catalyst (Ag/MS) and H₂O₂ (30%, 4.0 mmol) as an aqueous oxidant. The above-mentioned solution was reacted at 65°C and under the air atmosphere for 24 h. The catalyst was separated by filtration and washed with ethanol; to extinguish remained hydrogen peroxide, MnO₂ (ca. 20 mg) was added. Then, the solution was diluted with ethanol and analyzed by GC.

3. Results and Discussion

The FT-IR spectroscopy was utilized to analyze the surface modification of the catalyst (**Fig. 1**). In the FT-IR spectrum of the MS and Ag/MS, the characteristic bands peaking at 1624 cm⁻¹, and 1065 cm⁻¹ are assigned to the Si-O. In comparing the spectrum of the MS with those of Ag/MS, the appearance of the new peaks at 1624 cm⁻¹, 2342 cm⁻¹, and 1384 cm⁻¹ and shifting the peak from 1065 cm⁻¹ to 1014 cm⁻¹ verified MS modification [41-43].

The construction approach for Ag/MS catalyst is represented in **Scheme 1**. In this strategy, the Ag was supported on the surface of MS through a facile method by using sodium borohydride. The surface morphology of the catalyst was investigated by scanning electron microscopy (SEM). The SEM images depicted the morphology of the catalyst. The catalyst prepared from mesoporous silica/Ag clearly shows a homogenous morphology and confirms that was incorporated into the structure **Fig. 2**.

The energy dispersive spectroscopic (EDX) analysis was given in **Fig. 3**. The EDX analysis indicated the chemical composition of the catalyst, as can be seen in this figure the composition comprises is comprise of C, O, Si, and Ag.

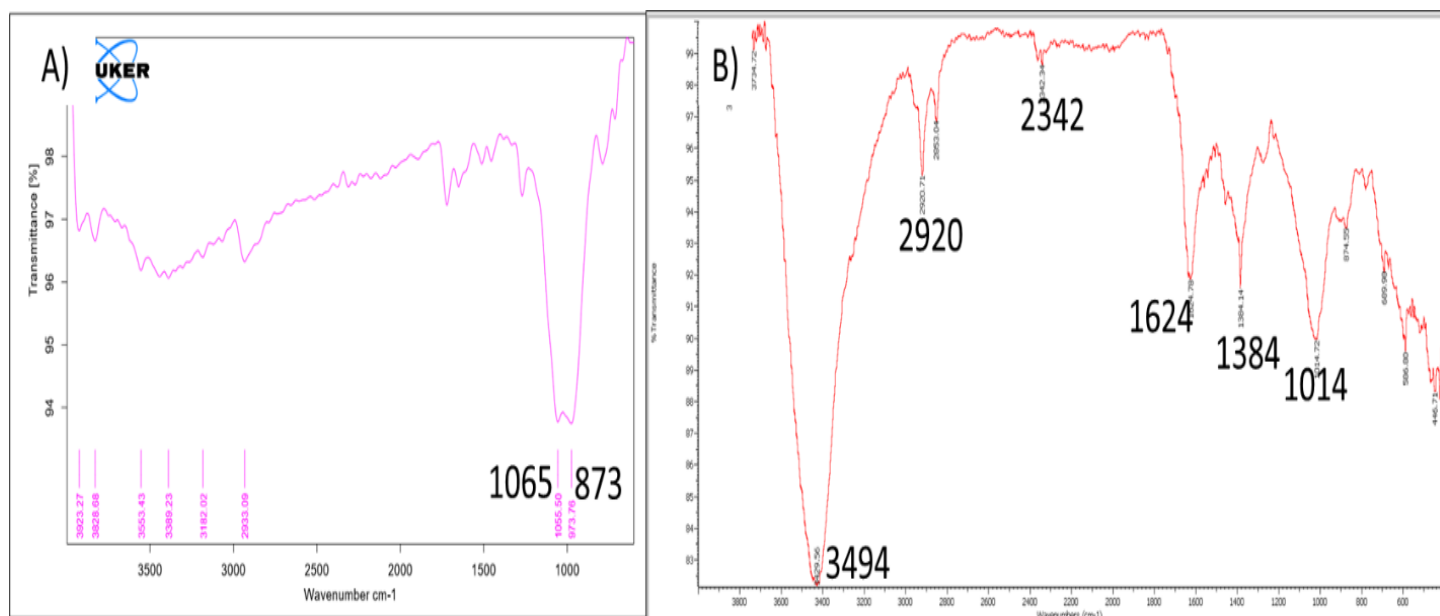


Fig. 1. The FT-IR spectra of A) MS and B) Ag/MS

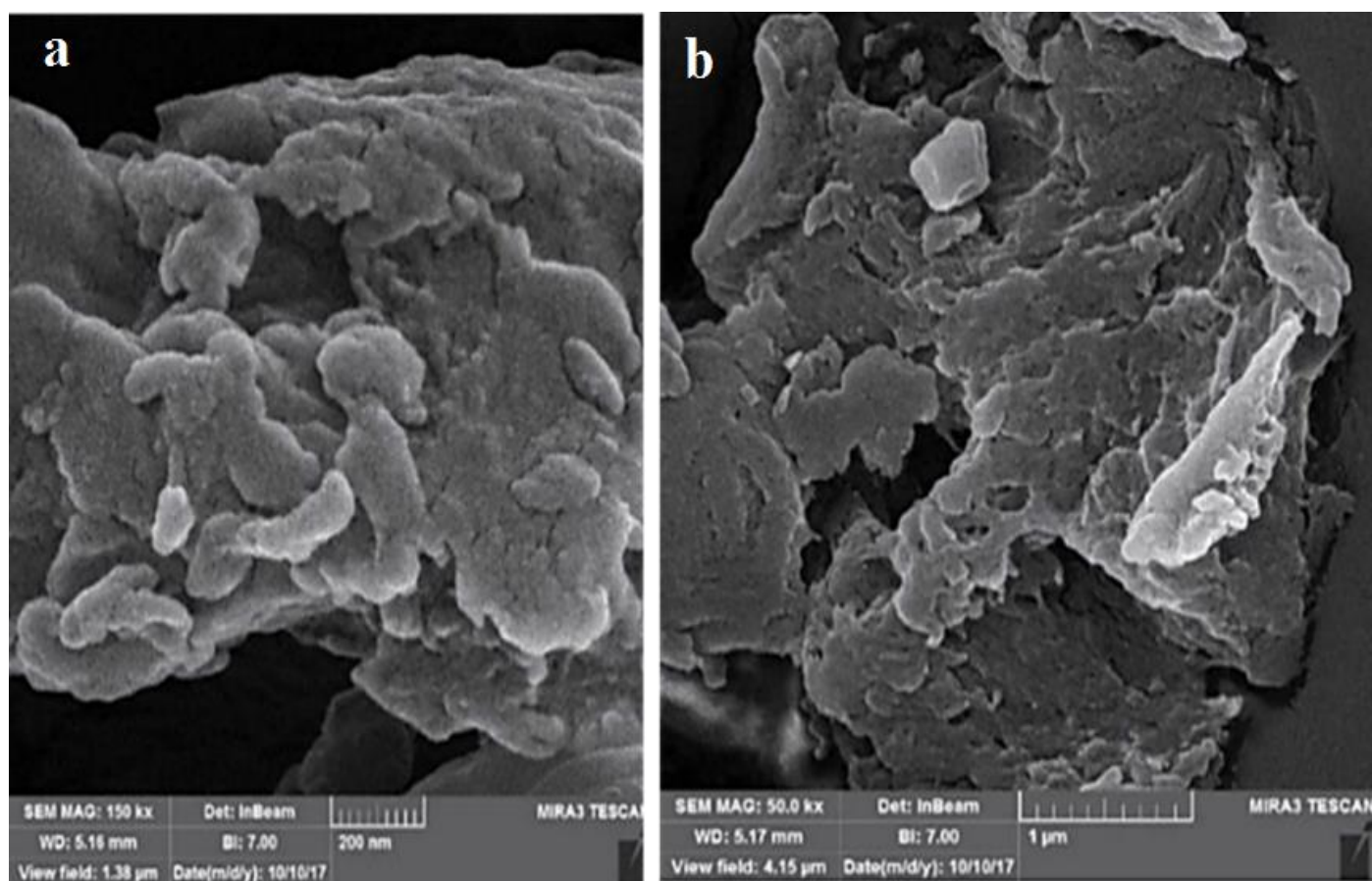


Fig. 2. SEM images of the catalyst a) 200 nm, b) 1 μm

The powder X-ray diffraction patterns of MS and Ag/MS are shown in Fig. 4. As can be seen, the broad peak in both spectra assigned amorphous silica. The X-ray diffraction patterns (B) of Ag/MS indicated its face-

centered cubic structure through $2\theta = 23.5, 28.3, 32.6,$ and 39.6 . This also confirmed the successfully tagged of Ag on the surface of MS [44].

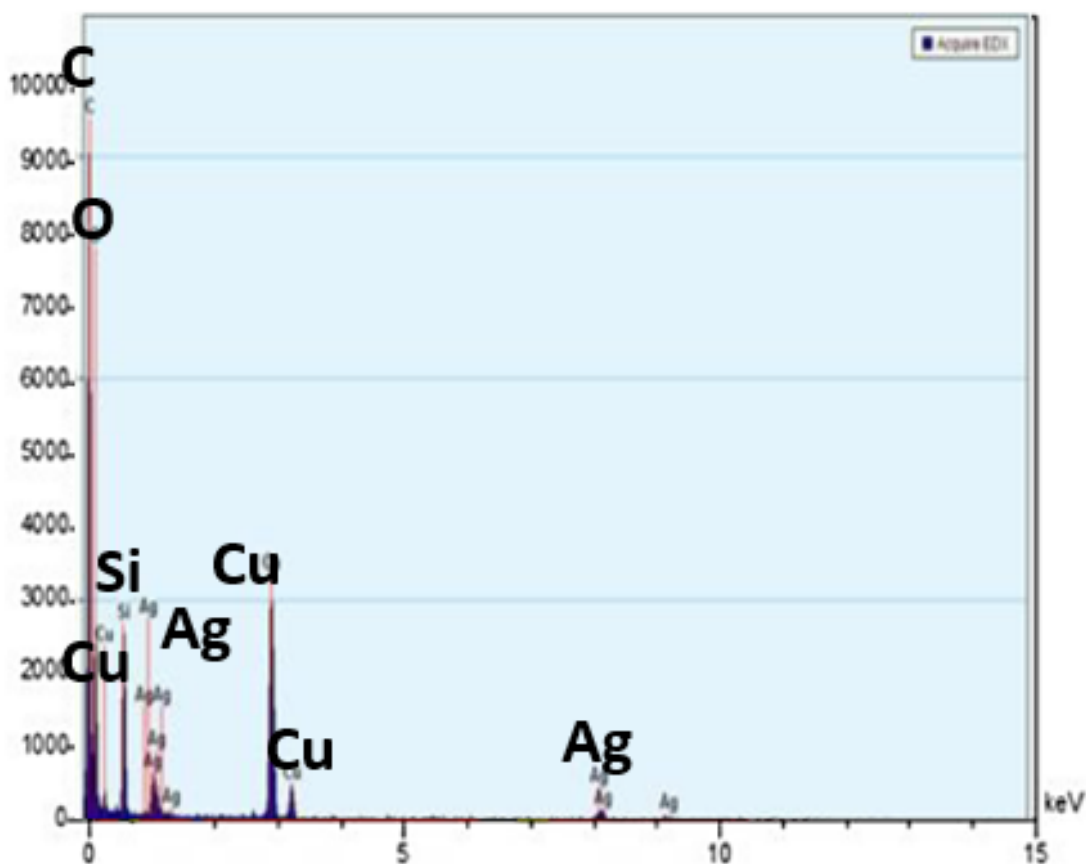


Fig. 3: EDX of Ag/MS

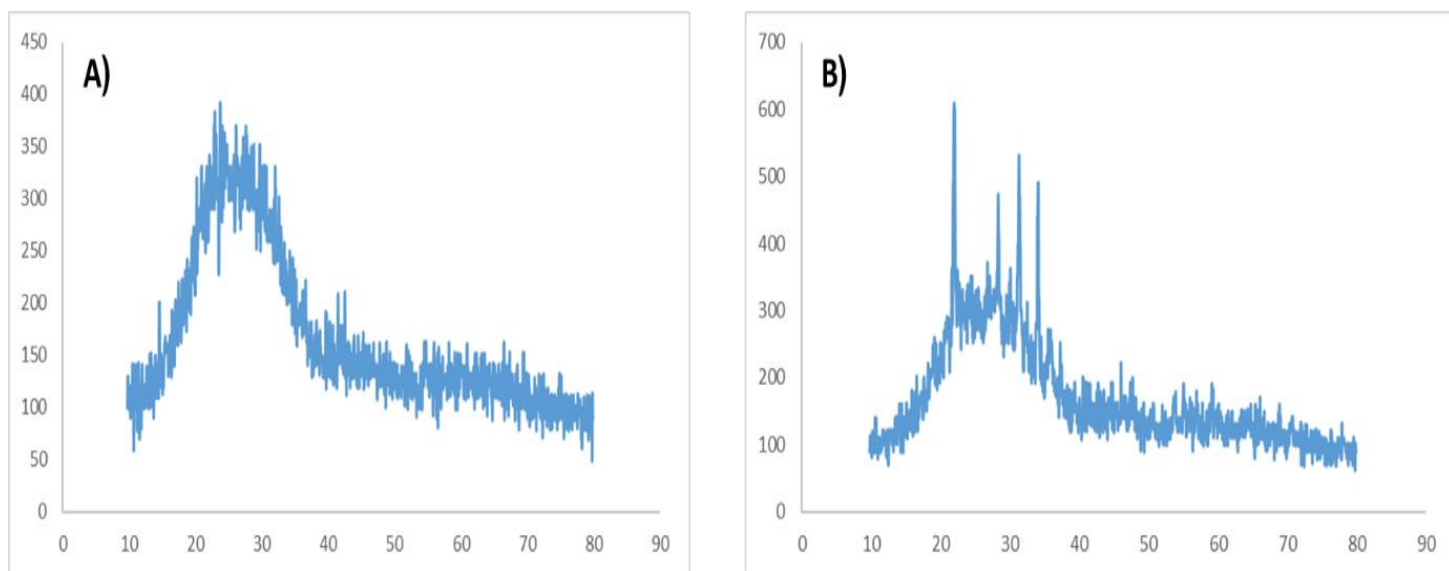


Fig. 4. The XRD pattern of catalyst A) MS B) Ag/MS

The nitrogen adsorption method (BET analysis) was applied to the characterization of the porous materials and pore structure (Fig. 5). The isotherm expressed a big jump in high pressure in the graph that shows that the

material is microporous. Also, it has a small hysteresis loop that shows it contains mesoporous materials as well. The average total pore volume is 0.2 cm³/g, and the average surface area is calculated as 31.2 m²/g.

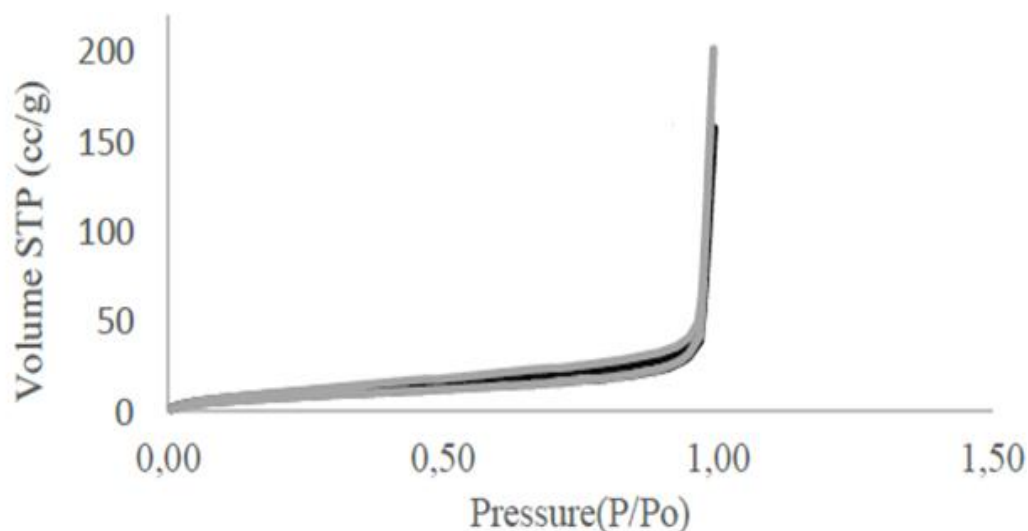


Fig. 5. Nitrogen adsorption and desorption isotherms (at 77K) for the catalyst

The activity of the synthesized catalyst has been investigated in the reaction of 1-hexene with hydrogen peroxide. As abovementioned, the catalytic dihydroxylation of olefins with hydrogen peroxide has been performed using various catalytic systems. However, to the best of our knowledge, their selectivity toward 1, 2-diols does not exceed 90% because of the construction of some by-products such as epoxides, alcohols, ketones, and/or others.

The model reaction was tested with Ag supported on mesoporous silica (Ag/MS) catalyst. For this study, 1-hexene was added to a suspension of the catalyst in 30% aqueous hydrogen peroxide and acetonitrile, the reaction mixture was reacted for 24 h at 65°C.

Various reaction conditions were optimized to find the best conversion and selectivity; the results were given in **Table 1**. Applying a catalyst without Ag

did not succeed to reach any selectivity. For indicating the critical role of a support bed, Ag powder (5 mg) without supporting was applied as a catalyst in the same reaction conditions, low yield of product and poor selectivity were obtained. After that, the amount of catalyst was optimized, and the best effective amount of catalyst was found as 10 mg. The different kinds of auxiliary solvents were also examined and acetonitrile was selected as the best one. The influence of reaction temperature was studied and 65 °C was found as the best reaction condition. These results were reported in **Table 1**.




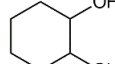


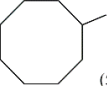
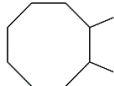
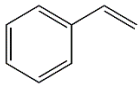


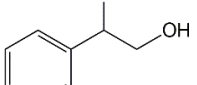
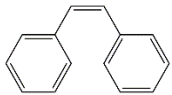
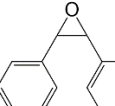
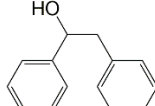
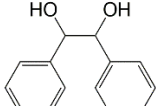
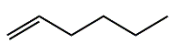
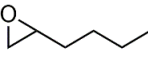
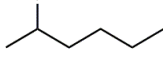
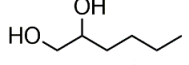
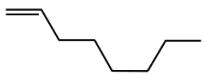

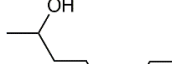
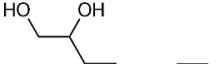
With optimized reaction conditions in hand, the general applicability of the catalytic system was investigated in the performance of oxidized various olefins to 1, 2-diol using aqueous H₂O₂. For all of the tested olefins, high conversion yields and selectivity of products were achieved (**Table 2**).

Table 1. Optimization of reaction conditions.

| Entry | Cat. (mg) | Solvent | T (°C) | Conv. ^a (%) | Selectivity ^a 3/1+2 |
|-------|-----------|--------------------|--------|------------------------|--------------------------------|
| 1 | 2 | CH ₃ CN | 25 | 83 | 93 |
| 2 | 5 | CH ₃ CN | 25 | 86 | 94 |
| 3 | 10 | CH ₃ CN | 25 | 90 | 90 |
| 4 | 10 | Toluene | 25 | 84 | 73 |
| 5 | 10 | Benzene | 25 | 71 | 64 |
| 6 | 10 | CH ₃ CN | 40 | 93 | 92 |
| 7 | 10 | CH ₃ CN | 65 | 92 | 97 |

^a Conversions were determined by GC

Table 2. Oxidation of olefines to 1, 2-diol by using Ag/MS^a.

| Entry | Olefin | Conversion ^b (%) | Selectivity ^b | | |
|-------|---|-----------------------------|---|---|--|
| 1 |  | 94 |  (0) |  (3) |  (97) |
| 2 |  | 91 |  (2) |  (5) |  (93) |
| 3 |  | 95 |  (5) |  (7) |  (88) |
| 4 |  | 89 |  (7) |  (10) |  (83) |
| 5 |  | 92 |  (0) |  (3) |  (97) |
| 6 |  | 94 |  (0) |  (5) |  (95) |

^a Reaction conditions: 0.01g catalyst (0.3 mol% Ag), H₂O₂ (30 %, 4 mmol) 2 mmol olefines, 65 °C, 24 h, CH₃CN (3 mL);

^b Conversions were determined by GC and are an average of at least three runs

A proposed model of the phase-boundary catalytic system and the reaction mechanism is given in **Scheme 2**. The Ag species at the surface of mesoporous silica are activated with H₂O₂ in the aqueous phase and reacted with olefine. As can be seen in **Scheme 2**, the reaction mechanism of the Ag/H₂O₂-catalyzed alkene epoxidation probably involves Ag–OOH species.

The efficiency of the catalyst was compared with some other catalytic systems which have been used for the synthesis of 1, 2-diols. These results are presented in **Table 3** and indicated excellent efficient conversion and selectivity of our heterogeneous catalyst in this reaction.

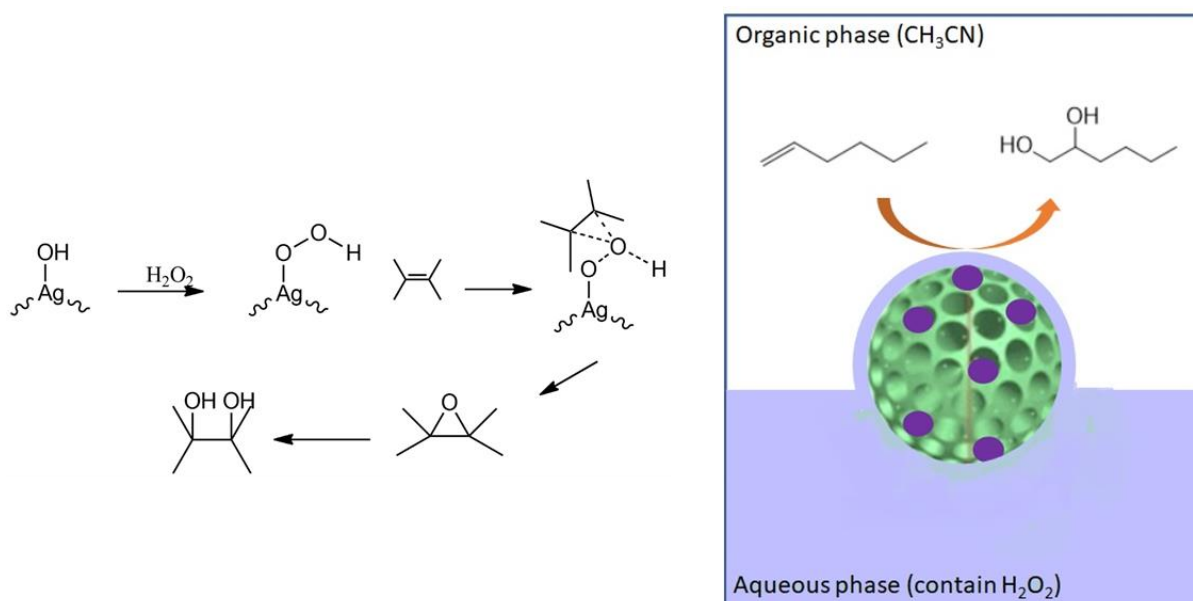
The recyclable investigation was carried out by 1-hexene, Ag/MS was removed from the reaction mixture, washed with EtOAc, dried, and used for to the next run, the results were was summarized in **Table 4**. The conversion of the reaction in the fourth run was 89%, it close to the 92% observed on the first run. To confirm the heterogeneous properties of the catalyst, a leaching experiment was done. In one test, the catalyst was suspended in H₂O₂/EtOAc and refluxed for 10 h. After the removal of the catalyst, alkene was added to the

solution and the reaction was performed and low reaction progress indicated no leaching.

In a final set of tests, the oxidation reaction in the absence of auxiliary solvents was investigated. We performed the reaction without using any other solvent which led to the desirable conversion and selectivity. It found that selective oxidation was also achieved without any additive solvent in comparison yields and selectivity at the model reaction (conversion of 1-hexene to hexane-1, 2-diol), this result is very valuable in ‘green’ chemistry.

4. Conclusions

In summary, to the best of our knowledge, this is the first report of excellent conversion and selectivity of oxidation reaction of olefines to 1,2-diols by using inexpensive and easily prepared Ag supported on mesoporous silica and aqueous H₂O₂. The introduced catalyst was heterogeneous and stable. The method has some advantages such as mild temperature reaction. Moreover, the used catalyst preparation process is easy comprising low-cost, steady, and commercially available compounds.



Scheme 2. The proposed model of the phase-boundary catalytic system and the reaction mechanism

Table 3. Comparison of catalytic activity of some reported heterogeneous catalyst in preparation reaction of 1,2-diol

| Entry | Catalyst | Conditions | Conv. (%) | Selectivity | Ref. |
|-------|--|---|-----------|-------------|-----------|
| 1 | PtNP in-situ photocatalyst (20 mg) | 80 °C, H ₂ O, 18 h | 68 | 82 | [45] |
| 2 | SiO ₂ /SO ₃ H (16 % wt.) | 30% aq H ₂ O ₂ , 70 °C, 22 h. | 90 | 36 | [46] |
| 3 | Al ₂ O ₃ (10 mg) | 30% aq H ₂ O ₂ , 25 °C, 24 h. | 82 | 42 | [47] |
| 4 | Co-Ag@ ZnO (7% wt.) | 30% aq H ₂ O ₂ , 80 °C, 24 h. | 94 | 64 | [48] |
| 5 | Ag/MS (10 mg) | 30% aq H ₂ O ₂ , 65 °C, 24 h. | 92 | 97 | This work |

Table 4. Recyclability of catalyst in the model reaction.

| Run | Conv. ^a (%) | Run | Conv. ^a (%) |
|-----|------------------------|-----|------------------------|
| 1 | 92 | 4 | 89 |
| 2 | 92 | 5 | 76 |
| 3 | 90 | - | - |

^aConversions were determined by GC.

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