Silver nanoparticles impregnated mesoporous SBA-15

A

Thesis submitted

in partial fulfilment of the requirement

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Master of Science in Chemistry

Submitted by
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All these thanks are, however, only fraction of what is due to almighty for granting me an opportunity and strength to successfully accomplish this assignment.

Sandeep Batish

Date: Sandeep Batish

Candidate's Declaration

I hereby declare that the work presented in the thesis entitled, "**Silver nanoparticles incorporated mesoporous SBA-15**" in partial fulfilment of the requirement for the award of the degree of **Masters of Science in Chemistry and being submitted to Thapar University, Patiala,** is my own work during the period of January 2012 to July 2012, under the supervision of **Dr. Satnam Singh**, Head and Associate Professor and **Dr. Bonamali Pal,** Associate Professor , School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the contents embodied in this thesis for the award of any other degree.

Patiala

Date:

Sandeep Batish

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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Certificate

This is to certify that the thesis entitled "**Silver nanoparticles incorporated mesoporous SBA-15**" being submitted by Mr. Sandeep Batish to **Thapar University, Patiala**, in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry, is a bonafide work carried out under our supervision, and that no part of this thesis has been submitted for the award of any other degree.

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List of Contents

List of abbreviations and symbols:

Ag/SBA-15/Hex	- Hexamine reduced silver nanoparticles incorporated SBA-15
Ag/SBA-15/Asc	- Ascorbic Acid reduced silver nanoparticles incorporated SBA-15
Ag/SBA-15/NH_3	- Ammonia reduced silver nanoparticles incorporated SBA-15
Ag/NP-1/SBA-15	- Silver nanoparticles incorporated SBA-15 (by method 1)
Ag/NP-2/SBA-15	- Silver nanoparticles incorporated SBA-15 (by method 2)
BET	- Brunaer, Emmett and Teller
°C	- Degrees Celcius
CO_2	- Carbon dioxide
Fig.	- Figure
NH_3	- Ammonia
nm	- Nanometer
Pa	- Pascals
Pc	- Phthalocyanines
SEM	- Scanning Electron Microscopy
μm	- Micrometer
XRD	- X-ray diffraction
γ	- Gamma

Abstract

Silver impregnated SBA-15 has been prepared by one- and two- pot synthesis. In one pot synthesis three different reducing agents viz., hexamine, ascorbic acid and ammonia were used for preparation of Ag incorporated SBA-15 and as prepared catalysts were named as Ag/SBA-15/Hex, Ag/SBA-15/Asc, and Ag/SBA-15/NH_3. However, in two pot synthesis, seed solution of Ag nanoparticles were introduced at two different stages during synthesis of SBA-15 and were abbreviated as Ag/NP-1/SBA-15 and Ag/NP-2/SBA-15. The synthesized samples were characterized by powder X-ray diffraction, BET surface area, SEM and EDX analysis. The surface areas of prepared catalysts were found to be 439 m^2/g (Ag/SBA-15/NH_3), 485 m^2/g (Ag/SBA-15/Asc), 510 m^2/g (Ag/SBA-15/Hex), 607 m^2/g (Ag/NP-2/SBA-15) and 626 m^2/g (Ag/NP-1). These values are lower than that of SBA-15 (702 m^2/g), suggesting the incorporation of Ag into SBA-15. All the prepared catalysts were tested for oxidation of cyclohexane to cyclohexanone. The highest conversion of 2.5% was obtained with Ag/SBA-15/Hex, whereas other catalysts showed 1.6-2.2% conversion. Hence, Ag/SBA-15/Hex was used for further oxidation of three cycloalkanols viz., cyclopentanol, cyclohexanol and cycloheptanol that resulted in 55%, 38.7%, 33.7% conversion, respectively into their respective cycloalkanones.

1. Introduction

Mesoporous materials are one of the types of porous materials with pore diameters in the range of 2-50 nanometres. The mesoporous silicas are made up of frameworks (pore walls) which are amorphous [Xia et al. (2003)]. These materials are special types of nanomaterials with ordered arrays of uniform nanochannels. They have important applications in a wide variety of fields such as separation, catalysis, adsorption and synthesis of advanced nanomaterials [Lu et al. (2004)]. These mesoporous materials exhibit high surface area (600–1300 m^2/g) and large pore size exhibiting widely potential applications in industrial catalytic reactions [Xiao et al. (2005)].

In 1992, scientists at Mobil Oil Research & Development announced the synthesis of the first broad family of mesoporous molecular sieves (M41S) using cationic surfactants to assemble silicate anions from solution [Beck et al. (1992); Kresge et al. (1992)]. Later on, Zhao et al. in 1998 reported the synthesis of Santa Barbara Amorphous type material number 15 (SBA-15) which is a type of mesoporous material with enhanced thermal and hydrothermal stability compared to other mesoporous silica. It can be readily prepared over a wide range of uniform pore size (4.6–30 nm) and pore wall thickness (3.1–6.4 nm), by using a variety of poly(ethylene oxide)–poly(propylene oxide)–poly (ethylene oxide) triblock copolymers (EO*x*PO*y*EO*x*) as templates.. It may be used as a promising catalyst support, particularly for reactions occurring at high temperatures [Wang et al. (2004)].

Mesoporous materials have several possible applications within heterogeneous catalysis, due to their high surface area and ordered pore structure [Vralstad et al. (2006)]. The advantages of using ordered mesoporous solids in catalysis are the relatively large pores facilitating the mass transfer and the very high surface area which allows a high concentration of active sites per mass of material. Mesoporous silica materials are not catalytically active by themselves. These materials, therefore, have to be functionalized in some way for application as catalysts. There are several different procedures that are applied to functionalize these supports. Two of the most commonly used for mesoporous materials are direct functionalization by metal incorporation and incipient wetness impregnation [Taguchi et al. (2005); Vralstad et al. (2006)]. The direct method is a “one-pot” procedure, where the metal precursors are added during synthesis and are incorporated into the framework. This one-step procedure is relatively simple, and it is also possible to control the pore size, pore structure, and the amount of metal during synthesis. Incipient wetness impregnation is a

widely used functionalization method for preparation of supported catalysts and is used for commercial purposes. In this post-synthesis procedure, a metal salt solution is added to the support in an amount to exactly fill the pore volume, and the material is then dried and calcined [Perego et al. (2004)].

2. Literature Review

Synthesis, characterization and application of porous materials have been strongly promoted for its wide use as catalysts, adsorbents and sensors. According to the classification made by IUPAC, porous solids can be divided into three main categories, depending on their pore size (diameter d): micro- (d < 2 nm), meso- (d = 2-50 nm), and macroporous materials (d > 50 nm). In particular, mesoporous materials are of the greatest attention because of uniform mesostructures, high surface areas, and tunable pore sizes. These properties make them promising templates to control shape and size dependent synthesis of metal nanoparticles. Mesoporous materials can be achieved through various types of surfactants (used as the template) and inorganic species. There are several pathways that may be classified according to interaction type between the surfactant and the inorganic framework. Huo et al. (1994) proposed mainly four different reaction pathways for synthesis of mesoporous materials.

1. The **(S^+I^-)** route. In this case, cationic surfactants (S^+) are used as structure directors for anionic inorganic species (I^-). This is the pathway for synthesis of M41S materials. This route involves the direct co-condensation of anionic inorganic species (I^-) with a cationic surfactant (S^+) to give assembled ion pair (S^+I^-). The original synthesis of M41S silicas in basic condition was the prime example [Kresge et al. (1992)]. Huo et al. (1994) were the first ones to extend the sol-gel method proposed by Kresge et al. (1992) to non-silica based materials. They reported the synthesis of lamellar tungsten (VI) oxide at pH above 8 (d_{100} = 28.3 A^o) and a mixture of lamellar and hexagonal tungsten (VI) oxide phases at pH 4-8 (d_{100} = 28.3 A^o). In the same way, cubic (a= 150.0 A^o), hexagonal (d_{100} = 46.0 A^o) and lamellar (d_{100} = 37.5 A^o) antimony (V) oxide were obtained at pH between 6.0 and 7.0. However, Huo et al. (1994) could not find any chemical or physical way to remove the organic phase without destroying the pore structure.

2. The **(S^-I^+)** route. In this pathway, anionic surfactants (S^-) interact with cationic inorganic species (I^-). In this route an anionic template (S^-) is used to direct the self-assembly of cationic inorganic species (I^+) via S^-I^+ ion pairs.

3. The **($S^+X^-I^+$)** route. Here both the surfactant and the inorganic species are cationic. These are mediated by negatively charged counter ions (X^- = Cl^-, Br^-, etc.).

4. The **($S^-M^+I^-$)** route. In the final case, both the surfactants and the inorganic species are anionic and positively charged counter ions (M^+ = Na^+, K^+, etc.) mediated the structure formation.

The pathways 3 and 4 involve counter ion (X^- or M^+) mediated assemblies of surfactant and inorganic species of similar charge. These counter ion-mediated pathways afford assembled solution species of type $S^+X^-I^+$ (where X^- = Cl^- or Br^-) or $S^-M^+I^-$ (where M^+ = Na^+ or K^+) respectively.

Beside the above said four-reaction pathways, another route (S^oI^o) has been proposed by Tanev et al. (1995) who have used neutral primary amine surfactant (S^o) and neutral inorganic species (I^o) as precursor for the preparation of mesoporous material.

Nanomaterials fabricated/supported inside the mesoporous materials are highly dispersed and stabilized in nature. The immobilisation of metal on mesoporous materials is a useful method for the preparation of heterogeneous catalyst. Work carried out by Jiang et al. (2004), Lou et al. (2007), and Riouxa et al. (2006) for the preparation SBA-15 supported palladium molybdenum oxide and platinum nanoparticles, provided insight into the relation between nanoparticles confined in various molecular sieves with their properties. Transition metals (Au, Ag, Cu etc.) dispersed mesoporous supports has shown unexpectedly high catalytic activity towards different reactions of both industrial and environmental importance [Aprile et al. (2009); Liu et al. (2008); Yong et al. (2010)]. Additionally, the incorporation of Ag nanoparticles on SBA-15 mesoporous silica has high potential to be used as the oxidation catalyst [Chimentao et al. (2005)]. The high percent conversion of carbon monoxide (CO) to carbon dioxide (CO_2) occurred on the surface of Ag nanoparticles [Chen et al. (2009)].

Oxidation of cyclohexane resulting into mixture cyclohexanone and cyclohexanol also known as K/A oil. These two compounds are important intermediates in the manufacture of nylon-6 and nylon-66 which have become important reference material in the industrial production of polymers, and the demand is increasing. The industrial scale preparation of cyclohexanol and cyclohexanone is carried out by oxidation of cyclohexane or by hydrogenation of phenol [Schuchardt et al. (2001); Lu et al. (2005)]. The earlier process was carried out at 150 ^oC and 1-2 MPa pressure, employing metal cobalt salt or metal-boric acid as homogeneous catalyst. However, a major drawback of the process is that to have the high selectivity (75–80%) for the K/A oil ratio, the conversion percentage must be in range of 3-6%, thus [Ingold et al. (1989); Sawatari et al. (2001)]. Many attempts have been made to

synthesize more efficient catalysts for the oxidation of cyclohexane. Lu et al. (2004) reported oxidation of cyclohexane with molecular oxygen using Au/MCM-41 resulting into 19% conversion with 21.3% and 6% selectivity towards cyclohexanol and cyclohexanone, respectively. Results with other mesoporous based catalyst are summarized in table 1.

Table 1: Metal incorporated mesoporous materials used for oxidation of cyclohexane along with selectivity towards cyclohexanol and cyclohexanone.

Metal	Support	Conversion (%)	Reaction Time (h)	Cyclohexanol/ Cyclohexanone	Reference
Au	SBA-15	4	6-8	85/10	Suo et al. 2004
Au	MCM-41	19	6	21.3/6	Lu et al. 2004
Au	γ-Al_2O_3	12.6	5	52.6/2.1	Xu et al. 2007
Au	SBA-15	10-20	3-6	33/50	Stoel et al. 2009
Au	SBA-15	34.5	2	18.6/61.5	Zhao et al. 2010
Cu	SBA-15	3.6	6	48.7/47.9	Gu et al. 2011

The intense literature regarding the use of other types of catalysts for the oxidation of cyclohexane is available. Bellifa et al. (2006) used a V_2O_5–TiO_2 catalyst which resulted with 8% conversion and 76% selectivity in the presence of acetic acid as solvent and acetone as initiator. Copper (II) complexes such as [Cu(BMPA)Cl_2] and {[Cu(BMPA)Cl_2][Cu(BMPA)(H_2O)Cl] [Cu(BMPA)Cl][$CuCl_4$]} with H_2O_2 were used to have 68.9% of total conversion of cyclohexane to cyclohexanone and cyclohexanol [Silva et al.(2007)]. The use of Co_3O_4 nanocrystals gave a 7·6% conversion yielding cyclohexanol and cyclohexanone at 120 ^oC in 6 h with molecular oxygen [Zhou et al. (2005)]. Chromium (II) containing complex, CrCoAPO–5(CH_3COOH) [Masters et al. (2001)] gave a 50% conversion, yielding 55%, 8%, 15% and 22% selectivity towards cyclohexanol, cyclohexanone, adipic acid and others, respectively at 115 ^oC and 1 MPa of oxygen. A zirconium complex bonded to modify carbamate silica gel gave a product distribution ratio of 6.6 : 1 of cyclohexanol/cyclohexene mixture with 21% conversion at 200 ^oC [Anisia and Kumar (2004)]. Titanium silicate gave 27·8% conversion with selectivity's of 44%, 45% and 11% towards cyclohexanol, cyclohexanone and other products, respectively in 100 ^oC with H_2O_2 as oxidant [Reddy and Sivasankar (1991)]. The Au/Al_2O_3 system using molecular oxygen in a solvent free system resulted in 12.6% conversion with a selectivity of 52.6% for cyclohexanol and 32.1% for cyclohexanone [Xu et al. (2007)]. Ebadi et al. (2007) reported Fe, Mn and CoPc supported on γ–alumina as catalysts for aerobic oxidation of cyclohexane

in the gas phase under atmospheric pressure (1Pa) with 38% selectivity for formation of cyclohexanol and cyclohexanone with a 29% conversion of cyclohexane.

Thus, it is clear that ample work has been done for the oxidation of cyclohexane to corresponding cyclohexanol and cyclohexanone using various types of metals viz., Fe, Co, Au based catalysts. Since, nanoparticles of Ag are stable than Cu and Fe and has an advantage over Au in terms of cost, hence Ag nanoparticles incorporated mesoporous materials deserve further investigation.

3. Objective

3.1 To prepare mesoporous SBA-15 and silver nanoparticles impregnated mesoporous SBA-15.

3.2 To study catalytic activity of silver nanoparticles impregnated mesoporous SBA-15 for oxidation of cyclohexane and cycloalkanols (cyclopentanol, cyclohexanol and cycloheptanol).

4. Experimental section

4.1 Materials and methods

Hydrochloric Acid (37%), Nitric Acid (69-70%), Ammonia (30%), Trisodium-citrate (99%), Cyclopentanol (99%), Triphenylphosphine (99%), Hexamine (99%), Sodium borohydride (98%), Cyclohexanol (99%) were obtained from Loba Chemicals Pvt. Ltd. Pluronic Acid (P123), Tetraethylorthosilicate (TEOS 99%) and CTAB (Cetyltrimethylammonium bromide 99%) were purchased from Sigma-Aldrich. Silver Nitrate (99%) was obtained from Fischer Scientific and Ascorbic acid (SD Fine Chemical Ltd.) and Cyclohexane (HPLC Grade) were purchased from MERCK. All chemicals were used without any further purification.

4.2 Preparation of catalyst:

4.2.1 Preparation of SBA-15

Mesoporous silica was prepared as under:

2 g of triblock copolymer P123 ($EO_{20}PO_{70}$-EO_{20}, Aldrich) was dissolved in 75 g of 1.6 M HCl followed by addition of 4.25 g of tetraethylorthosilicate (TEOS) under stirring at 40 ^{0}C. The solution was stirred for 24 h at 40 ^{o}C and heated at 100 ^{o}C for another 24 h under static conditions. The liquid was evaporated under stirring at 80 ^{o}C (instead of being filtered off in the traditional synthesis of SBA-15). The solid obtained was dried at 80 ^{o}C and calcined at 550 ^{o}C for 6 h to remove template.

4.2.2 Synthesis of SBA-15 impregnated Ag nanoparticles by in-situ reduction

In a typical experiment, 1 g of pluronic P123 (tri-block co-polymer) was dissolved in 30 ml of H_2O followed by addition of 2 ml concentrated nitric acid and the solution was stirred at 35 ^{o}C for 1 h. To this solution different reducing agents viz., ammonia (1 ml), ascorbic acid (0.7 g; 4 mmol) and hexamine (0.7 g; 5 mmol) were added in a series of experiments along with 20 mg of $AgNO_3$ and stirred for 3 h at 35 ^{o}C in dark to form silver nanoparticles by in-situ reduction. Afterwards, 2.3 ml of TEOS was added and stirred for 20 h at 35 ^{o}C. The mixture was kept at 100 ^{o}C for 48 h for crystallization. The resulting solid was filtered, washed several times with water followed by ethanol, and then dried at 50 ^{o}C for 10 h in vacuum oven. Finally, the solid was calcined in air at 550 ^{o}C for 5 h. These were designated as Ag/SBA-15/Hex, Ag/SBA15/Asc, Ag/SBA-15/NH_3 and were characterized by Powder X-ray diffraction and SEM-EDX.

4.2.3 Preparation of SBA-15 impregnated Silver Nanoparticles by two-step method

4.2.3.1 Seed solution of Ag Nanoparticles:

Seed solution of silver nanoparticles was prepared by literature reported method [Gorelikov and Matsuura (2008)]. For this preparation, aqueous solution of 9.75 ml of CTAB (80 mM) was added to 2.5 µL of 10 mM aqueous solution of $AgNO_3$ followed by addition of 600 µL of aqueous solution of $NaBH_4$ (10 mM) under vigorous stirring, resulting in the formation of yellow solution. Prepared seed solution was characterized by UV-Visible spectrophotometer and stored in refrigerator for further use.

42.3.2 Impregnation of Ag nanoparticles in channels of SBA-15

It was carried out by two ways:

(I) Preparation of Ag/NP-1/SBA-15: Ag nanoparticles seed solution (4 ml) and filtered mass during SBA-15 (before autoclaving step) were mixed along with 60 ml of water and subjected to hydrothermal treatment at 100 ^oC in a teflon lined autoclave (100 ml capacity) for 24 h. The catalyst thus obtained was washed successively with water and then calcined at 550 ^oC for 5 hours.

(II) Preparation of Ag/NP-2/SBA-15: In this method, seed solution of Ag nanoparticles (4 ml) was added after TEOS addition step during SBA-15 synthesis and rest of the experiment was performed as described for one pot synthesis.

5 Study of catalytic activity

5.1 Oxidation of cyclohexane

In a typical experiment, 10 mg of as-prepared catalyst and 40 ml of cyclohexane (20 mM) along with 150 mg of triphenylphosphine (to completely reduce the cyclohexyl-hydroperoxide intermediate formed) were autoclaved in Teflon lined container (100 ml) at 140-150 ^oC under atmosphere of O_2 (0.5 MPa) for 6 h and the products were analysed by UV-Visible spectrophotometer.

5.2 Oxidation of Cycloalkanols

In a typical reaction procedure for the oxidation, 40 ml aqueous solution (40 mM) of each cycloalkanol (cyclopentanol, cycloheptanol and cycloheptanol) and 10 mg of as-prepared Ag/SBA-15/Hex were autoclaved in the presence of oxygen atmosphere (0.5MPa.) at 140-150 ^oC for 6 h and the products were analysed by UV-Visible spectrophotometer.

6. Results and discussion

6.1 Catalytic Characterisation

6.1.1 Powder XRD analysis

Powder XRD of the prepared catalysts are shown in fig. 1. There are four major diffraction peaks at $2\Theta = 38^o$, 44.2^o, 64.4^o, and 77.6^o, corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) lattice planes respectively. These lattice planes confirm the presence of crystalline cubic Ag nanoparticles incorporated into channels of SBA-15. Lattice parameters were calculated as per eqn. 1 for Ag/SBA-15/Hex, Ag/SBA15/Asc and Ag/SBA-15/NH_3 and were found to be 1.3666, 1.3673 and 1.3651, respectively which confirms the fcc structure of Ag nanoparticles.

$$1/d^2 = (h^2 + l^2 + k^2) / a^2 \qquad \text{……. Eqn. 1}$$

where d = interplanar spacing

a = lattice parameter

h,k,l = miller indices

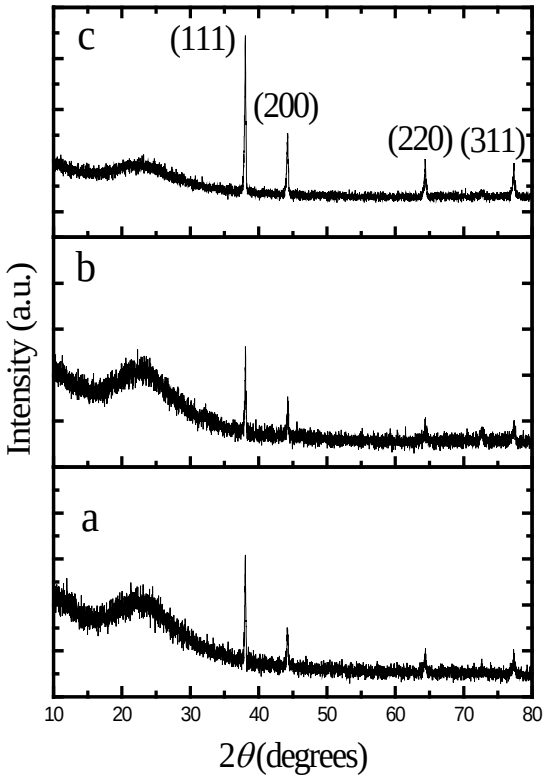

Fig.1. Powder XRD of (a) Ag/SBA-15/Asc (b) Ag/SBA-15/NH_3 (c) Ag/SBA-15/Hex

6.1.2. BET Surface Area

BET surface area for SBA-15, Ag/SBA-15/Hex, Ag/SBA15/Asc, Ag/SBA-15/NH_3, Ag/NP-1/SBA-15, Ag/NP-2/SBA-15 are shown in Table 2. The BET surface area of Ag/SBA-15/Hex (510 m^2g^{-1}), Ag//SBA-15/Asc (485 m^2g^{-1}) and Ag/SBA-15/NH_3 (439 m^2g^{-1}) is lower than bare SBA-15 (702 m^2g^{-1}), due to the incorporation of Ag-nanoparticles inside the mesoporous channels. On the other hand Ag/NP-1/SBA-15 and Ag/NP-2/SBA-15 have surface area higher than that of materials prepared by in situ reduction. This seems to be due to the incorporation of lesser Ag nanoparticles inside SBA-15.

Table 2: Physical properties and catalytic activity of as-prepared catalysts

Catalyst		Bare SBA-15	Ag/SBA-15/Hex	Ag/SBA-15/Asc	Ag/SBA-15/NH_3	Ag/NP-1/SBA-15	Ag/NP-2/SBA-15
Properties	S_{BET} (m^2g^{-1})	702	510	485	439	626	607
	EDX (at %)	Si=33.33 O=66.67	Si= 32.32 O = 65.66 Ag = 2.02	--	--	--	--
	Particle size from SEM (μm)	SBA~0.5	SBA~ 0.5 Ag ~ 0.2	--	--	--	--
Conversion (%) for cyclohexane oxidation		1.65	2.5	2.2	1.9	2.2	2.0

--not done

6.1.3. SEM and EDX studies

SEM of bare SBA-15 and Ag/SBA-15/Hex are shown in fig. 2 and fig. 3 (a, b) respectively. There are oval and elongated particle of size 0.5 µm in both SBA-15 and Ag/SBA-15/Hex. Some particle of silver can be seen on outside on the surface (Fig. 3a and 3b). SEM-EDX of bare SBA-15 and Ag/SBA-15/Hex are shown in Fig. 4a and Fig. 4b respectively. Presence of silver metal in Ag/SBA-15/Hex catalyst has been confirmed from fig. 4a and 4b.

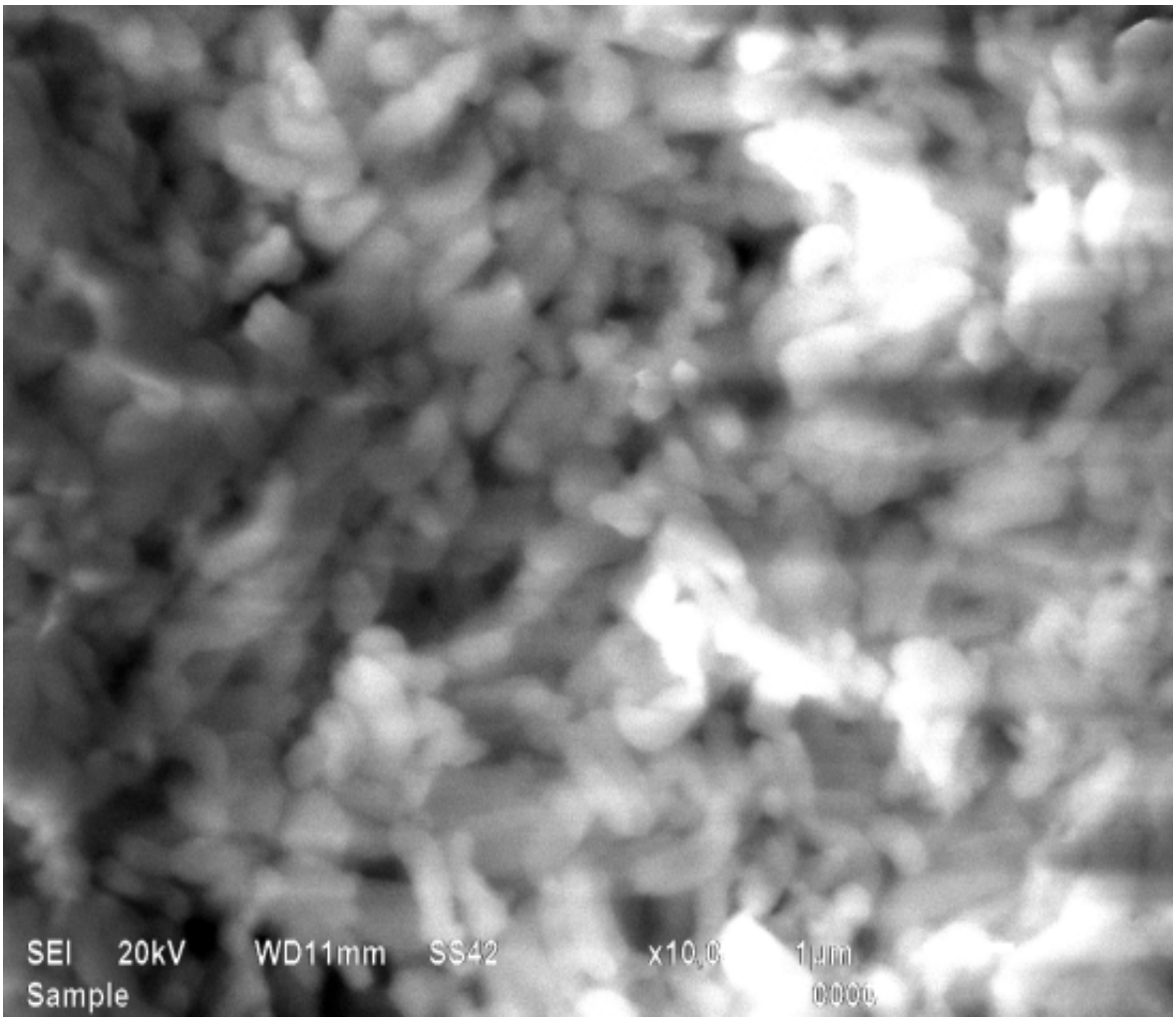

Fig. 2. SEM image of bare SBA-15

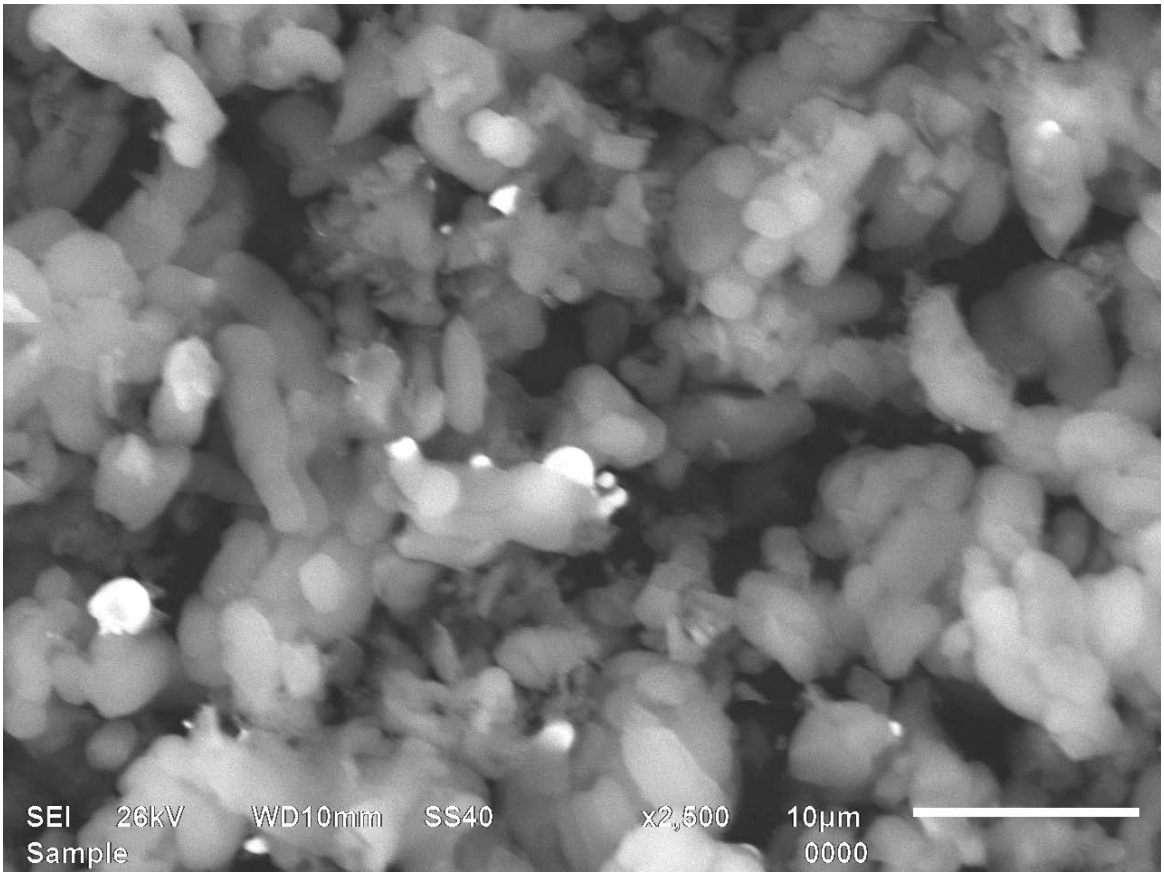

Fig. 3a. SEM image of Ag/SBA-15/Hex (10µm scale)

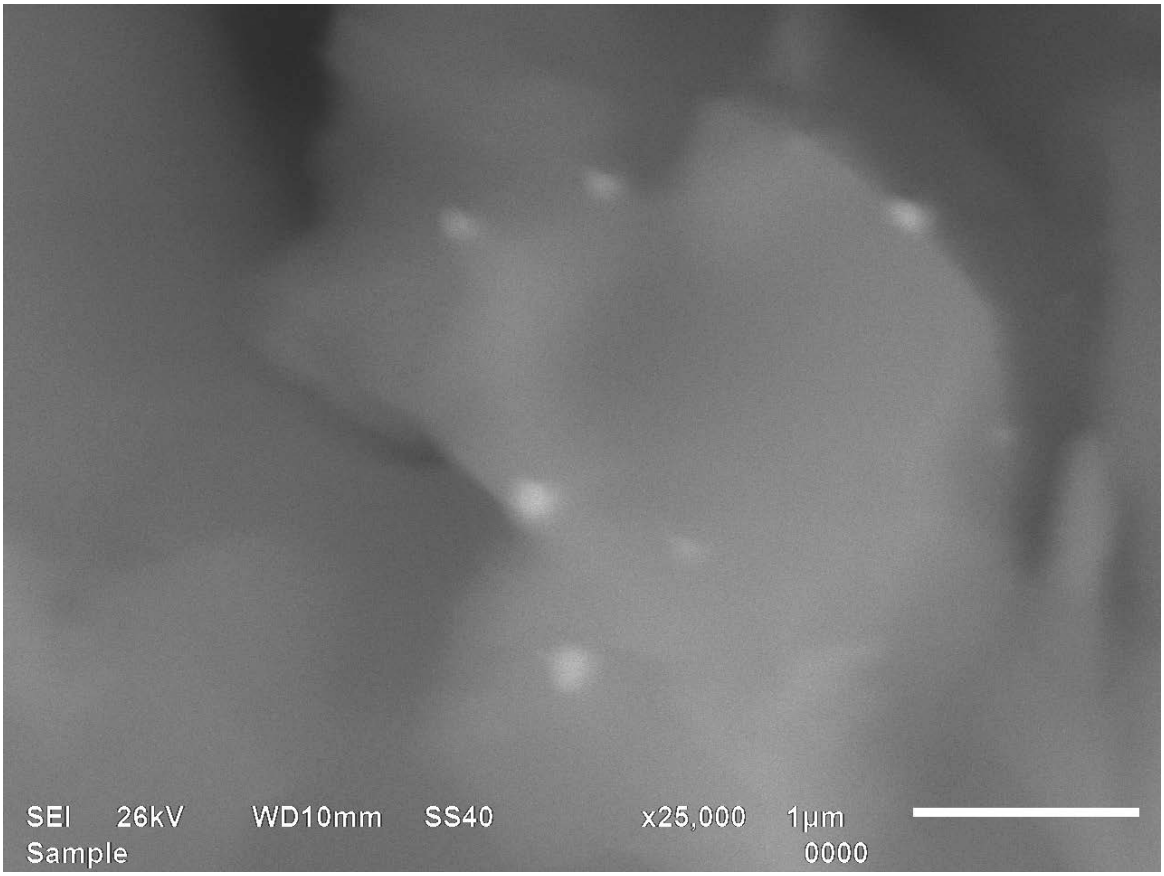

Fig. 3 b. SEM image of Ag/SBA-15/Hex (1µm scale)

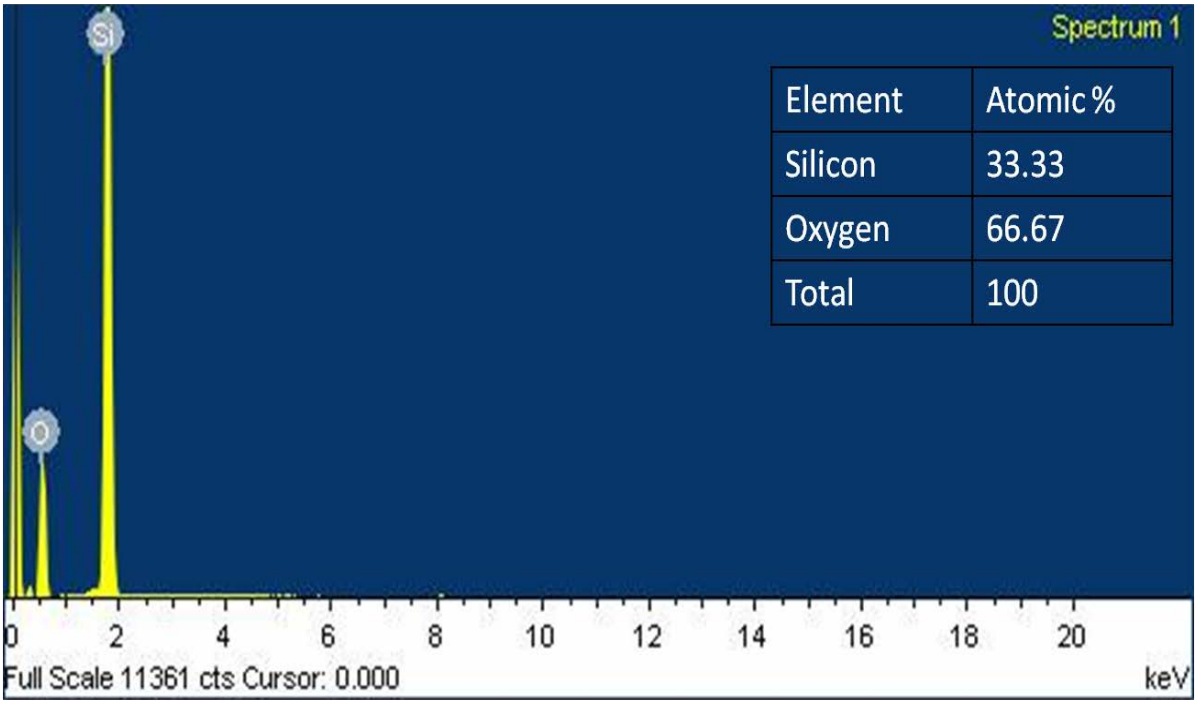

Fig. 4a. SEM-EDX of bare SBA-15

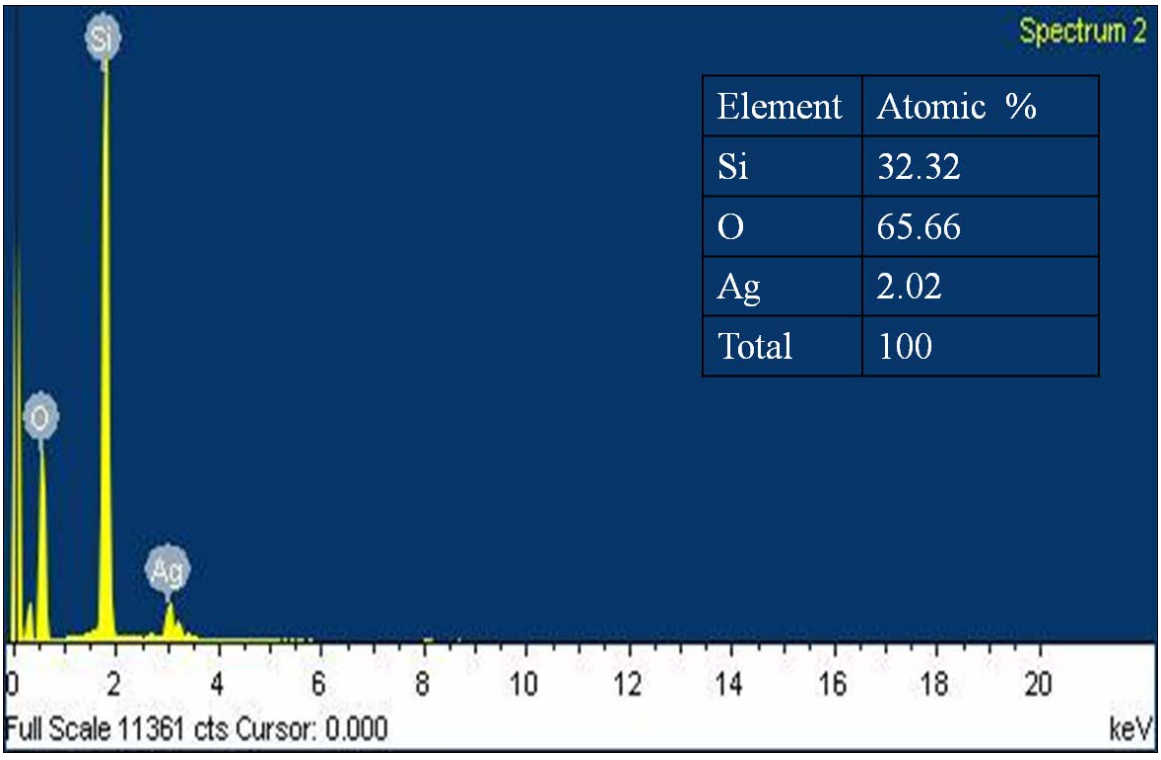

Fig. 4b SEM-EDX of Ag/SBA-15/Hex catalyst

6.2 Catalytic Activity

6.2.1 Oxidation of Cyclohexane

UV-Visible spectra of products obtained by oxidation of cyclohexane using all the synthesized catalysts are shown in Fig. 5 (a). Percentage conversion of cyclohexane into cyclohexanone using different catalysts was calculated from the standard calibration curve (fig. 5 b) and shown in fig. 5d. Highest conversion was obtained with the Ag/SBA-15/Hex catalyst which is higher than bare SBA-15 (fig. 5d). This may be due to the presence of finely dispersed silver nanoparticles in Ag/SBA-15/Hex catalyst by the use of hexamine as efficient reducing agent during its synthesis. Hence, silver incorporation in SBA-15 can be used as catalyst for cyclohexane oxidation though optimum size and weight percent of silver incorporation are yet to be experimented.

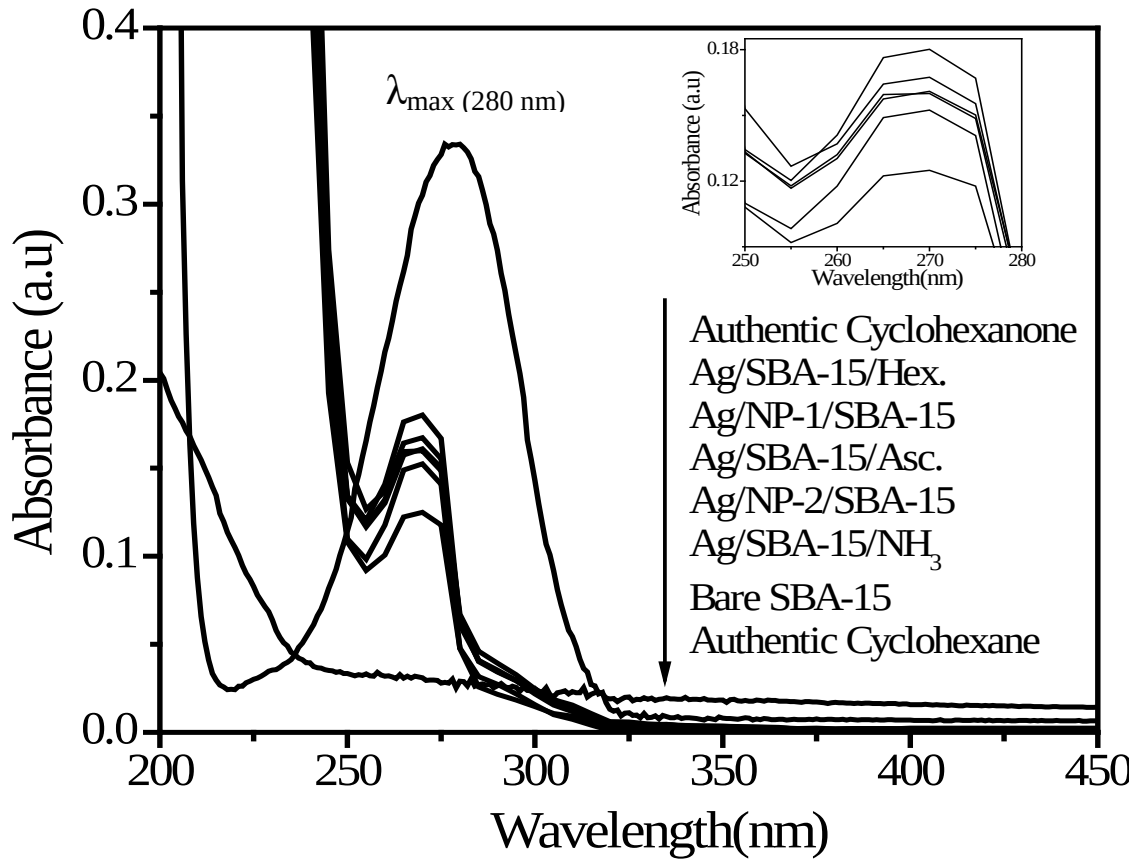

Fig. 5 (a) UV-Visible spectra of cyclohexane oxidation with various catalysts

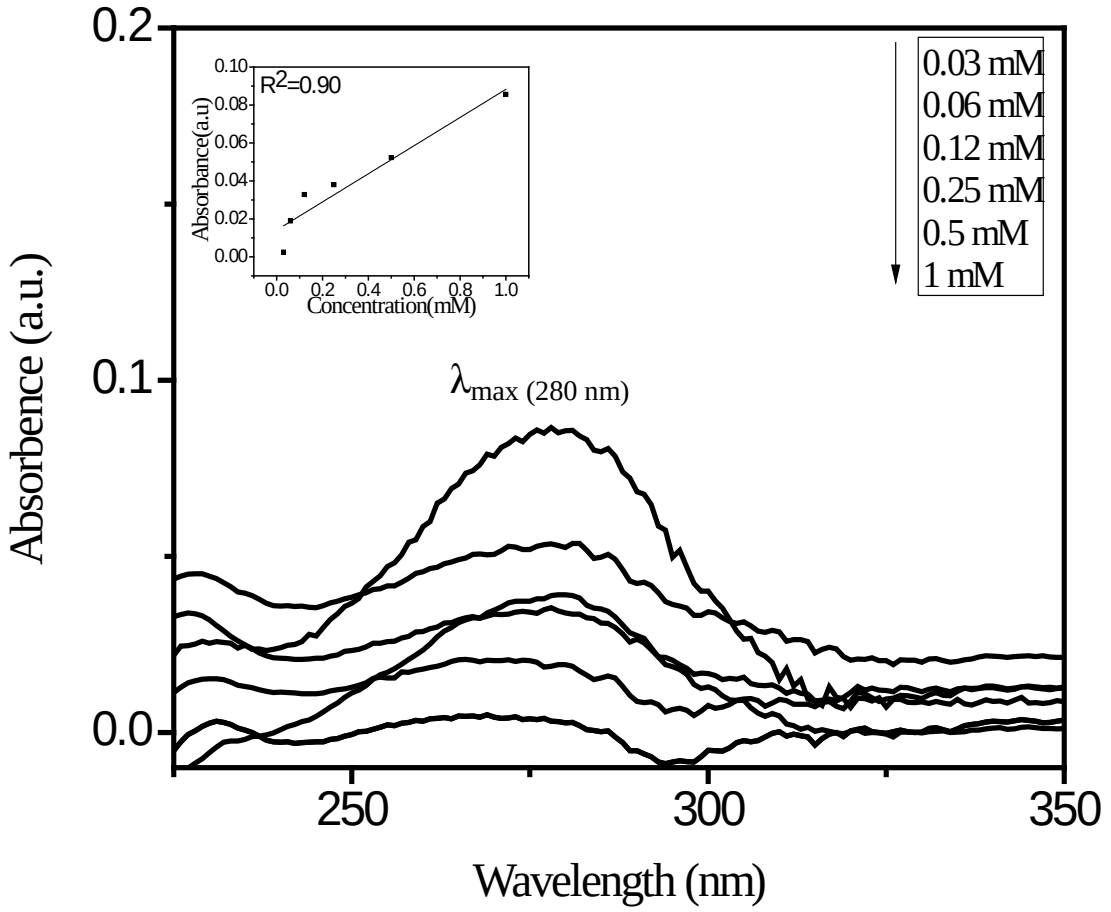

Fig. 5 (b): UV-Visible spectra of cyclohexanone at different concentrations

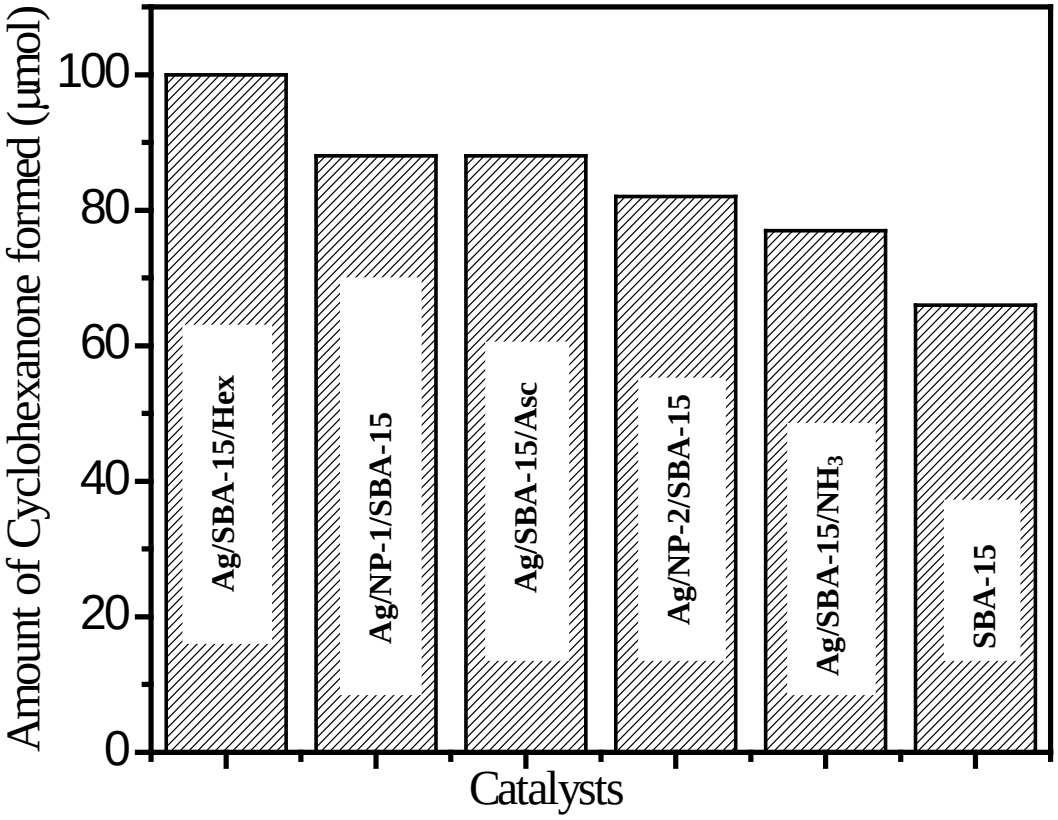

Fig. 5 (c) Amount of cyclohexanone formed using different catalysts

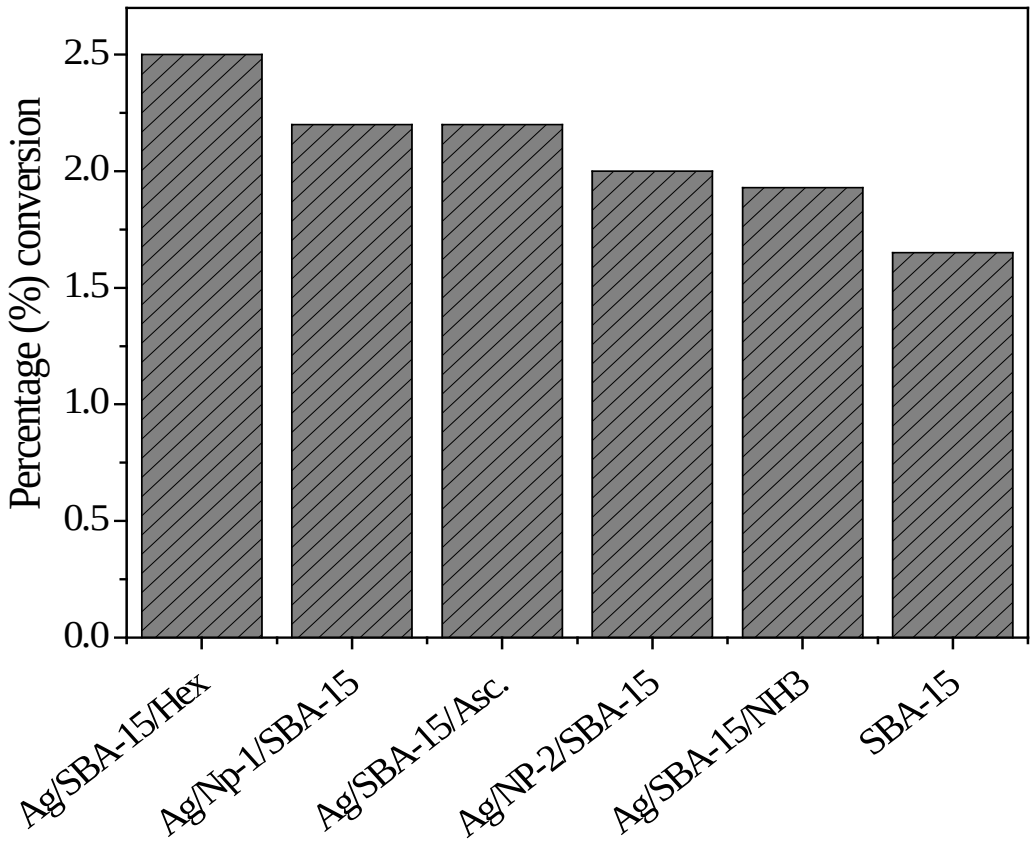

Fig. 5 (d) Percentage conversion of cyclohexane by various catalysts

6.2.2. Oxidation of cyclopentanol, cyclohexanol and cycloheptanol

Since, the activity of Ag/SBA15/Hex catalyst was highest out of all the prepared catalysts for oxidation of cyclohexane (table 2), hence was selected for studying oxidation of cycloalkanols. The catalytic activity of Ag/SBA-15/Hex catalyst was evaluated for the oxidation of cyclopentanol, cyclohexanol and cycloheptanol to corresponding cycloalkanones and UV-Visible spectra of products are shown in Fig. 6b, 7b and 8b respectively. Figure 6a shows the UV-Visible spectra of different concentrations (10-60 mM) of cyclopentanone at λ_{max} of 280 nm. However, the regression coefficient (R^2) calculated form calibration curve (inset Fig. 6a) is 0.9989, which clearly favours validation of calculations for the amount of cyclopentanone formed. Similarly, Fig. 7a and 8a shows the UV-Visible spectra (λ_{max} of 280 nm) for the different concentrations (10-60 mM) of cyclohexanone and cycloheptanone respectively. However, the regression coefficient (R^2) calculated form calibration curve for cyclohexanone (inset Fig. 7a) is 0.951 while that for cycloheptanone (inset Fig. 8a) is 0.95.

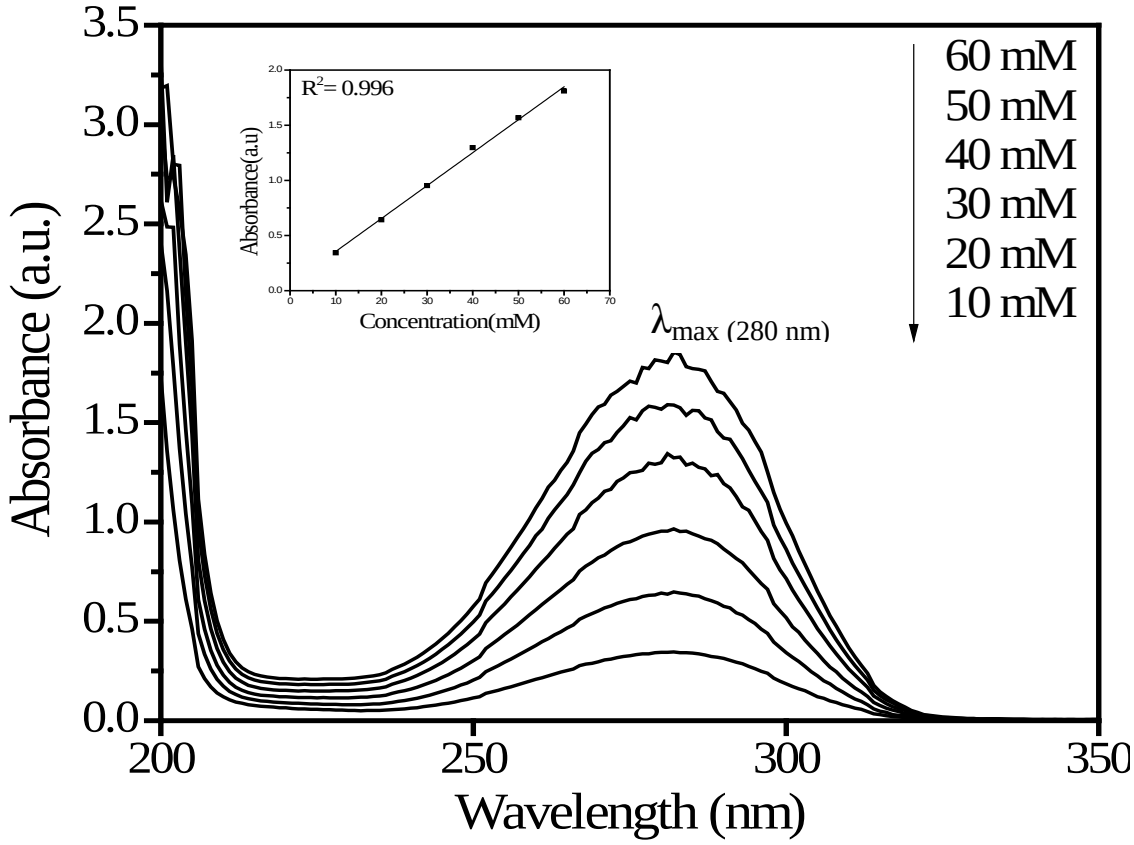

Fig. 6 (a): UV-Visible spectra of cyclopentanone at different concentrations

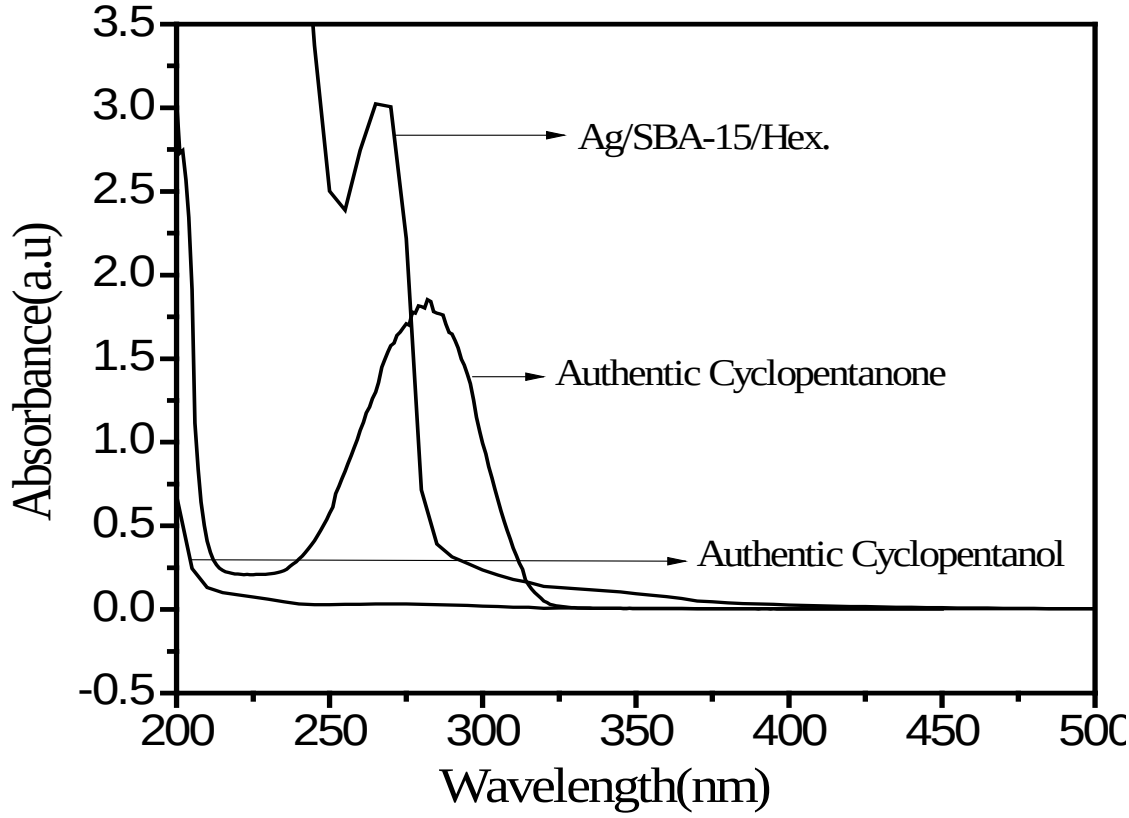

Fig. 6(b): UV-Visible spectra of cyclopentanol oxidation with Ag/SBA-15/Hex

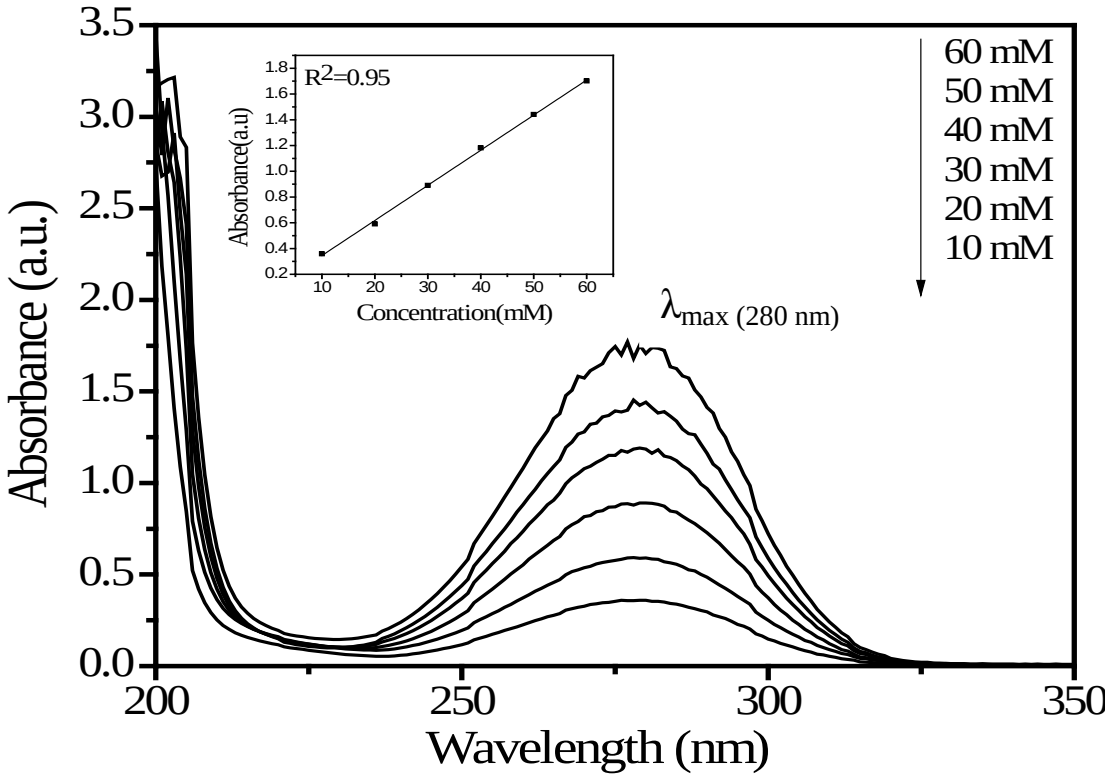

Fig. 7 (a): UV-Visible spectra of cyclohexanone at different concentrations.

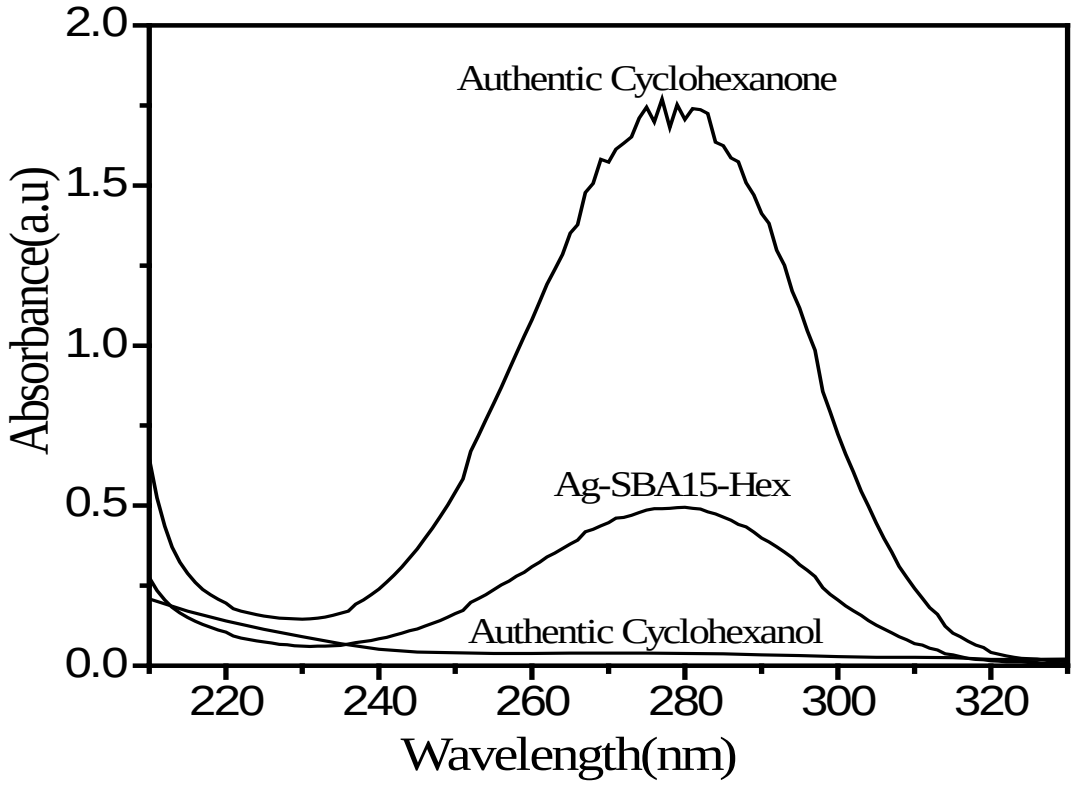

Fig. 7b: UV-Visible spectra of cyclohexanone oxidation with Ag/SBA-15/Hex

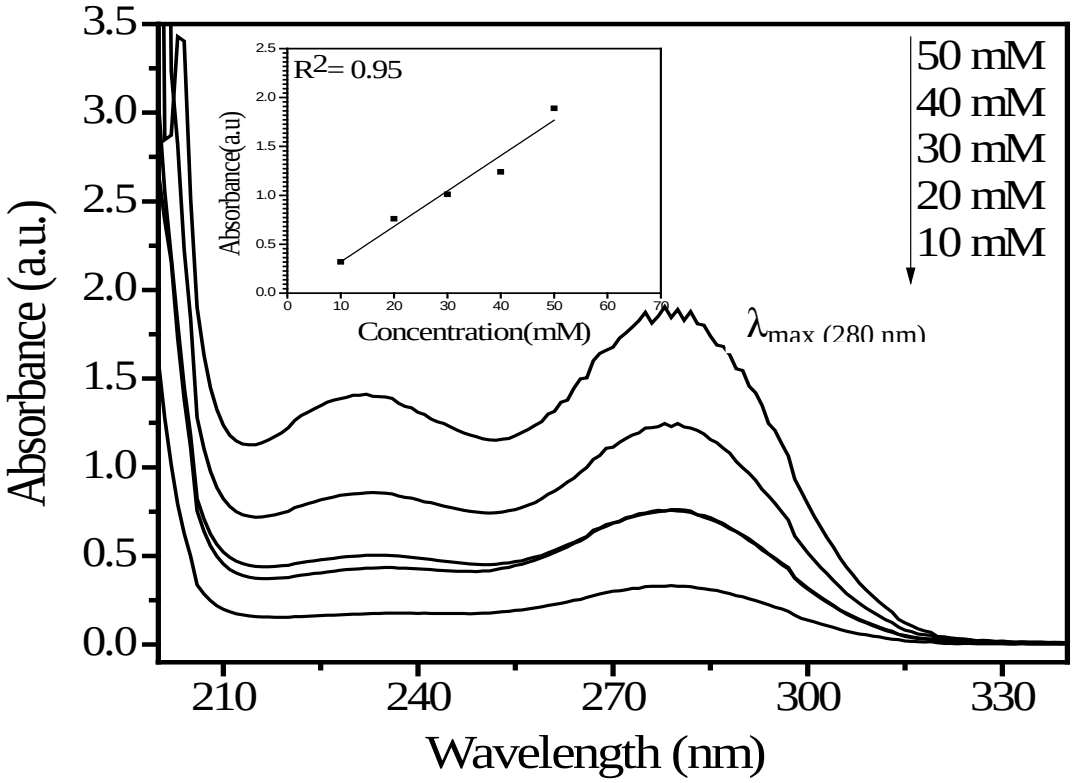

Fig. 8 (a): UV-Visible spectra of cycloheptanone at different concentrations.

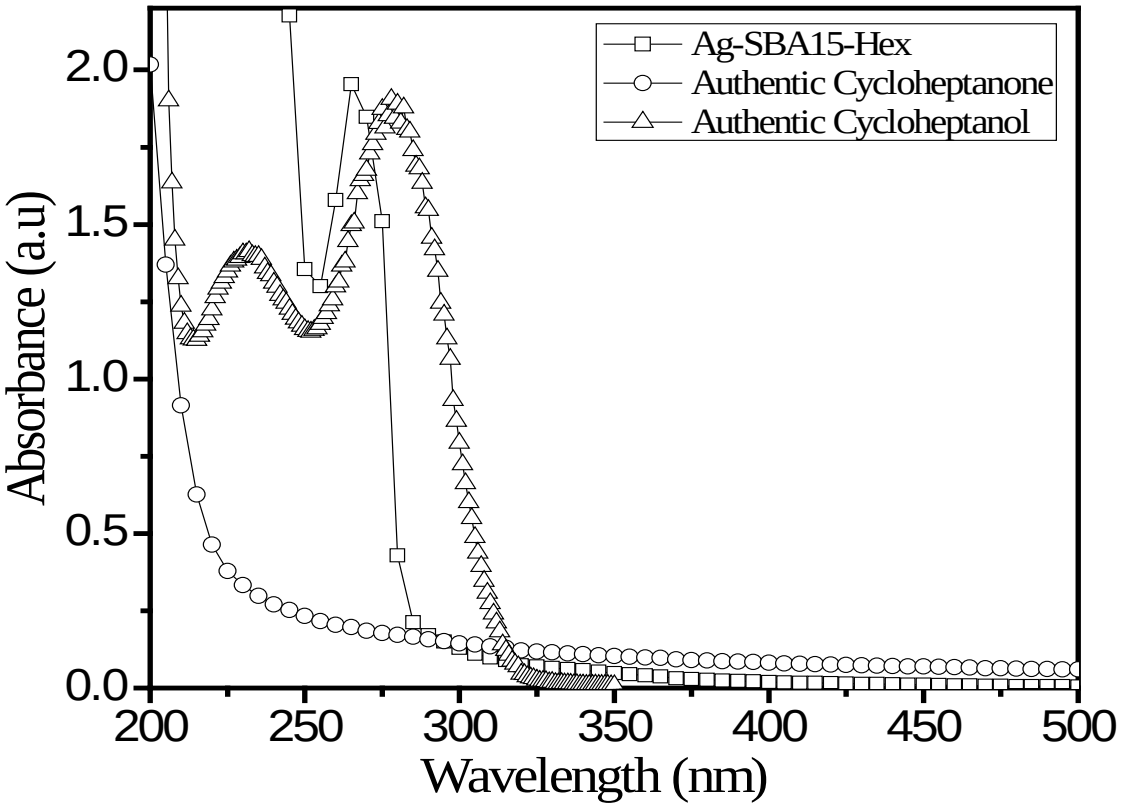

Fig. 8b: UV-Visible spectra of cycloheptanone oxidation with Ag/SBA-15/Hex

The amount of cyclopentanone, cyclohexanone and cycloheptanone formed from the oxidation of respective cycloalkanols was calculated from their respective UV-Visible spectra and calibration curve and was found to be 900, 620 and 528 µmol, for the cyclopentanone, cyclohexanone and cycloheptanone respectively. Conversion was 55%, 38.7% and 33.7% for the cyclopentanone, cyclohexanone and cycloheptanone respectively (fig. 9). Though the authentic peaks of cyclopentanone and cycloheptanone are observed at 280 nm but in the present experiment blue shift is obtained with λ_{max} = 260 nm which is probably due to the formation of intermediates like cyclopentanoic or cycloheptanoic acid respectively. Similar results have also been reported earlier [Bansal et al. (2007)]. It is clear from the above data that the efficiency of Ag/SBA15/Hex catalyst decreases with increase in the size of the ring. This can be explained by fact that due to high ring strain-unstability in cycloheptanol it gets degraded to CO_2 very fast before the cycloalkanone formation can takes place.

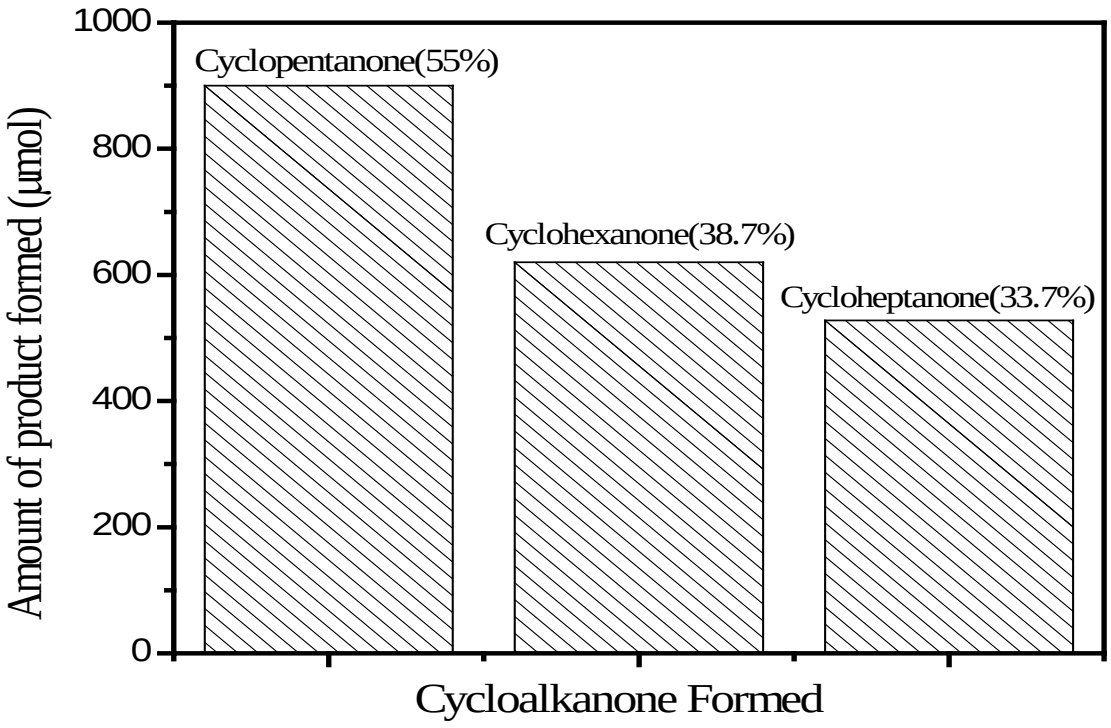

Fig. 9: Conversion (%) of cycloalkanols to corresponding cyaloalkanones

CONCLUSION

Silver nanoparticles impregnated SBA-15 were synthesised by one pot and two step methods through hydrothermal route. The catalytic activity of these prepared materials was assessed by oxidation of cyclohexane. Performance of the Ag/SBA-15/Hex catalyst was found to be better among all the prepared catalysts. This may be due to its preparation by one pot method which has better control over texture properties viz., surface area, pore size etc. of the synthesized material and by the use of hexamine that seem to act as efficient reducing agent. Other reducing agents viz., ascorbic acid and ammonia showed less conversion. Catalysts obtained by two step method viz., Ag/NP-1/SBA-15 and Ag/NP-2/SBA-15 showed less conversion which may be due the poor incorporation of silver nanoparticles into catalytic sites. Due to the better performance of Ag/SBA-15/Hex catalyst, it was also employed for the oxidation of three cycloalkanols viz., cyclopentanol, cyclohexanol and cycloheptanol which gave 55%, 38.7%, and 33.7% into their corresponding cycloalkanones.

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