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Short Communication

Selective benzylic oxidation of alkyl substituted aromatics to ketones over Ag/SBA-15 catalysts

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1. Introduction

Oxidation of benzylic C – H bond into corresponding ketone is one of the important transformations in organic synthesis [1], since, the oxidation products are essential intermediates for the manufacture of high-value fine chemicals, agrochemicals, pharmaceutical and high-tonnage commodity chemicals [2,3]. Generally, benzylic C – H bond oxidations are carried out with a large excess of metal based oxidants such as chromium reagents and manganese reagents [1]. Discharging of toxic metal residues, waste disposal and involvement of tedious workup procedures are the main disadvantages often encountered in the classical benzylic oxidations. At this juncture, development of eco-friendly supported catalysts those can be operated at mild conditions in combination with appropriate stoichiometric oxidant is the subject of interest.

Of late, mesoporous material based supported catalysts have been proven to be the most ideal catalysts because of their high surface area, high porosity, large and uniform channel size etc. [4–8]. These structural and textural characteristics of mesoporous supports provide a consistent and well-isolated environment for the fine deposition of active components and free access to the reactants [4]. Among the mesoporous material based catalysts, SBA-15 supported catalysts are under intensive investigation recently [9–12]. However,

ABSTRACT

Benzylic and cycloalkane C–H bonds have selectively been oxidized into corresponding ketones with t-BuOOH over Ag/SBA-15 catalysts, which were prepared by varying the loading of Ag (2, 4, 6 and 8% by weight) on SBA-15 support using an impregnation method. The retention of mesoporous structural ordering and crystalline behavior of Ag have been confirmed by N₂ adsorption and XRD studies. 4Ag/SBA-15 catalyst is found to be the best catalyst among the Ag/SBA-15 series. The influence of various parameters such as oxidant, solvent, temperature and time of reaction etc. have been systematically studied on Ag/SBA-15 catalyst. © 2012 Elsevier B.V. All rights reserved.

SBA-15 supported silver catalysts for the oxidation of benzylic C–H bonds have not yet been studied. Instead, other supported silver catalysts have been extensively studied as oxidizing catalysts and have been applied industrially to the epoxidation of ethylene [13,14]. It has also been recognized to show high activity in several reactions, such as hydrogenation of unsaturated aldehydes [15], partial oxidation of methanol to formaldehyde [16], and oxidative coupling of methane to ethane and ethylene [17], CO oxidation etc. [18,19].

Being an eco-friendly and high performance catalyst for the benzylic and cycloalkane C– H bonds oxidation, herein, the details of catalyst preparation, characterization and evaluation studies of Ag/SBA-15 has been delineated.

2. Experimental

2.1. Catalyst preparation

The siliceous SBA-15 has been synthesized in accordance with the literature procedures [20]. A solution of $EO_{20}PO_{70}EO_{20}$:2M HCI: TEOS: $H_2O = 2:60:4.25:15$ (mass ratio) was prepared, stirred for 12 h at 40 °C and then hydrothermally treated at 100 °C under static condition for 12 h, subsequently filtered, dried at 100 °C and calcined at 500 °C for 8 h to get the parent SBA-15 mesoporous silica support. The Ag/SBA-15 catalysts with the silver loading of 2, 4, 6 and 8 wt.% were deposited by impregnating the SBA-15 support with an aqueous solution of silver nitrate followed by evaporation to dryness at 100 °C for 12 h, calcination in air at 500 °C for 3 h and reduced at 300 °C in H₂ flow for 1 h.



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Fig. 1. N_2 adsorption-desorption isotherms of Ag/SBA-15 catalysts and their pore size distribution curves as in set.

2.2. Catalyst characterization

 N_2 adsorption–desorption isotherms were recorded for calcined catalysts using an ASAP 2020 V3.01 H adsorption unit (Micromeritics, USA). The X-ray diffraction (XRD) patterns were recorded at room temperature using a Rigaku, Multiflex, diffractometer with a nickel filtered CuK α radiation. Transmission electron microscope (TEM) analysis was made using a Philips Technai G2 FEI F12 at an accelerating voltage of 80–100 kV.

2.3. Evaluation of catalytic activity

The catalytic activity was determined in the liquid phase under solvent free conditions. In a typical experiment, 1 mmol of substrate and 50 mg of catalyst were taken in a 25 ml RB flask and added 3 mmol of aqueous t-BuOOH slowly under constant stirring at 90 °C for 5 h. The influence of solvents on the reaction was also studied taking 2 ml of solvents. The products were identified and analyzed by GCMS–QP-5050 (M/s. Shimadzu Instruments, Japan) with ZB-5 capillary column (25 m × 0.32 mm) supplied by M/s. J & W Scientific, USA. Toluene was used as an external standard for the quantification of the products.



Fig. 2. Low-angle XRD patterns of Ag/SBA-15 catalysts.

Table 1

Textural and structural characteristics of SBA-15 Ag/SBA-15 catalysts derived from $N_{\rm 2}$ adsorption–desorption isotherms and low-angle XRD analysis respectively.

| Catalyst | $\begin{array}{c} S_{BET} \\ (m^2/g)^a \end{array}$ | V _t (cm ³ /g) ^b | D _{BJH} (nm) ^c | d ₁₀₀ (nm) ^d | a ₀ (nm) ^e | t(nm) ^f |
|--|---|---|---------------------------------------|---------------------------------------|--------------------------------------|--------------------------|
| SBA-15 2Ag/SBA-15 4Ag/SBA-15 6Ag/SBA-15 8Ag/SBA-15 | 665 552 534 527 454 | 1.01 0.88 0.83 0.86 0.78 | 5.9 5.8 5.9 6.1 6.2 | 9.7 9.5 9.1 9.7 9.2 | 11.2 11.0 10.5 11.2 10.5 | 7.1 6.9 6.4 7.1 |

^a BET surface area.

^b The total pore volume.

^c BJH average pore diameter.

^d Periodicity of SBA-15 derived from low angle XRD.

The unit cell parameter ($a_0 = 2 d_{100}/\sqrt{3}$).

^f The pore wall thickness ($t = a_0 - D_{BJH}$).

3. Results and discussion 3.1. N₂ adsorption studies

The N₂ adsorption–desorption isotherms for the Ag/SBA-15 catalysts are shown in Fig. 1, which are of type IV adsorption isotherms with a H1 hysteresis loops, according to the IUPAC classification. These adsorption isotherms are having three well-distinguished regions $P/P_0 = 0-0.61$ (monolayer multilayer adsorption), $P/P_0 = 0.61-0.75$ (capillary condensation) and $P/P_0 = 0.75-1.0$ (multilayer adsorption on the external surface). The textural parameters like BET surface area, total pore volume, and average pore diameter determined from the BJH method are displayed in Table 1. There is a diminishing trend both in BET surface area and total pore volume with increase in the loading of Ag in Ag/SBA-15 catalysts series, which are expected due to the agglomeration of Ag particles and thereby partial blockage of pores. The pore size distribution curves are depicted in Fig. 1 as an inset, which are narrowly distributed with the distribution maxima at about 7.1 nm.

3.2. X-ray diffraction analysis

The low-angle X-ray diffraction patterns of Ag/SBA-15 catalysts along with parent siliceous SBA-15 are shown in Fig. 2, which exhibited three typical diffraction lines at $0.91-0.97^{\circ}$, 1.60-1.66 and $1.86-1.92^{\circ}$ respectively on the 2 θ scale that are indexable as (100), (110) and (200) reflections associated with p6mm hexagonal symmetry. The incorporation of the different amounts of Ag on the hexagonally ordered mesoporous SBA-15 did not considerably alter the structural ordering.



Fig. 3. Wide-angle XRD patterns of Ag/SBA-15 catalysts.



Fig. 4. TEM image and Ag particle size distribution (inset) of 4Ag/SBA-15 catalyst.

The wide-angle XRD spectra for the Ag/SBA-15 catalysts are shown in Fig. 3, which reveals that there are four well-distinguished diffraction lines on the 2 θ scale at 38.11, 44.25, 64.46 and 77.35° respectively, these are indexable as (111), (200), (220) and (311), corresponding to cubic Ag metallic (JCPDS No. 4-07830) crystals.

The morphology of Ag nanoparticles (4Ag/SBA-15) obtained from TEM analysis was displayed in Fig. 4, which demonstrates that most of the Ag nanoparticles are in prolate ellipsoidal shape. The others are in the form of spheres, which are lower in number. Due to sequential assemblage of prolate ellipsoidal shaped Ag nanoparticles the rope/wire like morphology was generated. It is evident that nanowires/nonorods of different metal nanoparticles are produced within the hexagonally ordered pores of SBA-15 support [21,22]. In the present study the size of nanoparticles that are seen from TEM image is bigger than that of the pore channels of SBA-15 support. The deposition of certain amount of Ag nanoparticles within the pores of SBA-15 may not be excluded. The histogram shown in Fig. 4 as an inset describes the particle size distribution. According to particle size distribution histogram most of the nanoparticles of Ag deposited on SBA-15 support are in the range of 30–50 nm.

3.3. Oxidation of benzylic C-H bond of ethylbenzene

Initially, the catalytic activity of various Ag/SBA-15 catalysts toward the oxidation of ethylbenzene to acetophenone has been investigated and depicted in Table 2, which reveals that the conversion of ethylbenzene is >90% on all Ag/SBA-15 catalysts series except over 2Ag/SBA-15 catalyst. The lower conversion of 2Ag/SBA-15 catalyst may be due to insufficient amount of Ag. The conversions of ethylbenzene on all the three higher loading catalysts (4Ag/SBA-15, 6Ag/SBA-15 and 8Ag/SBA-15) are more or less equal, but 4Ag/SBA-15 catalyst exhibited superior acetophenone selectivity (99%). The similar kind

Table 2

Effect of Ag loading on the oxidation of ethyl benzene over Ag/SBA-15 catalysts at 90 $^\circ C$ for 5 h using t-BuOOH as oxidant under solvent free conditions.

| Catalyst | Crystallite size (nm) ^a | Conversion (%) | ACP selectivity (%) ^b |
|------------|------------------------------------|----------------|----------------------------------|
| 2Ag/SBA-15 | 39 | 73 | 93 |
| 4Ag/SBA-15 | 37 | 92 | 99 |
| 6Ag/SBA-15 | 57 | 93 | 77 |
| 8Ag/SBA-15 | 65 | 93 | 80 |

^a Determined from Scherrer equation.

^b Acetophenone.

of high selectivity (100%) has also been reported in the biphasic oxidation with perfluoroalkyl phthalocyanine complexes [23]. Compared to 4Ag/SBA-15 catalyst the remaining two higher loading catalysts exhibited lower selectivity toward acetophenone, which may be due to agglomeration of Ag particles. The increased particle size with increase in Ag loading and decreased acetophenone selectivity can be seen from Table 2. In the subsequent study, other reaction parameters were optimized using 4Ag/SBA-15 catalyst.

Wide range of literature reveals that the selective production of acetophenone is a challenge on heterogeneous catalysts. High selectivity towards acetophenone is mainly hindered due to the formation other oxygenates via different oxidation sites depending on the type of catalyst used [24]. The other products that are generally formed from ethylbenzene oxidation are benzaldehyde, benzoic acid, phenylacetic acid, styrene, 1-phenylethane-1,-2-diol *p*-acetophenone, *m*-acetophenone etc. [25,26].

As evidenced from Table 3, the conversion of ethylbenzene and the selectivity of acetophenone are substantially increased with reaction time from 1 to 5 h, whereas the selectivity of 1-phenyl ethanol decreased, which implies that the major product (i.e. acetophenone) has been obtained via 1-phenyl ethanol. The impact of reaction temperature in the oxidation of ethylbenzene can also be seen from Table 3. At room temperature, the conversion of ethylbenzene is around 31%, which has been rose up to 63% when the reaction temperature increased to 60 °C. Surprisingly, the selectivity of acetophenone and 1-phenyl ethanol are in the same molar ratio (71:29) at 25 and 60 °C. Similar trend is observed at lower conversion levels, i.e., at 1 and 2 h reaction time. At 90 °C the conversion has

Table 3

Effect of reaction time and temperature on the oxidation of ethyl benzene over 4Ag/SBA-15 catalysts at 90 $^\circ\text{C}.$

| Reaction time (h) | Conversion (%) | ACP selectivity (%) ^a | PE selectivity $(\%)^{b}$ |
|-------------------|----------------|----------------------------------|---------------------------|
| 1 | 48 | 69 | 31 |
| 2 | 60 | 68 | 32 |
| 3 | 73 | 84 | 16 |
| 4 | 81 | 94 | 6 |
| 5 | 92 | 99 | 1 |
| 5 ^c | 31 | 71 | 29 |
| 5 ^d | 63 | 71 | 29 |

^a ACP = Acetophenone.

^b PE = 1-phenyl ethanol.

^c Reaction at 25 °C.

^d Reaction at 60 °C.

Table 4

Effect of solvent on the oxidation of ethyl benzene over 4Ag/SBA-15 catalysts using 70% t-BuOOH as oxidant at 90 °C.

| Solvent | Conversion (%) | ACP selectivity (%) ^a | PE selectivity $(\%)^{b}$ |
|--------------|----------------|----------------------------------|---------------------------|
| Toluene | 25 | 92 | 8 |
| DMF | 15 | 80 | 20 |
| DMSO | 52 | 77 | 32 |
| Acetonitrile | 85 | 86 | 12 |
| Water | 65 | 89 | 10 |
| DCE | 52 | 62 | 38 |
| No solvent | 92 | 99 | 1 |

^a ACP = Acetophenone.

^b PE = 1-phenyl ethanol.

significantly increased from 63 to 92%, but there is dramatic change in the selectivity ratio (99:1), which reinforces transformation of 1-phenyl ethanol into acetophenone at higher conversion levels.

To optimize the oxidant, different oxidants such as aqueous 30% H₂O₂, urea hydrogen peroxide, NaIO₄, K₂S₂O₈, molecular oxygen and t-BuOOH have been used. When the reaction was conducted using t-BuOOH as oxidant both conversion and selectivity are 92% and 99% respectively, but with other oxidants no appreciable conversion. Hence, t-BuOOH is the most appropriate oxidant among the oxidants used in this study.

The oxidation activity data of 4Ag/SBA-15 catalyst with different solvents is presented in Table 4, which reveals that the catalyst is highly effective under solvent-free conditions rather than with solvents. With all the solvents used the catalyst is active, comparatively acetonitrile seems to be better solvent. Interestingly, even in the water medium, the conversions and selectivities are significantly higher.

3.4. Oxidation of benzylic and cycloalkane C-H bonds

The optimized conditions have been applied for the other substrates and the details are depicted in Table 5. The catalytic activity



Scheme 1. Proposed C-H bond oxidation mechanism in the presence of t-BuOOH.

of 4Ag/SBA-15 towards the oxidation of halogen substituted ethylbenzenes at *p*-position is excellent, but little lower compared to ethylbenzene (entries 2–4). The catalyst exhibited outstanding performance in the case of electron donating group at *p*-position i.e. p-methoxyethylbezene (entry 5), similar trend has already been reported [27]. With increase in annelated aromatic rings, the decrease in activity is observed (entries 1, 7 and 8). In the case of diarylmethylenes like diphenylmethane and fluorine including indane are selectively oxidized at benzylic position with high yields (entries 9–11), which is well matched with the literature [28]. For the oxidation of cycloalkanes the catalyst is not so effective in producing cyclic ketones (entries12–14).

Table 5

Selective oxidation of different benzylic and cycloalkane C-H bonds over 4Ag/SBA-15 catalyst under solvent-free conditions.

| Entry | Substrate | Product | Time (h) | Conversion (%) | Selectivity (%) |
|-------|---------------------------------------|----------------------------|----------|----------------|-----------------|
| 1 | \bigcirc | \sim | 5 | 92 | 99 |
| 2 | CH | ch h | 5 | 88 | 95 |
| 3 | Br | Br | 5 | 87 | 94 |
| 4 | \leftarrow | H H | 5 | 85 | 95 |
| 5 | MeO | Meo | 5 | 97 | 99 |
| 6 | $\bigcirc \frown$ | | 5 | 90 | 93 |
| 7 | \bigcirc | | 7 | 90 | 96 |
| 8 | | m | 24 | 45 | 73 |
| 9 | $\bigcirc \bigcirc \bigcirc$ | | 5 | 95 | 99 |
| 10 | $\bigcirc \bigcirc \bigcirc \bigcirc$ | | 5 | 99 | 96 |
| 11 | $\langle \rangle \rangle$ | \sim | 5 | 99 | 95 |
| 12 | \bigcirc | = 0 | 24 | 43 | 72 |
| 13 | $\overline{\bigcirc}$ | $\bigcirc \circ$ | 24 | 40 | 69 |
| 14 | ŏ | $\tilde{\bigcirc}_{\circ}$ | 24 | 48 | 70 |

Substrate (1 mmol), t-BuOOH (3 mmol), catalyst (50 mg), temperature (90 °C).

The benzylic oxidation of C–H bond into corresponding ketone in the presence t-BuOOH followed the free radical mechanism. To verify this, an experiment was conducted by adding 4-t-butyl catechol to the reaction mixture. Due to addition of a free radical scavenger (4-t-butyl catechol) the conversion of ethylbenzene dropped significantly from 92 to 20%, which provides some information in support of a free radical mechanism for the benzylic C–H bond oxidation. On the basis of published literature [29–31] and the present results a mechanism is proposed as detailed in Scheme 1.

4. Conclusions

Ag/SBA-15 catalysts are proved to be useful eco-friendly catalysts for the oxidation of benzylic and cyclic C-H bond into corresponding ketones with t-BuOOH as an oxidant under solvent-free conditions.

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