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Short Communication

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

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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 $N_2$ 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.


## 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, 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 HCl: 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 $H_2$ flow for 1 h.

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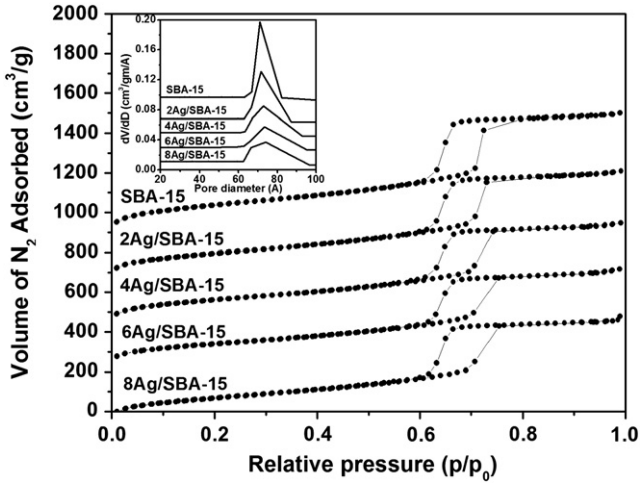


**Fig. 1.** $N_2$ adsorption–desorption isotherms of Ag/SBA-15 catalysts and their pore size distribution curves as in set.

### 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 CuKα 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.

**Table 1**
Textural and structural characteristics of SBA-15 Ag/SBA-15 catalysts derived from $N_2$ adsorption–desorption isotherms and low-angle XRD analysis respectively.

| Catalyst | $S_{BET}$ ($m^2/g$)[a] | $V_t$ ($cm^3/g$)[b] | $D_{BJH}$ (nm)[c] | $d_{100}$ (nm)[d] | $a_0$ (nm)[e] | t(nm)[f] |
|---|---|---|---|---|---|---|
| SBA-15 | 665 | 1.01 | 5.9 | 9.7 | 11.2 | 7.1 |
| 2Ag/SBA-15 | 552 | 0.88 | 5.8 | 9.5 | 11.0 | 6.9 |
| 4Ag/SBA-15 | 534 | 0.83 | 5.9 | 9.1 | 10.5 | 6.4 |
| 6Ag/SBA-15 | 527 | 0.86 | 6.1 | 9.7 | 11.2 | 7.1 |
| 8Ag/SBA-15 | 454 | 0.78 | 6.2 | 9.2 | 10.5 | 6.6 |

[a] BET surface area.
[b] The total pore volume.
[c] BJH average pore diameter.
[d] Periodicity of SBA-15 derived from low angle XRD.
[e] 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. $N_2$ adsorption studies

The $N_2$ 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°, 1.60–1.66 and 1.86–1.92° respectively on the 2θ 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.

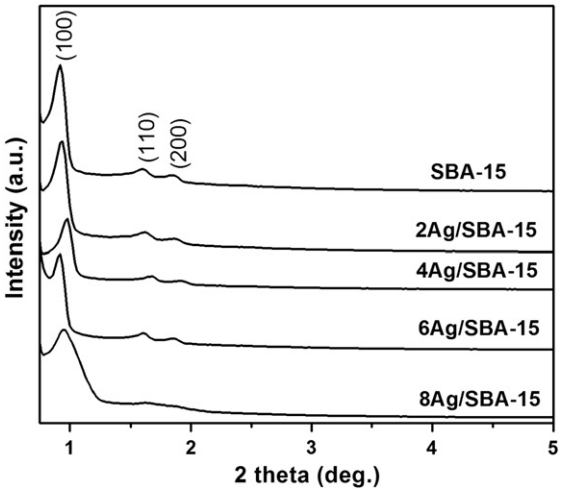


**Fig. 2.** Low-angle XRD patterns of Ag/SBA-15 catalysts.

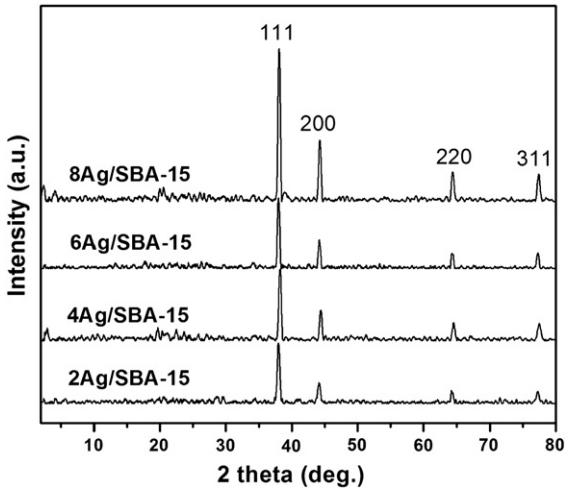


**Fig. 3.** Wide-angle XRD patterns of Ag/SBA-15 catalysts.