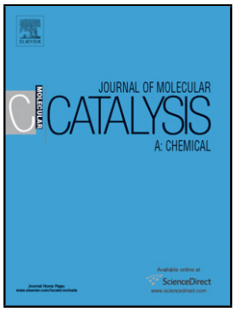

Title: Selective liquid phase oxidation of secondary alcohols into ketones by *tert*-butyl hydroperoxide on nano-fibrous Ag-OMS-2 catalyst

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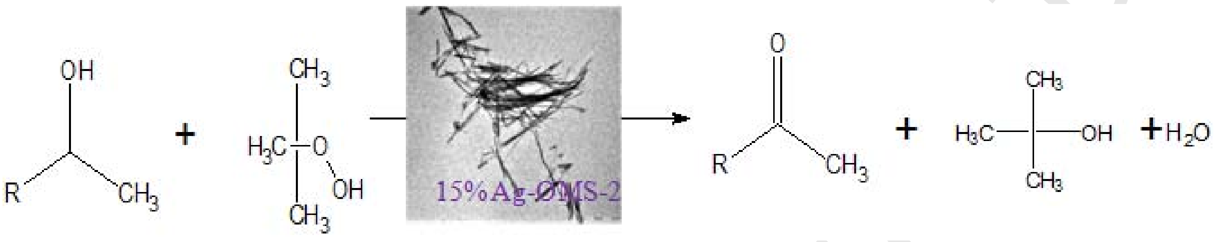
Highlights

- Single step selective oxidation of aliphatic and aromatic alcohol.
- Nano-fibrous 15% w/w Ag-OMS-2 is an efficient and reusable catalyst.
- 100% selectivity for oxidation of secondary alcohol into ketone.
- Various parameters affecting reaction were explored.
- Kinetic modeling and energy of activation is 12.65 kcal/mol.

Graphical abstract:

Selective liquid phase oxidation of secondary alcohols into ketones by *tert*-butyl hydroperoxide on nano-fibrous Ag-OMS-2 catalyst

Ganapati D. Yadav and Akhilesh R. Yadav



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September 9, 2013

Selective liquid phase oxidation of secondary alcohols into ketones by *tert*-butyl hydroperoxide on nano-fibrous Ag-OMS-2 catalyst

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Abstract

Selective oxidation of secondary alcohols to ketones using *tert*-butyl hydroperoxide was accomplished over active and reusable silver incorporated octahedral molecular sieve (Ag-OMS-2) catalyst. Different loadings of Ag (5 – 15 % w/w) were incorporated in OMS-2 by the precipitation method among which 15% w/w Ag-OMS-2 was found to be the best. The catalyst was fully characterized. It possesses nanofibrous crystalline structure with high surface area. Oxidation of 1-phenylethanol, as a model compound, was conducted at 75 °C into acetophenone by *tert*-butyl hydroperoxide over 15% w/w Ag-OMS-2. Effects of various parameters were investigated in detail. A mathematical model is built to interpret the kinetic data and develop mechanism. The reaction is intrinsically kinetically controlled and follows second order kinetics. The modelling will help reactor design and scale-up. As an extension to the studies, oxidation of various aliphatic and aromatic alcohols was studied in the liquid phase over 15%Ag-OMS-2 catalyst under optimized conditions. The catalyst is reusable up-to five runs without any loss in catalytic activity. The results obtained are novel.

Keywords: Oxidation, Secondary Alcohol, Oxidation, Octahedral molecular sieve (OMS-2), Kinetics, Redox catalyst.

1. Introduction

Selective conversion of alcohol into carbonyl compound is one of the most widely studied reactions in synthetic organic chemistry [1]. Aldehydes or ketones, as well as carboxylic acids, find wide applications in a variety of processes and products in the pharmaceutical, agrochemical, vitamin, and perfumery industries [2]. However, oxidations are carried out by using polluting and hazardous oxidising agents leading to high environmental factor (E-factor) and generation of large amounts of toxic waste [3]. Conventionally oxidation is carried out using stoichiometric amount of reagents such as chromic acid, permanganate, and ruthenium or nitrogen oxide with nitric acid, which produces environmentally deleterious heavy metal waste [4-8]. Many halogen-containing oxidising reagents and supported metal ions are reported for the oxidation of various aromatic and aliphatic substrates [9-27]. These methods are beset with several drawbacks such as use of expensive metal catalysts, severe reaction conditions and incompatible oxidising agent [28]. Hence there is tremendous scope to design and develop new catalytic oxidation processes which are safer, greener and economical. Recently Chen et al. [29] have reported advantage of ionic liquid as an additive in carbon nanotube supported palladium catalyzed aerobic oxidation of 1- phenylethanol; however, the reaction was carried out at very high temperature. Efforts are underway in many laboratories to develop novel catalysts which are tolerable to various functional groups and selectively able to oxidize the desired moiety. Selectivity engineering of catalytic process is the need of modern chemical industry to reduce waste minimisation. Yadav and Manyar [30] have reported synthesis, characterization and application of a novel V-OMS-2 based redox catalyst UDCaT-3 in selective oxidation, hydroxylation and hydrogenation reaction including mecapto compounds [31]. Octahedral molecular sieves (OMS) have been reportedly used for dehydration reactions. Further, OMS-2 having 2×2 tunnel structure doped with active metal or combination of metals is recently reported for reduction of acetophenone to 1-phenylethanol by Yadav and Mewada [32]. OMS and Octahedral layered (OL) materials based on porous mixed-valent manganese oxides are potentially useful catalysts due to their unique properties such as excellent semi-conductivity, particle size and porosity [33-35]. Catalytic properties of OMS and OL materials have been ascribed to the redox cycling of different oxidations states of manganese such as Mn^{2+}, Mn^{3+}, and Mn^{4+}. The smaller pore opening is possibly is responsible higher stability of OMS-2. It is reported that OMS-2 has better stability than OMS-1 materials [36]. The occurrence of counter cations such as alkali and alkaline earth metals and water is shown to be the cause for the stability and charge balance on structure of OMS-2. Inclusion of metals in the tunnel structure leads to increase in defects inside the catalyst surface thereby creating more number of active sites [30, 32, 37]. Our laboratory has reported hydrogenolysis of glycerol to 1, 2-propanediol over 30% w/wAg-OMS-2 as an excellent catalyst [38]. Selective hydrogenation of nitrobenzene to azobenzene over nano-fibrous Ag-OMS-2 is also reported [39]. Recently application of costly gold nanoparticle and N-hydroxyphthaliminde in ionic liquid was reported, which involves formation of undesired products and long reaction time [40].

The current work describes the use of nano-fibrous Ag-OMS-2 as the catalyst for the oxidation of various secondary aliphatic and aromatic alcohols to ketones. We have carried out both batch and continuous mode of operations to determine stability of the catalyst. Different loadings of Ag on OMS-2 were incorporated by the precipitation method. This paper reports a comprehensive account of this catalytic process.

2. Experimental Section

2.1. Chemicals. All chemicals were procured from reputed firms and used without further purification. 1-Phenylethanol, benzhydrol, 2-hydroxy-1-phenylethanol, 4-hydroxy-1-phenylethanol, 4-methoxy1-phenylethanol, 4-chloro-1-phenylethanol, 3-methyl-1-phenylethanol, potassium permanganate, silver nitrate, 2-propanol and nitric acid (70% w/v) were purchased from M/s s. d. Fine Chem Ltd., Mumbai, India.

2.2. Catalyst Synthesis.

Ag doped manganese oxide octahedral molecular sieves (OMS-2) was synthesized by precipitation method as follows [13]. Manganese acetate (21.0 g) was dissolved in 67.5 cm^3 deionised water and then concentrated nitric acid was added. Silver nitrate (9.97 g) was dissolved in 50 cm^3 distilled water and added to acidic manganese acetate at 30 ^oC. $KMnO_4$ (13.3 g) was taken in 275 cm^3 distilled water and added to the above solution dropwise at 70 °C and the black precipitate so obtained was agitated and refluxed at 100 °C for 24 h. The precipitate was washed several times with deionised water to pH of 7. The resulting material was filtered and dried at 120 °C for 12 h to obtain 15% w/w Ag-OMS-2 [32, 37, 38]. These catalysts have typical cryptomelane structure with a one-dimensional 2 × 2 channel structure.

2.3. Experimental Setup

All experiments were conducted in 50 cm^3 glass reactor. A four bladed –pitched turbine impeller was used for reaction. The temperature was maintained at the selected value. Weighed quantities of reactants and catalyst were charged to the reactor and then the temperature raised to the desired value. Thereafter the agitation was commenced. An initial sample was taken and further sampling was done periodically up to 4 h. A standard experiment was performed with 0.01 mol

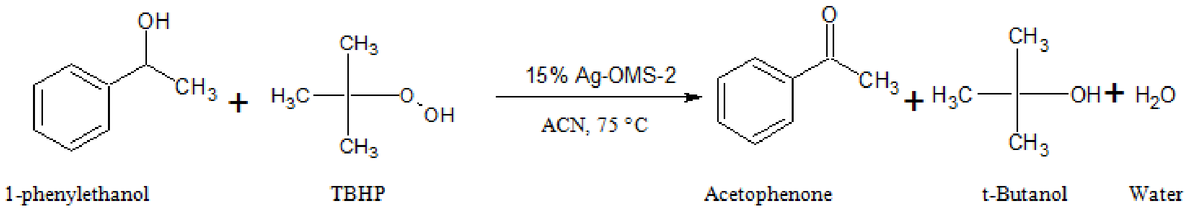
1-phenylethanol, 0.03 mol TBHP and catalyst quantity of 0.012 g/ cm^3. The temperature was normally maintained at 75 °C at 900 rpm as speed of agitation. The total volume of liquid phase was 15.0 cm^3 in which 0.2 cm^3 n-decane was used as internal standard. At the end of experiment, the catalyst was filtered and the organic layer was concentrated and purified by column chromatography.

2.5. Method of Analysis.

Clear liquid samples of reaction mass were analysed by GC (Chemito, model 1000) using FID and a capillary wax column BP-20 (0.25 mm diameter and 30 m length). The product was confirmed by GC–MS (Perkin Elmer instrument, Clarus 500) with BP-1 capillary column (0.25 mm i.d., 30 m length) and EI mode of MS. The injector and detector temperatures were maintained at 220 °C. The oven temperature was programmed from 90 °C to 220 °C, with a ramp rate of 15 °C/min. Nitrogen was employed as the carrier gas at a flow rate of 0.5 cm^3/s. The quantification of data was based on the disappearance of the limiting reactant. The products were also confirmed by GC-MS.

2.6. Reaction scheme: Oxidation of 1-phenylethanol using 15%Ag-OMS-2 is given by Scheme 1. In this reaction 1-butanol is the co-product along with water. The alcohol can be recycled.

Scheme 1. Oxidation of 1-phenylethanol with TBHP over Ag-OMS-2



3. Results and Discussion

3.1. Catalysts characterization

Ag-OMS-2 was characterized by various techniques such as SEM, TEM, ammonia-TPD, XRD, BET surface area, FTIR and elemental analysis and more details have been published recently by our group [32, 37, 38]. Only a few prominent features are presented here to put the current studies in perspective.

The catalyst was nano-fibrous and nano-crystalline as revealed by SEM (Fig. 1) and TEM (Fig. 2). The TEM also showed a fibrous nano-rod shaped structure.

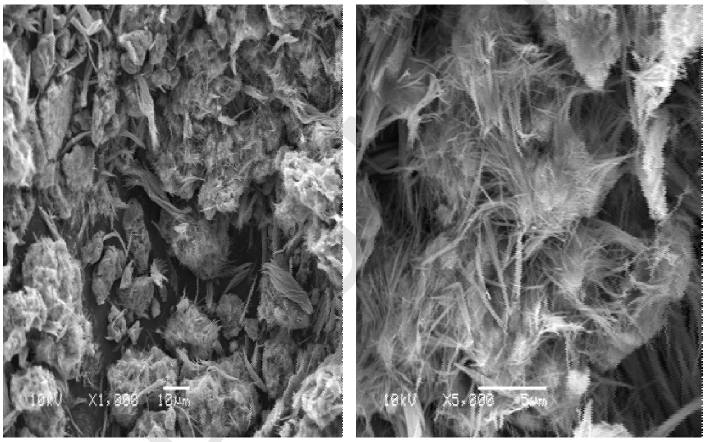


Fig. 1. SEM of catalyst 15%Ag-OMS-2

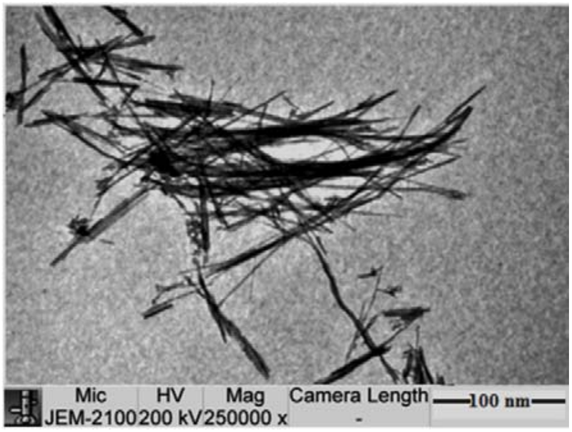


Fig. 2. TEM of catalyst 15%Ag-OMS-2

Replacement of K ions with metal ions Ag inside the tunnel framework is confirmed by EDX [32, 37]. The difference in physical and chemical properties of metal cation dopants was responsible for their content in OMS structure during synthesis. As a consequence, all metal cations have variations in their theoretical and actual compositions. For 15 % w/w Ag-OMS-2 synthesis, almost 15% Ag ions were retained in the catalyst. The size of Ag^+, which is smaller than K^+, is favorable to fit into the 4.6 A° tunnel of OMS-2 and also more surface area than parent OMS-2. TPD analysis of 15% w/w Ag-OMS-2 with ammonia and carbon dioxide as probe molecule confirmed the existence of mild acidic and basic sites [32, 37, 38]. Incorporation of silver into OMS-2 resulted in strong interaction of silver with OMS surface leading to a drastic decrease in reduction temperature from 280 °C of K-OMS-2 to 162 °C for 15% w/w Ag-OMS-2, which was revealed by TPR. The XRD of K-OMS-2 and Ag-OMS-2 had revealed well crystalline structure characteristic of octahedral molecular sieve material and the reflections and 2θ values obtained were characteristic of 2 × 2 tunnel structured manganese oxide phase (KMn_8O_{16}, JCPDS 34-168) [32, 37]. The crystal domain size of cryptomelane phase derived from the XRD peaks broadening was 20 nm [32, 37]. FT-IR studies showed OMS-2 structure was intact after inclusion of metal in the tunnel framework [32]. The BET surface area, pore volume and pore diameter for 15% w/w Ag-OMS-2 is much better than OMS-2. A surface area 118.8 m^2/g was obtained for 15% w/w Ag-OMS-2 as compared to 89.1 m^2/g of OMS-2 [32, 37, 38]. The adsorption-desorption isotherm was type III isotherm, suggesting a porous structure. Such type of adsorption occurs in cases where heats of adsorption are lower than the adsorbate heat of liquefaction.

3.2. Effect of oxidant

The rate of activation of reactant is governed by the nature of catalyst, oxidizing agent, and temperature. The effect of various oxidants on liquid phase oxidation of 1-phenylethanol, the model compound, was conducted at 75 °C. In this case, neither hydrogen peroxide nor air was found to be suitable as oxidising agent, with no conversion, whereas *tert*-butyl hydroperoxide (TBHP) was effective. A control experiment was also performed in the absence of catalyst to ascertain that the reaction did not proceed without catalyst.

3.3. Activity of Various Catalysts

The efficacies of UDCaT-3 and different Ag-OMS-2 are shown in Fig. 3. It is evident that

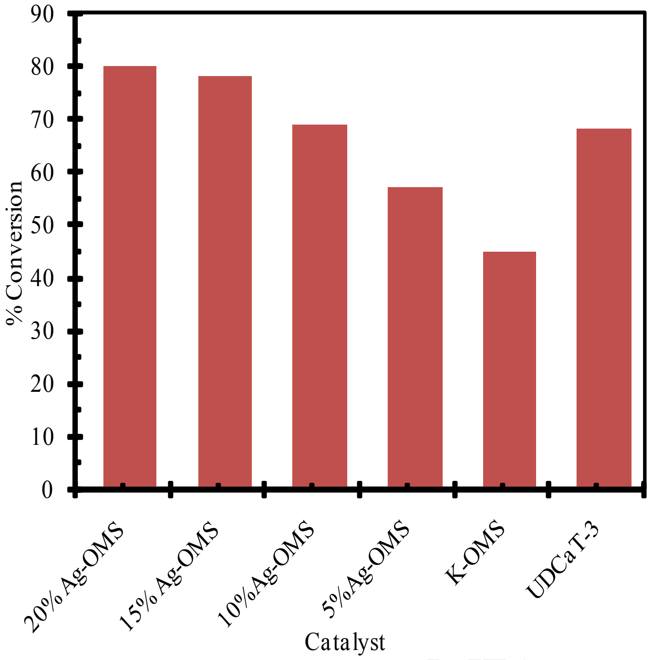


Fig. 3. Efficacy of various catalysts.

Reaction conditions: 1-Phenylethanol-0.01 mol, TBHP-0.03 mol, Catalyst loading: 0.012 g/cm^3, Speed of agitation-900 rpm, Temperature -75 °C, solvent-Acetonitrile.

incorporation of silver inside the framework of the catalyst enhances the activity of catalyst considerably. Mesoporous redox catalyst UDCaT-3 [30,31] lead to good conversion. A conversion of 45% was achieved in case of K-OMS, which is OMS-2, whereas with increasing Ag content in the OMS-2, there was increase in conversion and yield. There is a synergistic effect of silver in presence of manganese and potassium ions in the catalyst. The further increase in loading of silver ion does not so any significant difference in the conversion of oxidation reaction. Hence further reactions were performed with 15%Ag-OMS-2.

3.4. Effect of various solvents

The effect of solvents in the liquid phase oxidation of secondary alcohol using TBHP as oxidant is given in Fig. 4. Solvents such as acetonitrile, toluene, dioxane, DMF and DMSO were

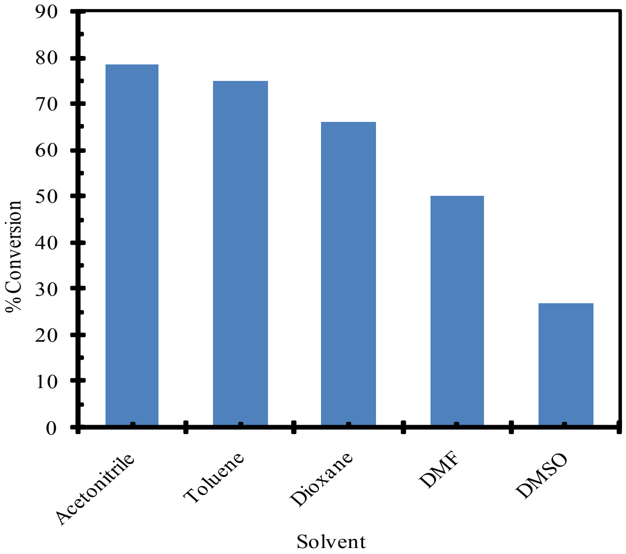


Fig. 4. Effect of solvent

Reaction conditions: 1-Phenylethanol-0.01 mol, TBHP-0.03 mol, Catalyst loading- 0.012 g/cm^3, Speed of agitation-900 rpm, Temperature -75 °C.

screened for the reaction. In case of non-polar solvent like toluene, 75% conversion was achieved, on the other hand, in polar aprotic solvents such as DMF and DMSO conversion of 50% and 27% was obtained, respectively. Acetonitrile was the best solvent under optimized reaction conditions; the results obtained were in accordance with the literature reports on use of acetonitrile.

3.5. Effect of Speed of Agitation

Fig. 5 depicts the effect of speed of agitation on conversion from 700 rpm to 1100 rpm at 75 °C at the catalyst loading of 0.012 g/cm^3 (Fig. 5).

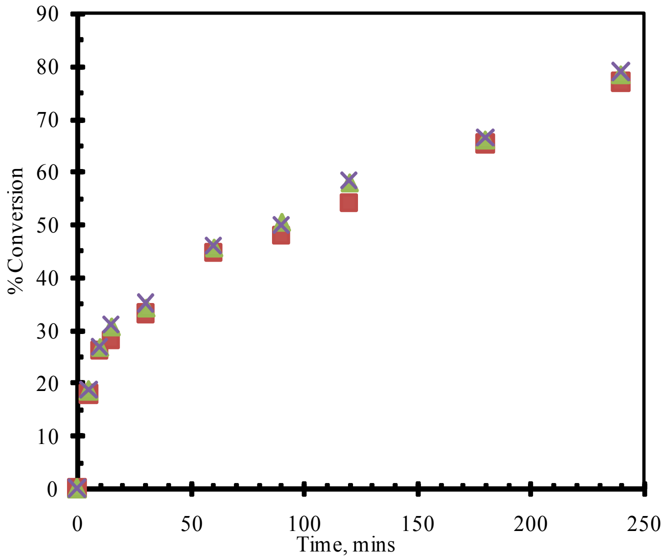


Fig. 5. Effect of speed of agitation

Reaction conditions: 1-Phenylethanol-0.01 mol, TBHP-0.03 mol, Catalyst loading - 0.012 g/cm^3, Temperature -75 °C, solvent-Acetonitrile. (■ 700rpm, ▲ 900rpm, +1100rpm)

In the range of 900 to 1100 rpm, the conversion was practically the same. Thus, the external resistance to mass transfer was absent beyond 900 rpm. However, to avoid catalyst abrasion and to ensure complete absence of mass transfer resistance, 900 rpm was used as minimum speed in further runs.

3.6. Effect of Catalyst loading

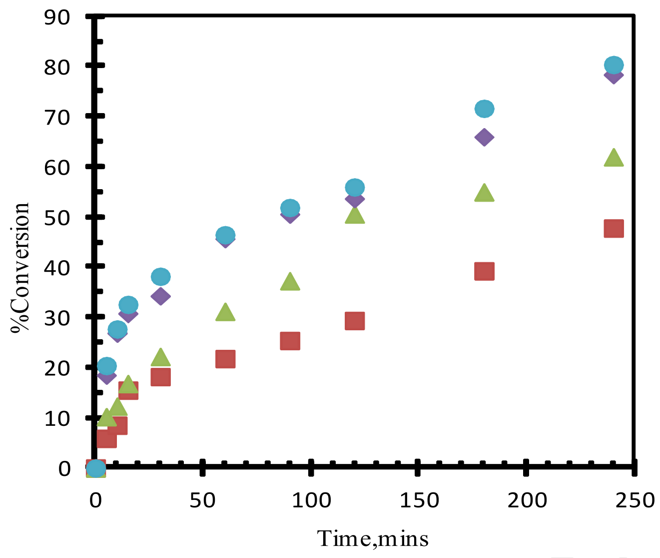


Fig. 6. Effect of catalyst loading

Reaction conditions: 1-Phenylethanol-0.01 mol, TBHP-0.03 mol, Speed of agitation-900 rpm, Temperature -75 °C, solvent-Acetonitrile. (■ 0.006g/ cm^3, ▲ 0.008g/ cm^3, ● 0.012g/ cm^3, ◆ 0.015g/ cm^3)

a mole ratio of 1-phenylethanol to TBHP of 1:3 (Fig. 6). Both conversion and rate of reaction increased up to 0.012 g/cm^3 with increase in catalyst loading due to the corresponding increase in active sites. The conversion and rate of reaction were nearly identical at 0.012 g/cm^3 and 0.015g/cm^3. It would suggest that the number of catalyst sites at catalyst loading of 0.015 g/cm^{3}was greater than that required by the reacting species. Theoretical calculations using Wiesz-Prater criterion were also done to show absence of intra-particle resistance [41].

3.7. Effect of mole ratio

The mole ratio of 1-phenylethanol to TBHP was changed from 1:1 to 1:3 with a catalyst loading of 0.012 g/cm^3 at 75 °C (Fig. 7**)**. The initial rate of the reaction increased with increase in mole

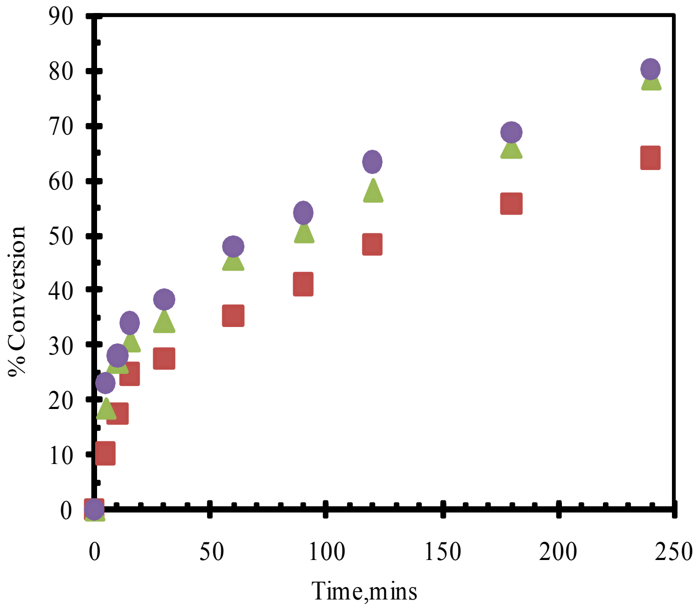


Fig. 7. Effect of mole ratio

Reaction conditions: 1-Phenylethanol: TBHP, Catalyst loading-0.012 g/cm^3, Speed of agitation-900 rpm, Temperature -75 °C, solvent-Acetonitrile. (■1:01, ▲1:02, ●1:03)

ratio. It can be concluded that there was not much difference in the conversions between mole ratios of 1:2 to 1:3. Therefore next set of reactions were conducted at a mole ratio of 1:3 of 1-phenylethanol to TBHP.

3.8. Effect of Temperature

The temperature effect on conversion and rate was studied from 65 °C to 80 °C (Fig. 8). With an

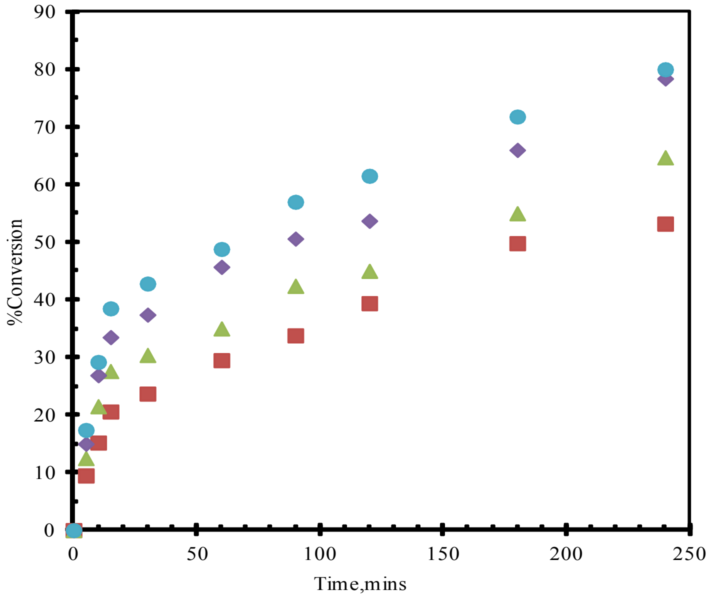


Fig. 8. Effect of temperature

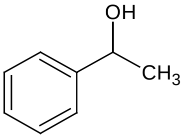
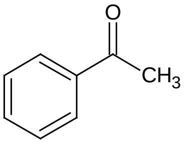
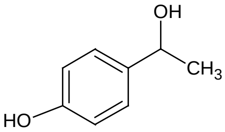
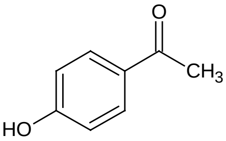
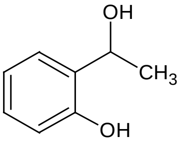
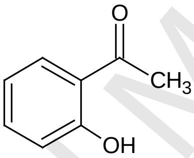
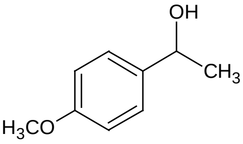
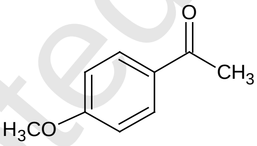
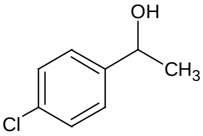
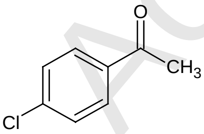
Reaction conditions: 1-Phenylethanol-0.01 mol, TBHP-0.03 mol, Catalyst loading 0.012 g/cm^3, Speed of agitation-900 rpm, solvent-Acetonitrile. (■65°C, ▲70°C, ◆75°C, ● 80°C)

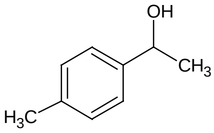
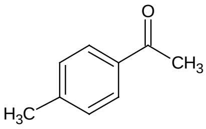
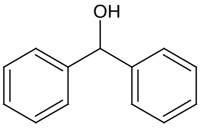
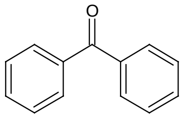
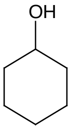
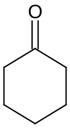
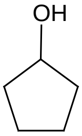
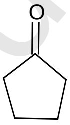
increase in temperature the rate of reaction and conversion increased significantly, which indicated that reaction was intrinsically kinetically controlled. This would be discussed later.

3.9. Substrate study

To explore the scope and generality of the developed protocol for the oxidation of secondary alcohols using nano-fibrous 15% w/w Ag-OMS-2, oxidation of various alcohols was studied at the same conditions (Table 1). Cyclic alcohols like cyclohexanol and cyclopentanol are efficiently oxidized with conversions of 90 % and 85 %, respectively. Good results were obtained for the

Table 1. Effect of various substrates

Entry	Alcohol	Ketone	Conversion %	Yield %
1.				
		78.9	71.5	
2.			82	69
3.			78	70
4.			85	74
5.				
		75	61	

6.			80	73
7.			80	67
8.			90	82
9.			89.2	80

Reaction Conditions: Alcohol-0.01 mol, TBHP-0.03 mol, Catalyst loading 0.012 g/cm^3, Speed of agitation-900 rpm, Temperature -75 °C, solvent-Acetonitrile. All products were confirmed by GC-MS

oxidation of substituted 1-phenylethanol. It should be recognized that temperature plays a very important role and higher conversions could be obtained at higher temperatures for less reacting molecules. The purpose here was to use the same reaction conditions to understand their reactivity. Selectivity is 100% for the oxidation of secondary alcohols because even though conversion is low, no other product except ketone was observed. Other groups present in the moiety such as phenolic –OH (entry 2 and 4), methyl (entry 6) and methylene (entry 8 and 9) are unaffected under the mild set of conditions used here.

3.10. Development of mechanistic model and kinetics of the reaction

The reaction of 1-phenylethanol with TBHP in presence of 15% Ag-OMS-2 gives acetophenone at 75 °C. It is assumed that reaction follows Langmuir-Hinshelwood-Hougen-Watson (LHHW) type mechanism with participation of two sites. Both reacting molecules are adsorbed on active sites and undergo surface reaction to produce acetophenone, tert-butanol and water. The concentration-time profiles of reactants and products confirmed that reactant and products are weakly adsorbed on the surface and get desorbed very fast. Thus, surface reaction of adsorbed species could control the overall rate of reaction.

Adsorption of 1-phenylethanol (A) on a vacant site S is given by

$$A+S \underset{K_A^{'}}{\overset{K_A}{\longleftrightarrow}} AS \qquad (1)$$

Adsorption of TBHP (B) on vacant site S

$$B+S \underset{K_B^{'}}{\overset{K_B}{\longleftrightarrow}} BS \qquad (2)$$

Surface reaction between AS and BS, in the vicinity of the active site, leading to formation of product “acetophenone (C), tert-Butanol (D), and water (W)” as follows

$$AS+BS+S \xrightarrow{k_2} CS+DS+WS \qquad (3)$$

Desorption of products from the surface of catalyst:

$$CS \xleftrightarrow{1/k_C} C + S \tag{4}$$

$$DS \xleftrightarrow{1/k_D} D + S \tag{5}$$

$$WS \xleftrightarrow{1/k_W} W + S \tag{6}$$

The total concentration of sites, C_t given by

$$C_t = C_S + C_{AS} + C_{BS} + C_{CS} + C_{DS} + C_{WS} \tag{7}$$

$$C_t = C_S + K_A C_A C_S + K_B C_B C_S + K_C C_C C_S + K_D C_D C_S + K_W C_W C_S \tag{8}$$

Therefore concentration of vacant site is given by

$$C_S = \frac{C_t}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D + K_W C_W)} \tag{9}$$

If equation (3) controls the rate of reaction, then the rate of reaction of A is given by

$$r_A = -\frac{dC_A}{dt} = k_2 C_{AS} C_{BS} C_S \tag{10}$$

$$r_A = -\frac{dC_A}{dt} = k_2 K_A K_B C_A C_B C_S^3 \tag{11}$$

After substituting the value of C_S from equation (9) we get

$$-\frac{dC_A}{dt} = \frac{k_2 K_A K_B C_A C_B C_t^3}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D + K_W C_W)^3} \tag{12}$$

When the reaction is far away from the equilibrium

$$-\frac{dC_A}{dt}=\frac{k_2K_AK_BC_AC_BC_t^3}{(1+\sum K_iC_i)^3} \tag{13}$$

$$-\frac{dC_A}{dt}=\frac{k_{R_2}wC_AC_B}{(1+\sum K_iC_i)^3} \tag{14}$$

Where $k_{R_2}w=k_2K_AK_BC_t^3$ and w is catalyst loading.

If adsorption and desorption of the species are very weak and values of equilibrium constants are very small then above equation can be given as

$$\frac{dC_A}{dt}=k_{R_2}wC_AC_B \tag{15}$$

Let $C_{B_0}/C_{A_0}=M$, the molar ratio of 1-phenylethanol at t=0. Then the above equation

$$\frac{dX_A}{dt}=k_{R_2}wC_{Ao}\left(1-X_A\right)\left(M-X_A\right) \tag{16}$$

$$\frac{dX_A}{dt}=k_1C_{Ao}\left(1-X_A\right)\left(M-X_B\right) \tag{17}$$

Integrating above equation

$$\ln\left\{\left(\frac{M-X_A}{M\left(1-X_A\right)}\right)\right\}=k_1C_{Ao}\left(M-1\right)t \tag{18}$$

The plot of $\ln\left\{\frac{\left(M-X_A\right)}{M\left(1-X_A\right)}\right\}$ against t was made at different temperature to get an excellent fit, thereby supporting the model (Fig. 9).

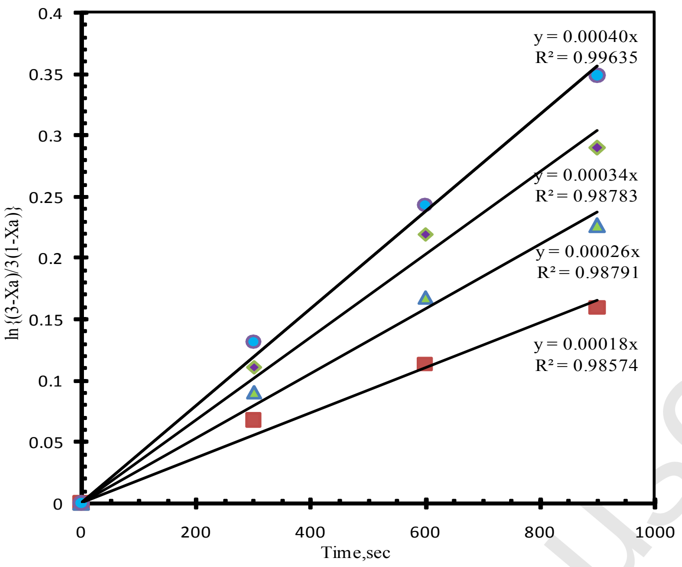


Fig. 9. Kinetic plot of ln{(3-X_a)/3(1-X_a)} Vs time

Reaction conditions: 1-Phenylethanol-0.01 mol, TBHP-0.03 mol, Catalyst loading 0.012 g/cm^3, Speed of agitation-900 rpm, solvent-Acetonitrile. (■ 65 °C, ▲ 70 °C, ◆ 75 °C, ● 80 °C)

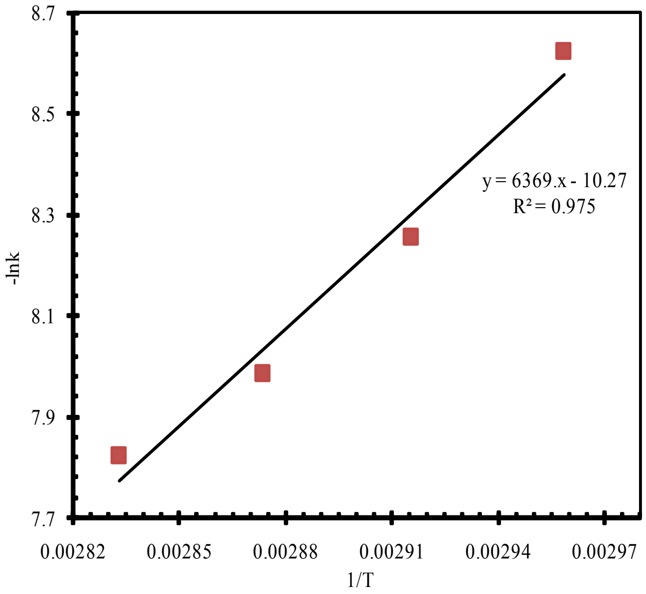


Fig. 10. Arrhenius plot (–lnk Vs. 1/T)

This is an overall second order reaction. Energy of activation was calculated by plotting Arrhenius plot as 12.65 kcal/mol for oxidation of 1-phenylethanol (Fig. 10).

3.11. Reusability of Catalyst

The reusability of 15% w/w Ag-OMS-2 was tested by conducting 6 runs. After each run the catalyst was filtered and refluxed with 50 cm^3 of acetonitrile in order to remove any adsorbed material from the catalyst surface, then it was dried in an oven at 120 ºC for 2 h. In a typical batch reaction, there was an inevitable loss of particles during filtration due to attrition. The catalyst was reused without any make up quantity and the experiments were done under otherwise similar conditions. The volume of reaction mixture was adjusted to make the catalyst loading of 0.012 g/cm^3. It was observed that there is only no decrease in the conversion (Fig. 11). Thus, the catalyst was active and reusable even after six runs for the liquid phase oxidation of secondary alcohols.

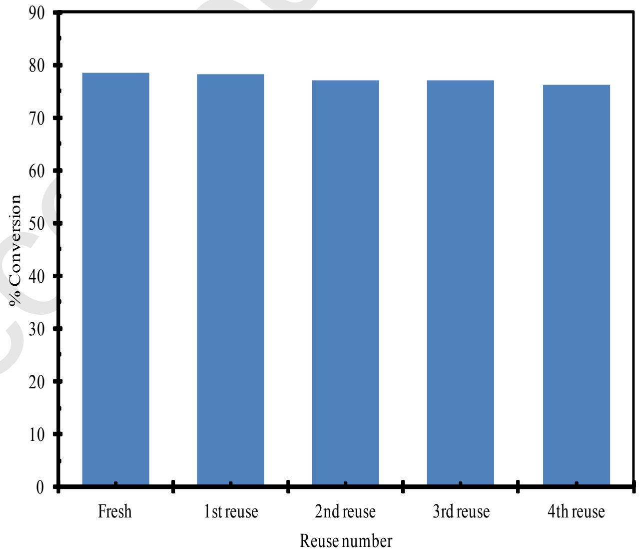


Fig. 11. Reusability of Catalyst

Reaction conditions: 1-Phenylethanol-0.01 mol, TBHP-0.03 mol, Catalyst loading 0.012 g/cm^3, Speed of agitation-900 rpm, Temperature -75 °C, solvent-Acetonitrile, Internal standard-n-Decane-200 μL.

4. Conclusion

The liquid phase oxidation of various secondary alcohols was carried out using Ag-OMS-2 at 75 °C with catalyst loading of 0.012 g/cm^3. TBHP was the most effective oxidising agent. Addition of silver ion from 5 to 15wt% in the pores of K-OMS significantly improves the redox property of catalyst and 15% w/w Ag-OMS-2 was the most active and selective catalyst. The synergistic effect among Ag, Mn and K ions was responsible for the enhancement in the activity of catalyst. Various parameters affecting the rate of reaction and conversion were discussed in detail. It was found that a mole ratio of 1:3 of alcohol to TBHP, speed of agitation 900 rpm, catalyst loading of 0.012 g/cm^3, and temperature of 75 °C in acetonitrile were the best conditions to get good activity of catalyst. Increase in temperature can be beneficial for oxidation of the least reactive alcohol since it can provide sufficient energy for higher conversion and rate. A detailed kinetic study was carried out, which indicates that reaction follows Langmuir-Hinshelwood-Hougen-Watson type of model with weak adsorption of all species. The energy of activation was found to be 12.65 kcal/mol for 1-phenylethanol. The optimized conditions were very effective for oxidation of various alcohols. So the catalyst is tolerable to various functional groups present in the molecule and has given well to excellent conversion for the oxidation reaction.

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Conflict of interest

The authors declare no conflict of interest.

Nomenclature

A	reactant species A, 1-phenylethanol
B	reactant species B, TBHP
C	acetophenone
D	t-butanol
AS	chemisorbed 1-phenylethanol
BS	chemisorbed TBHP
CS	chemisorbed acetophenone
DS	chemisorbed t-butanol
WS	product species D, product
W	product species W, water
S	vacant site
C_A	concentration of A in (mol/cm^3)
C_{Ao}	initial concentration of A in bulk liquid phase, (mol/cm^3)
C_{AS}	concentration of A at catalyst surface, (mol/cm^3)

C_B	concentration of B, (mol/cm^3)
C_{Bo}	initial concentration of B in bulk liquid phase, (mol/cm^3)
C_{BS}	concentration of B at solid surface, (mol/cm^3)
C_D	concentration of D, (mol/cm^3)
C_{CS}	concentration of C at solid surface, (mol/cm^3)
C_{DS}	concentration of D at solid surface, (mol/cm^3)
C_{WS}	concentration of W at solid surface, (mol/cm^3)
Cs	concentration of vacant sites, (mol/cm^3)
C_T	total concentration of sites, (mol/cm^3)
k_{R2}	reaction rate constant, cm^{6}gmol^{-1}s^{-1}
K_i	adsorption equilibrium constant for species i, cm^3/mol
w	catalyst loading g/cm^3 of the liquid volume
X_A	fractional conversion of A
$-r_A$	rate of surface reaction, g mol cm^{-3} s^{-1}
k_{R1}	second order surface reaction constants
K_A , K_B	Equilibrium constant for adsorption of A and B on catalyst surface (mol^{-1} min^{-1})
K_C, K_D, K_W	Equilibrium constant for adsorption of C, D, W on catalyst surface (mol^{-1} min^{-1})

S	Vacant site
X_A	Fractional conversion of A

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