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Short communication

Fabrication of Ag/WO₃ nanobars for Baeyer–Villiger oxidation using hydrogen peroxide



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1. Introduction

In the year 1899, Adolf Baeyer and Victor Villiger reported the oxidation of menthone to its corresponding lactone using Caro's acid [1]. Since then, Baeyer–Villiger (BV) oxidation has become one of the most potential reactions in organic synthesis, since valuable lactones or esters can be obtained directly from the corresponding ketones [2]. Generally, percarboxylic acids (i.e., meta-chloroperbenzoic acid, peracetic acid, etc.) are used for BV oxidation [2]. However, the use of percarboxylic acid or its salt as waste. Moreover, percarboxylic acids are expensive and/or shock-sensitive. In contrast, the use of H₂O₂ as oxidant bears some superiority in comparison to the per-acids [3]; thus, many researchers came forward to replace percarboxylic acids with aqueous H₂O₂ in BV oxidation reactions [4].

One-dimensional nanomaterials are currently of potential interest for the specific physical properties that they display compared to their bulk counterparts owing to the inherently rich in coordinatively unsaturated sites that can play an active role in catalytic reactions [5]. Recently we have developed Ag/WO₃ based 1D nanostructures to carry out some very important oxidation reactions like oxidation of propylene to propene-oxide [6], toluene to benzaldehyde [7] cyclohexene to adipic acid [8] and styrene to styrene oxide [9]. However, in one of our recent publications, we demonstrated that a phenomenon called "crystal-splitting mechanism" plays a key role in determining the morphology as well as the reactivity of the Ag/WO₃ catalyst [10]. Being inspired by our previous reports, we came forward to synthesize one-dimensional

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ABSTRACT

We report the preparation of Ag/WO₃ nanobars, mediated by cationic surfactant CTAB through hydrothermal route. XRD revealed the formation of metallic Ag supported on monoclinic WO₃ phase and TEM diagram showed the formation of bar-like structure, where supported Ag nanoparticles are in the range between 2 and 7 nm. The catalyst exhibited high activity for selective oxidation of cyclohexanone to caprolactone with H₂O₂. A cyclohexanone conversion of 97% with 99% caprolactone selectivity was achieved over this catalyst at 80 °C temperature. Moreover, the catalyst did not show any significant activity loss even after 5 reuses and proved its efficiency in the oxidation of other cycloalkanones also.

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Ag/WO₃ catalyst, which would be capable to display called "crystal-splitting mechanism" parameter; and we successfully prepared Ag/WO₃ nanobar catalyst, which is highly active in BV oxidation reaction. Herein, we report 97% conversion of cyclohexanone to caprolactone with 99% selectivity at 80 °C with H₂O₂ as oxidant, over Ag/WO₃ nano-bar catalyst.

2. Experimental

2.1. Preparation of the catalyst

The Ag/WO₃ nano-composite was synthesized modifying our own preparation method [6–10,11]. In a typical procedure, 9.8 g tungsten (VI) ethoxide (Alfa Aesar) and 0.40 g AgNO₃ (Sigma Aldrich) were dissolved in deionized water. Then the solution was made basic using NH₄OH solution followed by addition of 0.84 g CTAB. After the solution has been stirred for half an hour, aqueous hydrazine solution was added to it. All the reagents were added maintaining the molar ratio: Ag:CTAB:H₂O:N₂H₄ = 1:1:300:1. The resulting precursor solution was undergone hydrothermal treatment (180 °C for 4 h). After cooling naturally to room temperature, the white products were collected and dried at 100 °C for overnight. Finally, the sample was undergone calcinations under argon atmosphere at 500 °C for 6 h.

2.2. Reaction setup

Liquid phase oxidation reaction was carried out in a two-neck round bottom flask. The reaction temperature was ranged between RT and 100 °C. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis using a syringe. At the end of



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the reaction, the catalyst was separated by filtration and the products were analyzed by GC (FID) and GCMS.

3. Results and discussion

3.1. Catalyst characterization

The Ag/WO₃ nanocomposite was characterized by various techniques. The X-ray diffraction (XRD) pattern of the Ag-W catalyst (Fig. 1) showed the peaks at 2θ values of 23.1° , 23.7° , 24.4° , 33.3° and 34.0°, confirms the formation of monoclinic WO₃ (JCPDS No. 43-1035, space group: P21/n) (Fig. 1). The very small peaks at 2θ values at 44.5° and 64.3° correspond to metallic Ag crystal faces (200) and (220) respectively [JCPDS no. 04-0783]. No other peak due to other phase of tungsten-oxide was observed. After reaction, the oxidation state of metallic silver Ag(0), remained intact, which is confirmed from the XRD (Fig. 1b). X-ray photoelectron spectroscopy (XPS) analyses confirmed the presence of metallic silver in the fresh sample from the corresponding Ag 3d_{5/2} and Ag 3d_{3/2} binding energy values of 368.2 eV and 374.2 eV respectively (Fig. S1, Supporting Information) [6-11,12]. The W $4f_{5/2}$ and $4f_{7/2}$ spectra attributed to the binding energies 37.9 eV and 35.8 eV respectively suggesting that the tungsten in the tungsten oxide sample exists as W^{+6} (Fig. S2, Supporting Information) [6–11,13].

For further investigation of the surface property and to detect subtle phase information of the composite, Raman (Fig. 2) and FTIR (Fig. S5, Supporting Information) analyses were conducted. Generally, the 950–1050 cm⁻¹ Raman wave numbers of the transition metal oxide are assigned to be the symmetric stretching modes of metal and oxygen bonds [short terminal W = 0, $v_s(W = 0)$ terminal bands], and 750–950 cm^{-1} bands were either the antisymmetric stretching of W–O–W bonds $[v_s(W–O–W)]$ or symmetric stretching of –O–W– O- bonds $[v_s(-O-W-O-)]$ [14]. The Raman spectrum of the Ag/WO₃ NP catalyst detected vibrational peaks at 808, 724, 330, 300, 274, 136, 86 and 60 cm⁻¹. The two main intense peaks at 808 and 724 cm⁻¹, and the shoulder at 686 cm⁻¹, are typical Raman peaks of crystalline WO₃, which correspond to the stretching and bending vibrations of the bridging tungsten and oxygen atoms [15]. They are assigned to be the W–O stretching (υ), W–O bending (δ) and O–W–O deformation (γ) modes, respectively. Two peaks at 326 and 274 cm⁻¹ are assigned to be the bending $\delta(O-W-O)$ vibrations [14]. Those below 200 cm⁻¹ modes were attributed to the lattice vibrations [14]. After the reaction, the Raman spectrum of the spent catalyst was unchanged (Fig. 2b), reflected the structural stability of the catalyst under the reaction condition.

The topology of the catalyst was studied by scanning electron microscopy (SEM, Fig. S3a, Supporting Information) which showed a typical sample composed of nano-bars with width 80–150 nm. SEM–EDX







Fig. 2. Raman spectra of (a) fresh and (b) spent Ag/WO₃ nano-bars catalyst.

analysis of the composite (Fig. 3b, Supporting Information) revealed that, there appeared a distribution of Ag, W and O only, and no sort of C, N or Br, which are visualized from the corresponding SEM-EDX image of the uncalcined sample (Fig. S4, Supporting Information). This observation indicated the complete removal of the structure-directing template upon calcination. This experimental finding was further supported from FTIR and TGA/DTG analysis of the uncalcined catalyst (Fig. S5 & S6, Supporting Information). However, transmission electron microscopy (TEM) image (Fig. 3) revealed that the sample is comprised of several bar-like particles with 350-450 nm in length with 60-100 nm width in average. More interestingly, the reactive species (i.e. Ag NPs) were 2-7 nm in size and spherical in shape and were anchored upon these nano-bars. From the HRTEM (Fig. 3c) the interplanar spacing of the lattice fringe distance of 0.38 nm, corresponded to (020) lattice spacing of monoclinic WO₃, was clearly discriminated from 0.23 nm corresponded to (111) plane of Ag (Fig. 6d). Typically, the dispersion of Ag, W and O atoms in the catalyst was also analyzed by STEMelemental mapping (Fig. S15). It indicated that each of Ag, W and O species was homogeneously dispersed. Moreover, the fact that the catalyst retained its structure was interpreted in terms of TEM diagram (Fig. 3d), TEM-EDX (Fig. S7, Supporting Information) and particle size distribution (histogram, Fig. S8, Supporting Information) analyses of the spent catalyst.

3.2. Catalytic activities

The activity of the catalyst (AgW^{NB}) in selective oxidation of cyclohexanone has been shown in Table 1. No caprolactone was detected during neat reaction, reflecting the necessity of the catalyst (Entry 1, Table 1). Temperature played a crucial role in the oxidation reaction of cyclohexanone (Fig. S9, Supporting Information). Increment in temperature increased the yield of caprolactone and reached maximum (97%) at 80 °C. But above 80 °C, yield of caprolactone decreased rapidly due to the formation of cyclohexanone-2-ol, cyclohexanone-2-one etc. We also noticed that, optimum molar ratio of cyclohexanone: H_2O_2 was 1:4; probably, excess H_2O_2 was needed, since major amount of H_2O_2 decomposed over the catalyst at the reaction temperature. Maintaining all the optimum conditions, when the reaction was allowed to run for hours, we did not notice any marked effect in the yield of caprolactone after 9 h, probably due to the decomposition of H_2O_2 present in the reaction medium (Fig. S12, Supporting Information).

Notably, commercial catalysts, employed separately (Entry 2–4, Table 1), and even conventional Ag/WO₃ catalyst prepared in



Fig. 3. TEM image of (a-c) fresh and that of (d) spent Ag/WO₃ nano-bar catalyst.

impregnation process, did not show any remarkable activity in cyclohexanone oxidation reaction, excluding the catalytic contribution of the free Ag species to the C–O bond activation. It was also noticed that, higher loading of Ag decreased the yield of caprolactone, probably due to the fact that loading of Ag lead to the formation of Ag-agglomerates (as confirmed from TEM diagram, Fig. S13, Supporting Information) that decreased the active metal dispersion and thereby catalyst-efficacy. We also noticed that, when 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was used as a radical scavenger in the reaction, unhindering all the reaction conditions, remakable drop in the yield of caprolactone was noticed (Entry 9, Table 1).

In the light of the above experimental findings, we can draw the hypothesis that, Ag(0) is the reactive species in the catalyst and the reaction proceeds through a free-radical mechanistic pathway. We believe that, Ag(0) in the catalyst framework (suffers high strain, due to "crystal-splitting mechanism", also confirmed from TEM diagram Fig. S14, Supporting Information) interacts with the C–O bond of cyclohexanone lowers the activation energy of the oxidation reaction. At normal condition, H_2O_2 does not interact with cyclohexanone.

We believe that H_2O_2 dissociation is believed to occur over the Ag surface and probably follows the mechanism, suggested by Kazarnovsky (Supporting Information) [15]. During the oxidation process, dissociation

Table 1

Oxidation reactior	of cyclohexanone	over Ag-W	nano-bar	catalyst.
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Entry	Catalyst	C _B b (%)	S_{PC} (%)			Y _A d (%)	E _o e	TON	
			Caprolactone	Cy-1-one-2-ol	Cy-1,2-dione	Others			
1	No catalyst	-	_	_	_	_		-	-
2	Ag	-	-	-	-	-		-	-
3	Ag ₂ O	-	-	-	-	-		-	-
4	WO ₃	-	-	-	-	-		-	-
5	Ag-W ^{IMP}	18	5.5	15	5	74.5	1	0.24	1.6
6 ^f	Ag–W ^{NB}	97	99	0	0	0	97	24.0	153.1
7 ^g	Ag–W ^{NB}	93	95	2	1	2	88.3	22.1	140.8
8 ^h	Ag–W ^{NB}	>99	87	6	4	3	86.1	21.5	65.5
9 ⁱ	Ag-W ^{NB}	2.8	-	-	-	>99	-	-	-

TON: Turn over number.

^a Reaction condition: cyclohexanone = 1 g; solvent = MeCN; catalyst = 0.15 g; cyclohexanone: H₂O₂ mole ratio = 1: 4; time = 9 h; temperature = 80 °C.

^b $C_B =$ Conversion of cyclohexanone.

 c S_P = Selectivity of products.

^d $Y_A =$ Yield of caprolactone. ^e $F_A = H_a O_a$ efficiency = [mo

 $E_0 = H_2O_2$ efficiency = [moles of caprolactone formed / total moles of H_2O_2 added] × 100.

^f Fresh.

^g Spent (after 5 reuse) Ag–W Nano-bar catalyst (4.6% Ag loading).

^h 9.7% Ag loading.

Table 2

Oxidation reaction of various cyclic ketones over Ag-W Catalyst.^a

Entry	Cyclic alkanones	Product	C _A ^b	S _P ^c (%)	Y _A ^d (%)
1	0=	0	99	86	86
2	0		97	99	87
3	0		96	99	96
4			88	99	88
5			76	99	76

^a Typical reaction conditions: solvent (MeCN) = 10 ml, substrate (cyclohexane) = 1 g, catalyst = 0.15 g, cycloalkanone: H₂O₂ (molar ratio) = 1:4, reaction temperature = 80 °C; time = 9 h.

 $^{\rm b}$ C_B = Conversion of cycloalkanone based upon the FID–GC.

 c S_P = Selectivity of the product.

 d Y_A = Yield.

of H_2O_2 over Ag generates superoxide $(O_2^{\bullet-})$, which ultimately produces peroxide species 'OOH, which is supposed to be the active species for this reaction (Supporting Information) [16–19]. This 'OOH then attacks the carbon atom of C-O and forms caprolactone. We also noticed that higher loading of Ag decreased the yield of caprolactone, probably due to the fact that loading of Ag lead to the formation of Ag-agglomerates (as confirmed from TEM diagram, Fig. S13, Supporting Information) that decreased the active metal dispersion and thereby catalyst-efficacy. In other words we can say that very small silver nanoparticles able to activate H₂O₂ more efficiently, which is ultimately responsible for higher vield of the product. It is also believed that the active 'OOH species are stabilized by the solvent acetonitrile to a great extent [20]. Moreover, dissociation of H₂O₂ produce 'H radicals, that compel the formation of enol tautomer of the cycloalkanones. This explains the use of excess H₂O₂ in the cyclohexanone oxidation reaction. Oxidation of other similar substrates was explored by extending the reaction to a variety of other cycloalkanones and the results are presented in Table 2. Apparently, the Ag/WO₃ catalyst is effective for the oxidation of many of these substrates, which are usually difficult to accomplish with high yield to a specific oxygenate. Cycloalkanones showed very encouraging results with this catalyst.

3.3. Reusability test

At the end of the reaction, the catalyst was filtered during hot condition and the resulting filtrate was independently analyzed by ICP-AES. Only trace amounts of Ag (<3 ppb) were detected; which indicated that the catalyst is almost devoid of leaching properties; this may be attributed due to the fact that, Ag remains strongly anchored upon WO₃ support; the catalyst did not show any significant loss in its activity even after 5 successive runs (Entry 7, Table 1 & Fig. S12, Supporting Information) and the catalyst was proved to be truly heterogeneous.

4. Conclusions

In summary, we have developed a surfactant-promoted simple preparation method to prepare 2–7 nm Ag nanoparticles supported on monoclinic WO₃ nanobars having high thermal stability and good catalytic activity for the single step conversion of cyclohexanone to caprolactone using H_2O_2 , exhibiting 97% cyclohexanone conversion and 99% selectivity towards caprolactone at 80 °C. The catalyst can be reused several times without any activity loss, which is a prerequisite for practical application. Moreover, the catalyst also showed excellent activity in case of other cycloalkanones also. This oxidation protocol is also much cleaner than the traditional oxidation processes using stoichiometric oxidants and peracids, which would produce copious amounts of undesired by-products. The proposed method is also advantageous from the standpoint of low cost, environmental benignity and operational simplicity; furthermore, it can be applicable to large-scale reactions. This environmentally benign, "green" route to caprolactone production may be a potential alternative to the existing conventional process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2015.09.001.

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