Preparation of One-dimensional (1D) Cu-WO_3 Nanorods Catalyst for the Selective Oxidation of Ethylbenzene

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Abstract: We present here a facile hydrothermal synthesis method to prepare Cu (II) nanoparticles supported on W (VI) oxide nanorod catalyst. Detailed characterization of the material was carried out by XRD, XPS, SEM, TEM, TGA, and ICP-AES. The catalyst was highly active for selective oxidation of ethylbenzene to acetophenone with H_2O_2 at 90 ºC. The influence of reaction parameters were investigated in detail. The reusability of the catalyst was studied and it was found that the catalyst did not show any significant activity loss even after 5 reuses. An ethylbenzene conversion of 86.5% with 100% acetophenone selectivity was achieved over this catalyst at 90 ºC.

Keywords: Cu (II) Nanoparticles, W (VI) oxide nanorods, Ethylbenzene, Acetophenone, Selective oxidation.

1. INTRODUCTION

Oxidation of saturated hydrocarbons to the corresponding oxygenates selectively is among the most challenging reactions in the chemical industry [1, 2]. Recently, the selective oxidation of ethylbenzene to acetophenone has drawn immense attention because the acetophenone serves as a crucial platform as it is used as an intermediate for the manufacture of some perfumes, pharmaceuticals, resins, alcohols, esters, and aldehydes [3-5]. Industrially, acetophenone is synthesized by Friedel–Crafts acylation of arenes by acyl halides or acid anhydrides with Lewis acids or by oxidation of alkylarenes with stoichiometric inorganic oxidants such as permanganate or dichromate [6-8]. But, these reagents are not only relatively expensive but they also produce huge amount of noxious and corrosive wastes. Moreover, it is very inconvenient to separate the catalysts from the reaction mixture. Many researchers came forward to sort out this problem and reported acetophenone production from ethylbenzene using several oxidants like TBHP [9,10], H_2O_2 [11], and molecular O_2 [12,13]. Recently, Chen *et al*. reported oxidation of ethyl benzene over Co-SiO_2-based nanocomposite catalyst [14] and Luo *et al*. reported oxidation of ethyl benzene using carbon nanotubes with air as oxidant [15]. But so far, none of the reported processes have been developed largely because either high reaction temperature have been employed or due to poor selectivity of acetophenone despite higher conversion, or severe leaching of the catalyst. Therefore, there is potential interest in the development of more efficient, readily separable, reusable catalysts for the catalytic oxidation of ethylbenzene. H_2O_2 is an economically and environmentally desirable oxidant in comparison to other oxidants [16]. Additionally, the activated C–H bonds (that is, adjacent to a heteroatom, a π-system and/or an electron-rich tertiary C–H bond) are hydroxylated selectively by H_2O_2 in most metal-catalyzed oxidation systems [16].

Previously, we showed the preparation of Cu/WO_3 nanoparticles catalyst and its high activity in oxidation of cyclohexane to adipic acid [17]. But the catalyst has not been well explored for the selective catalytic oxidation of ethylbenzene by virtue of benzylic C^{sp3}—H activation.

Herein we report the cationic surfactant CTAB promoted, hydrothermal-based preparation of Cu/WO_3 nanorods catalyst and its catalytic application in the oxidation of ethyl benzene at liquid phase with H_2O_2 as oxidant. An ethylbenzene conversion of 86.5 % with an acetophenone selectivity of 100 % was achieved over this catalyst.

2. EXPERIMENTAL

2.1. Materials

Hydrogen Peroxide (50 wt % in water) was bought from Merck KGaA, Darmstadt, Germany. $Cu(NO_3)_2$. $3H_2O$, sodium tungstate dihydrate (Na_2WO_4. $2H_2O$), hexadecyltrimethylammonium bromide (CTAB), hydrazine hydrate, ethylbenzene (purity > 99.9%), DMSO (HPLC grade) were bought from Sigma-Aldrich Co.

2.2. Catalyst Preparation

The Cu-W catalyst was prepared hydrothermally following our own preparation method [17]; In a typical preparation method, 1.5 g of Cu $(NO_3)_2$. $3H_2O$ and 14.3 g Na_2WO_4. $2H_2O$ at a desired molar ratio (taking 4%

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Cu loading on WO_3 by weight) were dissolved in 34g water. Then 1.72 g dissolved CTAB was poured in the solution by intensive stirring for 2h to form gel. A solution of hydrazine monohydrate (80% aqueous solution) was added to the well-stirred mixture at RT by simultaneous, vigorous agitation. All the reagents were used maintaining the ratio: Cu: CTAB: hydrazine: H_2O = 1: 0.75: 1: 300. The mixture was stirred for 30 min and subsequently sealed in a Teflon lined stainless-steel autoclave (250 mL capacity). The autoclave was kept at oven with 180° C for 18h and then allowed to cool to RT. The light sky blue fluffy solid products (precipitates) were collected by centrifugation at 5000 rpm and washed with water and ethanol several times prior to drying in air at 100 °C for 6h. The resulting dry powder was transferred to a quartz reactor inside a tubular resistance furnace for calcination (600 °C in air at ramp of 1 °C min^{-1}).

2.3. Characterization Techniques

Powder X-ray diffraction spectra were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K_α radiation source with a wavelength of 1.5418 Å. Diffraction patterns in the 2°–80° region were recorded at a rate of 0.5 degrees (2θ) per minute. The resulting XRD profiles were analyzed to identify the crystal phase of the compound using reference standards. X-Ray photoelectron spectra were recorded on a Thermo Scientific K-Alpha X-Ray photoelectron spectrometer and binding energies (±0.1 eV) were determined. The resulting spectra were analyzed to identify the different oxidation states of the copper and tungsten ions present in the sample. Prior to the analysis, the spectra were calibrated with reference to C1s observed at a binding energy of 284.5 eV. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanumhexaboride (LaB_6) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer. Transmission electron microscopy (TEM) images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. The particle size and distribution of the samples were analyzed by TEM. Chemical analyses of the metallic constituents were carried out by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES); model: PS 3000 uv, (DRE), Leeman Labs, Inc, (USA). Thermo gravimetric analyses (TGA) of the uncalcined catalyst were carried out in a Pyris Diamond, Perkin Elmer Instruments, and Technology by SII (Seiko Instruments Inc), USA instrument-balance by heating 2.15 mg samples at 5 °C min^{-1} in flowing air.

2.4. Liquid Phase Oxidation of Ethylbenzene

Oxidation of ethylbenzene reaction was carried out in a two neck round bottom flask, equipped with refrigerant, containing 0.2 g catalyst, 15 ml solvent (DMSO) and 1 g ethylbenzene to which H_2O_2 (50% aq. solution) was added drop wise. The flask was then placed in a preheated oil bath and vigorously stirred with a magnetic stirrer. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis using a syringe. After reaction completion, the solid particles (catalyst) were separated by filtration and the products were analysed by Gas Chromatograph (GC, Agilent 7890) connected with a HP5 capillary column (30m length, 0.28 mm id, 0.25 μm film thickness) and flame ionisation detector (FID). The ethylbenzene conversion and acetophenone formation were calculated using a calibration curve (obtained by manual injecting the authentic standard compounds). The product was identified by injecting the authentic standard samples in GC and GC-MS.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

The XRD of the catalyst was carried out to determine the crystallite phase of the Cu-W nanocomposites (Figure **1**). Sharp peaks at 2θ = 23.1°,

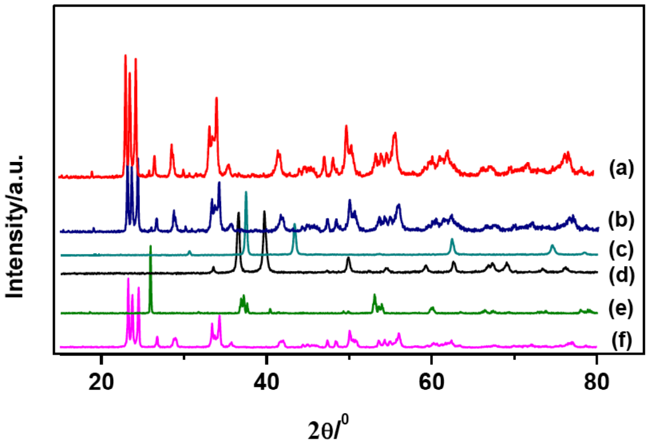


Figure 1: XRD of (**a**) fresh and (**b**) spent Cu/WO_3 nanorods and that of (**c**) Cu_2O (commercial), (**d**) CuO (ommercial), (**e**) WO_3 (commercial), and (f) WO_2 (commercial).

23.7°, 24.4°, 33.3° and 34.0°, confirm the formation of monoclinic WO_3 (JCPDS No. 43-1035, space group: P21/n). Moreover, XRD reflections with comparatively low peak strength due to crystalline CuO (monoclinic) were also noticed at 2θ = 35.57°, 38.75°, 48.7°, 68.2° etc. [JCPDS card no. 89-2530]. Furthermore, other crystalline by-products or other phases of copper/tungsten oxides were not detectable by XRD, indicating the high purity of our synthetic procedure.

XPS was used to detect the surface composition and the chemical state of the catalyst. The XPS binding energies (BE) of some characteristic core levels of Cu and W in the Cu-W samples have been presented (Figure **2 a** & **b** respectively). The Cu 2p XPS results indicate that the binding energy of the Cu 2p electron in the sample, and the peaks center at approximately 935.7 eV corresponding to $Cu2p_{3/2}$ [17]. The existence of satellite peaks in the spectra suggests that copper exists in the samples as Cu (II). The value of the binding energy (~935.7 eV) is much greater than that of pure CuO (933.8 eV), which indicates that the Cu (II)-species are surrounded by tungsten oxide. 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} [17]. XRD and XPS data support the fact that, the main phase is comprised of monoclinic W (VI) oxide and the supported metal is of Cu (II) oxide.

The topology of the catalyst was studied by SEM (Figure **3a**), which showed a typical sample composed of almost uniform rod-like structure (1.5-2 μm in length and diameter 50-80 nm). SEM-EDX analysis (Figure **3b**) of the composite revealed that, there appears a distribution of Cu, W and O only, and no sort of C or Br. This observation indicated the complete removal of the structure-directing template (s). This experimental finding was further supported from TGA analysis of the

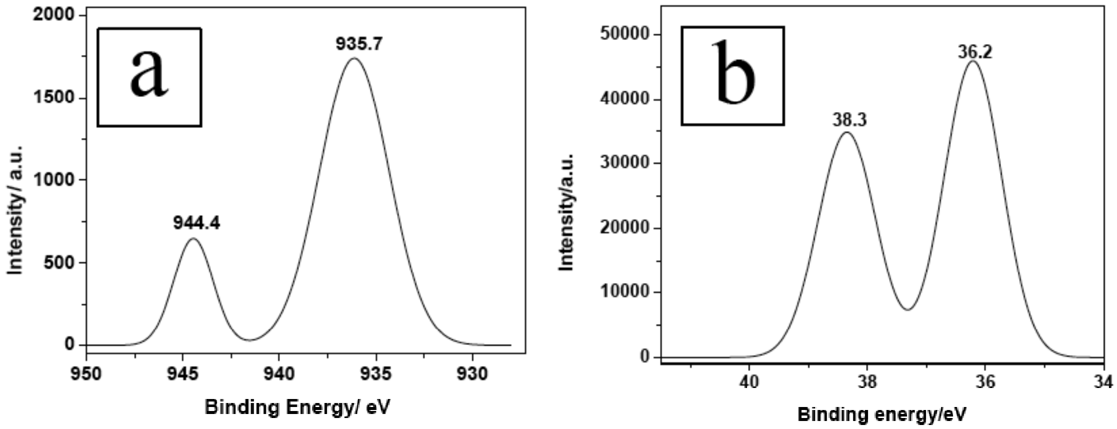


Figure 2: Cu $2p_{3/2}$ and (**b**) $W4f_{7/2}$ and $W4f_{5/2}$ Cu/WO_3 nanorods.

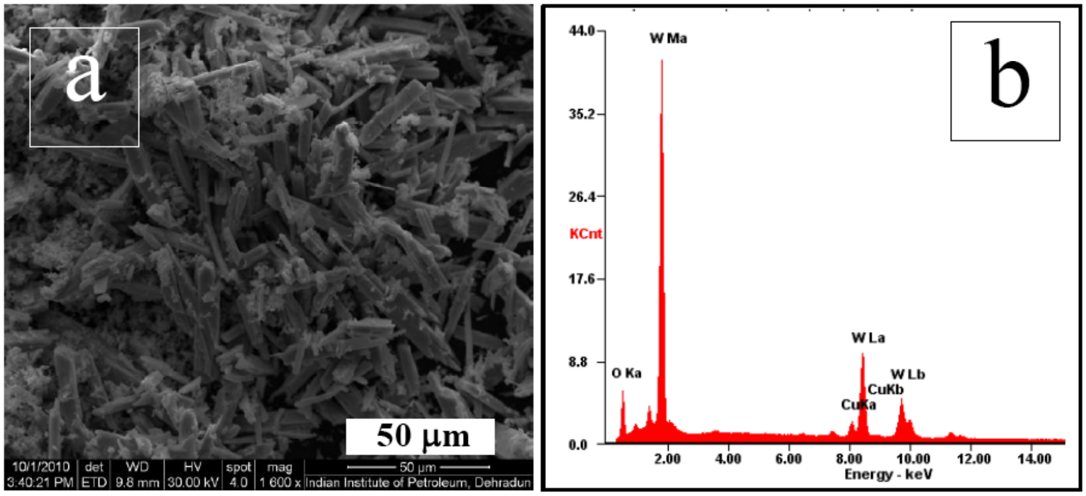


Figure 3: (**a**) SEM and (**b**) SEM-EDAX diagram of Cu/WO_3 nanorods.

unalcined catalyst (Figure **4**). However, TEM image revealed that the sample (nanorods) is comprised of several spherical black patches (Figure **5b**) with 2-5 nm in size in average. To get further information about the catalyst structure, a representative high resolution TEM (HRTEM) image taken from a nanoparticle is shown in Figure **5c**. The lattice fringes with a d-spacing of 0.23 nm, corresponding to the spacing of the [111] planes of monoclinic CuO is conveniently discriminated from that of the [020] planes of monoclinic WO_3 with a d-spacing of 0.30 nm [17].

The assembly of all the catalyst-characterization data led to the conclusion that, the main phase of the catalyst is comprised of monoclinic W (VI) oxide, whereas a small amount of CuO is dispersed (as active component) on this phase of the catalyst surface.

3.3. Catalytic Studies

The activities of Cu-WO_3 catalyst in the direct oxidation of ethylbenzene to acetophenone in liquid phase by using H_2O_2 as oxidant have been summarized in Table **1**. Notably, commercial WO_3, CuO, Cu_2O and Cu/WO_3 catalyst prepared by physical mixing did not show any activity (Table **1**, entry 1-4). This experimental finding reflected the small size as well dispersed Cu (II) oxide nanoparticles (on WO_3 nanorods support). The comparatively smaller size of Cu (II) oxide nanoparticles catalyst possess comparatively high specific surface area which corresponds to higher dispersion of the catalyst that leads to the availability of more exposed surface active sites, where the catalytic reaction takes place.

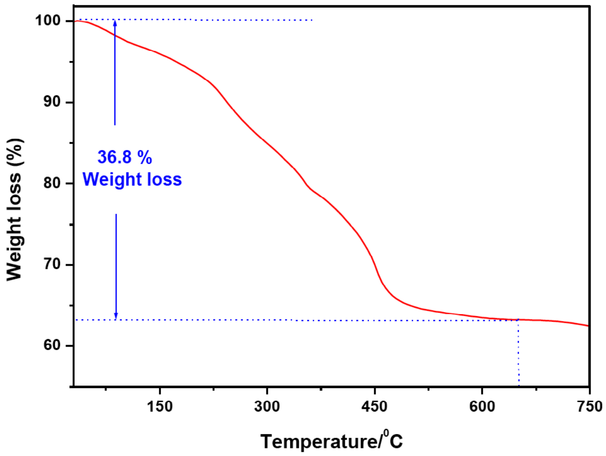


Figure 4: TEM diagram of (**a-c**) Cu/WO_3 nanorods (with increased magnifications) and (**d**) spent Cu/WO_3 nanorods.

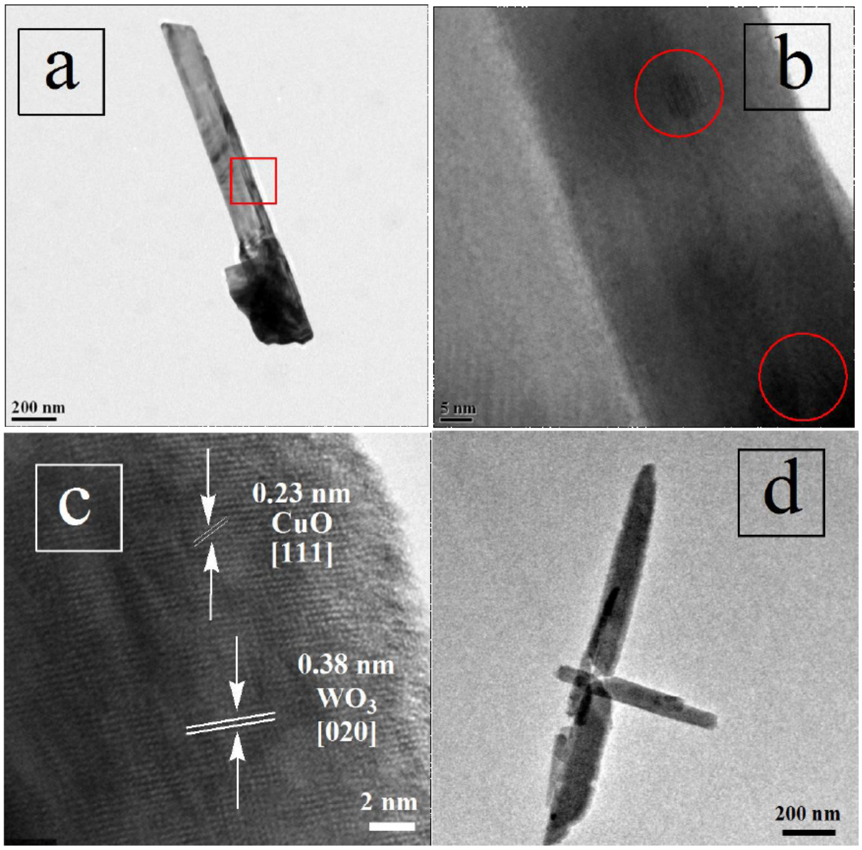
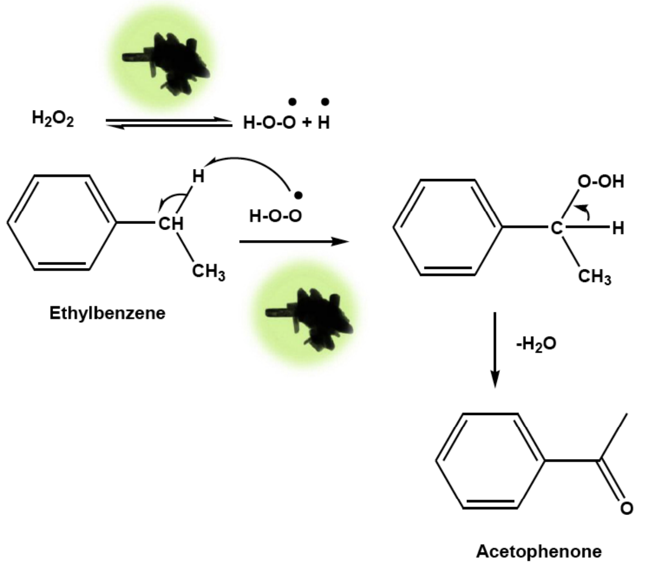


Figure 5: TGA diagram of uncalcined Cu/WO_3 nanorods.



Scheme 1: Mechanism of the catalytic oxidation of ethylbenzene to acetophenone over Cu/WO$_3$ nanorods catalyst.

Table 1: Catalytic Oxidation of Ethylbenzene to Acetophenone[a]

Entry	Catalyst	Cu loading(%)[b]	C_{EB} (%)[c]	S_P(%)[d]	
				AP	Others
1	CuO^{COM}	>99	13.5	20	80
2	Cu_2O^{COM}	>99	12.8	28.5	71.5
3	WO_3^{COM}	-	35	38	62
4[e]	Cu/ WO_3^{PM}	15	35.5	55	45
5[f]	Cu/ WO$_3$	3.7	86.5	100	-
6[g]	Cu/ WO$_3$	3.7	78	97	3
7[h]	Cu/ WO$_3$	3.7	88	96	4
8	No Catalyst	-	-	-	-

[a] Typical reaction conditions: substrate (ethylbenzene) = 1g, solvent (DMSO) = 15ml, catalyst= 0.2g, ethylbenzene: H_2O_2 (ratio of mole) = 1:5, temperature = 90 °C, time = 12 h. [b] Loading of Cu determined from ICP-AES. [c] C_{EB} = Conversion of ethylbenzene based upon the FID-GC using chloroform as external standard = [Moles of ethylbenzene consumed (reacted)/initial moles of ethylbenzene used] x 100. [d] S_P = Selectivity = [Moles of products produced/ moles of ethylbenzene reacted] x 100; [e] Cu (II)/WO$_3$ catalyst prepared by physical mixing (PM) of CuO and WO$_3$. [f] Fresh and [g] Spent (after 5 recycles) Cu/WO$_3$ nanorods catalyst. [h] Time=24h.

We believe that, Cu (II) is the reactive species in the catalyst, which interacts with the C-H bond of cycloalkanes and lowers the activation energy of the oxidation reaction [17]. At normal condition, H_2O_2 does not interact with ethylbenzene. H_2O_2 dissociation is believed to occur homogeneously over Cu-WO$_3$ catalyst and follows the mechanism proposed by Kazarnovsky [18]. The generated $\dot{O}H$ radicals behave as electrophiles and proceed towards the more reactive α-C-atom of (-CH_2CH_3 group). As a result, a homolytic cleavage of the C-H bond occurs. The concomitantly formed radicals react with excess $\dot{O}H$ radicals to produce acetophenone over the catalyst surface. This explains the use of excess H_2O_2 in the ethylbenzene oxidation reaction.

4. CONCLUSIONS

In summary, we have developed a surfactant-promoted simple preparation method to prepare Cu/WO$_3$ nanorods catalyst (with supported Cu(II) oxide is 2-5 nm) having high thermal stability and good catalytic activity for the single step conversion of ethylbenzene to acetophenone using H_2O_2, exhibiting 86.5 % ethylbenzene conversion and 100 % selectivity towards acetophenone at 90 °C. The catalyst can be reused several times without any activity loss, which is appreciating. The proposed method is also advantageous from the standpoint of low cost, environmental benignity and operational simplicity. This environmentally benign, “green” route to acetophenone production may be a potential alternative to the existing conventional process.

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