

Oxidation of Cyclohexane Over Nanoclusters of Cu (II) Supported on Nanocrystalline Tungsten Oxide with H₂O₂ as Oxidant

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Abstract: A facile hydrothermal synthesis method is developed for the preparation of Cu (II) nanoclusters (with average particle size 6 nm) supported on nanocrystalline tungsten (VI) oxide. Detailed characterization of the material was carried out by XRD, SEM, TEM, ICP-AES and TGA. The catalyst was highly active for selective oxidation of cyclohexane to adipic acid with H₂O₂. The reusability of the catalyst was tested by conducting same experiments with the spent catalyst and it was found that the catalyst did not show any significant activity loss even after 5 reuses. A cyclohexane conversion of 62.5 % with 27 % adipic acid selectivity was achieved over this catalyst at room temperature

Keywords: Cu (II) Nanoclusters, Nanocrystalline tungsten (VI) oxide, Cyclohexane, Cyclohexanone, H₂O₂, Selective oxidation, Heterogeneous catalysis.

INTRODUCTION

The selective transformation of inert C-H bonds of alkanes into useful functional groups are of much potential interest as alkanes are comparatively less expensive and more readily available than the current petrochemical feedstocks [1-4]. The catalytic oxidation of alkanes under mild conditions remains a major challenge in industrial and synthetic chemistry [5, 6]. The oxidation of cyclohexane represents a typical example for this type of reactions which have become a myth to several researches these last years [7, 8]. The oxidation of cyclohexane produces cyclohexanol and cyclohexanone (collectively called KA oil or "olone"), which are further used to produce adipic acid and caprolactum, which in turn are the starting materials for the synthesis of nylon-6 and nylon-66 polymers, respectively [9,10]. That means, selective oxidation of cyclohexane is the center-piece of the commercial production of Nylon. The conventional industrial process for C-H oxidation to a mixture of K and A, the so-called KA-oil (6× 10t/y), employs soluble cobalt or manganese salts as homogeneous catalysts under severe conditions (140–180° C and 10–20 atm of air) and produces KA-oil with 75–80% selectivity, limiting the conversion to 5–7% in order to prevent over-oxidation of the target products [11]. Beyond low conversion, this process also generates several by-products like mono- and dicarboxylic acids, esters, and other oxygenated materials. This low conversion and selectivity, leaching of metal, and over-oxidation of products in the existing catalytic systems reinforce the need for new catalytic systems, including

heterogeneous catalyst and clean oxidant [12-14]. Therefore, the selective oxidation of cyclohexane at mild condition with high energy efficiency has thus become a challenge to the researchers [14]. To overcome this problem, many researchers came forward and applied certain oxidants like H₂O₂, [15, 16] TBHP, [17, 18] and molecular O₂ [19-21]. Although oxidation of cyclohexane with the greenest oxidant molecular oxygen have demonstrated important progress, but these systems display shortages and their applications are limited. That's why, the technology with which cycloalkanes has been oxidized by O₂ to produce their corresponding oxygenates has not been improved well till now. Therefore, a huge task in this field is to design the heterogeneous catalyst that affords the primary product with high selectivity at cost of high conversion of the hydrocarbon. Our previous report indicated that, Cu (II) nanoclusters supported on nanocrystalline Cr₂O₃ catalyst efficiently converts cyclohexane and furnishes high yield of cyclohexanone [22] but the catalyst suffers severe leaching. Moreover, the catalyst was inactive to produce adipic acid. Recently, we reported synthesis of adipic acid from cyclohexene with very high yield [23]. To the best of our knowledge, there is no report for the preparation of adipic acid via direct oxidation of cyclohexane. Herein, we report a cyclohexane conversion of 62.5 % with 27 % adipic acid selectivity over Cu (II) nanoclusters supported on tungsten oxide nanoparticles catalyst at room temperature.

EXPERIMENTAL

Materials

Hydrogen Peroxide (50 wt % in water) was bought from Merck KGaA, Darmstadt, Germany. CuCl₂ · 2H₂O, WCl₆, cetyltrimethylammonium bromide, hydrazine

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hydrate, ammonium hydroxide, cyclohexane (purity > 99.9%), acetonitrile (HPLC grade) were purchased from Sigma-Aldrich Co. All the chemicals were used without further purification.

Catalyst Preparation

The Cu-W catalyst was prepared hydrothermally by modifying our own preparation method; [24]. In a typical preparation method, 1.3 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 17 g WCl_6 at a desired molar ratio (taking 5% Cu loading on WO_3 by weight) were dissolved in 43g water to give a clear dark blue solution. The pH of the medium was made 8, by gradual addition of NH_4OH solution dropwise; the colour of the solution became greenish gradually. Then 2.2 g dissolved CTAB was poured in the solution by intensive stirring for 2h to form gel. A solution of hydrazine monohydrate (80% aqueous solution), 0.5 g was added drop wise 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 vigorously for 30 min and subsequently sealed in a Teflon lined stainless-steel autoclave (250 mL capacity). The autoclave was heated to and maintained at 200° 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. The calcination was operated at 700 °C in air at ramp of 1 °C min^{-1} .

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. The line width of the most intense XRD peak was taken for estimation of crystallite size by the Scherrer equation. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (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.

Liquid Phase Hydroxylation

Liquid phase oxidation reaction was carried out in a two neck round bottom flask, equipped with refrigerant, containing 0.2 g catalyst, 10 ml solvent (MeCN) and 1 g cyclohexane to which H_2O_2 (50% aq. solution) was added dropwise (1:3 molar ratio wrt cyclohexane) to prevent immediate H_2O_2 decomposition. The flask was then emerged in a preheated oil bath and vigorously stirred. The reaction temperature was carried out at RT. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis using a syringe. At the end of the reaction, 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 product identification was carried out by injecting the authentic standard samples in GC and GC-MS. For the reusability test, the catalyst was repeatedly washed with acetonitrile and acetone and dried overnight at 120 °C and used as such, without regeneration. In order to check the metal leaching the mother liquor was then analyzed using ICP-AES.

RESULTS & DISCUSSION

Catalyst Characterization

The powder X-ray diffraction pattern of the Cu-W catalyst is shown in Figure 1. PXRD pattern exhibited the typical diffraction lines of the pure WO_3 phase [13] and that of Cu (II) oxide [JCPDS-89-2530]. The crystallite size of Cu (II) species was determined using the Scherrer equation (based on $2\theta=36.11^\circ$) and a mean particle size of 5.5 nm was observed, which

matched well from that derived from TEM image. Also, we did not notice any phase change of the catalyst during catalysis, as confirmed from the respective XRD diffractogram, only a bit decrease in the intensity in the diffractogram was speculated (Figure 1b).

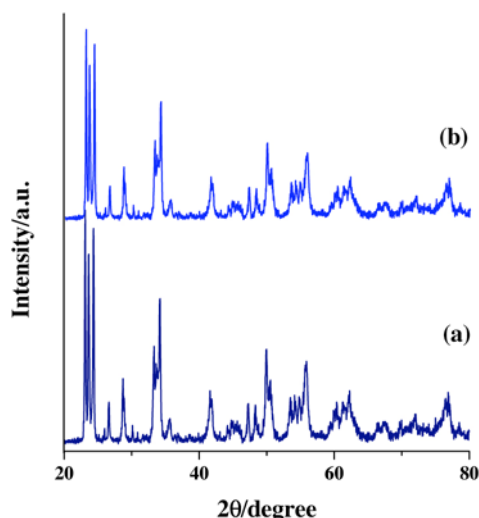


Figure 1: XRD pattern of the (a) fresh and (b) spent (after 5 recycles) Cu/WO₃ catalyst.

A representative SEM (Figure 2) image has been plotted to show the morphology of the catalyst. SEM images revealed that the sample is composed of almost homogeneously distributed uniform nanoparticles.

SEM-EDX diagram has been plotted (Figure 2c) as an evidence of the presence of Cu, W and O in the sample.

Transmission Electron Microscopy (TEM) images of the catalyst (Figure 2d, e) revealed the formation of uniform particle sizes. Magnified TEM images (Figure 2e) the supported Cu (II) nanoparticle and the WO₃ support are clearly visible. From the HRTEM diagram (Figure 2e, inset), two different patches with corresponding to two different interplanar spacings, $d = 0.23$ nm and $d = 0.38$ nm are noticed; these may be attributed to the presence of Cu (II) species with [200] plane [25] and W (VI) oxide with [002] plane.[26]. Furthermore, the TEM diagram of the spent catalyst (Figure 2f) was almost same with that of the fresh one (Figure 2d), indicating the fact that, the catalyst was devoid of any severe structural change during catalysis (Table 1).

The assembly effect of the surfactant (as imaged by SEM) and the embedment of CTAB molecules on the pre-calcined catalyst surface were further confirmed from TGA analysis. TGA analysis (Figure 3) was operated to understand the various decomposition regimes. The TGA diagram showed that the weight loss has three regimes, first being the loss of water followed by the decomposition of reactants to form NO_x and organic compounds at 150 to 250 °C and finally the combustion of CTAB between 250°–350 °C. A further small mass loss was observed between 400°–

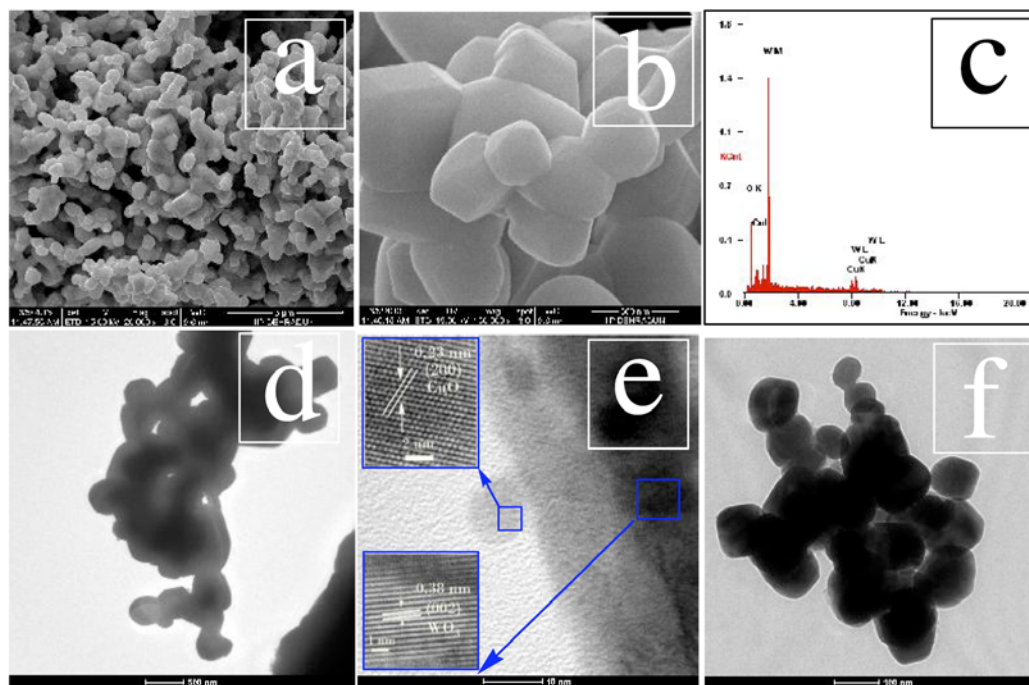


Figure 2: (a), (b) SEM image, (c) SEM-EDAX image, (d), (e) TEM image of the fresh and (f) TEM image of the spent (after 5 recycles) Cu/WO₃ catalyst.

Table 1: Reaction Conditions of Catalytic Oxidation of Cyclohexane^a

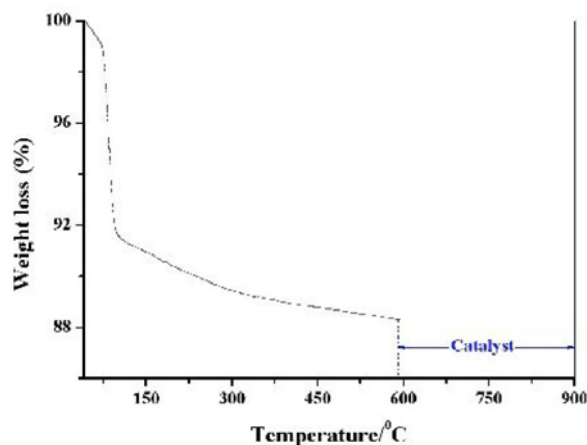
Entry	Catalyst	Cu Loading(%) ^b	C _H (%) ^c	S _p (%) ^d			
				Cy-ol	Cy-One	AA	Others
1	CuO ^{COM}	>99	3.5	10	35	-	55
2	Cu ₂ O ^{COM}	>99	2.8	8.5	28	-	63.5
3	WO ₃ ^{COM}	-	15	18	22	2.5	57.5
4 ^e	Cu/ WO ₃ ^{PM}	15	15.5	25	15	2.8	57.2
5 ^f	Cu/ WO ₃	3.8	62.5	58	4	27	11
6 ^g	Cu/ WO ₃	3.8	58.5	55	7	25.5	12.5
7 ^h	Cu/ WO ₃	3.8	64	38	15	27.5	19.5
8	No Catalyst	-	-	-	-	-	-

^aTypical reaction conditions: substrate (cyclohexane) = 1g, catalyst= 0.2g, cyclohexane: H₂O₂ (molar ratio) = 1:3, reaction temperature = RT, time = 6 h. ^bLoading of Cu determined from ICP-AES. ^cC_H = Conversion of cyclohexane based upon the FID-GC using chloroform as external standard = [Moles of cyclohexane reacted/initial moles of cyclohexane used] x 100. ^dS_p = Selectivity = [Moles of products produced/ moles of cyclohexane reacted] x 100; ^eCu (II)/WO₃ catalyst prepared by physical mixing (PM) of CuO and WO₃. ^fFresh and ^gSpent (after 5 recycles) Cu/WO₃ nanoparticles catalyst. ^hTime=12h.

550 °C due to the elimination of remaining carbon and organic compounds. Further weight loss was not observed when the temperature was further increased from 600°-900° C, indicating the generation of the Cu/WO₃ catalyst in that temperature range. The total mass loss is 11.8 % upto 900 °C.

Catalytic Oxidation

Table 1 shows the activities of the Cu/WO₃ nanoparticles catalyst in the direct oxidation of cyclohexane in liquid phase by using H₂O₂ as oxidant. Blank experiment was performed without the catalyst (Table 1, entry 8) and it was found that there was no conversion of the reactant, reflecting the necessity of the catalyst. Commercial CuO, Cu₂O, WO₃ did not show any special activity for cyclohexane oxidation (Table 1, Entry 1-3). Commercial WO₃ furnished very low amount of adipic acid (AA). Commercial CuO, mixed with commercial tungsten oxide by physical mixing (Table 1, entry 4) and was introduced as a catalyst in the oxidation reaction; but still, no improvement in the catalytic activity was noticed. Introducing the prepared Cu/WO₃ nanoparticles catalyst, significant increment in the catalytic activity was noticed (Table 1, entry 5). We continued the reaction for six hours. We also noticed that the catalyst did not show any severe loss in its activity, even after 5 reuses (Table 1, entry 6). Maintaining all the optimum conditions, when we increased the reaction time (12h) no appreciable conversion of cyclohexane was noticed (Table 1, entry 7), probably due to the decomposition of H₂O₂ over the catalyst account for this reason. The detailed mechanistic path of the reaction and effect of other reaction parameters are under study.

**Figure 3:** TGA of the uncalcined Cu/WO₃ catalyst.

Reusability Test

At the end of the reaction, the catalyst was filtered in the hot condition and was the resulting filtrate was independently analyzed by inductively coupled plasma (ICP) (and atomic absorption spectroscopy for free or dissolved metal ions. Only trace amounts of Cu²⁺ (<3 ppb) were detected; which indicated the fact that, the catalyst is almost devoid of leaching properties; this may be attributed by the fact that, Cu²⁺ remains strongly anchored upon WO₃ support. Recycling and reusability of the catalyst was examined by introducing the used catalyst subsequently 5 times to carry out the catalytic oxidation. The reusability of the catalyst was studied without regeneration of the catalyst in the same experimental condition. Before each recycle, the catalyst was recovered facily from the reaction mixture (after 6h) by centrifugation, repeatedly washed

with ethanol and acetone and kept for drying at 120 °C for overnight. The catalyst did not show any significant loss in its activity even after 5 successive runs and the catalyst was proved to be truly of heterogeneous nature.

CONCLUSION

In summary, we have developed a surfactant-promoted simple preparation method to prepare ~ 7 nm Cu (II) nanocrystals supported on W (VI) oxide nanoparticles having high thermal stability and good catalytic activity for the single step conversion of cyclohexane to adipic acid using H₂O₂, exhibiting 62.5 % cyclohexane conversion and 27 % selectivity towards adipic acid at room temperature. 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 cyclic alkanes 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 catalyst preparation is also relatively simple and does not involve the use of any expensive precursor materials. The proposed method is also advantageous from the standpoint of low cost, environmental benignity and operational simplicity. Moreover, the catalyst does not show any significant activity loss even after 5 reuses, reflecting its true heterogeneous character.

ACKNOWLEDGEMENTS

SSA thanks CSIR and SG thanks UGC, New Delhi, India, for their respective fellowships. .B. thanks CSIR, New Delhi, for financial support in the form of the 12 FYP Project (CSC- 0125, CSC- 0117). The Director, CSIR-IIP is acknowledged for his help and encouragement. The authors thank Analytical Section Division, IIP for the analytical services.

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