

Green Oxidation of Benzyl Alcohols using Molecular Oxygen as Oxidant and Catalysed by Supported Copper and Silver Catalysts

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1. Background of the study:

The selective oxidation of benzyl alcohols to benzyl aldehydes is very important because benzyl aldehydes are key ingredients and intermediates in the food, pharmaceutical, perfume, and other industries. Benzaldehyde is the second most used aromatic molecule in the cosmetics and flavour industries for its bitter-almond flavor. Efficient catalytic systems for the production of high-grade benzyl aldehydes are sought for their sustainable industrial production. A common route for benzaldehyde production is the hydrolysis of benzal chloride obtained from toluene chlorination. This route is hampered by contamination from the chlorinated by-products and benzoic acid.

Benzaldehyde is also synthesised, through the oxidation of toluene, to obtain the aldehyde as a by-product in the benzoic acid industry. However, this route is not sustainable because it employs harsh reaction conditions and the aldehyde selectivity is poor.

Recent research efforts have been focused more on catalysts based on gold, palladium and platinum resulting into expensive catalysts with low selectivity to the most valuable products. This makes the developed systems less attractive industrially. Moreover Pt group metal will be very scarce in the near future due to low reserves.

Herein, we report a cheap, recyclable, and efficient catalyst system using cheap metals and molecular oxygen as a green oxidant.



2. Preparation and Characterisation of the Catalysts:

The support was prepared by precipitation of sodium phosphotungstate hydrate (2.5 g) in deionised water (25 mL) at 95 °C by addition of a solution of excess silver nitrate (3 mL, 2.5 g) recovering the solid by centrifugation, washing with deionised water, drying overnight at ambient temperature and further at 120 °C for 3 h to obtain the POM support.

The Cu nanoparticles (NPs) were prepared by adding copper (II) nitrate hydrate

to a mixture of polyethylene glycol (PEG) (20 mL) and polyvinyl pyrrolidone (PVP) (7 g). The resultant mixture was heated at 140 °C for 1 h. The colour changed from light blue to green, through yellow and finally to ochre indicating formation of Cu NPs. To the resultant mixture, silver nitrate solution (0.0025 g, 1 mL) was added dropwise and the stirring continued for another 2 h. The colour of the Ag-Cu NPs was golden brown. Using the same procedure, monometallic Ag and Cu NPs were also prepared separately.

The POM support (1.25 g) was dispersed in deionised water (25 mL) and stirred at 350 rpm for 10 min, followed by drop-wise addition of the mixture containing the Ag-Cu NPs. The mixture was allowed to stir for another 2 h and the resultant solid recovered by centrifugation. The obtained solid was dried at 80 °C overnight and then at 120 °C for 4 h. It was then calcined at 400 °C for 4 h and reduced in H₂ at 400 °C in a horizontal furnace for another 4 h to give the Ag-Cu catalysts supported on the POM, **Ag-Cu/POM**. The nanoparticles were also deposited on talc (Sigma Aldrich) and the catalyst designated **Ag-Cu/talc**.

The catalysts were characterized by a combination of FTIR, XRD, UV-Vis, TEM, STEM, XRF, and TGA..

3. Oxydation of benzyl alcohols:

The oxidation reaction was performed in a three neck flask at ambient pressure and oxygen gas was introduced from a cylinder with the use of a Schlenk-line set up.

The catalysts are heterogeneous, stable and don't show tendency to leach or deactivate. The Ag-Cu/POM catalyst could be recycled at least 4 times with negligible deactivation (table 2). When tested on various derivatives of benzyl alcohol, similar results were obtained. The representative results are given in table 1.

Table 1: Representative Results for the Oxidation Reaction

Entry	Catalyst	Temperature °C	Time (h)	Benzyl alcohol conversion (%)	Benzaldehyde selectivity (%)
1	Ag-Cu/POM	85	1	57.3	>99
2	Ag-Cu/POM	85	2	82.3	>99
3	Ag-Cu/POM	85	4	98.0	>99
4	Ag-Cu/POM	85	5	>99.9	>99
5	Ag-Cu/Talc	65	3	51.8	>99
6	Ag-Cu/Talc	65	6	81.3	99
7	Ag-Cu/Talc	65	8	93.2	98.8
8	Ag-Cu/Talc	65	12	>99.9	98.6

Parameters: Benzyl alcohol (2 mmol), catalyst (100 mg), K₂CO₃ (100 mg), deionized water (0.5 mL), toluene (5 mL).

Table 2: Reusability of the catalysts

Recycle	%Conversion	%Benzaldehyde selectivity
1 ^a	100	>99
2 ^a	100	>99
3 ^a	100	>99
4 ^a	100	>99
5 ^a	98	>99
1 ^b	100	>99
2 ^b	100	>99
3 ^b	97	>99

a – using Ag-Cu/POM. b – using Ag-Cu/talc

The developed catalyst systems have potential for industrial application

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