

Gum-Supported Melamine: A Recyclable Reagent for Selective and Metal-Free Oxidation of Benzyl Alcohols [†]

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[†] Presented at the title, place, and date.

Abstract: Novel melamine functionalized gum (gum@Melamine@Cu(II)) is synthesized, and its catalytic performance is investigated in the oxidation of benzyl alcohols. The gum@Melamine was prepared through grafting of 3-chloropropyltrimethoxysilane on gum followed by treatment with melamine. The synthesized gum@Melamine@Cu(II) was used to achieve an effective and selective method for the oxidation of different alcohols. All substituted benzyl alcohols were oxidized in good yields under mild conditions at room temperature. This gum@Melamine@Cu(II) has great stability and could be recycled five times without noteworthy loss of activity.

Citation: Ghafuri, H.; Rostami, Y.; Ghanbari, N.; Abbasi, B.; Tajik, Z.; Ramsheh, N.A. Gum-Supported Melamine: A Recyclable Reagent for Selective and Metal-Free Oxidation of Benzyl Alcohols. *Chem. Proc.* **2021**, *3*, x. <https://doi.org/10.3390/xxxxx>

Academic Editor: Julio A. Seijas

Published: 15 November 2021

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Keywords: melamine; gum; oxidation of benzyl alcohols

1. Introduction

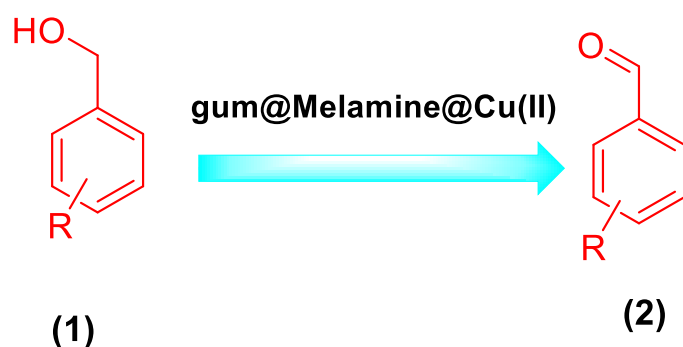
In recent decades, the use of suitable catalytic support has become more important and interesting for chemistry researchers [1]. Therefore, the preparation and use of catalysts with suitable support have been considered. Cherry gum is widely used as heterogeneous catalytic support due to its advantages such as excellent physical, chemical, and thermal stability, abrasion resistance, high hardness and low density, versatile performance, low cost for synthesis, and recyclability [2,3].

On the other side, preparation of catalyst with use of a magnificent agent is really essential, agents that are nontoxicity, low cost, and economical. Without a doubt, melamine is one of these agents with mentioned properties.

In the last decade, with the development of oxidation processes, the use of these reactions has attracted much attention. In addition, the synthesis of their product with high yield is really important and considerable. Oxidation of benzyl alcohol to aldehydes and acid carboxylic is one of these oxidation reactions [4–6].

Some of these reactions are done under conditions such as high temperature, the use of unfavorable solvents for the environment, and the use of oxidants that produce undesirable by-products; Due to these limitations, using efficient catalysts, suitable oxidants, and environmentally friendly solvents is a priority target.

In this paper, we prepared gum-melamine as a heterogeneous recyclable catalyst and used it to oxidize benzyl alcohol and its derivatives (Scheme 1).



Scheme 1. Synthesized derivatives in oxidation reaction.

2. Experimental

2.1. General

All reagents were purchased from Fluka and Merck companies and used without further purification. Thin layer chromatography (TLC) was used for the purity determination of substrates, products and reaction monitoring over silica gel 60 F254 aluminum sheet. Melting points were measured in open capillary tubes with Electro thermal 9100 melting point apparatus.

2.2. Synthesis of gum@Melamine@Cu(II)

The gum (1 g) was dispersed in toluene (40) mL. After complete dispersion, melamine (1 g) and Triethylamine (3 mmol) were added to them and was refluxed for 24 h. Then was washed with ethanol and dried at 80 °C for 24 h. gum@Melamine (0.5 g) was dispersed in 10 mL distilled water, then Cu(OAc)₂ (0.5 g) was added slowly and stirred at room temperature for 24 h. Then, the mixture was filtered, washed with H₂O and EtOH, and dried at 60 °C for 5 h.

2.3. General Procedure for Derivatives Synthesis

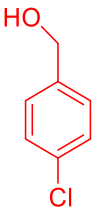
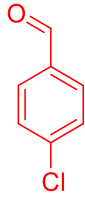
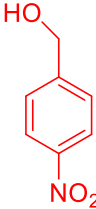
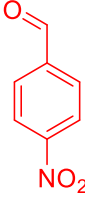
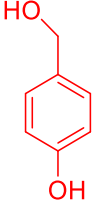
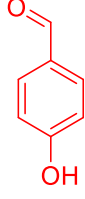
The oxidation of alcohols to aldehydes was conducted in 50 mL flask in an oil bath. 1mmol of aldehyde, 5 mL CH₃CN and 50 mg gum@Melamine@Cu(II) were added to flask and stirred. After completion the reaction which was followed by TLC, the mixture was filtered and the products were purified.

3. Results and Discussion

In order to extend the application of gum@Melamine@Cu(II), the effect of substrate was also studied under optimal conditions (Table 1). As can be seen, the reaction conditions were compatible with both electron acceptor and electron donor substituents aromatic ring.

Table 1. oxidation of different benzyl alcohols catalyzed by gum@Melamine@Cu(II) under optimized conditions.

Entry	Substrates	Products	Yield of Products
1	<p style="text-align: center;">(1a)</p>	<p style="text-align: center;">(2a)</p>	98

2	 <p>(1b)</p>	 <p>(2b)</p>	96
3	 <p>(1c)</p>	 <p>(2c)</p>	91
4	 <p>(1d)</p>	 <p>(2d)</p>	93

* **Reaction conditions:**), aldehyde (1 mmol), catalyst (50 mg). and CH₃CN (5 mL) under reflux conditions.

4. Conclusions

In summary, a heterogeneous gum-melamine catalyst was prepared and used for the oxidation of benzyl alcohol and its derivatives with a high yield. The main advantages of this catalyst are its reusability, simple separation from the reaction mixture, and short reaction time. In addition, the use of an easy and convenient method for the preparation of the catalyst is another advantage of this catalyst over other reported catalysts.

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Data Availability Statement:

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