

Research Article

Synthesis of Heterogeneous Copper Catalyst Based on Amino-Functionalized Triazine Rings Supported by Silica-Gel for Oxidation of Alcohols

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Amino-functionalized triazine supported on silica-gel was prepared. This new triazine derivate was applied as a coordinating agent for copper (II) and was characterized by different methods. The copper (II) content of the material was determined by atomic absorption. This novel transition metal supported on heterogeneous surface was used as an effective catalyst for oxidation of benzylic alcohols in the presence of H₂O₂. This catalyst can be reused without any significant loss of activity.

1. Introduction

1,3,5-Triazine derivatives have found widespread applications in the pharmaceutical, textile, plastic, and rubber industries and are used as pesticides, dye stuffs, optical bleaches, explosives, and surface active agents [1].

Recently, there has been a growth of interest in the use of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) in a wide range of functional group transformations. The ease of displacement of chlorine atoms in cyanuric chloride by various nucleophiles, in the presence of an acid acceptor, makes this reagent useful for the preparation of mono-, di-, and tri-substituted 1,3,5-triazines [2]. Cyanuric chloride is one of the most widely used linking agents, as it can react with carbon active surface [3, 4], clay [5], quartz surface [6], modified resins [7, 8], glass slide [9], and with a variety of substances, including hydroxyl and amino compounds, alkyl and aryl Grignard reagents, and organic hydrazine derivatives [3]. Interestingly, in most of these cases, the use of cyanuric chloride presents advantages compared to other classical methods in terms of cost, yield, and mildness. Thus, in the light of these results, the discovery of new applications for cyanuric chloride in organic synthesis is of interest.

Selective oxidation of alcohol into an aldehyde or ketone is an important transformation in organic synthesis, and various methods are known for this particular conversion. Aldehydes are an important class of compounds used as food additives and as intermediates in organic syntheses such as Aldol condensation, Micheal addition, Cannizaro and Perkins reactions. To achieve selective oxidations, various homogeneous catalysts and combined catalysts have been reported in the literature [10–16]. Homogeneous catalysts have enormous relevance in various organic reactions. However, homogeneous catalysts have some disadvantages in that they can decompose during the course of the reaction and are not easily recovered after the reaction for reuse. This leads to the loss of metal and ligands and incorporation of impurities in the products. Also, these oxidation reactions are often performed in solvents such as chlorinated hydrocarbons, which can have an adverse environmental impact when practiced on an industrial scale. Immobilization of homogeneous catalysts on solid supports often presents advantages due to easy separation from the product mixture by simple filtration, high catalytic activity, stability, and selectivity in comparison to unsupported metal complexes where the industrial demand of recyclability for continuous operation

TABLE 1: The effect of solvent for oxidation of benzyl alcohol^a.

Solvent	Time (min) ^b	Yield (%)
Acetonitrile	65	55
Solvent free	45	42
Toluene	85	70
Acetone	240	73
<i>n</i> -Hexane	35	80

^aAll reactions were carried out in the reflux condition in the presence of 0.15 g catalyst and 3 mmol H₂O₂.

^bTime of maximum conversion.

can be met. Due to these inherent advantages of heterogeneous catalysts over homogeneous catalysts, a great deal of effort has been devoted to the development of heterogeneous catalysts. In the literature, many heterogeneous catalysts have been proposed for oxidation of alcohols to aldehydes or ketones. For example, benzylic alcohols were oxidized to the corresponding carbonyl compounds in good to high yields by environmentally friendly and green oxidant, H₂O₂ catalyzed by montmorillonite K-10 supported cobalt (II) chloride in a rather long reaction time [17]. Selective oxidation of benzyl alcohol to benzaldehyde catalyzed by Cr(salen) complexes immobilized on MCM-41 was performed by H₂O₂ but showed low conversion [18]. Also, oxidation of alcohols by Cu(II) complexes immobilized by different ligands on silicate layers of bentonite was reported in the presence of tert-butylhydroperoxide (TBHP) as an oxidant with good selectivity but low conversion [19].

In order to provide a more environmentally benign "green" process for alcohol oxidations, a variety of methods for using transition metal catalysts with more mild oxidants such as H₂O₂ have been investigated [20]. Hydrogen peroxide is an attractive, atom-economic, and environmentally benign oxidant as it is cheap, easily available, nontoxic which produces only water as a by-product [21].

The problems associated with homogeneous catalysts prompted us to investigate and design a novel heterogeneous oxidizing catalyst for conversion of alcohol to aldehyde with improved selectivity and conversion efficiency. The goal of this work is to support copper (II) on a silica-gel surface via a novel modification technique using an aminated triazine ring in order to increase adhesion with deposited metal.

2. Experimental

2.1. Materials and Solvents. The reagents and solvents were purchased from Merck, Fulka, and Aldrich Chemical companies and were used as received. Silica-gel (particle size 20–63 μm, 70–230 mesh pore size 100 Å), ethylenediamine (EDA), cyanuric chloride, triethylamine (TEA), and copper acetate were purchased from Merck Chemical Company and used without further purification. In order to dry tetrahydrofuran (THF), it was distilled off over sodium in the presence of benzophenone after its color changed to deep blue.

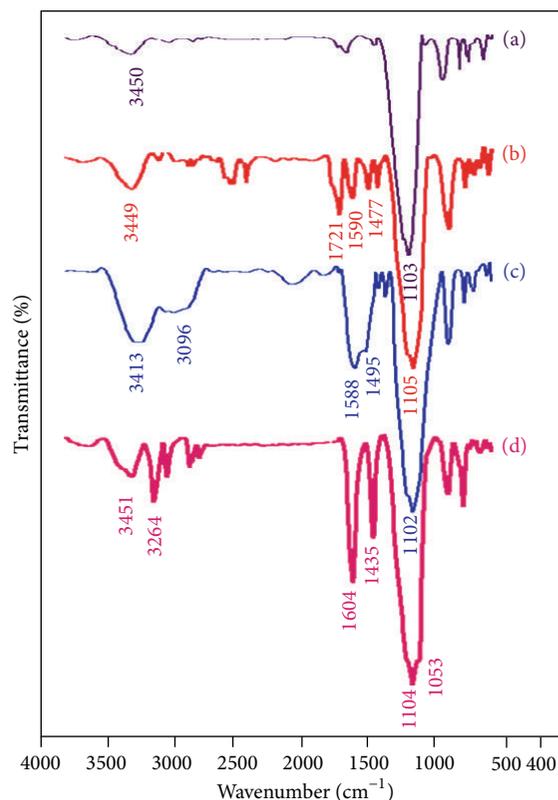


FIGURE 1: FT-IR spectra for (a) silica-gel, (b) CC-silica, (c) AT-silica, and (d) Cu/AT-silica.

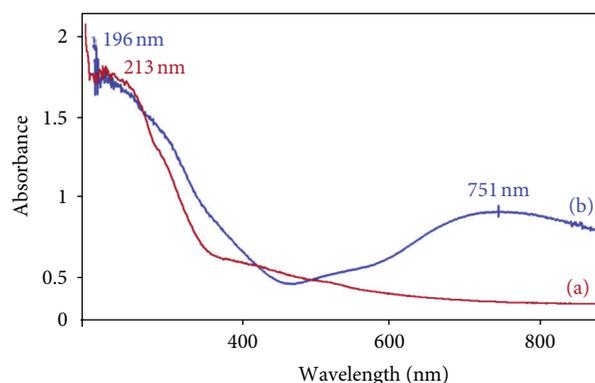


FIGURE 2: DR UV-vis spectra of (a) AT-silica and (b) Cu/AT-silica.

2.2. Preparation of Cyanuric Chloride Supported on Silica-Gel. Silica-gel (1.2 g) and 10 mL dry tetrahydrofuran (THF) in a 25 round bottom flask were cooled in an ice bath. TEA (0.5 mL) was added and stirred for 10 min. Then, cyanuric chloride (1.2 g, 6.5 mmol) was added, and the mixture was stirred for 1 h in an ice bath and 2 h at room temperature. The solid was filtered, washed with dry THF, and dried at 60°C for 1 h to give 1.87 g of cyanuric chloride grafted on silica-gel (CC-silica).

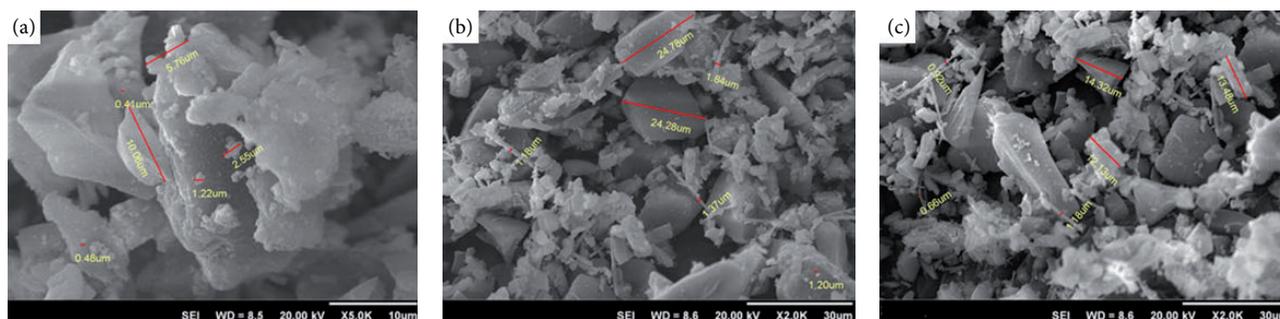
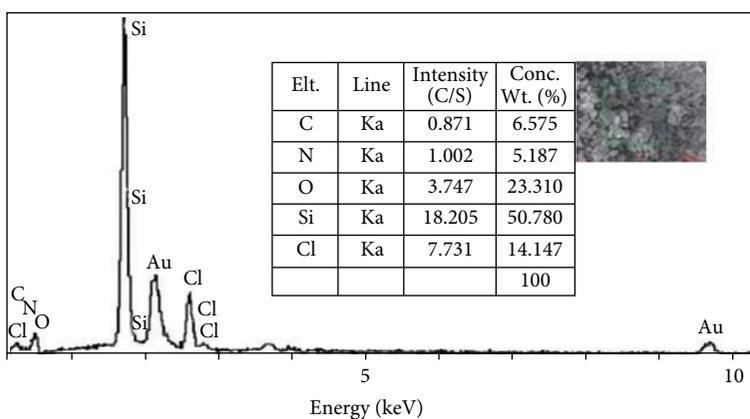
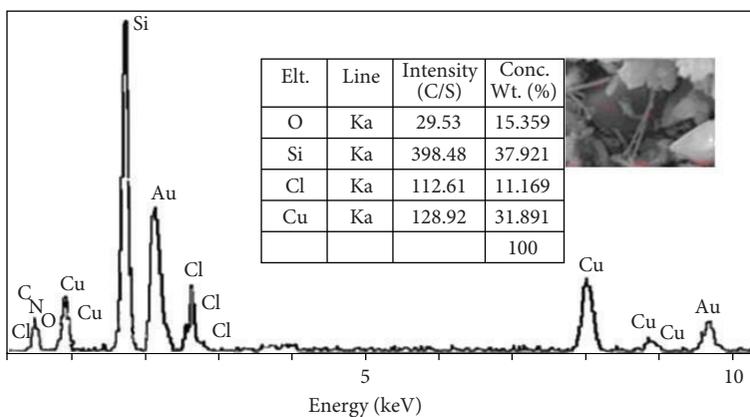


FIGURE 3: SEM images of (a) AT-silica and (b, c) Cu/AT-silica.



(a)



(b)

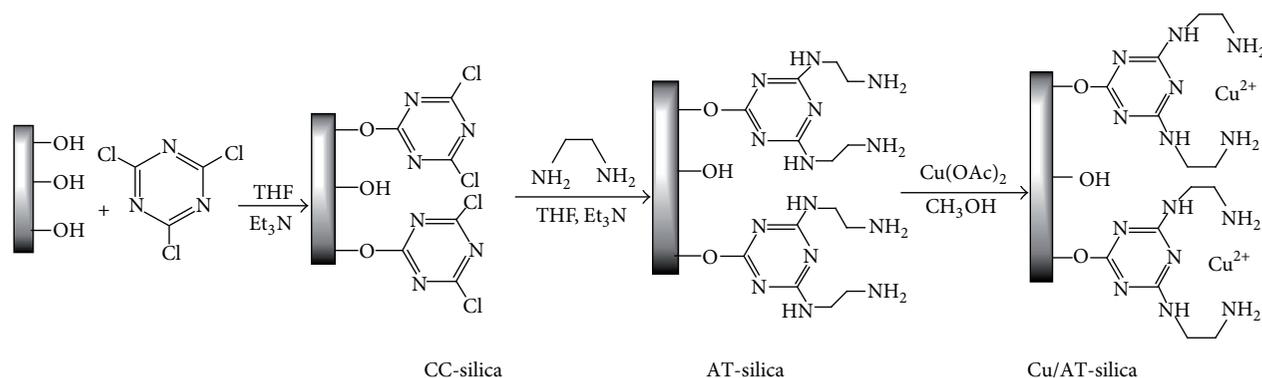
FIGURE 4: EDX images of (a) AT-silica and (b) Cu/AT-silica.

2.3. Reaction of CC-Silica with Ethylenediamine. In the second step 1.5 g of CC-silica in 10 mL dry THF was reacted with 1.5 mL EDA in the round bottom flask. The reaction mixture was stirred in an ice bath for 1 h and warmed to room temperature; TEA (1 mL) was added and stirred for overnight. Then, it was refluxed for 45 min, and the solid was filtered to give 1.9 g animated-triazine supported on silica-gel (AT-silica).

Basic content of AT-silica was estimated by back titration using NaOH. In a typical procedure, 5 mL of HCl (0.12 N) was added to 0.2 g of modified silica and stirred for 30 min. The

catalyst was removed and washed successively with deionized water. The excess amount of HCl was titrated with NaOH (0.1 N) in the presence of phenolphthalein as an indicator. The basic content of catalyst was found to be 2.75 mmol g⁻¹.

2.4. Coordination of Cu(II) onto AT-Silica. 1.4 g (7.0 mmol) of Cu(OAc)₂ in 3 mL of methanol was added to the 1.2 g AT-silica in a round bottom flask equipped with a condenser. The reaction mixture was refluxed for 6 h. The solid was filtered and extracted with methanol in soxhlet for 10 h, then



SCHEME 1: Preparation of Cu/AT-silica.

TABLE 2: The effect of catalyst amount on oxidation of benzyl alcohol^a.

Entry	Catalyst amount (g)	Yield (%)	Selectivity (%)
1	—	5	100
2	0.05	58	100
3	0.10	72	100
4	0.15	80	100
5	0.20	83	100

^a Reaction conditions: benzyl alcohol = 1 mmol, solvent = *n*-hexane, amount of H₂O₂ = 3 mmol, time = 35 min at reflux condition.

it was dried at 60°C for 1 h to give Cu(II) supported on AT-silica (Cu/AT-silica). The copper content of Cu/AT-silica was determined by atomic absorption (Perkin Elmer) and found to be 2.8 mmol Cu²⁺/g.

2.5. A typical Procedure for Oxidation of Alcohol. Benzyl alcohol was selected as a model substrate for oxidation reaction and for the optimization of the process. A typical experimental procedure was as follows: to the mixture of catalyst (0.15 g), *n*-hexane (2 mL), and benzyl alcohol (1 mmol), 3 mmol hydrogen peroxide (30% solution) was added slowly. The reaction components were stirred at reflux condition for a period of time. The reaction process was monitored by thin-layer chromatography (TLC, silica-gel 60 F₂₅₄) and/or gas chromatography (GC, CP WAX 52, VARIAN CP 3800). After completion of reaction, the mixture was filtered and the filtered washed with ethyl acetate. Evaporation of solvent gives the corresponding aldehyde.

3. Results and Discussion

Silica-gel surfaces are modified with an aliphatic amine (EDA) by cyanuric chloride as a linking agent via a two-step chemical reaction. Cyanuric chloride was chemically bound with surface hydroxyl groups of silica-gel followed by reaction with EDA (Scheme 1). Cyanuric chloride contains three chlorine atoms which can be substituted by nucleophiles in a stepwise manner. This stepwise reactivity is used to initially couple the cyanuric chloride to the silica-gel at moderate

temperatures via reaction with the surface hydroxyl groups. The remaining chlorine groups on the coupled triazine are subsequently substituted by EDA at higher reaction temperatures. This new triazine derivate was applied as a coordination agent for copper (II) in methanol.

3.1. Characterizations of Catalyst. The structure of this catalyst was confirmed by FT-IR spectroscopy (PerkinElmer Spectrum Version 65). The spectrum of silica-gel shows absorption bands, around 1103 cm⁻¹ (Si-O) and 3450 cm⁻¹ (Si-O-H). After reaction of silica-gel with cyanuric chloride, new peaks at 1721 cm⁻¹, 1477 cm⁻¹, and 1590 cm⁻¹ (C-Cl, C = N stretching of triazine ring) as well as existing bands at 1103 cm⁻¹ to 1105 cm⁻¹ were appeared.

The FT-IR spectrum of AT-silica displays a broad absorption (with two weak peaks) around 3300–3400 cm⁻¹ (stretching N-H) and two peaks at 1495 and 1588 cm⁻¹ (C = N stretching and N-H vibration). After reaction of AT-triazine with Cu(II), the C = N stretching absorption bond shifted to lower frequency (1435 cm⁻¹), while vibrational N-H absorption shifted to higher frequency (1604 cm⁻¹), which confirms the chemical interactions of aromatic electrons and nitrogen lone pair electrons with vacant copper orbitals (Figure 1).

Figure 2 presents the DR UV-vis spectra of AT-silica and Cu/AT-silica run by UV-vis Spectrophotometer, JASCO, V-670 (190–2700 nm), Japan. The absorption around 213 nm in AT-silica is attributed to *n*-π* and π-π* electron transfers for the aromatic ring and amine groups. In DR UV-vis spectrum of Cu/AT-silica, new absorption around 751 nm appears which can be assigned to d-d transitions after loading of copper.

3.2. SEM Characterization. Morphology and location of metallic species on the surface of the catalyst were analyzed by scanning electron microscopy (SEM) using an AIS-2100 (SIE mode), Korea microscope equipped with an energy dispersive X-ray analyzer (EDX). Figure 3 shows the SEM images of (a) AT-silica and (b, c) the immobilized copper on AT-silica (Cu/AT-silica). Clear changes in the morphologies of the catalyst after introduction of metals were observed by SEM.

TABLE 3: Oxidation of various alcohols using H₂O₂ catalyzed by AT-silica supported Cu(OAc)₂^a.

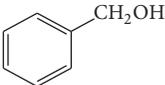
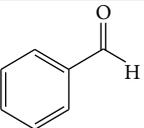
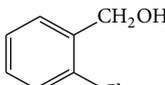
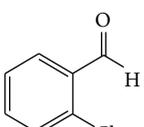
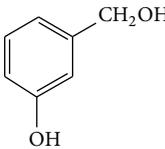
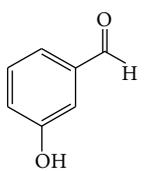
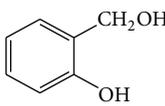
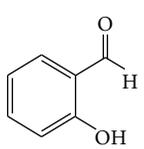
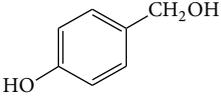
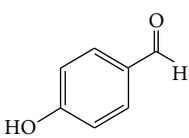
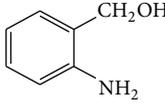
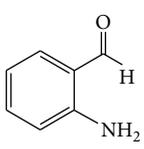
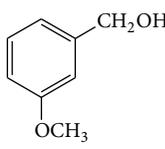
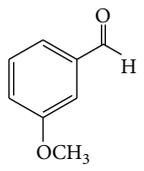
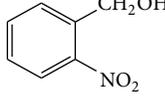
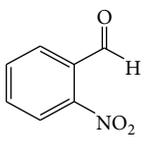
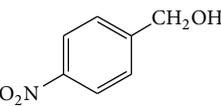
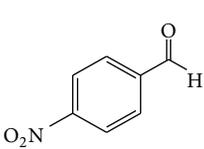
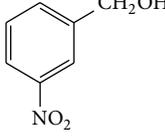
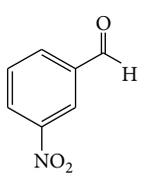
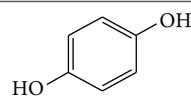
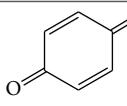
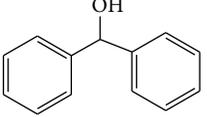
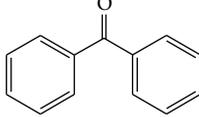
Entry	Alcohol	Product	Time (min) ^c	Yield (%) ^{d,e}
1			35	80
2			30	71
3 ^b			75	83
4			2	98
5			2	98
6			5	98
7			30	81
8			30	46
9			45	60
10			30	53

TABLE 3: Continued.

Entry	Alcohol	Product	Time (min) ^c	Yield (%) ^{d,e}
11			2	98
12			80	67

^a Reaction conditions: alcohols = 1 mmol, amount of catalysis = 0.15 g, H₂O₂ = 3 mmol, solvent = *n*-hexane, all reactions were carried out in reflux condition, except entries 5, 9, 11, which were performed in room temperature.

^b Acetone was used as a solvent.

^c Time of maximum conversion (determined by TLC and/or GC).

^d Isolated yield.

^e All of the reactions give corresponding aldehyde in 100% selectivity.

TABLE 4: Catalyst reusability of Cu/AT-silica^a.

Entry	Time (min)	Yield (%)	Selectivity (%)
1	35	80	100
2	35	80	100
3	35	72	100
4	35	65	100

^a Reaction conditions: alcohols = 1 mmol, amount of catalysis = 0.15 g, H₂O₂ = 3 mmol, solvent = *n*-hexane, all reactions were carried out in reflux condition.

Comparisons of EDX analysis of AT-silica with Cu/AT-silica (after extracting with methanol in soxhlet) confirm addition of copper to the catalyst, which suggested the formation of metal complexes with the anchored ligand (Figure 4).

3.3. Investigation of Catalytic Activity for Oxidation of Alcohols. In order to investigate the effect of solvent for oxidation reaction, different solvents such as acetonitrile, toluene, acetone, *n*-hexane, and solvent-free condition were chosen for oxidation of benzyl alcohol (Table 1). The result shows the best solvents for this reaction were *n*-hexane and toluene. In solvent-free condition, the yield of product is low.

The effect of catalyst amount on oxidation of benzyl alcohol was investigated (Table 2). The results show that with increasing of the amount of catalyst to 0.15 g, the yield of reaction increased in fixed time. But further increasing in amount of the catalyst to 0.20 g did not show any considerable effect on the reactivity.

After the investigation of the effects of different parameters for the oxidation of benzyl alcohol, as a standard substrate, the best conditions were chosen and various alcohols were oxidized in the presence of a catalytic amount of Cu/AT-silica and H₂O₂ as an oxidant in refluxing *n*-hexane. Table 3 summarizes the result of various benzylic alcohols oxidation using Cu/AT-silica. The reaction yields were slightly dependent on substituents (-Cl, -OH, -OCH₃, -NO₂, and -NH₂) and on their positions.

Primary benzylic alcohols with electron donating substituent such as *o*- and *p*-hydroxy, and *o*-amino were converted to the corresponding aldehydes in excellent yield (entry 3–6). On the other hand, the highest decelerating effect was observed with strong electron accepting nitrosubstituents (entry 8–10), whereas halogen substituents cause medium yields (entry 2). Similarly, the oxidation of secondary benzylic alcohol was also giving the corresponding ketone (entry 12). The overoxidation of aldehydes into carboxylic acids was not observed, and all of the corresponding aldehydes were obtained in excellent selectivity.

3.4. Catalyst Recycling. One of the main reasons for supporting a homogeneous metal complex on the silica-gel is to enhance the life of the resulting catalyst. To investigate the reusability of silica-gel-based complex catalysts, the catalyst was separated by filtration after the first run, dried under vacuum, and then subjected to a second run with further addition of substrates in appropriate amounts under optimum reaction conditions, and the yield and structure of the final products were compared with those of the original run. As shown in Table 4, the catalyst could be used for oxidation of alcohols up to four times without loss of its selectivity.

4. Conclusions

In this study, a novel heterogeneous catalyst (Cu/AT-silica) containing amino-functionalized triazine supported on silica-gel synthesized via reaction of cyanuric chloride with silica-gel is followed by reaction with ethylenediamine and coordination of copper (II). FT-IR spectroscopy and X-ray diffraction show the structure of Cu/AT-silica and confirm that the ligand is attached to the silica surface. DRUV-Vis, atomic absorption, and EDX analysis also approve the existence of copper on the resulting catalyst. This new triazine derivate was applied as a highly efficient catalyst for the selective and environmentally friendly oxidation of benzylic alcohols to corresponding aldehydes and ketones with hydrogen peroxide. The main advantages of this catalytic system are easy catalyst preparation, mild reaction conditions, and easy

workup procedure, low cost of the catalyst, and finally it can be recycled and reused several times without loss of activity.

Acknowledgment

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