



Copper-doped CaO as a nanocrystalline heterogeneous catalyst for amidation of natural triglycerides

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ABSTRACT

Alkylamides or fatty acid diethanolamides were synthesized from a variety of natural triglycerides (vegetable oil) using copper-loaded CaO nanocrystallites as a heterogeneous catalyst. The Cu-doped CaO (Cu@CaO) nanocrystallites were observed to be efficient heterogeneous catalysts and led to the complete conversion of vegetable oil to fatty acid diethanolamine in 2.0 h at 110 °C. The Cu@CaO nanocrystallites were prepared using the wet-impregnation method by loading copper nitrate on CaO in the weight percentage (wt%) range of 1.0 to 5wt% and characterized with DLS, powder XRD, FESEM, and TEM analytical techniques. Prepared Cu@CaO were found to be nanosized crystalline material with ~45 nm of average particle size. 4wt% of copper nitrate loaded CaO calcined at 500 °C was observed to show higher catalytic activity and convert the natural triglycerides to alkyl amides.

Keywords - copper loaded CaO; nanocrystallites, triglycerides; amidation; heterogeneous catalyst

I. INTRODUCTION

Natural triglycerides viz., vegetable oils [1] and various other biomass [2-4] have been found to convert into useful value-added products using chemical processes. Vegetable oils as well as animal fats are being used in the industries as a feedstock to synthesize fatty acid diethanolamides, fatty acid alkyl esters, nitriles, alcohols, and amines which are valuable products to prepare numerous commodity chemicals like paints, surfactants, resins, biofuels, and different polymers [2, 5].



Further, long-chain alkyl amides have a broad range of applications such as they are used in fungicides, cosmetics, lubricants, detergents, water repellents, corrosion inhibitors, shampoos, and anti-blocking agents [6-9]. Also, fatty acid alkyl amides possessed excellent ignition properties in comparison to simple esters and hence were designated to be more useful in biofuel advancement technologies [8]. Moreover, alkyl amide derivatives of vegetable oils animal fats, or fatty acids are free from sulfur or any aromatic complexes and therefore help to reduce the greenhouse impact, exhibiting an enhancement in the cold flow properties, cetane number, and an advantageous effect on the emission of particulate matter [10]. The industrialized preparation of fatty acid alkyl amides required a two-step synthesis, first the transformation of triglycerides into fatty acid alkyl esters followed by their high-temperature heating to prepare the resultant fatty acid diethanolamides [8].

To avoid a high-temperature process, some other methodologies have been reported to prepare fatty acid alkyl amides from fatty acid alkyl esters or fatty acids or natural triglycerides via reactions with different amines have been suggested previously [11, 12]. At the industrial level, homogeneous catalysts viz., sodium methoxide/ethoxide [13], acid chlorides [14], and calcium chloride [15] are employed for the fatty acid alkyl amides preparation. Enzymes have also been commonly reported [16, 17] as heterogeneous catalysts for the aminolysis of triglycerides though needed extended reaction duration. Likewise, solvent-free reaction conditions [18], dithiocarbamates [19], Sm^{III} complexes [20], Cr-MIL-100 and Cr-MIL-101 [21], Fe-beta zeolites [22], the Deoxo-Fluor reagent [bis(2-methoxyethyl)amino-sulfur trifluoride] [23], Sn^{IV} complexes [24], and other catalysts [19] have been used to procure the required amide. However, there are some drawbacks connected with these methodologies such as lower yields, longer reaction periods, laborious product separation, lack of catalytic recyclability, excess use of reactants/solvents, product contamination, and the formation of undesired side products. Hence, it is required to extend new, highly active, efficient, environmentally green, eco-friendly, and recyclable heterogenous catalytic approaches for the amidation/aminolysis of fatty acids and nature derived triglycerides [25, 26]. In recent years, heterogeneous catalytic processes have attracted great attention as they are nonhazardous, highly selective, reusable, and easily separable from reaction mixture [27-30].

In the present report, copper-loaded CaO has been prepared in nanocrystalline form using the incipient-wet impregnation synthetic method and utilized as heterogeneous catalysts for the amidation of natural triglycerides.



The effect of Cu metal ion impregnation on CaO, catalyst concentration, calcination temperature, and reaction time has been studied for the amidation of vegetable oil.

II. EXPERIMENTAL SECTION

Preparation of catalyst

Copper (Cu) doped CaO nanocrystallites were synthesized by following the modified incipient-wet impregnation method [31]. In a typical synthesis, CaO slurry (10 mg in 40 mL ethanol) was ultra-sonicated for 1.0 h then 10 mL of copper nitrate solution in ethanol of required concentration was added dropwise into CaO slurry and stirred continuously for 3.0 h at room temperature (25 °C). The resulting final mixture was dried at 100 °C and then calcined at 500 °C for 6.0 h. The Cu@CaO powdered nanocrystallites thus obtained were analyzed by powder-XRD (X-ray diffraction), DLS (dynamic light scattering), FESEM (field emission scanning electron microscopy), and TEM techniques (transmission electron microscopy).

Aminolysis reaction

The Cu@CaO mediated aminolysis reactions of vegetable oil (cottonseed oil) with varying molar concentrations of diethanolamine, calcination temperature, and catalyst amounts were carried out at 110° C. All chemical reactions were carried out till the completion by changing one reaction parameter at a time to determine the optimum reaction conditions needed to complete the amidation/aminolysis in the lowest possible time. The reaction products from the aminolysis reaction were characterized by FTIR (Fourier transform infrared) and proton nuclear magnetic resonance (¹H-NMR) spectroscopic techniques and the reaction yield was quantified with FTIR spectroscopy.

III. RESULTS AND DISCUSSION

Structural analysis of catalyst

Dynamic light scattering analysis (DLS) has been carried out to measure the particle size distribution of CaO and Cu@CaO and illustrated that the average particle size of CaO and Cu@CaO was ~101 nm and ~45 nm, respectively (Figure 1a and 1b). The effect of Cu loading on CaO and calcination temperature on the crystal

structure of CaO has been observed with powder XRD analysis (Figure 2a). The presence of CaO in the cubic crystalline phase was confirmed because of the presence of peaks at 2θ values of 37.5° , 53.9° , 32.2° , and 67.4° (JCPDS card no. 821691) as shown in Figure 2a. After Cu loading (4 wt%) the calculation at 500°C showed the existence of only the cubic phase. However, the peaks of Cu@CaO become broader as compared to CaO which inculcates the existence of Cu@CaO in nanocrystallites form.

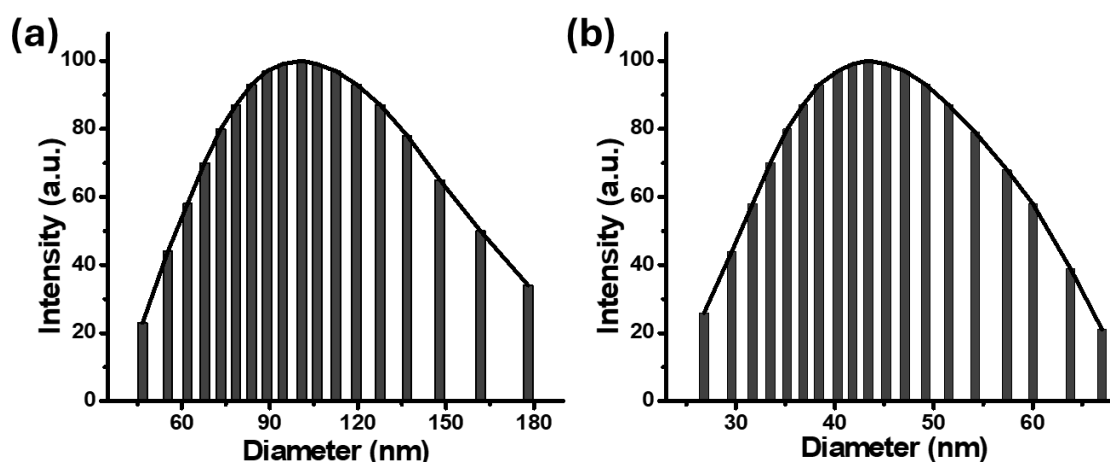


Figure 1. Particle size distributions of (a) CaO and (b) Cu@CaO nanocrystallites.

There were no diffraction patterns associated with Cu were observed in the XRD spectrum which could be because of the high degree dispersion of Cu on CaO, or it might be under the detection limit of XRD. However, the variation in Cu ion concentration and calcination temperature has no significant impact on particle size or crystallinity.

The exact particle size and surface morphology of Cu@CaO nanocrystallites were analyzed by FESEM and TEM. The surface morphology of Cu@CaO nanocrystallites has been found to be porous crystalline irregular morphology with particle size varying from 50-300 nm as shown in Figure 2b. TEM image showed that the Cu@CaO nanocrystallites were agglomerated and possess an average particle size of ~ 50 nm (Figure 2c).

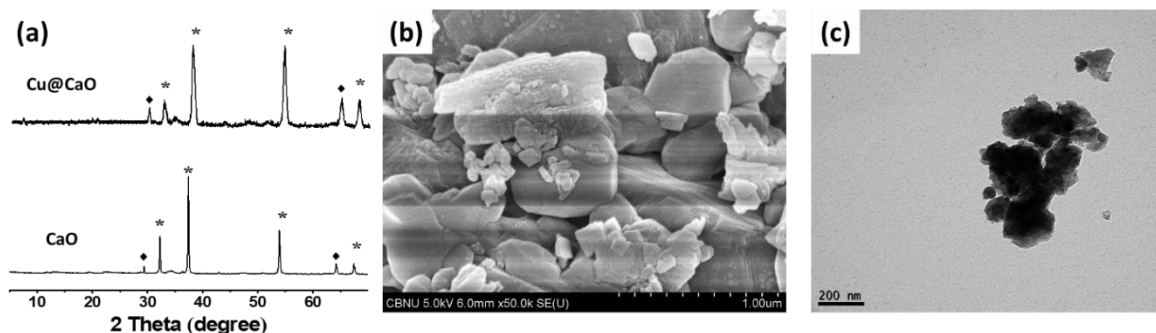
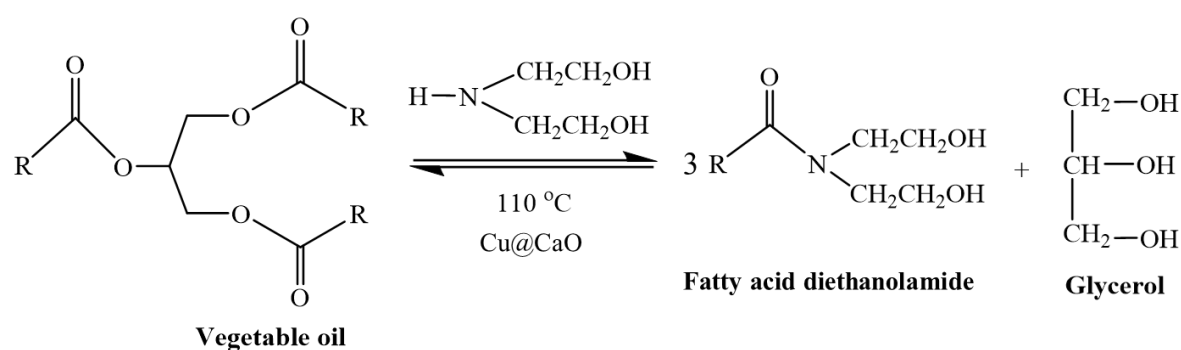


Figure 2. (a) Comparative powder XRD patterns of CaO with Cu@CaO. (b) FESEM image of Cu@CaO. (c) TEM image of Cu@CaO.

Aminolysis reaction

The amidation reactions of natural triglycerides with different Cu@CaO nanocrystallite concentrations and different molar concentrations of diethanolamine were performed at 110° C for 2.0 h. All amidation reactions for studying various reaction parameters were carried out with diethanolamine in the presence of 4 wt% of Cu@CaO catalyst at 110 °C for 2.0 h (Scheme 1). The schematic for the amidation of vegetable oil performed with diethanolamine (12:1 diethanolamine to oil molar ratio) by using the 5 wt% of the Cu@CaO nanocrystallite at 110 °C has been shown in Scheme 1.



Scheme 1. Aminolysis of vegetable oil using Cu@CaO nanocrystallites in the presence of diethanolamine at 110 °C for 2.0 h.

The vegetable oil amidation reaction progress was examined by taking out samples from the reaction solution after certain time gaps and analyzed with FTIR and $^1\text{H-NMR}$ spectroscopic techniques. The Cu@CaO nanocrystallites were removed from the reaction samples by centrifugation at 5000 rpm/10 min and the resulting organic layer was washed multiple times with deionized water and then dried over sodium sulfate. As obtained amide derivatives were characterized by FTIR (Figure 3) and $^1\text{H-NMR}$ (Figure 4) analysis techniques. The ester carbonyl peak shifting to the ester amide peak from 1741 cm^{-1} to 1619 cm^{-1} suggested the formation of fatty acid diethanolamides (Figure 3). The formation of the derivative of diethanolamine has also been supported by the existence hydroxide ($-\text{OH}$) group peak at 3408 cm^{-1} as shown in Figure 3.

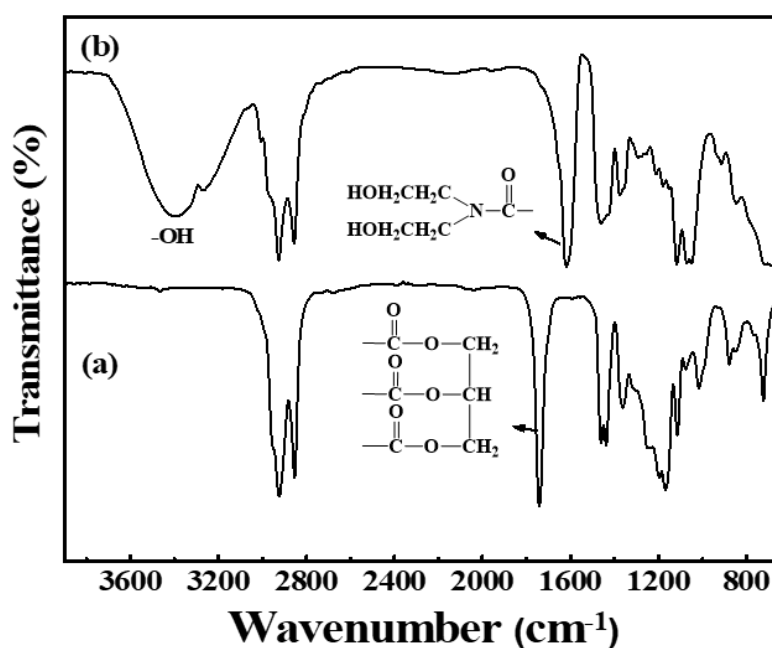


Figure 3. Comparative FTIR spectrum of (a) vegetable oil and (b) fatty acid diethanolamide derivative of vegetable oil.

Alternatively, the $^1\text{H-NMR}$ spectrum showed the presence of multiplets at 3.47 and 3.77 ppm due to $-\text{NCH}_2-$ and $-\text{CH}_2\text{OH}$ protons, respectively (Figure 4), and the disappearance of characteristic glyceridic peaks at 4.15, 4.33 and 5.35 ppm (Figure 4) reinforced the conversion of triglyceride molecule to corresponding fatty acid

diethanolamides. The NMR and FTIR analysis suggested the complete conversion of vegetable oil to fatty acid diethanolamide derivatives in the presence of Cu@CaO nanocrystallites.

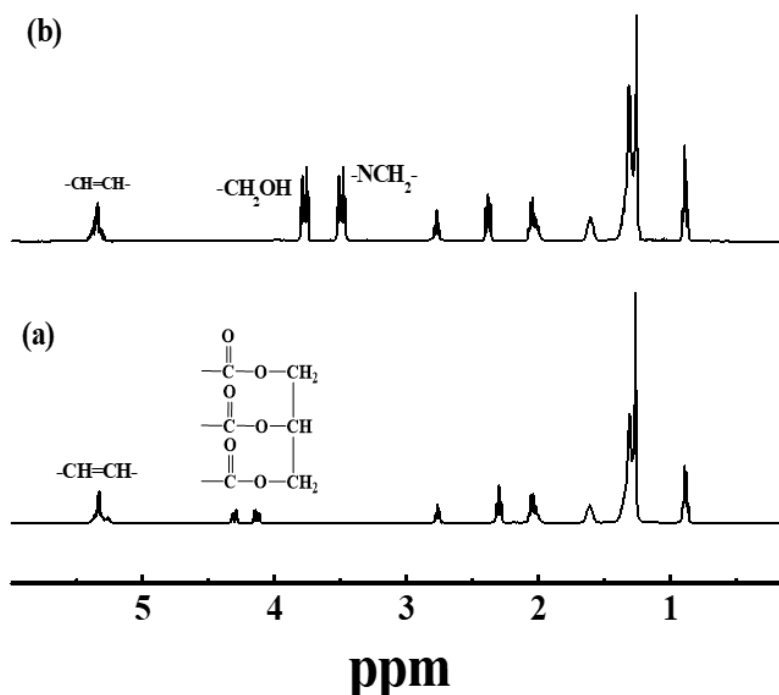


Figure 4. Comparative ¹H-NMR spectrum of (a) vegetable oil and (b) fatty acid diethanolamide derivative of vegetable oil.

Optimization of different parameters

The prepared Cu@CaO nanocrystallites were employed for the amidation of vegetable oil with diethanolamine. The Cu@CaO nanocrystallites were calcined at three different temperatures viz., 300, 500, and 700 °C and tested for the aminolysis of vegetable oils. Among all the prepared catalysts Cu@CaO nanocrystallites calcined at 500 °C was found to be the most efficient with complete conversion (99%) of vegetable oil to fatty acid diethanolamide and selected for further optimization studies (Figure 5a). The lesser catalytic activity at high calcination temperatures might be because of the sintering of Cu@CaO nanocrystallites.

To optimize the Cu metal ion concentration in CaO for higher catalytic activity, a series of vegetable oil amidation reactions were performed by varying the Cu²⁺ concentration from 1.0 to 5.0 wt%. There was a significant surge

in the fatty acid diethanolamide yield from 46% to 99% as the Cu^{2+} concentration increased from 1.0 to 4.0 wt%, respectively (Figure 5b). Further enhancement in Cu^{2+} concentration has no impact on catalytic activity, and hence 4.0 wt% Cu-loaded CaO was chosen as the optimized amount of Cu for maximum catalytic efficiency.

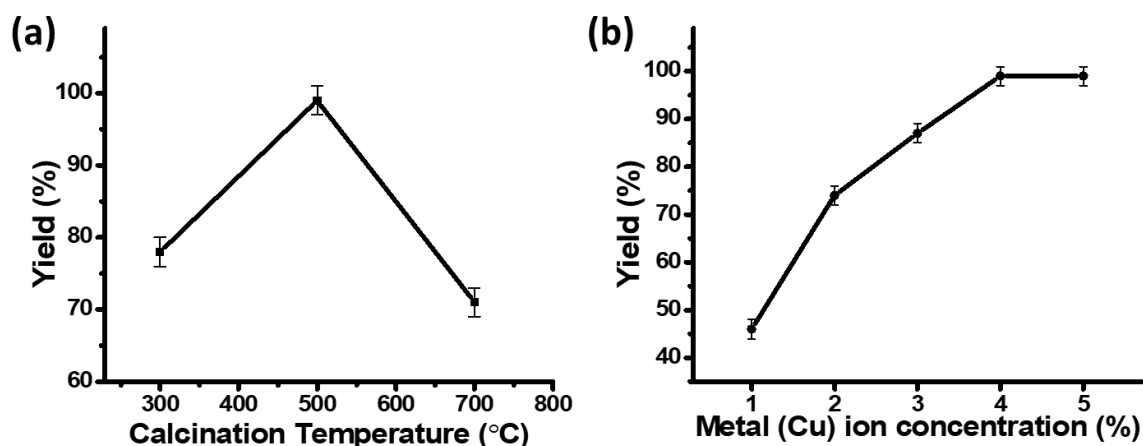


Figure 5. Effect of (a) calcination temperature and (b) Cu ion concentration in CaO on the amidation of vegetable oil.

Different catalyst amounts of Cu@CaO nanocrystallites from 1-7 wt% were tested to figure out the optimized catalyst amount. The fatty acid diethanolamide yield escalated from 24% to 99% when the Cu@CaO nanocrystallites amount was enhanced from 1.0 wt% to 4.0 wt%. Further increase in the Cu@CaO nanocrystallites amount has no significant impact on the reaction rate (Figure 6a). Five different diethanolamine: vegetable oil molar ratios were tested to optimize the amount of diethanolamine for maximum conversion rate in minimum reaction time. As the molar ratio was enhanced from 3:1 to 12:1 the fatty acid diethanolamide yield was also increased from 34% to 99% in 2.0 h, respectively (Figure 6b). In the next reaction parameter, reaction time was varied from 0.5 h to 3.0 h for the Cu@CaO mediated amidation of vegetable oil. The fatty acid diethanolamide yield was observed as 36% after 0.5 h which enhanced significantly after 1.0 h to 64% and reached 99% after 2.0 h of reaction time (Figure 6c). The diethanolamine to vegetable oil molar ratio of 12:1, calcination temperature of 500 °C, 4.0% of Cu loading on CaO, 5.0 wt% of catalyst amount, and 110 °C of reaction temperature were the

optimized reaction conditions for the fatty acid diethanolamides synthesis from vegetable oil in 2.0 h of reaction time.

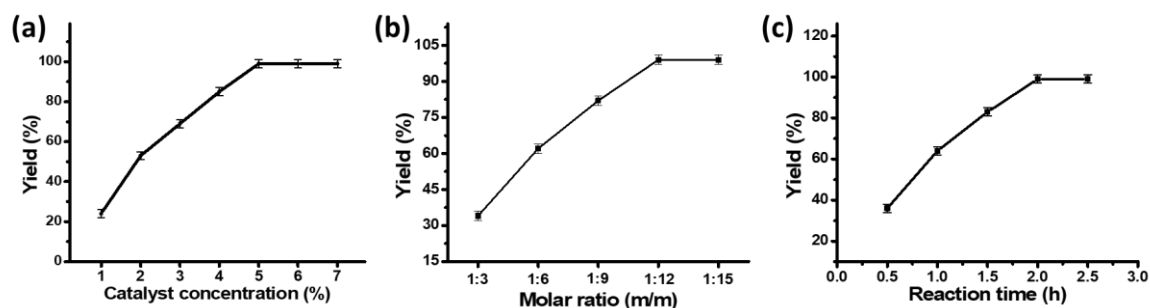


Figure 6. Effect of (a) catalyst concentration, (b) diethanolamine: vegetable oil molar ratio, and (c) reaction time on the complete aminolysis of vegetable oil.

IV. CONCLUSIONS

The Cu-loaded CaO nanocrystallites were prepared by employing a simple incipient-wet impregnation synthetic method and used as a solid heterogeneous catalyst for the amidation of vegetable oil. Copper nitrate solution in ethanol was added to the CaO slurry in ethanol and after ultra-sonication and stirring the resulting final mixture was dried and calcined at different temperatures to prepare Cu@CaO nanocrystallites. Prepared Cu@CaO nanocrystallites were observed to have a crystalline structure with cubic phase, porous structure, and ~50 nm size. Cu@CaO nanocrystallites with 4.0% copper loading on CaO and calcined at 500 °C were found as a highly efficient heterogeneous catalyst for the amidation of vegetable oil as it took only 5.0 wt% of catalyst amounts for complete conversion of vegetable oil-based natural triglycerides with 12:1 molar ratio of diethanolamine: vegetable oil at 110 °C after 2.0 h of reaction time. The complete conversion of vegetable oil to fatty acid alkyl amides suggested that Cu@CaO nanocrystallites can be useful for other similar chemical transformations of natural triglycerides or fatty acids such as transesterification, esterification, and epoxidation.

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