



Catalytic wet oxidation of ferulic acid (a lignin model compound) in the presence of non-noble metal based catalysts at mild conditions

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HIGHLIGHTS

- Synthesis and characterization of non-noble metal based supported catalysts.
- Catalytic wet oxidation of ferulic acid (lignin model compound) at mild conditions.
- Theoretical estimation of the mineralization of ferulic acid (in terms of CO₂).
- HPLC analysis and determination of reaction kinetics.
- Catalyst thermal regeneration, characterization and reuse in the oxidation process.

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ABSTRACT

The present study investigated the performance of activated carbon and alumina supported non-noble metal based catalysts during the catalytic wet oxidation (CWO) of ferulic acid (a lignin model compound). The heterogeneous catalysts, Cu/Ce/AC, Cu/Ce/Al₂O₃, Cu/Mn/AC and Cu/Mn/Al₂O₃ (mass ratio = 3:3:4), were prepared by metal impregnation while Cu/Mn/Ce (mass ratio = 3:3:4) catalyst was synthesized by co-precipitation method. The CWO reaction was performed in a batch reactor at mild conditions (temperature = 120 °C and oxygen pressures = 0.5 MPa) with a catalyst concentration of 3 g/l for 3 h duration. Among all the catalysts, Cu/Ce/AC catalyst showed the maximum chemical oxygen demand (COD) and total organic carbon (TOC) removals (88% and 82%, respectively) from the wastewater. The ferulic acid removal was resulted from a combination of reactions (such as oxidation, hydrolysis, decarboxylation and adsorption). During the CWO reaction, oxalic acid was identified as the major by-product but mean oxidation state of carbon and TOC balance calculation indicated also the presence of other compounds. A significant difference in the surface characteristics of the fresh and thermally regenerated catalysts (after CWO) was observed. The first time reuse of Cu/Ce/AC catalyst caused ~6% lesser reduction in TOC than the fresh catalyst though no considerable reduction in the catalytic activity could be observed after second reuse of the catalyst. The future study should plan for the determination of the change in biodegradability after the treatment and the effectiveness of CWO on real pulping effluent.

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1. Introduction

Catalytic wet oxidation (CWO) is considered a promising hydrothermal method for the destruction of recalcitrant organic or inorganic compounds generally found in industrial wastewater. Typically wet oxidation (WO) process can be performed at 125–320 °C temperature and 0.5–20 MPa total pressures by passing air or molecular oxygen [1]. The operating temperature and pressure conditions of the reaction can be reduced by introducing a suitable catalyst. Pulp mill effluents contain compound like lignin

which is highly resistant to the conventional biological oxidation. Therefore, the wastewater needs to be pre-treated by a suitable physico-chemical process. In the present study, the heterogeneous oxidative degradation of ferulic acid (a lignin model compound) at mild reaction conditions is explored.

Several ongoing efforts have assessed the performance of the transition metal based homogeneous and heterogeneous catalysts for CWO process [2–7]. The homogeneous catalysts have exhibited very good activity for the removal of recalcitrant pollutants but such catalysts are not preferred due to the difficult recovery of active metal from the treated wastewater. The leached metal concentration can enhance toxicity of the treated wastewater. The noble metal based catalysts have shown comparable performance

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but their use is limited by the high cost of catalysts. Therefore, the current research emphasizes on the development of less expensive non-noble metal based heterogeneous catalysts for CWO process.

Among the transition metals, copper has been reported as one of the active metals for the catalytic oxidation process [3,6,8–11]. However, only few studies reported the stability and reusability of WO catalysts. In a study, the several combinations of a heterogeneous catalyst comprising Cu and Ce were synthesized and tested for the oxidative degradation of phenol [3]. 60%CuO/40%CeO₂ catalyst (w/w) showed the highest phenol reduction among all combinations. Verenich et al. [12] evaluated the performance of different transition metal based heterogeneous catalysts for CWO of pulp mill wastewater. The activated carbon (AC) supported copper catalyst showed promising performance. In another study, AC and ceria supported transition metals (Cu and Mn) based catalysts were used for the degradation of pretreated pulping effluent (chemical oxygen demand (COD) = 2700 mg/l) [10]. The ceria and AC supported copper catalysts exhibited the highest COD removals. In the follow up study, 60%CuO/40%CeO₂ catalyst was also used for the diluted black liquor (COD = 7000 mg/l) at a lower temperature (=140 °C) [13].

In the above studies, the detailed catalyst characterization and its deactivation were not reported. In addition, the information on the degradation pattern of lignin (a major persistent compound in pulping liquor) is lacking. Only few research groups have performed CWO studies for the lignin model compounds (such as ferulic acid and alkali lignin) [7,14–16]. According to the literature, AC and alumina (Al₂O₃) supported copper and manganese catalysts can be effective for the CWO of lignin model compounds. Apart from this, ceria may promote the oxidation due to its oxygen carrying capacity. The motivation of the present study was to investigate the changes in heterogeneous catalysts after regeneration and their performance in CWO after repeated reuse.

In the present study, the catalytic activity of the fresh as well as spent heterogeneous catalysts was investigated during CWO of the ferulic acid. The fresh and regenerated catalysts were characterized before and after the oxidation process. The WO and CWO reaction kinetics were also studied using a lumped kinetic model.

2. Materials and methods

2.1. Materials

The analytical grade ferulic acid (99% purity) was supplied by Sigma-Aldrich Mumbai, India. For the preparation of catalysts, Cu(NO₃)₂·3H₂O, CeCl₃·7H₂O, MnSO₄·H₂O, and NH₄OH (30%) were purchased from Merck Chemicals, Mumbai, India. Besides, Al₂O₃ and peat derived AC were supplied by Zeolite and Allied Products, Mumbai, India and Merck Chemicals, Mumbai, India, respectively.

The synthetic wastewater was prepared by dissolving 1 g of ferulic acid in 1 L of tap water. The major characteristics of the synthetic wastewater were as follows: pH = 4.13, COD = 1550 mg/l and total organic carbon (TOC) = 530 mg/l.

2.2. Experimental methods

2.2.1. Catalyst preparation

Out of the five heterogeneous catalysts used for the CWO study, Cu/Ce/AC, Cu/Ce/Al₂O₃, Cu/Mn/AC and Cu/Mn/Al₂O₃ (mass ratio = 3:3:4) were prepared by impregnation method as outlined in earlier research studies [12,17–19]. Only Cu/Mn/Ce (mass ratio = 3:3:4) catalyst was prepared by co-precipitation method according to the previously reported procedure [6,10,14].

In impregnation method, the stoichiometric amounts of respective metal salts (Cu(NO₃)₂·3H₂O, CeCl₃·7H₂O and MnSO₄·H₂O) were dissolved separately in the distilled water and the resulting

solutions were mixed with either of the two supports (AC or Al₂O₃) in the desired proportion. The mixture then was continuously stirred magnetically for 12 h to allow the penetration of metal precursor into the support. In the next step, the mixture was oven-dried (at 103–105 °C temperature) for 24 h. The dried mass was ground by means of a pestle and mortar before calcining at high temperature for 2 h in a muffle furnace. The calcination temperature for AC and Al₂O₃ supported catalysts was 300 °C and 500 °C, respectively.

To synthesize Cu/Mn/Ce catalyst by co-precipitation method, the stoichiometric amounts of Cu, Mn and Ce metal salts were dissolved in distilled water and agitated with a magnetic stirrer to ensure complete mixing. The solution pH was adjusted around 8.0 with ammonia solution (2 M) to precipitate the respective metal hydroxides. The suspension was then left undisturbed for 2 h to allow the settling of the precipitate. Moreover, the solution was filtered (filter size = 0.45 µm) to recover the residual suspended solids. The retained mass at the filter paper was washed five times with distilled water to remove excess ammonia. The resulting wet slurry was oven-dried at a temperature of 103–105 °C for 24 h. The dried mass was ground and calcined in a muffle furnace at 500 °C temperature for 2 h.

The actual composition of the catalysts was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The synthesized catalysts were characterized to identify the phase formation by X-ray diffraction (XRD) technique. Brunauer–Emmett–Teller (BET) surface area, average particle diameter and the particle size distribution of the catalysts were also measured.

2.2.2. Wet oxidation (WO) experimentation

WO/CWO batch studies were performed in a 0.7 L capacity high pressure stainless steel (SS) reactor (material of construction: SS-316). The instrument was equipped with the provisions for temperature control and mixing speed adjustment. Separate ports for liquid sampling and air/oxygen injection were also provided on the reactor cap. A digital display unit was attached with the reactor assembly to monitor temperature, pressure and stirrer speed during the reaction. The pressure in the reactor was controlled by two valves provided at the oxygen cylinder and the reactor cap. For instantaneous cooling of the liquid samples, a condenser (with water flowing in the outer shell) was also attached to the sample port.

For a typical WO/CWO runs, 250 ml of the synthetic wastewater was charged into the reactor without or with 3 g/l fresh catalyst (for CWO runs). The reactor assembly was made leak proof before raising the reactor temperature to 120 °C from the ambient condition (~30 °C). The approximate time to achieve the desired temperature was 45 min. A 'zero time' sample (~5 ml) was withdrawn just after attaining the reaction temperature. Then the pure oxygen was purged into the reactor at an initial oxygen pressure of 0.5 MPa while the total pressure was maintained at 0.69 MPa. The reactor contents were mixed vigorously by a mechanical stirrer (rotating speed = 1000 rpm) continuously during the reaction. All CWO runs were conducted in triplicate and COD of each sample was determined thrice. The periodic liquid sampling was done to record change in pH, TOC and COD with time for the first run only. No samples were withdrawn during the remaining two runs so that the spent catalyst could be quantified and reused.

In addition, an effort was made to quantify the intermediates and by-products formed during the catalytic run performed with Cu/Ce/AC catalyst using high performance liquid chromatography (HPLC).

2.2.3. Catalytic tests at ambient and elevated temperatures in the absence of oxygen

The removal of ferulic acid from the synthetic wastewater was also investigated in the absence of oxygen at ambient (~30 °C) and

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