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Ferulic Acid Degradation By Wet Oxidation Process

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Abstract: In the present study, the effectiveness of wet oxidation (WO) process was studied for ferulic acid (a lignin model compound) degradation at mild operating conditions (120°C temperature and 0.7 MPa total pressures) in a stainless steel high pressure batch reactor (capacity = 0.7 L). The oxidative degradation was performed in the presence of heterogeneous catalysts and the results were compared with the non-catalytic oxidation. Two heterogeneous catalysts (30%Cu/ 30%Ce/ 40%AC and 30%Cu/ 30%Ce/ 40%Al_2O_3) were synthesized by wet impregnation method and used for WO of synthetic wastewater containing 1 g/l ferulic acid. Initial pH and TOC of the wastewater were 4.13 and 530 mg/l, respectively. X-ray diffraction of the synthesized catalyst powders confirmed the presence of desired species. Under the mild operating conditions, Cu/Ce/AC showed the best TOC reduction (~ 82%). In the presence of Cu/Ce/Al_2O_3 catalyst, TOC reduction was slightly lower (~ 78%) though the same was only ~ 52% for the reaction performed in the absence of catalyst. The adsorption of organics on the catalyst support (i.e., activated carbon and alumina) contributed ~ 12 – 14% TOC removal during catalytic runs. The final pH of the treated wastewater was also noted and the results indicated the formation and accumulation of the low molecular weight carboxylic acids in the wastewater.

Keywords: Ferulic acid; Heterogeneous catalysts; Wastewater treatment; Wet oxidation.

1. Introduction

Pulp and paper industries are considered one of the major consumers of natural resources (wood, water and fossil fuels) and are the big contributor of environmental pollution. The wastewater generated from pulp and paper industries contains a range of organic compounds including lignin, cellulose, phenols and sulfides. Lignin is persistent component and not amenable by biological degradation. Hence it should be removed by some appropriate chemical or physico-chemical method before subjecting to the conventional biological process.

In the recent past, some studies have been performed on the degradation of lignin model compounds (like ferulic acid and alkali lignin) by wet oxidation (WO) process[1-4]. WO is a hydrothermal treatment process that mineralizes the persistent and non-biodegradable suspended or dissolved organic or inorganic compounds into harmless gaseous products in the presence of a source of oxygen. Typical WO reaction is conducted in a temperature and pressure range of 120 - 325°C and 0.5 - 20 MPa, respectively[5]. The process is not used widely due to high capital and operating costs. Hence, the focus of current research is on the development of efficient non-noble metals based heterogeneous catalysts which should also be thermally stable and easily recoverable.

In the present study, the degradation of a synthetic wastewater containing ferulic acid was investigated during non-catalytic and catalytic wet oxidation process at mild temperature and pressure conditions.

2. Experimental section

2.1. Materials

Ferulic acid was supplied by Sigma Aldrich Mumbai, India. The synthetic wastewater was prepared by dissolving 1 g of ferulic acid in 1 L tap water. pH and total organic carbon (TOC) of the wastewater were 4.13 and 530 mg/l, respectively.

The analytical grade copper nitrate, cerium chloride and activated carbon (AC) were purchased from Merck chemicals, Mumbai, India whereas activated alumina was supplied by Zeolite and Allied Products, Mumbai, India. All these chemicals were used for the synthesis of catalysts. Two heterogeneous supported catalysts, Cu/Ce/AC (30/30/40 by weight) and Cu/Ce/Al_2O_3 (30/30/40 by weight) were prepared using impregnation method[4].

2.2. Wet oxidation (WO) runs

The hydrothermal oxidation reaction was carried out in a 0.7 L high pressure reactor made of stainless steel (SS - 316). The reactor assembly is well equipped with a temperature controller, heating jacket, agitating mechanism, liquid sampling port and gas injection port. For a typical WO/CWO run, 250 ml of synthetic wastewater was charged to the reactor without or with 3 g/L catalyst. The reactants were then heated up to a reaction temperature of 120°C. The time required to achieve the reaction temperature from the ambient conditions was ~ 45 min. Then the total reactor pressure was increased to 0.7 MPa by introducing oxygen out of which the oxygen partial pressure was 0.5 MPa. After pressurizing the reactor, the reactants were agitated at a stirrer speed of 1000 rpm for 3 h duration. The final samples were analyzed for TOC and pH.

2.3. Analytical methods

The synthesized catalysts were characterized for identifying the phase formations and surface area. X- ray diffraction (XRD) analysis and Brunauer, Emmett and Teller (BET) surface area techniques were used for these purposes. The XRD spectra of the catalysts were obtained on Philips (PANalytical "Xpert Pro", Netherland) diffractometer. The X-ray source used was Cu Kα and the scan angle (2θ) was varied from 20 - 90°. BET surface area was measured by N_2 adsorption on a Micrometric ASAP-2020 machine (USA).

pH of the wastewater was measured by a digital pH meter (Polmon, LP-1395, India) whereas TOC of untreated and treated samples was measured using a Shimadzu TOC analyzer, purchased from Japan.

3. Results and discussion

3.1. Catalyst characterization

XRD spectra of the two heterogeneous catalysts are presented in Fig. 1. The prominent 2θ peaks demonstrates the presence of various metal species in the synthesized catalyst powders.

The short peaks of copper oxide (CuO) could be observed at 35.8° and 39° whereas the strong distinct peaks of cerium oxide (CeO_2) were obtained at 2θ angles of 28.7°, 32.5°, 47.7° and 56.5°. On the other hand, the peaks of support (i.e. alumina and AC) were not very clear and the intensity of these peaks was very low. XRD spectra of both the catalysts were also compared with that reported by other researchers.[4,6-10]

BET surface area of 30% Cu/ 30% Ce/ 40% AC and 30% Cu/ 30% Ce/ 40% Al_2O_3 were ~ 18.5 and ~ 37.9 m^2/g, respectively. The results obtained from catalyst characterisation are summarized in Table 1.

Table 1: Summary of the results from the catalyst characterization

Catalyst	XRD analysis*	BET surface area (m^2/g)
Cu/Ce/AC	CeO_2 (28.7, 32.5, 47.7 and 56.5), CuO (35.8 and 39.0) and AC (45.5)	18.5
Cu/Ce/Al_2O_3	CeO_2 (28.7, 32.5, 47.7 and 56.5), CuO (35.8 and 39.0) and Al_2O_3 (42.5 and 69.6)	37.9

[* The values given in brackets are of 2θ angle at the peaks of respective constituents]

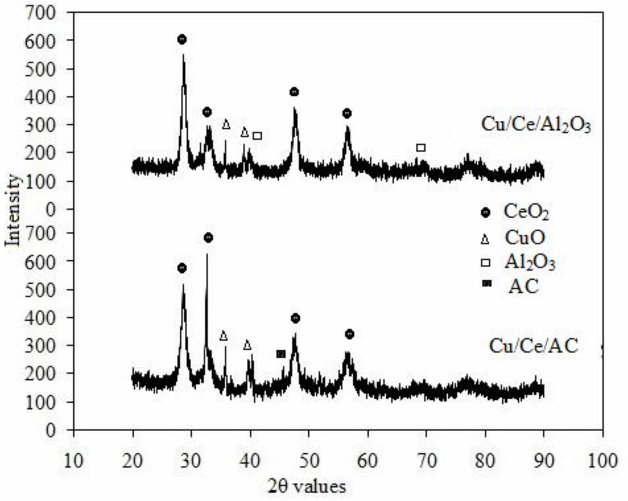

Figure 1. XRD spectra of Cu/Ce/AC and Cu/Ce/Al$_2$O$_3$ catalysts

3.2. Treatment of synthetic wastewater

3.2.1. Comparison of non-catalytic and catalytic reactions

The activity of two synthesized catalysts was observed during catalytic WO under mild operating conditions (T = 120°C, P = 0.7 MPa, catalyst conc. = 3 g/l and reaction time = 3 h) and the results were compared with that obtained from non-catalytic oxidation run. The percent reductions in TOC during the runs are shown in Fig. 2. The maximum TOC reduction of 82% was obtained after 3 h of reaction in the presence of Cu/Ce/AC catalyst though TOC removal from the synthetic wastewater with Cu/Ce/Al$_2$O$_3$ catalyst was slightly lower (~ 78%). During non catalytic WO, TOC reduction was only 52% under similar temperature and pressure conditions. The final TOC of the treated wastewater was 93, 113 and 253 mg/l, respectively when treated with Cu/Ce/AC, Cu/Ce/Al$_2$O$_3$ and without catalyst.

The enhancement in TOC reduction during catalytic WO is due to the adsorption and the subsequent reaction between reactant molecules on active sites of the catalyst surface[3]. To find out the contribution of adsorption on TOC reduction (for catalytic runs only), the catalysts were recovered after the reaction and subjected to TOC analysis. From the results, it was found that ~ 12% of the total TOC (i.e., ~ 64 mg/l) was adsorbed on Cu/Ce/AC catalyst whereas ~14% TOC (i.e., ~ 74 mg/l) was retained un-reacted at Cu/Ce/Al$_2$O$_3$ catalyst surface. Hence, it can be deduced that ~ 70% and 64% TOC reductions were occurred due to the oxidation of parent compound (i.e., ferulic acid) into the other low molecular weight compounds, CO$_2$ and H$_2$O.

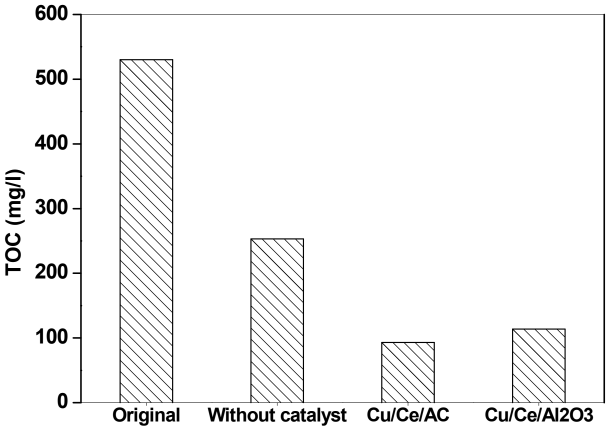

Figure 2. TOC reductions during non-catalytic and catalytic WO of synthetic wastewater (Ferulic acid concentration = 1 g/l, initial pH = 4.13, initial TOC = 530 mg/l, T = 120^{o}C, total pressure = 0.7 MPa, catalyst concentration = 3 g/l, stirring speed = 1000 rpm and reaction time = 3 h)

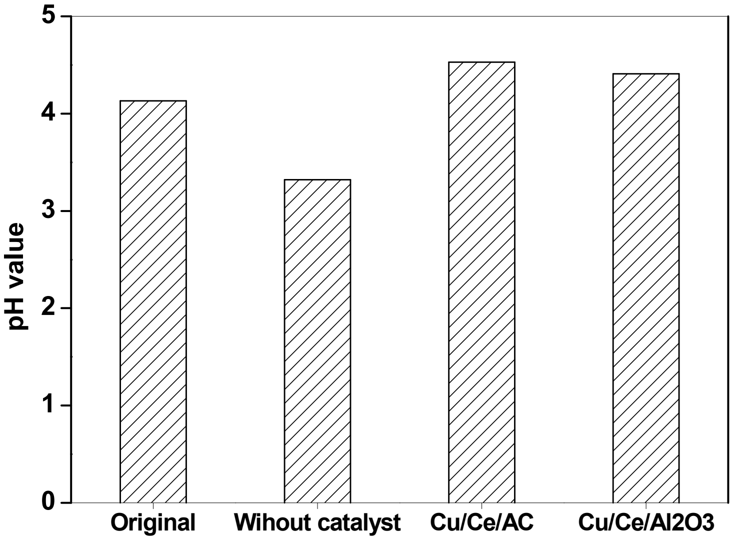

Figure 3. Change in pH after non-catalytic and catalytic WO of the synthetic wastewater (T = 120°C, total pressure = 0.7 MPa, catalyst concentration = 3 g/l and reaction time = 3 h)

3.2.2. Change in pH during WO/CWO runs

pH of the treated wastewater was determined to get an idea of the nature of species present. The initial pH of the wastewater was 4.13 and it was increased to 5.4 and 4.7 with the addition of Cu/Ce/AC and Cu/Ce/Al_2O_3 catalysts, respectively. After the reaction the pH was decreased to 4.5 and 4.4, respectively for the two catalysts. In case of non-catalytic reaction, the final wastewater pH was ~3.4 from the initial value (i.e., 4.13). The final pH of the wastewater treated with catalytic and non catalytic WO is illustrated in Fig. 3. It can be noted that the overall reduction in pH was quite low. This indicates the formation of low molecular weight carboxylic acids (weak acidic species) which may be accumulating in the treated wastewater though some portion of the ferulic acid and other intermediates may have been completely mineralised in CO_2 and H_2O.

4. Conclusions

The major conclusions drawn from the study are listed below:

- The heterogeneous catalysts used in the present study (i.e., Cu/Ce/AC and Cu/Ce/Al_2O_3) were found efficient in TOC removal from ferulic acid laden synthetic wastewater at mild operating conditions.
- Cu/Ce/AC catalyst showed the best performance with an overall TOC reduction of ~ 82% compared to Cu/Ce/Al_2O_3 catalyst (TOC reduction = ~ 78%). In the absence of catalyst, TOC reduction was only 52%.
- Adsorption of organic compounds on the catalyst also contributed to the TOC reductions during catalytic oxidation runs (~ 12% and 14% respectively for Cu/Ce/AC and Cu/Ce/Al_2O_3 catalysts).
- Lowering the treated wastewater pH indicates the degradation of ferulic acid in low molecular weight carboxylic acids. However, the pH decrease during catalytic runs was lower compared to non-catalytic runs possibly due to higher mineralization of parent compound as well as intermediates formed during the run.

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