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Catalytic Wet Oxidation of Ferulic Acid (A Model Lignin Compound) Using Heterogeneous Copper Catalysts

Suresh Bhargava,^{*,†} Harit Jani,[†] James Tardio,[†] Deepak Akolekar,[†] and Manh Hoang[‡]

Department of Applied Science, RMIT University, Melbourne, VIC 3001 Australia, and CSIRO Manufacturing and Materials Technology, Clayton, VIC 3168 Australia

Catalytic wet oxidation (CWO) of ferulic acid (a model lignin compound) was investigated at low temperature and pressure (100 °C, 172 kPa P O₂). Nine homogeneous catalysts were screened at three different catalyst loadings. Homogeneous copper ions were observed to be the most active catalysts; various copper based heterogeneous catalysts were also prepared and tested. The most active catalyst was Cu–Ni–Ce–Al₂O₃; however, this catalyst also exhibited the highest extent of copper leaching. Cu–Mn–Al₂O₃ was the most stable catalyst tested and was second only to Cu–Ni–Ce–Al₂O₃ in terms of activity among nine heterogeneous catalysts studied. Heterogeneous catalytic activity compared with the activity due to leached metal ions was observed to be dominant for both of the above-mentioned catalysts.

1. Introduction

Because of lignin degradation, pulp and paper mill effluents contain a range of organic compounds. The choice of treatment method is governed by factors such as the organic or inorganic content, their concentration, their toxicity, and environmental discharge standards. The technologies available to date are mostly based on single or hybrid treatments involving one or a combination of chemical treatments, physical treatments (adsorption–separation, reverse osmosis, distillation, etc.), biological treatments (anaerobic and/or aerobic), incineration, and wet oxidation (WO)/catalytic wet oxidation (CWO). Lignin degradation compounds are usually phenolic in nature, and because of their high toxicity, strong color, and high resistance to biological treatments, they need to be removed from the effluent before discharge.^{1,2}

Wet oxidation (WO) is an established liquid-phase process for the aerobic oxidation of organics-laden waste streams.³ Harsh conditions—temperatures of up to 350 °C and pressures up to 20 MPa—are, however, usually required to achieve acceptable levels of oxidation using reasonable residence times. These conditions impose increased capital costs and lead to difficulties in the technical design of operating equipment; hence, there is significant interest in reducing the severity of the reaction conditions through the use of a catalyst.^{3–5}

The catalytic wet oxidation (CWO) technique, an alternative to the WO technique, efficiently removes organics from an industrial stream using catalysts to obtain better oxidation rates at lower temperatures and pressures. This lowers the capital and operating costs of this technology. The catalyst aids by increasing the overall rate of the process while allowing the use of milder conditions and by favoring reactions that increase product yield. CWO is, thus, more economically and environmentally attractive.

There has been a significant amount of research conducted on noble and transition metal based supported catalysts for use in CWO over the last three decades, with transition metals being of more interest to industry because of their lower cost. One of

the major issues associated with CWO catalysts is the stability of the active metal components.^{6,7} This is one of the main reasons there have been very few commercial WO catalysts developed and that there is a significantly higher amount of commercial WO units compared to CWO units.⁸ Copper based catalysts have shown the highest level of total organic carbon (TOC) removal compared to any other transition metal based catalysts for various industrial effluents.^{9–11} In spite of such a high level of activity, supported copper catalysts are not very popular among industry because of leaching of copper ions to aqueous discharge. Copper is highly toxic to marine life, and government regulation on permissible copper discharge is quite low.¹² In literature, various authors have reported a very high level of copper ions leaching, which is 40–250 ppm of copper ions concentration, for supported copper catalysts. The reported studies were conducted using a particular type of copper catalysts under different reaction conditions.^{11,13–16} But there is a significant gap in terms of activity and stability studies of various multimetallic supported copper catalysts for the same oxidative conditions and comparison of the same. In this paper, we have discussed activity and stability of various supported copper catalysts for the CWO of ferulic acid, a lignin oxidation product. Further enhancement in the knowledge on the catalyst stability and activity will lead to the development of more active and robust catalysts, which can be used efficiently to treat the industrial aqueous effluents.

2. Experimental Section

CWO reactions were carried out in a 1.2 L continuously stirred Teflon coated stainless steel 316 autoclave (Parr Autoclave, Moline, IL) equipped with a gas manifold and liquid sampling port. A schematic diagram of the autoclave assembly used is presented elsewhere.⁹ In the standard reaction, a predetermined amount of catalyst was placed in the reactor vessel, followed by 0.4 L of 1000 ppm ferulic acid in water. The headspace area was evacuated to ~0 kPa, and the vessel and its contents were heated to 100 °C, unless specified, with the stirrer set at 800 rpm. Once the target temperature was reached, oxygen was introduced and maintained at a constant partial pressure of 172 kPa for the duration of the test (2 h). Because some of the catalysts tested were chloride salts, which can corrode stainless steel under the reaction conditions used,

* To whom correspondence should be addressed. E-mail: suresh.bhargava@rmit.edu.au.

[†] RMIT University.

[‡] CSIRO Manufacturing and Materials Technology.

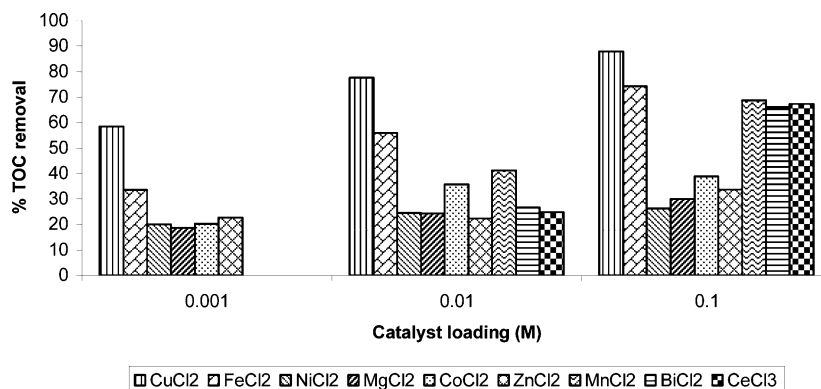


Figure 1. Catalyst loading (mol %) vs percent TOC removal for oxidation of ferulic acid [reaction conditions: temperature = 100 °C, oxygen partial pressure = 172 kPa, reaction time = 2 h, stirrer speed = 800 rpm (TOC removal for blank WO is 3%)].

Table 1. Extent of Metal Ions Leached from Various Catalysts for CWO of Ferulic Acid [Reaction Conditions: Temperature = 100 °C, Oxygen Partial Pressure = 172 kPa, Reaction Time = 2 h, Stirrer Speed = 800 rpm]

catalyst	composition (wt %)	leaching ppm (% leached)		
Cu–Ni–Al ₂ O ₃	Cu = 18.25% Ni = 19.5%	Cu 16.5 (4.54)	Ni 9.98 (2.56)	
Cu–Co–Al ₂ O ₃	Cu = 23.5 Co = 3.75%	Cu 29.86 (6.35)	Co 9.61 (12.82)	
Cu–Mn–Al ₂ O ₃	Cu = 24% Mn = 24.75%	Cu 1.55 (0.32)	Mn 5.94 (12)	
Cu–Mn–kaolin	Cu = 8.25% Mn = 4.5%	Cu 15.86 (9.61)	Mn 53 (58.89)	
Cu–Al ₂ O ₃	Cu = 52.5%	Cu 38.14 (3.63)		
Cu–kaolin	Cu = 18%	Cu 19.42 (5.39)		
Cu–Co–Mn	Cu = 54.4% Co = 28.65% Mn = 16.90%	Cu 8.2 (0.75)	Co 10 (1.74)	Mn 34.83 (10.3)
Cu–Fe–Mn	Cu = 40.9% Fe = 32.1% Mn = 27%	Cu 6.46 (0.78)	Fe 0.25 (0.04)	Mn 32.86 (6.09)
Cu–Ni–Ce–Al ₂ O ₃	Cu = 2.125% Ni = 0.475% Ce = 1.175%	Cu 11 (21)	Ni 3.1 (32.63)	Ce 3.4 (14.47)

the autoclave vessel walls were protected by means of a removable glass lining and the internal components (stirrer assembly, cooling lines, thermowell, etc.) were coated with Teflon.

The following chemicals were used as purchased: ferulic acid (Sigma Aldrich; >98% pure), orthophosphoric acid (85%; Ajax Finechem), and sodium peroxodisulfate (purchased from Merck). MilliQ water was used for all prepared solutions. Catalysts used in these experiments were copper(II) chloride 2-hydrate, iron(II) chloride 4-hydrate, manganese(II) chloride 2-hydrate, cerium(III) chloride 7-hydrate, cobalt(II) chloride 6-hydrate, magnesium(II) 6-hydrate, and bismuth(III) chloride (all from BDH Chemicals Ltd.).

The total organic carbon (TOC) concentration was analyzed using an O. I. Analytical model 1010 (U.S.A.) total carbon analyzer. A Hewlett-Packard GC-5890 system, with HP-5970 mass selective detector and SGE BPX5 30 m × 0.25 mm i.d. × 0.25 μm film column, was used for GC-MS analysis. Fourier transform infrared (FT-IR) analysis was performed on a Perkin-Elmer 1725X with Spectrum v2.00 software. The amount of organic carbon adsorbed on the catalyst surface was measured using the TOC analysis. In a typical experiment, 20 mg of catalyst was added to 2.5 mL of aqua regia solution and then diluted to 50 mL using MilliQ water. The pH was adjusted to 3 using NaOH prior to the TOC analysis.

2.1. Catalyst Preparation. The single-metal (Cu), bimetallic (Cu–Ni, Cu–Co, and Cu–Mn), and multimetals (Cu–Ni–Ce) alumina supported catalysts, Cu and Cu–Mn kaolin supported catalysts, and multimetals oxide (Cu–Co–Mn and Cu–Fe–Mn) catalysts were prepared in-house. The general procedure followed for the preparation of these catalysts is as follows.

2.1.1. Single-Metal (Cu) Supported Catalysts. The single-metal heterogeneous catalysts were prepared by precipitation of appropriate metal salts (0.25 M) by sodium hydroxide solution (0.25 M) in the presence of appropriate pure and active alumina/kaolin support under constant temperature with continuous stirring.

2.1.2. Bimetallic (Cu–Ni, Cu–Co, and Cu–Mn) Supported Catalysts. The bimetallic metal heterogeneous catalysts were prepared by coprecipitation of appropriate metal (Cu–Ni, Cu–Co, and Cu–Mn) salts (0.25 M) by sodium hydroxide solution (0.25 M) in the presence of appropriate pure and active alumina/kaolin support under constant temperature with continuous stirring.

2.1.3. Multimetallic (Cu–Ni/Ce) Supported or Nonsupported (Cu–Co–Mn and Cu–Fe–Mn) Catalysts. The multimetallic metal heterogeneous catalysts were prepared by the coprecipitation of appropriate multimetal(s) (Cu–Ni–Ce, alumina supported; Cu–Co–Mn and Cu–Fe–Mn, nonsupported catalysts) salts (0.25 M) by sodium hydroxide solution (0.25 M) in the presence of appropriate pure and active alumina (in the absence of alumina support in the case of nonsupported catalysts) under constant temperature with continuous stirring.

After precipitation, the catalysts were washed thoroughly, dried at room temperature, heat-treated up to 673 K at the rate of 5 K/min, and then held at this temperature for 4 h. The homogeneous catalysts were prepared by dissolving the appropriate metal salt in water and were utilized as homogeneous catalysts.

3. Results and Discussion

3.1. Homogeneous Catalysts. Chloride salts of Cu²⁺, Fe²⁺, Ce³⁺, Co²⁺, Mg²⁺, Bi²⁺, Mn²⁺, Ni²⁺, and Zn²⁺, at three different concentrations, have been used as homogeneous catalysts for CWO of ferulic acid (Figure 1). The most effective catalysts were found to be Cu²⁺, Fe²⁺, and Mn²⁺, removing more than 86%, 73%, and 69% TOC, respectively, at 100 °C after 120 min reaction for 0.1 mol/L catalyst concentration. The order of catalytic activity was observed to be Cu²⁺ > Fe²⁺ > Mn²⁺ > Ce²⁺ > Bi²⁺ > Co²⁺ > Zn²⁺ > Mg²⁺ > Ni²⁺. Ni²⁺ ions displayed the lowest catalytic activity, removing 26% TOC at 100 °C after 120 min of reaction using 0.1 mol/L catalyst concentration; this was still considerably higher than the 3% TOC removal that occurred for the blank test.

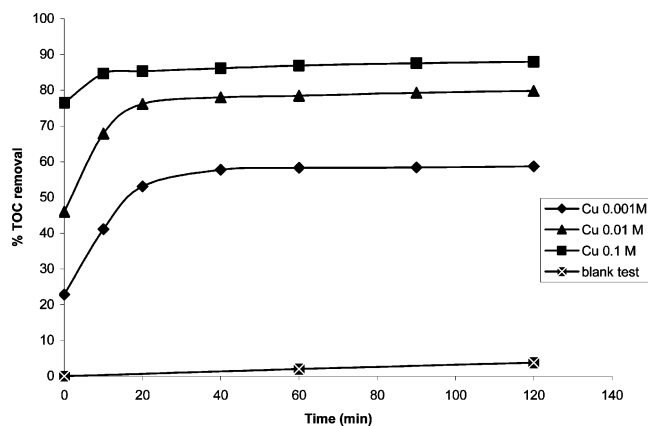


Figure 2. Percent TOC removal–time profile of ferulic acid [reaction conditions: temperature = 100 °C, oxygen partial pressure = 172 kPa, reaction time = 2 h, stirrer speed = 800 rpm, and various Cu^{2+} ions loading].

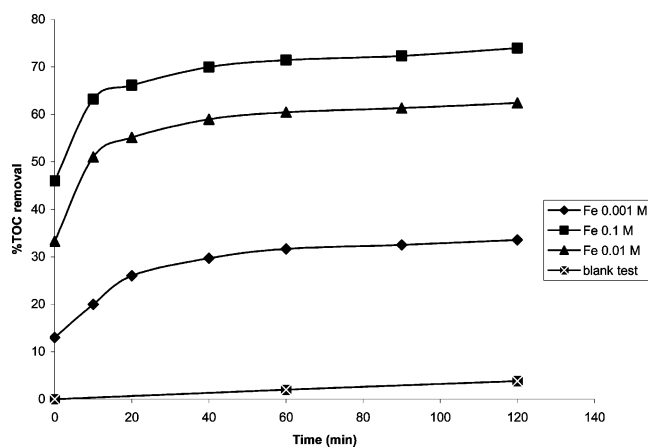


Figure 3. Percent TOC removal–time profile of ferulic acid [reaction conditions: temperature = 100 °C, oxygen partial pressure = 172 kPa, reaction time = 2 h, stirrer speed = 800 rpm, and various Fe^{2+} ions loading].

Figures 2 and 3 show the TOC removal as a function of time for Cu^{2+} and Fe^{2+} metal ions, respectively, at three different concentrations. It can be seen from Figures 2 and 3 that the total TOC removal increases with increasing catalyst loading. Also, the time-zero TOC removal, in the absence of oxygen during the heat-up period, is directly proportional to catalysts loading. This is most likely due to either the combination of catalytic decarboxylation or the direct oxidation by Fe/Cu.

On the basis of the high TOC removal achieved using homogeneous Cu, the further study was focused on developing stable copper based heterogeneous catalysts.

3.2. Heterogeneous Catalysts and Leaching. The catalytic activity and the extent of metal ions leaching are two main issues of any heterogeneous catalytic system applied in the aqueous phase. In this study, a series of different copper based catalysts using aluminum oxide and kaolin as support were developed and studied.

The TOC removal as a function of time for all these catalysts is shown in Figure 4. Cu–Ni–Ce– Al_2O_3 and Cu–Mn– Al_2O_3 are the most effective catalysts, achieving 81% and 75% TOC removal, respectively, after 120 min of CWO at 100 °C. Table 1 gives the detailed information about metal ions loading on the catalyst surface and concentration of metal ions leached into the solution. Figure 5 shows the concentration of Cu^{2+} ions leached to the liquid phase as a function of time. Under the testing conditions used in this study, 20% of supported Cu^{2+} ions from Cu–Ni–Ce– Al_2O_3 catalyst was leached in comparison to only 0.20% for Cu–Mn– Al_2O_3 catalyst. The higher

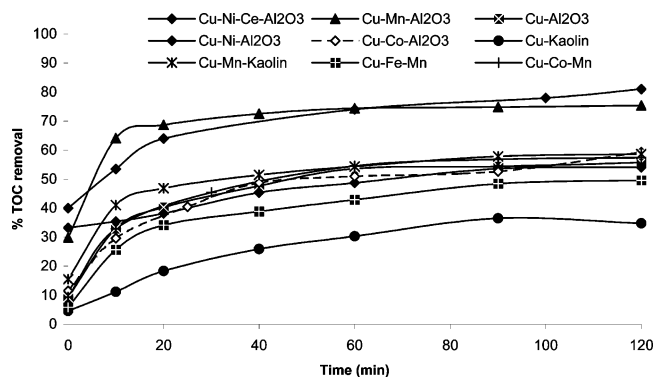


Figure 4. Percent TOC removal–time profile for catalytic wet oxidation of ferulic acid [reaction conditions: temperature = 100 °C, oxygen partial pressure = 172 kPa, reaction time = 2 h, stirrer speed = 800 rpm, catalysts loading = 2 g/L catalysts].

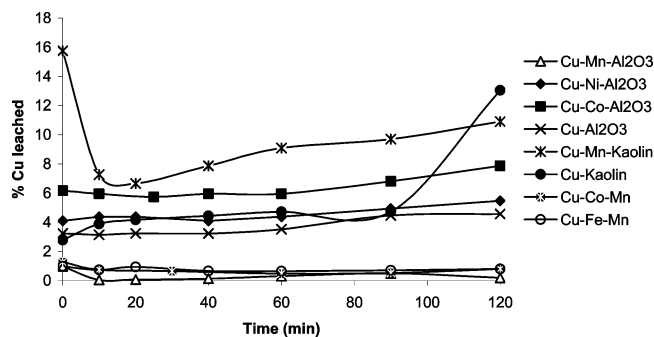


Figure 5. Percent Cu^{2+} ions leached with respect to time for various heterogeneous catalysts [reaction conditions: temperature = 100 °C, oxygen partial pressure = 172 kPa, reaction time = 2 h, stirrer speed = 800 rpm, catalyst loading = 2 g/L catalysts, (~21% supported Cu^{2+} of Cu–Ni–Ce– Al_2O_3 leached under the same conditions, not shown in the figure)].

copper leaching from the Cu–Ni–Ce– Al_2O_3 catalysts might be due to the observed low pH compared to the Cu–Mn– Al_2O_3 catalyst test or the synergistic effect of Mn^{2+} on the surface, which will be discussed in the following section. The pH at time zero for Cu–Ni–Ce– Al_2O_3 was 3.47 and dropped down to 3.10 over 2 h of CWO reaction, and the pH at time zero for Cu–Mn– Al_2O_3 catalysts was 5.50 and dropped down to 3.50 after 2 h of CWO reaction.

Leaching of Cu^{2+} was considerably reduced in the catalysts containing Mn^{2+} . This effect has not been previously reported in CWO literature. Among the catalysts tested, Cu^{2+} leaching was lower for Cu–Fe–Mn, Cu–Co–Mn, and Cu–Mn– Al_2O_3 catalysts. Cu^{2+} ions leaching from Cu–Mn– Al_2O_3 was very little compared to that from Cu– Al_2O_3 . Another interesting result is that Cu^{2+} , Mn^{2+} , and Fe^{2+} ions were the most effective catalysts in the homogeneous phase, but the heterogeneous catalyst containing Cu–Mn–Fe was not an effective catalyst; this is because of availability of more catalytic active sites in the homogeneous catalysts. This result indicates that oxides of these metals are not as effective without being supported on a high-surface-area material.

Because Cu^{2+} is known to function as a catalyst in the liquid phase, the observed activity may be due to a combination of both heterogeneous and homogeneous components. Further investigation was focused on the catalytic wet oxidation mechanism for Cu–Ni–Ce– Al_2O_3 and Cu–Mn– Al_2O_3 catalysts. Figure 6a shows the catalytic wet oxidation of ferulic acid using the homogeneous component, the heterogeneous component, and the leached component. Here, the heterogeneous component is Cu–Ni–Ce– Al_2O_3 with a loading of 2 g/L, the homogeneous component is the chloride salts of Cu^{2+} , Ni^{2+} ,

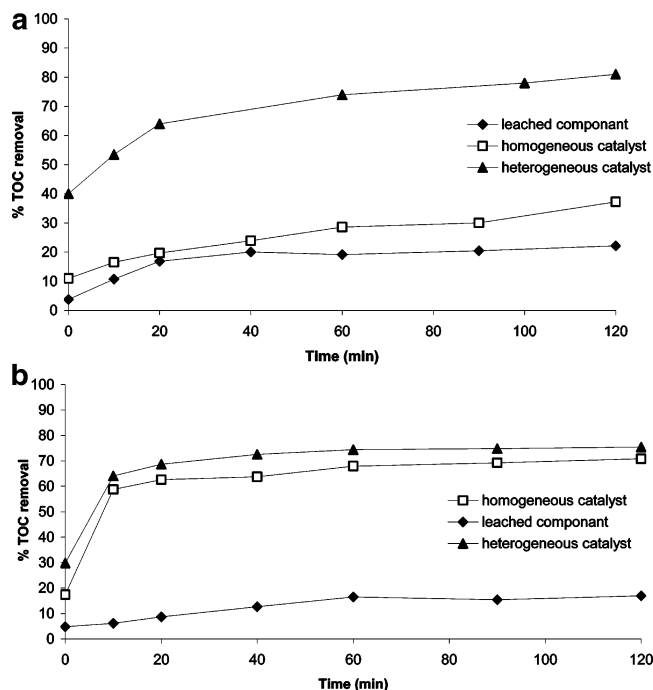


Figure 6. (a) Effectiveness of homogeneous catalyst, heterogeneous catalyst, and leached component for Cu-Ni-Ce-Al₂O₃ catalyst [reaction conditions: temperature = 100 °C, oxygen partial pressure = 172 kPa, reaction time = 2 h, stirrer speed = 800 rpm]. (b) Effectiveness of homogeneous catalyst, heterogeneous catalyst, and leached component for Cu-Mn-Al₂O₃ catalyst [reaction conditions: temperature = 100 °C, oxygen partial pressure = 172 kPa, reaction time = 2 h, stirrer speed = 800 rpm].

and Ce³⁺ ions at the same concentration as if there is no aluminum oxide support available for 2 g/L of Cu-Ni-Ce-Al₂O₃ catalyst, and the leached component is chloride salts of metal ions of the same amount as that leached for CWO experiments with 2 g/L of Cu-Ni-Ce-Al₂O₃ loading. Figure 6b shows similar results for the Cu-Mn-Al₂O₃ catalyst. For both of these catalysts, a significant difference (~60%) was observed between TOC removal for the heterogeneous component and the leached component of the catalyst, leading to the conclusion that the role of heterogeneous activity is dominant.

Because Cu-Ni-Ce-Al₂O₃ has shown the highest activity in terms of TOC removal and this activity is mainly from supported copper (heterogeneous activity) compared to leached metal ions, further investigation was carried out to study the catalytic oxidative (adsorption/oxidation/desorption) mechanism of Cu-Ni-Ce-Al₂O₃ catalyst. Special experiments were performed to determine the fate of adsorbed ferulic acid in the latter stages of the CWO under oxygenated conditions. These experiments were conducted as follows: the reaction solution containing 1000 ppm ferulic acid was heated up to 100 °C in to the reactor with catalyst and no oxygen and then cooled down to room temperature. The recovered catalyst was then filtered and suspended in 400 mL of water. The solution of water plus filtered catalyst was then heated up to 100 °C, and 42 psi of oxygen was added and maintained throughout the test. Approximately 100 mL of solution was removed at times 0, 15, 30, and 60 min, and the catalyst was separated from these and analyzed for TOC. The amounts of organic (% of actual ferulic acid concentration, 1000 ppm) adsorbed to the catalyst at various stages of the reaction are given in Table 2. FT-IR analysis of the recovered catalyst samples also confirmed that the catalyst initially adsorbed ferulic acid, and this adsorbed ferulic acid was gradually released during the course of the test.

Table 2. TOC Adsorbed on the Filtered Catalyst Surface [Reaction Conditions: Temperature = 100 °C, Oxygen Partial Pressure = 172 kPa, Reaction Time = 2 h, Stirrer Speed = 800 rpm]

catalyst filtered at different time	% TOC adsorbed on catalyst surface
catalyst (not exposed to ferulic acid)	0
time zero	39
15 min	29
30 min	14.9
60 min	12.2

3.3. Catalyst Life Cycle. Cu-Ni-Ce-Al₂O₃ catalyst reusability tests were performed up to the fourth reuse. The filtered catalyst was reused with fresh ferulic acid under the same reaction conditions. In these tests, because no catalyst washing was carried out, the adsorbed organics from the previous run were carried over from the catalyst to the next runs. Although significant amounts of active component were leached out from the catalyst as mentioned earlier, the catalyst activity is still high.

4. Conclusions

Several different homogeneous and heterogeneous catalysts have been studied. Cu²⁺ was found to be the most effective homogeneous catalyst. The order of homogeneous catalytic activity observed was Cu²⁺ > Fe²⁺ > Mn²⁺ > Ce²⁺ > Bi²⁺ > Co²⁺ > Zn²⁺ > Mg²⁺ > Ni²⁺. Nine different copper based catalysts using aluminum oxide and kaolin as support were developed and tested. Cu-Ni-Ce-Al₂O₃ and Cu-Mn-Al₂O₃ were the most effective catalysts, achieving 81% and 75% TOC removal, respectively, after 120 min for CWO of ferulic acid at 100 °C. The higher catalytic activity of these catalysts was mainly due to their heterogeneous effectiveness. Cu-Mn-Al₂O₃ was the most stable catalyst, and leaching of Cu²⁺ was reduced considerably in the presence of Mn²⁺.

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