

# Activity and stability of iron-containing pillared clay catalysts for wet air oxidation of phenol

Jing Guo<sup>\*</sup>, Muthanna Al-Dahhan

*Chemical Reaction Engineering Laboratory (CREL), Department of Chemical Engineering, Campus Box 1198, Washington University, St. Louis, MO 63130, USA*

Received 10 August 2005; received in revised form 11 October 2005; accepted 13 October 2005  
Available online 1 December 2005

## Abstract

Catalytic wet air oxidation of an aqueous phenol solution over Fe–Al pillared catalyst was conducted in a stirred tank and packed bed reactor. Semi-batch experiments in the stirred tank reactor were designed to investigate the effects of temperature, air pressure, initial phenol concentration, catalyst loading, and catalyst size on the conversion of total organic carbon. The catalyst exhibited an important activity in degrading total organic carbon at mild conditions. Its internal mass transfer resistance was assessed over different catalyst sizes via a chosen criterion. Packed bed runs were conducted under selected temperature and pressure (170 °C, 3.2 MPa) over a long duration (240 h). Various characterization methods were employed for fresh and aged pillared clay catalysts. Occurrence of catalyst deactivation by carbonaceous deposits during the packed bed operation was observed through scanning electron microscopy (SEM) and elemental analysis. Insignificant metal leaching was observed because trace amounts of metal elements were detected in the hot acidic liquid solution.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Catalyst characterization; Carbon deposition; Pillared clay; Phenol treatment; Wet air oxidation

## 1. Introduction

Catalytic wet air oxidation (CWAO) uses dissolved oxygen to abate organic pollutants contained in wastewater streams. The proper choice of catalyst is of great importance for the design and scale-up of the CWAO process. One challenge that a catalyst faces is the severity of the CWAO conditions. The reported features of CWAO operation are high temperature (200–325 °C) and high pressure (5–20 MPa) [1]. Although a diversity of catalysts has been developed for the oxidation of various organic compounds in wastewater [2], the lack of catalysts that are active and durable under these process conditions has prevented CWAO from being fully implemented for environmental remediation.

Catalyst deactivation may occur due to a diversity of factors, including reduction of the catalyst specific surface area or poisoning of the catalytic agents by halogen-containing compounds formed during CWAO [1]. Deactivation may also

result from surface deposition and strong adsorption of a polymeric carbon layer [3], which rapidly decreases the pollutant removal rate. Furthermore, the dissolution of some metal oxides from catalysts into the hot acidic reaction medium prevents the use of catalysts, which can be transformed to a soluble state during reaction in the presence of oxygen. For example, supported copper oxide is an active catalyst for phenol oxidation in the temperature range 160–250 °C [1]. Despite the fact that such Cu-based catalyst is very active in batch processes, tests using continuous reactors reveal that there is a substantial loss of activity due to the dissolution of the catalytic species in the acidic reactive medium [4]. Its activity after five to seven runs reportedly decreased by 40% [5]. Active carbon and graphite supports were resistant to leaching in acidic medium, but they were slowly oxidized at temperatures higher than 150 °C and therefore could not be used for continuous operation over a long period of time [6]. Several catalysts with noble metals (oxides of Mn/Ce and Co/Bi) have been developed to exhibit much higher activity than a homogeneous copper catalyst for phenol oxidation at temperatures of 180–250 °C [1]. Even though the commercial application of these noble metal catalysts is costly, they can

<sup>\*</sup> Corresponding author. Tel.: +1 314 9354729; fax: +1 314 9357211.

E-mail address: [jingguo@che.wustl.edu](mailto:jingguo@che.wustl.edu) (J. Guo).

overcome the activity loss and achieve the destruction of aromatic and aliphatic organic compounds with significant selectivity to CO<sub>2</sub> [7].

Further improvement of catalyst performance is still needed for milder operating conditions (e.g., lower temperature and pressure) of the wet oxidation process over inexpensive catalysts. Among various porous compounds, pillared clays are novel materials with potential for use as supports due to their tunable pore dimension and their specific catalytic properties, which depend on the type of silicate layers and pillaring agents. The width of the pillar is approximately 7–8 Å and the free distance between pillars is 10–22 Å [8]. Their distribution in the space between the clay sheets and the host lattice can accommodate large molecules susceptible to undergo chemical transformations. In fact the original intent in creating pillared clays was to provide a range of pores so that heavy crude oils containing large refractory molecules could be processed by fluid catalytic cracking. Extensive examination of cracking reactions has shown that gas oil cracking by pillared clay catalysts gives highly selective yields of gasoline under moderate conditions [9].

Recently, metal oxide pillars, such as Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, have been successfully introduced between the silicate layers. Collaborated efforts have been made to evaluate such catalysts for the oxidation of phenol, a model pollutant due to its toxicity and prevalence in industrial processes. The novel catalyst has remarkable activity and can achieve complete destruction of phenol and phenol intermediates at mild temperatures by peroxide oxidation [10,11]. In this work, the catalyst activity in degrading TOC by air oxidation under a group of operating conditions is investigated. The effect of intra-particle diffusion on catalyst activities is also reported. In order to further understand the catalyst's performance, the stability of catalyst structure through long time application in treating aqueous phenol solutions is studied by various characterization techniques. Such studies are necessary to enable development of viable catalytic wet air oxidation processes.

## 2. Experimental

### 2.1. Catalyst preparation

Generally the properties of pillared clays are related to the nature of their constitutive elements (the clay layer and pillar) and to the bond between these two. Modifications of the properties of pillared clay were directed to the synthesis of pillars derived from various metallic hydroxides. Catalyst synthesis comprises two essential steps. The first is a cationic exchange of the natural clay by hydroxyl cations, and the second is a calcinations, which is stable to transform the hydroxides into oxide pillars anchored to the clay sheets. Diffusional limitations during the exchange, the structure of the oxide pillars, the distribution of pillars within the particles, and the existence of migrating H<sup>+</sup> during the calcinations are all factors that affect the properties of the final product.

Al–Fe pillared clay catalyst extrudates were prepared and provided by Professor N. Papayannakos' group at the National

Technical University of Athens (NTUA), Athens, Greece. A stock clay suspension (2 wt.%) was prepared and kept under stirring for 48 h before the upper half of the clay suspension was used. The cationic solution containing AlCl<sub>3</sub> and FeCl<sub>3</sub> (molar ratio of 9:1) was slowly titrated with NaOH solution at 70 °C until the OH/cation mole ratio was equal to 1.9. After aged under stirring for 24 h, the cationic complexes were mixed with clay suspension. Through a 1 h intercalation period and a 24 h aging period, the intercalated clay was washed thoroughly with water to remove chloride ions on the clay surfaces, dried at 60–70 °C for 24 h, and finally calcined at 500 °C for 1 h. The catalyst composition is (wt.% on dry basis): SiO<sub>2</sub>, 52.50; Al<sub>2</sub>O<sub>3</sub>, 27.56; Fe<sub>2</sub>O<sub>3</sub>, 7.02; CaO, 0.35; MgO, 2.5; K<sub>2</sub>O, 1.38; Na<sub>2</sub>O, 0.27; and TiO<sub>2</sub>, 0.17 [10].

### 2.2. Apparatus and procedure

By feeding fresh air, the experiments were carried out batchwise for the liquid and continuously for the gas in an autoclave stirred tank reactor at constant temperature and air pressure. The reactor was loaded with 600 cm<sup>3</sup> of feed solution and a given mass of catalyst. The reactor temperature was automatically controlled, while cold water circulation through a coil placed inside the reactor was used for properly quenching the reaction. Each run lasted for 4 h. At preset time points, liquid samples were withdrawn, rapidly cooled, filtered and analysed. The temperature, oxygen partial pressure, and catalyst loading were varied over wide experimental intervals. To characterize the catalyst intraparticle resistance, a number of catalyst sizes were used. Throughout the operation, the stirrer was operated at 800 rpm continuously to minimize the catalyst external mass-transfer resistance and to ensure uniform temperature and concentration profiles in the liquid phase.

The pillared clay catalyst is aimed to be suitable for continuous packed-bed application. The long-duration catalyst activity for phenol oxidation was tested in an isothermal packed-bed reactor of 25 mm diameter and 30 cm length, with either cocurrent downflow or upflow. The reaction solution containing 500 ppm phenol in water was fed to the catalyst extrudates with a liquid hourly space velocity (LHSV) of 0.3 h<sup>-1</sup>. Beginning with fresh catalyst packing, the reactor was operated continuously for 240 h under the selected conditions of temperature (170 °C) and total pressure (3.2 MPa). Both the autoclave stirred tank reactor and the packed-bed reactor are made of stainless steel.

### 2.3. Analyses

The liquid, gas, and catalyst samples collected during the CWAO process were subject to a diversity of analyses, as shown in Fig. 1. The concentration of phenol and other reaction products in the liquid phase (e.g., benzoquinone, acetic acid) was monitored by high-performance liquid chromatography (HPLC). Total organic carbon (TOC) was identified by the difference between the total carbon (TC) and inorganic carbon (IC) in the liquid sample. Fresh and used catalysts were characterized with respect to their Brunauer–Emmett–Teller

Download English Version:

<https://daneshyari.com/en/article/44193>

Download Persian Version:

<https://daneshyari.com/article/44193>

[Daneshyari.com](https://daneshyari.com)