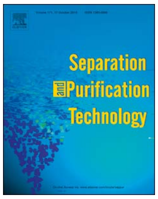
Separation and Purification Technology 197 (2018) 36–46

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Novel metal modified diatomite, zeolite and carbon xerogel catalysts for mild conditions wet air oxidation of phenol: Characterization, efficiency and reaction pathway

Raluca Pleşa Chicinaş[a], Emese Gál[b], Horea Bedelean[c], Mircea Darabantu[d,*], Andrada Măicăneanu[a,e,*]

[a] *Babeş-Bolyai University, Department of Chemical Engineering, 11 Arany János St., 400028 Cluj-Napoca, Romania*
[b] *Babeş-Bolyai University, Department of Chemistry and Chemical Engineering, Hungarian Line of Study, 11 Arany János St., 400028 Cluj-Napoca, Romania*
[c] *Babeş-Bolyai University, Department of Geology, 1 M. Kogălniceanu st., 400048 Cluj-Napoca, Romania*
[d] *Babeş-Bolyai University, Department of Chemistry, 11 Arany János St., 400028 Cluj-Napoca, Romania*
[e] *Indiana University of Pennsylvania, Department of Chemistry, Indiana, PA 15705, USA*

ARTICLE INFO

Keywords:
Phenol
Catalytic Wet Air Oxidation (CWAO)
Diatomite
Zeolite
Carbon xerogel

ABSTRACT

Metal (Co, Ce, Ni, Fe, Zn, Mn and Cu) containing Diatomite (**D**), Zeolite (**Z**) and Carbon Xerogel (**CX**) catalysts were prepared, characterized (SEM-EDX, TEM, FTIR and XRD) and tested as new catalysts in Catalytic Wet Air Oxidation (CWAO) of phenol in aqueous solution. Maximum values of Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC) efficiencies were obtained in the case of **Fe-D**, **Cu-Z**, and **Co-CX** catalysts. Reaction pathway and kinetics for CWAO of phenol revealed a pseudo first-order catalytic process and a k_{cat} between 0.0473×10^{-3} and 1.4183×10^{-3} L/min g. (Di)carboxylic acids, acetic and oxalic were identified as oxidation organic products.

1. Introduction

Phenol, a pollutant originating from numerous industrial processes, is a typical model pollutant of non-biodegradable wastewaters for their advanced treatment because it is considered to be an intermediate product in the oxidation pathway of aromatic hydrocarbons [1].

Wet Air Oxidation (WAO) as one of the available technologies used for the treatment of wastewaters [3] is suitable for high organic loads (10–100 g/L COD) and/or toxic contaminants at high flow rates requiring, however, elevated pressure (0.5–20 MPa) and high temperatures (125–320 °C) [2–4]. Although with low operation costs and minimal air pollution discharges, the high capital costs and safety implications related to severe operating conditions limit the practical usage of this method [3]. Consequently other wet air oxidation techniques were considered.

The use of *Catalytic Wet Air Oxidation* (CWAO) was intensively studied in the last years. Indeed, CWAO technique reduces the severity of the reaction conditions, promotes an easier decomposition of organic and refractory pollutants, thus reducing the costs of the wastewater treatment [5]. Due to milder operating conditions and shorter residence time [5,6], the operating cost of CWAO is about half of that of WAO process. Also, if conducted in fixed bed, the process is not mandatory to a separation step [3,4].

Recent studies on CWAO process of organic compounds using Al—Fe pillared clays [7], $MnCeO_x$ [8], CeO_2 nanorods [9], $CuO/\gamma\text{-}Al_2O_3$ [10], Ru/CeO_2 [11], Fe/C beads [12], $Ru/TiO_2{-}CeO_2$, $Ru/TiO_2{-}ZrO_2$ [13], $Pt/Ce_xZr_{1-x}O_2$ [14] or Ag nanoparticles supported on zirconia-ceria [15] catalysts were focused on phenol [7–12], aniline [13], succinic acid [14] or methyl-tert-buthylether [15] removal at high temperature and pressure (100–200 °C, 0.5–5 MPa), most of them using pure oxygen or high purity air as oxidation agent. Although there is a great interest in the CWAO process, not many studies consider mild operating conditions. Cui et al. [16], Anushee et al. [17,18] and Kurian et al. [19] used Fe_2O_3 nanoparticles, $ZnO{-}CeO_2$, $CuO{-}CeO_2$ and $Ce_xFe_{1-x}O_2$, respectively to study phenol, color and chlorinated compounds removal at 32–90 °C and atmospheric pressure. Maximum removal up to 74% for TOC and 94% for COD were achieved.

Diatomite (bio-silica) is an abundant mineral from natural sources, consisting of 87–91% SiO_2 along with small quantities of alumina and iron oxide. Diatomite has a high porosity (25–65%), small particle size, large surface area and high adsorption capacity. It is chemically stable and environmentally friendly. Diatomite has been widely used as

---

[*] Corresponding authors at: Babeş-Bolyai University, Department of Chemistry, 11 Arany János St., 400028 Cluj-Napoca, Romania (M. Darabantu). Indiana University of Pennsylvania, Department of Chemistry, Indiana, PA 15705, USA (A. Măicăneanu).
E-mail addresses: darab@chem.ubbcluj.ro (M. Darabantu), sanda.maicaneanu@iup.edu (A. Măicăneanu).

https://doi.org/10.1016/j.seppur.2017.12.050
Received 14 June 2017; Received in revised form 1 December 2017; Accepted 27 December 2017

filtering material, adsorbent and catalyst support [20–22].

Natural Zeolites comprise a family of crystalline aluminosilicates whose structure defines channels opened to the external surface of the particle, thus allowing mass transfer from the exterior to the interior of the crystal [23–25]. This open porosity determines a very large surface area of the Zeolites, e.g. in comparison with that of non-porous materials [25]. Due to the ionic relationship between the charges compensating cations and the rigid Zeolite framework, it is possible to operate the metathesis of one cation by another one without producing any alteration of the rigid framework [10,11]. Specifically, *Clinoptilolite* is the most abundant natural Zeolite [26], whose utilization for removal of organic dyes, ammonium and heavy metal ions was already reported [27–30].

Carbon materials, such as activated carbon, *Carbon Xerogels* (**CX**) and carbon nanotubes, have been successfully used for the oxidation of organic compounds in CWAO, Catalytic Wet Peroxide Oxidation (CWPO) and catalytic ozonation conditions [31]. Carbon Xerogels are one of the most interesting types of the above-mentioned innovative materials and have received considerable attention over the last two decades [32] and they can be obtained by the so called *sol-gel* protocol [33–36]. Metals-doped carbon xerogels to be used as catalysts can be prepared by impregnation or by adding a soluble metal salt to the initial reaction mixture [32].

Depending on specific conditions, in the CWAO process of phenol, several processes may occur, such as full mineralization of phenolic species with formation of CO_2 and H_2O, formation of polymers (easily separable from aqueous media) and generation of easily biodegradable compounds, such as carboxylic acids. Obviously, the most desirable path is, by far, the complete catalytic oxidation of phenols, i.e., producing CO_2 and H_2O only [37]. For this reason, the optimal reaction conditions should be identified and applied.

Taken into account all of the above, the aim of the present work consists of (i) preparation and characterization of new Diatomite, Zeolites and Carbon Xerogel based catalysts, (ii) study of efficiency of these catalysts in the CWAO of phenol in aqueous phase at ambient pressure and low temperatures and (iii) identification of the reaction pathway for the CWAO of phenol.

2. Experimental

2.1. Starting materials

A representative sample of Zeolitic volcanic tuff (hereafter referred as to Zeolite, **Z**), that of Clinoptilolite type (collected from Măcicaş deposit, Cluj County, Romania) and a Diatomite sample (**D**, collected from Minișul de Sus deposit, Arad County, Romania) were used as support for catalysts preparation.

All reagents, namely K_2CO_3 (anhydrous), formaldehyde [as $-(CH_2O)_n-$ 37% g/g solution], $Ce(NO_3)_3·6H_2O$, $Ni(NO_3)_2·6H_2O$, $CuSO_4·5H_2O$, $Cu(NO_3)_2·3H_2O$, $Zn(NO_3)_2·6H_2O$, $Co(NO_3)_2·6H_2O$, $Mn(NO_3)_2·4H_2O$, $Fe(NO_3)_3·9H_2O$, 2,4-Dihydroxybenzoic acid, Phenol were of analytical grade.

Phenol, Propionic acid (both Merck), Fumaric acid, Malonic acid, Maleic acid, Acetic acid, Oxalic acid, Formic acid, Acrylic acid, Hydroquinone, Catechol, 4-Hydroxybenzoic acid, 1,4-Benzoquinone and Formaldehyde (all Sigma Aldrich) were used as standards for HPLC investigations. Acetonitrile (ACN, HPLC grade) was purchased from VWR International. Water was purified using a Milli-Q filter system.

2.2. Catalysts preparation

2.2.1. Preparation of metal modified Diatomite (*Me-D*) catalysts

The raw Diatomite sample was crushed, grounded and passed through mesh sieves (0.4–0.6 mm fraction was collected, selected based on preliminary tests using a series of grain sizes). Next, in order to obtain the chosen catalysts, Diatomite sample was subjected to an adsorption process, as described in our previous work [38], upon treatment with a 0.5 N aqueous solution containing a selected metal cation (Co^{2+}, Ce^{3+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and Cu^{2+} respectively) using a solid: solution mass ratio of 1:10. The adsorption procedure was conducted in an ultrasonic bath at room temperature at 100 W power for 10 min. After the ultrasonic treatment, samples were separated from the precursor solution by settling, washed several times with distilled water, dried at 105 °C (24 h) and calcined at 250 °C (4h, with a heating rate of 4 °C/min). The **Me-D** catalysts thus obtained are listed in Table SM-1.

2.2.2. Preparation of metal modified Zeolite (*Me-Z*) catalysts

The raw Zeolite sample was crushed, grounded and passed through mesh sieves (0.4–0.6 mm fraction was collected, selected based on preliminary tests using a series of grain sizes). Then, the Zeolite sample was washed with distilled water, dried at 105 °C for 24 h. Dried sample was then treated, at pH = 10 (NaOH), with a 1 M NaCl aqueous solution under stirring (330 rpm) for 2 h with a solid: solution mass ratio of 1:10. Finally, the resulted sample was washed with distilled water (until chlorine anions were no longer detected with $AgNO_3$) and dried at 105 °C for 24 h (modified after Mondale et al. and Panayotova et al. [39,40]). The resulted **Na-Z** form of the Zeolite was thus obtained and further used. This preliminary cationic exchange was included in the catalyst preparation process based on previously reported data [39,40] that demonstrate the higher efficiency of the Na modified Zeolite (**Na-Z**) form with respect to the raw Zeolite sample.

Next, **Na-Z** sample was subjected to a cation exchange process, as described in our previous work [38,41], upon treatment with a 0.5 N aqueous solution containing the same selected metal cations and solid: solution mass ratio as in the case of Diatomite. The cationic exchange procedure was conducted using a 3D shaker (50 rpm) for 24 h. After that, samples were separated from the precursor solution by settling, washed several times with distilled water, dried at 105 °C (24 h) and calcined 250 °C (4h, with a heating rate of 4 °C/min). The **Me-Z** catalysts thus obtained are listed in Table SM-2.

2.2.3. Preparation of Metal-doped Carbon Xerogels (*Me-CX*) catalysts

The chemistry followed in this study, sol-gel protocol, is resumed in Scheme 1.

First, Potassium-doped Organic Xerogel (**K-OX**) was obtained by applying the sol-gel method (**I-III**). Thus, potassium-2,4-dihydroxybenzoate (K-2,4-DHBA), obtained from the partial neutralization of 2,4-dihydroxybenzoic acid (2,4-DHBA) upon treatment with an aqueous K_2CO_3 solution (**I**) and formaldehyde were used as starting materials for the polycondensation reaction in the presence of K_2CO_3 as catalyst (**III**) [42]. The sol-gel process (**III**) took place in sealed glass bottle. The resulted wet **K-OX** doped gel was then immersed in a 0.1 M doping metal salt aqueous solution (**IV**). The immersion process was repeated 3 times at 24 h intervals, with fresh metal salt solution. Thus, potassium cations from the wet gel were replaced by the corresponding metal through cation exchange process and the metal doped gel was obtained. This material was dried under ambient conditions (20 ± 2 °C) and then pyrolyzed (**V**) at 750 °C in argon atmosphere for 2 h. The resulted Metal-doped Carbon Xerogels, **Me-CX** ($\mathbf{Me}^{n+}$: Co^{2+}, Ce^{3+}, Ni^{2+}, Fe^{3+} and Zn^{2+}), are listed in Table SM-3. A blank **K-CX** sample was also prepared from **K-OX** using the same stages (**I-III**, **V**) described above, without the $1/n\ \mathbf{Me}^{n+} \leftrightarrows \mathbf{K}^{+}$ cationic exchange step (**IV**).

2.3. Apparatus for structural characterization

Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDX) analyses were performed using a JEOL JSM-6510 scanning electron microscope equipped with a Bruker EDX system on gold coated samples.

Transmission electron microscopy (TEM) was performed using a