Applied Clay Science 120 (2016) 121–134

Contents lists available at ScienceDirect

Applied Clay Science

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

The effect of ultrasonic treatment on iron–chromium pillared bentonite synthesis and catalytic wet peroxide oxidation of phenol

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ARTICLE INFO

Article history:
Received 2 July 2015
Received in revised form 4 November 2015
Accepted 5 November 2015
Available online 17 November 2015

Keywords:
Fe/Cr-pillared bentonite
Phenol
Ultrasonic treatment
CWPO

ABSTRACT

In this study, compared to traditional methods, Fe/Cr-pillared bentonite synthesis whose Fe/Cr mol ratio is 1/9 is carried out by considerably reducing the water consumption and synthesis time. Fe/Cr-pillared bentonites were characterized by scanning electron microscope with energy dispersive system (SEM–EDS), powder X-ray diffraction (XRD) and N_2-adsorption/desorption isotherm. The characterization results indicated that the Fe/Cr-DC sample prepared by adding dry clay to the pillaring solution directly exhibits comparable surface properties to those of the sample (Fe/Cr-SS) prepared by adding the pillaring solution on clay dispersion slowly. Catalytic behavior of Fe/Cr-pillared bentonites was tested for the catalytic wet peroxide oxidation (CWPO) of phenol with ultrasonic heating. No significant difference is observed among the phenol conversions for all of the synthesized samples. Phenol conversion increased with increasing temperature until 45 °C, but further increasing the temperature in higher than 45 °C was not very effective. The phenol conversion at pH 5 was higher than at pH 7. Additionally, a nearly complete removal of phenol was obtained over 2 h using Fe/Cr-DC catalysts, at the experimental conditions of T = 45 °C, pH 5, m_{cat} = 5 g/L, [H_2O_2/phenol] = 16, during reaction peroxide addition (2×10^{-4} mol/h) and ultrasonic heating. It is obtained that, aromatic intermediate products as catechol, hydroquinone and benzoquinones which are obtained in the beginning of oxidation oxidated into carboxylic acids. However, carboxylic acids such as oxalic and formic acid showing resistance to oxidation results by the level of total organic carbon (TOC) conversion being low.

1. Introduction

Pillared interlayered clays (PILC) are low-cost, microporous solid catalysts with unique properties and structures, formed by intercalation of metal polycations into swelling clay minerals, notably smectites (Garrido-Ramírez et al., 2010). In the synthesis of pillared interlayered clays, traditional or ultrasonic/microwave heating techniques can be used during aging of the pillaring solution and ion exchange. When using a traditional heating technique, the time of aging may change by hours or days depending on the pillars (Vicente et al., 2013; Gil et al., 2010; Ding et al., 2015; González-Rodríguez et al., 2015; Khankhasaeva et al., 2015). With an ultrasonic/microwave heating technique, aging occurs in minutes. Similarly, during the process of ion exchange, using ultrasonic/microwave techniques is much faster than traditional techniques. Another disadvantage of pillared interlayered clays at the industrial scale is that the clay dispersion is diluted from having used so much water during the synthesis process, and adding pillaring solutions to the clay suspension takes a long time (Fetter and Bosch, 2010). While water consumption can be decreased by using concentrated clay suspensions and dry clay, directly adding clay or/and pillaring solutions also decreases the time required for the synthesis process (Aouad et al., 2005; Sanabria et al., 2008; Olaya et al., 2009a). By including concentrated clay dispersions/dry clay along with ultrasonic/microwave heating techniques during the processes of pillaring solution aging and ion exchange, it is possible to synthesize pillared interlayered clays, which are used as catalysts for the degradation of recalcitrant organic compounds (Singh et al., 2004; Pérez et al., 2008; N. Sanabria et al., 2009, N.R. Sanabaria et al. 2009; Tomul, 2012a).

Phenol, which is used by the petrochemical, paint, paper, fabric and chemical industries, is the most common compound found in wastewater. Phenol is listed as a primary pollutant by the EPA (US Environmental Protection Agency). It is considered toxic at concentrations above 2 mg/L, and when present in water, it can create harmful chlorine solutions during disinfection by chlorination (Zhou and Smith, 2002; Melero et al., 2007; Zhou et al., 2011). In terms of human health and the environment, it is critical to clean up phenol, which can be found in almost all industrial wastewater and is a hard-to-remove pollutant. Currently, advanced oxidation processes (AOPs) are commonly used for organic pollutants such as phenol that resist traditional biological and chemical techniques. Catalytic wet peroxide oxidation (CWPO) is one of these successful AOPs, utilizing steady catalysis for the reduction of pollutants in industrial wastewater in the presence of an active catalyst (Catrinescu et al., 2011; Banković et al., 2012; Galeano et al., 2010,

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http://dx.doi.org/10.1016/j.clay.2015.11.007
0169-1317/

2014). Using ultrasonic processes in CWPO both increases oxidative degradation and causes the formation of much less harmful intermediates (Goel et al., 2004; Kidak and Ince, 2006; Nikolopoulos et al., 2006). Therefore, interest in CWPO with ultrasonic treatment has been increasing, and it is of vital importance to develop catalysts that can be used in such reactions (Rokhina et al., 2009).

Pillared clays are one of the materials that have the potential of widespread technological applications as catalyst and catalyst support in catalytic oxidation reactions due to their catalytic properties such as high surface area, porous structure, thermal, hydrothermal and mechanical durability. In literature, the use of pillared clays by compound transition metals (Al–Fe–, Al–Ce–Fe–, Fe, Cu, Al–, Al–Zr–, Zr–Fe–, Cu–Ce/Zr, Fe/Cr–) and CWPO of phenol has been carried out by many researcher and these research show that pillared clay catalysts give high activity (Catrinescu et al., 2003; Carriazo et al., 2005a, 2005b; Tatibouët et al., 2005; Timofeeva et al., 2005, 2009a, 2009b; Molina et al., 2006; Sanabria et al., 2008; Luo et al., 2009; Perathoner and Centi, 2010; Tomul, 2011a, 2012a, 2012b). As chromium being a good oxidant catalyst, in literature, although there are limited works where Fe/Cr-pillared clays is used as a catalyst in oxidation reactions, there are not so many works in which the method of CWPO backed up by ultrasonic operation is used in elimination of organic pollutants. Nikolopoulos et al. (2006) used the powder and pressed Fe–Al pillared clays as catalyst in CWPO reaction, backed up by ultrasonic operation and observed that ultrasonic operation increased the activity of pressed catalysts. In 4 h, 6.8% conversion without ultrasonic operation corresponding to 41.6% conversion values with ultrasonic operation at the same time has been reached. Mei et al. (2004), in CWPO reaction, backed up by microwave, with delaminated Fe–Ti pillared clays, full phenol conversion and high chemical oxygen demand removal efficiency were obtained and it was observed that the reaction time was greatly reduced. In literature, the synthesis studies executed by less water consumption and short synthesis time show that pillared clays synthesized by traditional method are synthesized by constructions which have comparable chemical, textural and surface properties and these catalysts have executed high catalytic behavior in various reactions. However, these studies are limited.

Therefore, in this study, the synthesis of Fe/Cr-pillared bentonites was carried out using ultrasonic treatment during both the aging and the intercalation of the pillaring solution. Furthermore, during the intercalation stage, the pillaring solutions were added to 10% clay dispersions, and dry clay was added to pillaring solutions in a drop-wise and direct manner to yield a 10 mmol ratio of (Fe + Cr)/g bentonite. The prepared pillared bentonites were characterized using SEM–EDS, XRD and N_2-adsorption/desorption measurements. In addition, experiments were also performed to demonstrate the catalytic behavior of different Fe/Cr-pillared bentonites in the catalytic oxidation of phenol using a combination of ultrasound and hydrogen peroxide. The effects of catalysts, temperature, and pH and the addition of H_2O_2 on the technique of CWPO combined with ultrasonic heating were investigated. The phenol oxidation intermediates generated by CWPO of phenol were identified, and the degradation pathways were discussed.

2. Experimental section

2.1. Materials and chemicals

The raw material used to prepare the Fe/Cr-pillared bentonites was Hançılı Green Bentonite (HGB) mined by ÇANBENSAN Company from the Hançılı region, Turkey and was used without any further purification or cation exchange. For the experiments of pillaring, chromium (III) chloride hexahydrate and sodium hydroxide were purchased from Merck. Iron (III) chloride hexahydrate and sulfuric acid were obtained from Sigma-Aldrich. For the catalytic experiments, phenol, and hydrogen peroxide (H_2O_2, 35%, v/v) from Merck. Phenol and intermediate compounds such as catechol, hydroquinone, p-benzoquinone, oxalic acid, maleic acid, fumaric acid, formic acid, and acetic acid standard stock solutions were obtained from Absolute. Acetic acid, methanol and phosphoric acid of chromatographic grade were purchased from Merck. Calibration solutions were prepared from standard stock solutions by dilution. All the chemicals were used as received without further purification. Doubly distilled water was used during the preparation of all liquid solutions.

2.2. Preparation of Fe/Cr-pillared bentonites

The preparation of Fe/Cr-pillared bentonites was performed via an ultrasonic heating technique, modifying the procedure according to the procedure of Olaya et al. (2009a) and Tomul (2011b, 2012a). Aging and intercalation of pillaring solutions were performed in an ultrasonic bath whose water temperature was adjusted before. Pillaring solutions were prepared via the drop-wise addition (flow rate of 1 mL/min) of a 0.4 M NaOH solution into a solution of $FeCl_3 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$ salts at a 1/9 Fe/Cr molar ratio, producing an $OH^-/(Fe^{3+} + Cr^{3+})$ ratio of 2.0. The catalytic properties of catalysts prepared by conventional methods (Tomul, 2012b), the different Fe/Cr ratios of Fe/Cr- and Fe-pillared bentonite samples tested by CWPO of phenol, and the catalytic activity of Fe/Cr-pillared bentonite for the ratio of Fe/Cr equal to 1/9 at the CWPO of phenol were higher than those of the other samples. Therefore, in this study, the Fe/Cr ratio was chosen to be 1/9. To facilitate the polymerization of Fe and Cr cations in pillaring solution and accelerate the process, Fe/Cr-pillaring solutions were aged via ultrasound using an ultrasonic bath (Bandelin Sonorex, operating frequency 35 kHz) at 70 °C for 20 min. The temperature of pillaring solution reached 60 °C after 20 min. After Fe/Cr-pillaring solutions were cooled to room temperature, during the intercalation stage, the pillaring solutions were added to 10% clay dispersions, and then dry clay was added to the pillaring solutions (1) drop-wise and (2) in a direct way to yield a 10 mmol ratio of (Fe + Cr)/g bentonite (75 mL pillaring solution/1 g of clay). The resulting dispersions were allowed to rest for 30 min in an ultrasonic bath at 25 °C to perform ion exchange. These aging and intercalation times were determined according to literature (Katdare et al., 2000; Olaya et al., 2009a, 2009b; Tomul, 2011a, 2012a). The dispersions were separated from the liquid phase by a vacuum filter, after which they were washed to remove the chlorine ions, dried at room temperature and calcined at 400 °C (heating ramp of 3.33 °C/min) for 2 h. The final samples are denoted as Fe/Cr-DC (prepared by adding dry clay directly to the pillaring solution), Fe/Cr-SC (prepared by adding dry clay slowly to the pillaring solution), Fe/Cr-DS (prepared by adding pillaring solution directly to a 10% w/w clay dispersion) and Fe/Cr-SS (prepared by adding pillaring solution slowly to a 10% w/w clay dispersion).

2.3. Characterization studies

The surface morphology of the raw and the Fe/Cr-pillared bentonites was obtained by SEM using a Philips XL-30S FEG instrument. The chemical composition of raw and pillared bentonites was determined by semi-quantitative EDS (Philips XL-30S FEG energy dispersive X-ray spectrometer) analysis, which shows the composition of a certain region in a depth between 500 nm and 1000 nm (Huerta et al., 2003). X-ray diffraction patterns (XRD) for the samples were obtained from 1° to 70° of 2θ using a Rigaku Ultima IV diffractometer with a Cu-Kα radiation (40 kV, 40 mA) at a scanning speed of 0.02°/s. XRD patterns were used to determine the basal spacing (d_{001}) values. Moreover, mineralogical composition of raw bentonite was found to be approximately 80% montmorillonite and 20% quartz via external standard method (Brindley, 1980) within its XRD pattern. N_2-adsorption/desorption isotherm measurements of HGB and of Fe/Cr-DC, Fe/Cr-SC, Fe/Cr-DS and Fe/Cr-SS were performed at 77 K using a Quantochrome Autosorp 6B instrument. Before each measurement, the samples were dried at 105 °C for 24 h and then degassed under vacuum for 5 h at 300 °C. N_2-