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Research article

Ultrasonic impregnation of MnO_2/CeO_2 and its application in catalytic sono-degradation of methyl orange

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ABSTRACT

MnO_2/CeO_2 catalyst was prepared by ultrasonic impregnation method. The traditional and stirring impregnation methods were used as control. Results showed that ultrasonic impregnation was the best synthesis method. The impregnation time was shortened from 120 min (traditional method) to 20 min, the specific surface area of catalyst was three times larger, and the catalytic activity of catalyst was also the highest. Furthermore, MnO_2 had crystalline structure and distributed uniformly on the support, CeO_2. The preparing conditions were further examined and the optimal conditions were found to be: 20 min of ultrasonic impregnation, 4.3 mol/L of manganese nitrate concentration and 450 °C of calcination temperature. The so prepared catalyst removed 94% of methyl orange in 30 min with a dosage of 0.5 g/L. The efficiency was 77.7% and 85.9% for traditional and stirring impregnation method under the same experimental conditions. The reaction process involved two stages: adsorption-dominated and degradation-dominated stages. The reaction rate constant of adsorption-dominated stage had little difference. However, compared with traditional impregnation, the reaction rate constant of degradation-dominated stage improved from 0.01 to 0.14 min^{-1} by ultrasonic impregnation. Mechanism analysis showed that the activity of ultrasonic impregnation MnO_2/CeO_2 was improved by the effects of acoustic cavitation and ultrasound oscillation on solid–liquid transport and distribution status.

1. Introduction

In recent years, ultrasonolysis has attracted intensive interests in wastewater treatment due to advantages including high efficiency, simple equipment, stable operation, and no secondary pollution (Nikpassand et al., 2016; Safaei-Ghomi and Masoomi, 2015). However, in many cases long treatment time was required and thus the energy cost was very high (Al-Juboori et al., 2015; Lastre-Acosta et al., 2014). The ultrasonolysis process can be improved by using a suitable catalyst, known as sonocatalyst (Khataee et al., 2015a). Various catalysts have been investigated, including Fe_3O_4/polyaniline (Wang et al., 2015), Er-doped ZnO (Khataee et al., 2015b), Sm-doped ZnO (Khataee et al., 2016), etc. MnO_2 is an excellent catalyst in degradation of organic matters because of its strong oxidation and adsorption ability (Zhang et al., 2014; Zhu et al., 2015). The multiple oxidation states of Mn element (Mn^{4+}, Mn^{3+} and Mn^{2+}) in manganese dioxide promote its activity in heterogeneous catalytic oxidation of organic pollutants (Su et al., 2016). CeO_2 is widely used as support in catalysts due to its high oxygen transport and storage capacities (Perkas et al., 2006; Song et al., 2016). MnO_2/CeO_2 was found an efficient sonocatalyst (Zhao et al., 2015, 2014), and nearly 99% of methyl orange was removed within 60 min with 1.0 g/L of catalyst, 2.6 of pH value, and 1.3 W/mL of ultrasonic density.

The common preparation methods for supported catalysts are deposition precipitation and impregnation. Deposition precipitation is beneficial for chloride ion removal but requires strict conditions and the repeatability is poor. In comparison, impregnation is much simpler, and has high utilization of active species, low cost, and high productivity. However, many studies have shown that this method caused low dispersion of manganese oxide since the impetus of transmitting mass was rather small in preparation (Zhang et al., 2011a,b). Catalytic process is a surface phenomenon, so high dispersion of active species is essential (Rahmani et al., 2014).

Ultrasonic technology is an environment friendly method for synthesizing catalysts, and can reduce the consumption of chemical

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reagents and energy (Lee and Jo, 2017). The physic-chemical effects of ultrasonic cavitation can accelerate dispersion of active component on the surface of support, hence obtaining catalysts with good dispersion on the surface and nano-scale oxides in the structure. The cavitation effect of ultrasound can generate high temperatures (5000 K) and pressures (180 MPa) (Gogate et al., 2011). The high temperature and pressure break the chemical bonds easily and causes the reactions to proceed. Since collapsing of cavitation bubble happens in less than a nanosecond, the temperature decreases quickly, which prevents the agglomeration of particles. Breaking agglomeration can improve the dispersion of active component and the activity of catalyst (Morelli and Prado, 2012). High pressures are favorable for the active component to enter into the pores of the support, so more active components are doped. Specific surface area of catalysts is increased since shockwave of ultrasound cut support particles into smaller one. Chong et al. (2016) found that FeCeOx prepared by ultrasonic impregnation showed a better diclofenac removal capacity than traditional method.

In this paper, MnO_2/CeO_2 was prepared by the ultrasonic impregnation method. For comparison, the catalyst was also prepared by traditional and stirring impregnation methods. The catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) to examine the structure and dispersed state of active component. The preparation process was optimized, including ultrasonic impregnating time, concentration of impregnating solution and calcinations temperature of the catalyst. The prepared catalyst was then applied for catalytic sono-degradation of methyl orange. The reaction kinetics were examined. Finally, the mechanism was investigated.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade. Methyl orange, a typical dye with high toxicity and carcinogenicity, was adopted as the target pollutant in this paper. Cerium nitrate, manganese nitrate and methyl orange were purchased from Tianjin Guangfu Fine Chemical Co. and Guoyao Chemical Industry Co. LTD, respectively. Solutions were prepared with water purified by a Millipore Molli Q UV Plus system.

2.2. Preparation of catalysts

The catalysts were obtained by ultrasonic impregnation, traditional impregnation, and stirring impregnation methods. The preparation process of CeO_2 powder was same as previous report (Zhao et al., 2014). Mixture of 150 mL NaOH (0.2 mol/L) and 150 mL $Ce(NO_3)_2$ (0.065 mol/L) was stirred at 300 rpm and 35 °C for 4 h, the solution was then centrifuged at 5000 rpm for 30 min to separate the products. The settled products were washed thrice using distilled water to remove byproducts, then dried at 100 °C in an air atmosphere for 3 h to obtain CeO_2.

Subsequently, CeO_2 was dipped in 50 mL manganous nitrate solution by different impregnation methods. For traditional impregnation and stirring impregnation methods, the mixture was stationary and stirred at 300 rpm for 20 min, respectively. Then the mixtures were filtered, and the products were calcined for 2 h at 450 °C. For the ultrasonic impregnation method, the beaker was immersed in a 40 kHz ultrasonic generator (FB-1500, Aoran Technology Ltd, Shanghai) for different times (5, 10, 20 and 120 min). Various concentrations of impregnating solution (2.15, 3.225 and 4.3 mol/L) and calcination temperature (350, 450 and 550 °C) were examined. The sound density for ultrasonic impregnation was 0.23 W/mL. Finally, catalysts were obtained.

2.3. Catalyst characterization

The catalyst was characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The specific surface area, porosity of and average pore size of samples were measured by BET (3H-2000PS2, BeiShiDe Instrument-S&T Company). The nitrogen adsorption/desorption isotherms were obtained at 77 K. To get the structural features and mineralogy of sample, the catalyst was identified by XRD analysis using a Bruker D8 Advance X-ray diffractometer at 2θ from 10° to 90°. The surface morphology of samples was obtained by a Hitachi S 4700 SEM analyzer at different scales and magnifications. The oxidation state of the components was detected by XPS using A1Kα radiation.

2.4. Experimental runs

Certain amount of catalyst and 100 mL of 20 mg/L methyl orange solution were added in 250 mL glass beaker. The beaker was then probed in an ultrasonic generator (S600H, Aoran Technology Ltd, Shanghai). The ultrasound frequency was 23 kHz, the power was 120 W, and the temperature was kept at 25 °C by water circulating cooler. The experimental conditions were as following unless stated otherwise: methyl orange concentration = 20 mg/L, pH = 3, and MnO_2/CeO_2 dosage = 0.5 g/L. The pH value was selected following previous study (Zhao et al., 2014).

The concentration of methyl orange was detected at 464 nm by a Pu Xi TU-1900 UV–vis spectrophotometer (Beijing Purkinje General Instrument Co., China). The removal efficiency (%) of methyl orange dye was defined as follows: Removal efficiency (%) $= \frac{C_0 - C_t}{C_0}$, where C_0 and C_t are the initial and final concentration of methyl orange.

Duncan's multiple range tests (DMRT) were used for pairwise or individual (one-to-one) comparisons. Significant difference was considered at $p < 0.05$.

3. Results

3.1. Comparison of three impregnation methods

Three methods, ultrasonic impregnation, traditional impregnation, and stirring impregnation methods, were used to prepare MnO_2/CeO_2. The obtained catalysts were applied in catalytic sono-degradation of methyl orange. Fig. 1(a) reports the results. The removal efficiency of catalyst made by ultrasonic impregnation increased most quickly and reached 93.86% after 30 min. The removal efficiency of the other two catalysts (made by traditional impregnation and stirring impregnation) was 77.72% and 85.93%, respectively. The removal efficiency of methyl orange was only 27% in CeO_2 sonocatalytic process. Further, 1.0 g/L catalyst-$_{\text{traditional impregnation}}$ was needed to reach the same result (Zhao et al., 2014) as that by 0.5 g/L catalyst-$_{\text{ultrasonic impregnation}}$ when all other conditions were the same. Thus, ultrasonic impregnation decreased 50% catalyst. The catalyst activity was significantly improved through ultrasonic impregnation. Furthermore, the impregnation time decreased from 2 h (traditional impregnation) to 20 min (ultrasonic impregnation), saving 100 min.

Fig. 1(b) (c) are the SEM images of catalysts made by traditional impregnation and ultrasonic impregnation. Clearly the loaded MnO_2 on CeO_2 was more by ultrasonic impregnation method than by traditional method. The distribution of MnO_2 on CeO_2 was more uniform, and the catalyst particles size was smaller. Ultrasound has