



Research article

Comparative evaluation of synthesis routes of Cu/zeolite Y catalysts for catalytic wet peroxide oxidation of quinoline in fixed-bed reactor

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ABSTRACT

In order to find a better alternative of conventional aqueous ion-exchange method, several Cu/zeolite Y samples were synthesized by different routes and examined for the catalytic wet peroxide oxidation of quinoline aqueous solution in continuous fixed-bed reactor. The characterization of catalysts using ICPMS, XRD, N₂ sorption, UV–vis DRS, FESEM and XPS techniques reveals the profound influence of preparation methods on synergy between copper-support interfaces. Aqueous ion-exchange (CuY_{AIE}) and wet-impregnation (CuY_{IMP}) methods promoted isolated Cu^{1+/2+} species; however, large crystallites of CuO were present on the external surface of precipitation-impregnation (CuY_{PI}) catalyst. Interestingly, CuY_{PI} showed hierarchical porosity and increase of surface area from 567 to 909 m² g⁻¹. The generation of mesoporosity in CuY_{PI} was result of higher desilication from zeolite framework due to synergetic effect of copper and NaOH. Almost comparable mineralization (61–65%) and H₂O₂ stoichiometric efficiencies (44.2–45.7%) were observed for CuY_{AIE} and CuY_{IMP} samples. Higher catalytic activities of both catalysts in comparison to CuY_{PI} suggest that isolated sites are the most redox-active sites for H₂O₂ activation and play more important role than high surface area, i.e., for CuY_{PI}. Wet-impregnation was found better than aqueous ion-exchange method. CuY_{IMP} exhibited high operation stability with >60% mineralization at LHSV = 4 h⁻¹, particle size = 1.2–1.7 mm, H₂O₂/quinoline = 48 and T = 80 °C. Copper leaching was majorly influenced by LHSV and particle size. The system was following Eley-Rideal mechanism and kinetic parameters were calculated using model based on this mechanism.

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1. Introduction

Advanced oxidation processes (AOPs) have been recognized as highly efficient and environmental-friendly techniques for the destruction of toxic organic pollutants from industrial effluent (Oturán and Aaron, 2014). These techniques are based on the use of powerful oxidizing hydroxyl radicals (*OH) generated through different modes of operation (Moreira et al., 2017). Among them, catalytic wet peroxide oxidation (CWPO) is a promising option because of its ability to completely degrade the pollutants to CO₂, N₂ and inorganic ions at mild operating condition (temperature (<373 K) and atmospheric pressure) (Ribeiro et al., 2016). In the CWPO process, hydroxyl radicals are generated by the set of redox processes between hydrogen peroxide and transition metal. Iron species supported on different materials, such as metal oxides

(Pouran et al., 2014), clays (Navalon et al., 2010), mesoporous silica (Zhong et al., 2011), activated carbon (Ramirez et al., 2007) and polymers (Gumy et al., 2005) have been extensively tested and showed significant catalytic activities. However, the requirements of highly acidic pH condition (3–4), high concentration of H₂O₂, complex formation ability of iron with organic acidic intermediates and slow reduction of Fe³⁺ to Fe²⁺ are major limitations for their application at industrial scale (Lyu et al., 2015).

Recently, copper, which also behaves like a Fenton reagent, has been reported suitable for industrial applications due to its wide-working pH range as well as good redox properties (Xia et al., 2011; Bokare and Choi, 2014). Unlike iron, copper does not form strong complexes with organic acid intermediates. Thus, it does not block the generation of hydroxyl radicals and can provide high mineralization (Bokare and Choi, 2014; Nichela et al., 2013). Table S1 shows a comparative evaluation of performance of Fe and Cu containing heterogeneous catalyst. Designing a highly active and stable copper containing oxide catalyst has become a hotspot in the field of Fenton chemistry. In recent years, copper containing

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zeolites, such as Cu/13X (Valkaj et al., 2011a), Cu/ZSM-5 (Wang et al., 2004), Cu-exchanged zeolite Y (Guzmán-Vargas et al., 2015) and CuFe/ZSM-5 (Dükkanci et al., 2010a) have attracted the attention of researchers owing to their high catalytic activity and stability. Particularly promising is copper exchanged zeolite Y which exhibits better utilization of hydrogen peroxide than popular Cu/ZSM-5 and shows higher degradation of toxic compound (Valkaj et al., 2011b). A further discussion is required in context of more advanced preparation methods as well as use of continuous reactor to increase their suitability for the large scale processes.

Aqueous ion exchange (AIE) is a traditional method for the incorporation of metals cations in zeolites. This method is based on the principle of inserting metals cations to neutralize the negative charge appearing on the oxygen atoms of the zeolite framework (Macdonald et al., 2014). Although conventionally used, AIE has several limitations. The procedure requires large solvent volume and consequently generates large amount of hazardous copper-containing residual solution (Mhamdi et al., 2009). The slow metal exchange rate makes it time-consuming and the poor control over metal loading causes difficulty in acquiring targeted metal content (Gao et al., 2015; Shwan et al., 2015). In addition, the requirement of additional filtration steps and treatment of residual solution make it uneconomical for large scale applications. Clemens and co-workers (Clemens et al., 2015) recently implemented a solid-state ion-exchange approach for copper loaded chabazite zeolite to circumvent the drawbacks of AIE process.

In order to overcome the shortcomings of the AIE route, two more facile approaches, wet-impregnation and precipitation-impregnation have been explored in the present study. Wet-impregnation is a popular method for the synthesis of supported catalysts. The small volume of solvent is completely evaporated in wet impregnation and thus, has advantages of no residual solvent, less processing time and absence of filtration step (Singh et al., 2016). Precipitation is also a well-known method for the preparation of metal oxides. This method involves the addition of an alkaline compound for the precipitation of metallic species. In addition, alkaline treatment of zeolite is a popular post-synthetic approach for the generation of hierarchical porosity in microporous zeolite (Verboekend and Pérez-Ramírez, 2011). Furthermore, the combination of impregnation with precipitation can provide good control of metal loading without generating residual solvent. Therefore, in the present research, precipitation-impregnation has been developed as a strategy to simultaneously remove the limitations of AIE as well as of microporosity in considerable extent. The alkaline treatment on the zeolite Y has not been explored extensively. Qin et al. (2011) reported that alkaline treatment of pristinene Y result in minor development of mesoporosity ($S_{meso} = 60 \text{ m}^2 \text{ g}^{-1}$). We have first time shown the synergetic effect of copper and NaOH on the generation of substantial mesoporosity and increase in surface area of protonized (partially dealuminated) zeolite Y. Since these preparation methods give rise to different copper species, an emphasis has been given to identification of these.

Most of the CWPO studies have been carried out in batch reactors. These reactors have been reported to be associated with several drawbacks such as excess of non-degradable intermediates (Yan et al., 2015), post-treatment filtration for catalyst recovery (Esteves et al., 2016) and long reaction period which results in the decrease of long-term stability of the catalyst (Yan et al., 2014). All these shortcomings can be overcome by fixed-bed reactor (FBR). The FBR allows catalyst reusability without need of filtration step and prevents unnecessary loss of catalyst. At the same time the higher treatable working volume, simple operation (no moving parts), less oxidant requirement, good catalyst stability, suitability for long-term operation (called workhorse of chemical industry) and short reaction time make it more economical than batch

reactor (Halim et al., 2009; Tisa et al., 2014). Few researchers have discussed the performance of FBR for treatment of wastewater (Yan et al., 2014; Botas et al., 2010; Mesquita et al., 2012; Satishkumar et al., 2013). However, all of them use iron containing solid matrix as catalyst and phenol as a model pollutant. In the present work, quinoline, a nitrogen heterocyclic compound (NHC), has been used as target pollutant. The degradation of quinoline is of particular interest because it is highly toxic, carcinogenic and mutagenic to human being, and found in large volume in wastewaters from textile, coking, pharmaceuticals and petroleum industries (Zhao et al., 2012; Zhang et al., 2016). To the best of authors' knowledge, the CWPO of toxic pollutants in continuous FBR using Cu/zeolite Y has not been reported.

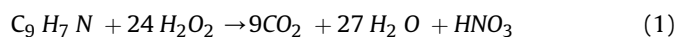
In this work, copper was immobilized over zeolite Y by different methods and the resulting Cu/zeolite Y were characterized for the in-depth understanding of the influence of these preparation methods on crystalline structure, hierarchical porosity and coordination environment of copper species. The performance of catalysts prepared by these methods have been examined and compared in terms of catalyst activity and stability for the continuous oxidative degradation of quinoline in FBR. The best catalyst is identified and the effects of different operating conditions (liquid hourly space velocity (LHSV), particle size, H_2O_2 /quinoline molar ratio and temperature) were measured on mineralization efficiency (total organic carbon degradation), H_2O_2 conversion and leaching of active species. Moreover, the long term stability, kinetics and mechanism of CWPO of quinoline have been discussed.

2. Methods and materials

The protonic form of zeolite (HY) was used as supporting material and this was prepared from NaY by following the procedure previously reported by our group (Singh et al., 2016). Copper was deposited over HY using three different routes, viz. aqueous ion exchange, wet impregnation and precipitation-impregnation. The catalyst preparation procedures and characterization techniques have been explained in supporting information (section S1 and S2).

2.1. Catalytic activity tests and residence time determination

CWPO of quinoline aqueous solution (3.87 mM, pH 7.0) was carried out in an up-flow packed-bed glass column reactor. The catalyst was placed inside bed in the form of spherical pellets and a layer of inert glass beads was placed at top and bottom of this bed for uniform liquid distribution. The glass tube was surrounded by jacketed annular tube, where hot silicone oil was circulating at high flow rate to heat the catalyst bed. The specifications of the packed-bed reactor and operating condition of CWPO experiments have been listed in Table 1. The column diameter/particle diameter ratio was kept larger than 8 to avoid the wall effect. The temperature of the packed-bed (40–80 °C) was maintained by circulating oil in outer jacket. The mixture quinoline and H_2O_2 was placed in oil bath to keep the whole system at isothermal condition. The initial pH of the mixture was set using 0.1 M H_2SO_4 or 0.1 M NaOH solution. The concentration of H_2O_2 was varied from 0.5 to 3 times of its stoichiometric dose, which was theoretically required for 100% mineralization of quinoline solution (according to Eq. (1)). The stoichiometric amount of H_2O_2 is 92.88 mM.



The reactants mixture was fed to the packed-bed reactor using a peristaltic pump (Gilson, USA) at the different space velocities, corresponding to flow rates (Q) = 0.97–3.89 $\text{cm}^3 \text{ min}^{-1}$. These space velocities were varied to evaluate the influence of residence

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