Process Safety and Environmental Protection xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Sono-dispersion of ceria and palladium in preparation and characterization of Pd/Al_2O_3-clinoptilolite-CeO_2 nanocatalyst for treatment of polluted air via low temperature VOC oxidation

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ARTICLE INFO

Article history:
Received 15 March 2015
Received in revised form 12 December 2015
Accepted 20 June 2016
Available online xxx

Keywords:
Pd/Al_2O_3-clinoptilolite-CeO_2
Ultrasound
Nanocatalysts
Toluene
Total oxidation

ABSTRACT

Pd/Al_2O_3-clinoptilolite-CeO_2 nanocatalyst was successfully synthesized via ultrasound assisted wet impregnation method to be utilized for total oxidation of toluene. Chemical analysis like XRD, FESEM, EDX, BET and FTIR techniques are used to determine physico-chemical properties of synthesized samples. Chemical analysis confirms the presence of all the elements in natural and treated clinoptilolite. XRD patterns prove the formation of ceria as a crystalline phase with an average crystallite size of 19.5 nm. FESEM images show the surface nanometric size of catalyst particles. EDX analysis indicates homogeneous dispersion of elements over nanocatalyst. BET surface area presented large surface for nanocatalysts. The results confirm the positive effect of ultrasound irradiation on surface morphology and elemental dispersion. Catalytic performance tests indicated high removal efficiency of nanocatalyst in total oxidation of toluene. High conversion at low temperatures (200–225 °C) and thermal stability are reasons for this observation.

1. Introduction

Volatile organic compounds (VOCs) are an important atmospheric pollutant and they are dangerous for human life. Thermal oxidation, catalytic oxidation and biological treatments are some methods have been utilized for VOCs removal. In recent years, many studies have been focused on catalytic oxidation of VOCs (Abbasi et al., 2011a; Yosefi et al., 2015). Different methods for catalyst preparation and their effects on catalyst activity are investigated (Azalim et al., 2011; Burgos et al., 2002; Delimaris and Ioannides, 2008, 2009; Hosseini et al., 2012; Hussain et al., 2011; Perez et al., 2011; Rahmani et al., 2014; Spivey, 1987; Zuo et al., 2012).

Conventional technologies for abatement of VOCs from waste gases, such as incineration, adsorption, absorption and ozonation have been used. However, oxidation at lower temperatures (200–300 °C) (Asgari et al., 2013b; Rahmani et al., 2014) than those of thermal

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http://dx.doi.org/10.1016/j.psep.2016.06.028
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Please cite this article in press as: Hosseini, M., et al., Sono-dispersion of ceria and palladium in preparation and characterization of Pd/Al_2O_3-clinoptilolite-CeO_2 nanocatalyst for treatment of polluted air via low temperature VOC oxidation. Process Safety and Environmental Protection (2016), http://dx.doi.org/10.1016/j.psep.2016.06.028

oxidation (300–400 °C) (Spivey, 1987) causes lower NO_x production. Furthermore, catalytic oxidation provides safer and more economical process compared to thermal oxidation.

High dispersion of active sites on support by different methods such as polyol method (Hosseini et al., 2012), using ultrasound waves for Co–Mg mixed oxide (Perez et al., 2011), plasma-ultrasound hybrid synthesis method (Rahmani et al., 2014) are some examples for different synthesis methods. Application of ultrasound assisted impregnation decreases the particle size and modifies particles distribution on support for better catalyst performance (Abdollahifar et al., 2014; Ghodrati et al., 2011; Parvas et al., 2014). Adsorption/desorption (Zuo et al., 2012), membrane gas stripping (Subrahmanyam et al., 2006) and cryogenic condensation and adsorption (Dwivedi et al., 2004; Gupta and Verma, 2002; Zaitan et al., 2013) are some different processes for VOCs removal from air. The effect of non-thermal plasma on catalyst properties and catalytic process was investigated (Vandenbroucke et al., 2011).

The reported VOCs, as air pollutants, are mainly acetone, formaldehyde, dichloromethane, trichloroethylene, tetrachloroethylene, benzene, toluene, etc. (Vandenbroucke et al., 2011). The common materials used for synthesis of catalysts in VOCs oxidation are zeolites, alumina, ceria and some metal oxides such as palladium and platinum oxides. For example, Pd/Ceria-clinoptilolite for P-xylene abatement from waste gas stream (Asgari et al., 2013b), Al_2O_3-supported transition metal oxide catalysts for catalytic incineration of toluene (Wang, 2004) and Mn, Fe and Co exchanged clinoptilolite catalyst for catalytic combustion of toluene (Özçelik et al., 2009) are some of the reported researches. The other materials used for VOC oxidation are TiO_2, ZrO_2 as support and Cu and Mn as active phase (Doggali et al., 2012). Al_2O_3-supported Cu–Co bimetallic catalysts prepared with polyol process for removal of BTEX and PAH in the incineration flue gas (Özçelik et al., 2009) are an example for these cases.

Catalytic oxidation of VOCs is investigated in many researches. For example, synthesis of Pd/Ceria-clinoptilolite catalyst for p-xylene abatement (Asgari et al., 2013b), total oxidation of xylene by nanostructured ceria/clinoptilolite catalyst (Asgari et al., 2013a), using of Pt/alumina-ceria nanocatalyst for oxidation of toluene, xylene and benzene (Abbasi et al., 2011b) and synthesis of ceria nanoparticles for toluene removal (Abbasi et al., 2012) are some researches which were carried out in this topic.

Clinoptilolite is a natural zeolite which can be utilized as adsorbent and catalytic materials. Because of the tri-dimensional micro-pore structure, controllable acidity and large specific surface area, zeolites provide a suitable template for the fabrication of supported catalysts (Rahmani et al., 2015). Ceria can be used as support or promoter in catalytic processes (Baneshi et al., 2014a; Jamalzadeh et al., 2013; Parvas et al., 2014). Its unique property of storing and releasing oxygen (redox property) helps the thermal resistance of the supports, the dispersion of supported metals, the oxidation and reduction of supported noble metals and the decrease in coke formation on the catalyst surface (Aghaei and Haghighi, 2015; Baneshi et al., 2014b; Khajeh Talkhoncheh and Haghighi, 2015). Ceria has the excellent thermal and mechanical resistance and increases thermal stability of the support (Rahmani et al., 2014). However, alumina with a high surface area, ceria nanoparticles as a promoter and treated clinoptilolite as support that act also as an active phase obtain suitable conditions for oxidation reaction. Addition of palladium in the structure increases the catalyst activity.

In this paper, Pd/Al_2O_3-clinoptilolite-CeO_2 nanostructured catalyst has been synthesized to remove toluene from air via oxidation rout at low temperatures. The composite of Al_2O_3-clinoptilolite-CeO_2 were not investigated in the literatures. The synthesized samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX), Brunauer–Emmett–Teller (BET) and Fourier transform infrared (FTIR).

2. Materials and methods

2.1. *Materials*

Natural zeolite used in this work was clinoptilolite from Mianeh mine (East Azarbaijan, Iran), ammonium chloride (NH_4Cl), hydrochloric acid (HCl) for acid treatment of clinoptilolite, hydrogen peroxide (H_2O_2), cerium (III) nitrate hexahydrate as cerium precursor, γ-alumina, palladium chloride ($PdCl_2$) as palladium precursor and deionized water. All the materials were from Merck Company and were not purified further.

2.2. *Clinoptilolite treatment*

As can be seen in Fig. 1(a) at first step, natural clinoptilolite was treated by 1 M ammonium nitrate aqueous solution. In this step, the ratio of NH_4NO_3 solution to clinoptilolite is 10 ml to 1 g. The mixture was heated for 8 h at 70 °C and then separated by filtration. After this stage, the separated material was washed by deionized water. Drying at 110 °C for 24 h under air flow and calcination at 550 °C for 4 h under air flow are final steps of natural clinoptilolite treatment. Treated clinoptilolite is shown by CLT-I. In the second stage in Fig. 1(b), the CLT-I was treated by hydrochloric acid. In this step, 1 g CLT-I was added to 10 ml of 1 M HCl aqueous solution and then was heated for 2 h at 80 °C. Filtration, washing with deionized water until pH 7, drying at 110 °C for 24 h and calcination at 500 °C for 3 h are next steps of procedure. The treated clinoptilolite after this stage is shown by CLT. Chemical analysis was

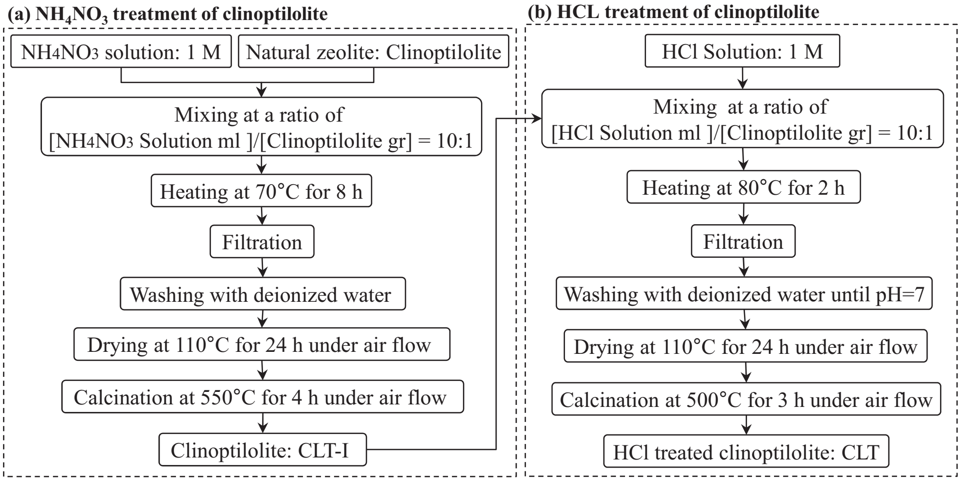

Fig. 1 – Treatment of clinoptilolite using ion exchange and acid treatment.

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