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Comparative sonochemically synthesis of CeO_2-doped Pd/clinoptilolite and Pd/Al_2O_3 nanocatalysts used in total oxidation of toluene at low temperatures for polluted air treatment

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ABSTRACT

A series of palladium based nanocatalysts which were loaded on CeO_2 doped alumina or clinoptilolite supports were synthesized by the ultrasonic assisted impregnation method. The influence of different ceria doped supports via total oxidation of toluene was investigated. Therefore, physiochemical properties of prepared nanocatalysts were evaluated by XRD, FESEM, BET and FTIR analyses. The FESEM images stated that synthesized naocatalysts had nanometric particles. The average size of catalyst particle was obtained to be 34.5 nm. BET analysis introduced a considerable rise in clinoptilolite surface area after treatment and demonstrated large surface area for Al_2O_3 and its composites. CeO_2 acts not only as a fine support due to its stability and surface area, but also had catalytic role because of its reducibility properties. Among synthesized catalysts, $Pd/Al_2O_3–CeO_2$ sample resulted the lowest particle size, highest surface area and consequently highest oxidation performance and stability.

1. Introduction

Nowadays, environmental problems become the major challenging issue all over the world. Among air, water and soil pollution as environmental risks facing human life, air pollution plays an important role especially through its growth at the industrial states and megacities with catastrophic effects on human health. Fast emission of air contaminants compared with soil and water is another important reason to notice this part of environmental issues. The volatile organic compounds (VOCs) comprise significant part of global environmental issues (Cunningham, 1995; Jones, 1999; Karimnezhad et al., 2014; Yosefi et al., 2015a). These pollutants made up of three major resources: industrial processes, transportation, and domestic activities (Gentner et al., 2009; Nørgaard et al., 2009). The consequence would be ozone formation and photochemical smog generation by the sunlight incidence leading the environmental problems (Jeon et al., 2014; Li et al., 2009; Ling and Guo, 2014; Zou et al., 2014). There are several methods to remove VOCs with their own advantages and drawbacks.

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VOCs abatement technologies such as adsorption, absorption, incineration, ozonation and catalytic oxidation, can reduce VOCs emission to secure grades (Karimnezhad et al., 2014). Catalytic oxidation through low temperature and high efficiency would be a promising procedure converting VOCs to safe products as CO_2 and H_2O (Oguz et al., 2000; Yosefi et al., 2015c). Among common supports Al_2O_3, ZrO_2, CeO_2, SiO_2 and TiO_2 are widely used at catalytic oxidation of VOCs through their high surface area, oxidation ability, mechanical stability, etc. (Huang et al., 2008; Jin et al., 2007). The importance of CeO_2 would be through its oxidization ability, high stability against thermal sintering and catalytic reactivity for reactions like methane combustion (Garcia et al., 2005; Pecchi et al., 2005; Tamura and Tomishige, 2015). The reducibility of CeO_2 enhances the oxidation of VOCs and corporates active phase, leading highly efficient catalysts (Aghaei and Haghighi, 2015; Baneshi et al., 2014; Yosefi et al., 2015b). The reduction of Ce^{4+} to Ce^{3+} demonstrates CeO_2 catalytic activity especially for oxidation/reduction applications (Abbasi et al., 2012; Bulfin et al., 2013; Chen et al., 2012; Tamura and Tomishige, 2015):

$$CeO_2 \leftrightarrow CeO_{2-x} + \frac{x}{2}O_2 \quad 0 \le x \le 5$$

However, it was proven that a reverse relation between the ceria particle size and Ce^{3+}/Ce^{4+} ratio (Hayat et al., 2014; Schubert et al., 2006). The noble metal oxidation/reduction also aims decreasing coke formation on catalyst surface (Abbasi et al., 2011). In many cases, CeO_2 is supported on Al_2O_3, which has a high surface area to ensure effective contact between waste gas flow and catalyst active sites (Abbasi et al., 2011; Dai et al., 2013; Rahmani et al., 2014). Furthermore, literature has reported proper removal ability for zeolites. Zeolite supported catalysts are extensively used to remove pollutants such as VOCs, due to their high activated sites density, high thermal stability and suitable selectivity (Barzegar et al., 2014; Hernández-Beltrán and Olguín, 2007; Korkuna et al., 2006). Clinoptilolite as one of the common natural zeolites would be a fine candidate to degrade air pollutants. In addition, clinoptilolite has other properties such as being readily available, cost effectiveness and simple mining production, therefore; it could be a reliable case to corporate composite supports (Asgari et al., 2013a; Hernández-Beltrán and Olguín, 2007; Jamalzadeh et al., 2014). Various investigations reported fine catalytic activity for supported noble metals for oxidation of VOCs as well as other catalytic applications (Abbasi et al., 2011; Barakat et al., 2011; Chen et al., 2012; Huang et al., 2008). In present work, CeO_2 was synthesized by redox reaction and doped on Al_2O_3 and treated clinoptilolite (CLT) to form two kind of support for palladium as an active phase. The ultrasound assisted impregnation method was applied as an effective synthesis method and the fabricated catalysts were analyzed by XRD, FESEM, EDX, BET and FTIR. The catalytic performance of these two supported catalysts was evaluated in total oxidation of toluene process. The main purpose of this paper is to compare the influence of ceria doped clinoptilolite and alumina as supports of palladium catalysts in terms of physicochemical and catalytic properties for toluene abatement.

2. Materials and methods

2.1. Materials

Palladium chloride $PdCl_2$, cerium (III) nitrate hexahydrate $Ce(NO_3)\cdot 6H_2O$ and γ-Al_2O_3 were used as palladium, ceria and high surface area support (alumina) precursors, respectively. Natural zeolite (clinoptilolite) was prepared from Azarshahr (East Azerbaijan, Iran) in the powder form and used after treatments. Toluene was used as an artificial VOC source. All materials were purchased from Merck Company and used without any further purification.

2.2. Clinoptilolite treatment

Raw clinoptilolite were finely powdered with agate mortar and thereafter were pestled, sieved and separated to particles smaller than 100 μm. Obtained powder was refluxed with pure deionized water for 12 h at 75 °C, filtered and dried at 110 °C for 4 h and stored as CLT-R. As illustrated in Fig. 1, raw clinoptilolite (CLT-R) was treated by two steps, ion exchange treatment with ammonium nitrate (NH_4NO_3) and acid treatment using hydrochloric acid (HCl). First, clinoptilolite added to 1 M solution of NH_4NO_3 at a ratio of [NH_4NO_3 sol. 1 M]/[Clinoptilolite gr] = 10:1 and mixed at 70 °C for 8 h. Then, the mixture was filtrated, washed, dried at 110 °C for 24 h and finally was calcined at 550 °C for 4 h both under airflow. The prepared clinoptilolite at this stage was powdered with agate mortar and named as CLT-I. At the second part, the Si/Al ratio of CLT-I was increased via acid treatment using HCl solution at a ratio of [HCl solution ml]/[Clinoptilolite gr] = 10:1 and mixed for 2 h at 80 °C. Then, the filtered mixture was washed with deionized water until pH 7, dried at 110 °C for 24 h and calcined at 500 °C for 3 h under airflow. The prepared sample was powdered with agate mortar

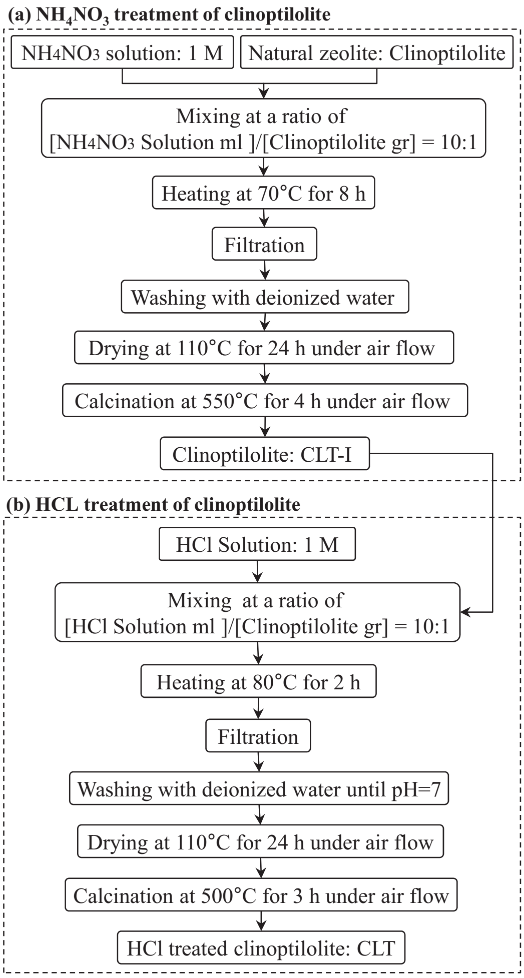

Fig. 1 – Treatment of clinoptilolite using ion exchange and acid treatment.

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