Journal of Industrial and Engineering Chemistry 20 (2014) 2735–2744

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Synthesis and physicochemical characterizations of nanostructured Pd/carbon-clinoptilolite-CeO_2 catalyst for abatement of xylene from waste gas streams at low temperature

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ARTICLE INFO

Article history:
Received 28 April 2013
Accepted 4 November 2013
Available online 12 November 2013

Keywords:
Pd/carbon-clinoptilolite-CeO_2
Pine cone
$ZnCl_2$
Catalytic oxidation
Xylene

ABSTRACT

Xylene removal from waste gas streams was carried out via catalytic oxidation over Pd/carbon-clinoptilolite-CeO_2. The synthesized samples were characterized by XRD, FESEM, BET, FTIR and TG techniques. The XRD patterns confirmed the formation of nano ceria with an average crystallite size of 11.6 nm. FESEM results indicated a good morphology for prepared carbon with deep pores, confirmed structure modification of zeolite, and showed that nanocatalyst has nanometric particles with an average size of 60.85 nm. Reaction data illustrated 98% abatement of xylene at 250 °C. The stability test of catalyst demonstrated that the removal efficiency has remained constant for 1200 min.

1. Introduction

Volatile organic compounds (VOCs) are recognized as major sources of air pollution, mainly caused by industrial emissions [1,2]. Due to their toxicity to human health and involvement in the formation of photochemical smog, decreasing VOCs emissions is urgent [3,4]. Previous studies have proved that the central nervous system is a major target of xylene toxicity, one of the aromatic VOCs, through inhalation and oral routes. Xylene causes impaired short-term memory, impaired reaction time, alterations in body balance, and has many other chronic effects [5,6].

Numerous treatment techniques have been developed for degradation of organic pollutants from stationary sources [7–13]. In recent years, catalytic oxidation is more considered to be an effective way for reducing the emissions of VOCs because of its high efficiency and flexibility in a wide range of applications at low temperatures [3,14–16]. The desired reaction is the complete oxidation of the toxic organic pollutants into CO_2 and H_2O [3,17–19]. The selection of catalyst depends on the nature of the pollutants, cost and availability. Besides, the catalyst should retain its activity for a longer period. There are several factors which influence catalyst activity like active phase loading and oxidation state as well as surface area of the catalyst, promoters and dispersion of active compound [20,21].

Using catalysts with mixed supports, we could benefit from numerous properties simultaneously. For instance, in a catalyst comprising palladium (active phase), AC (support), clinoptilolite (co-support) and ceria (promoter), we could have a novel nanocatalyst with unique properties such as the high activity, thermal stability, the high surface area, and micro pore volume as well. Furthermore, high redox properties of these catalysts to reach a relatively low-cost and highly effective catalyst are remarkable for the oxidation of VOCs.

Activated carbon (AC) can act as catalyst by itself or as a support of other catalytically active phases. Its excellent properties make this material become more and more interesting. Activated carbon is made from a variety of raw materials that are heated and further treated [22]. Generally, physical and chemical activation have been used to produce ACs [23,24]. Due to easy recovery of added chemicals and low-temperature process to result in a better porous structure, chemically activation is preferable [24]. In chemical activation, the raw material is impregnated with an activating agent ($ZnCl_2$, KOH, H_3PO_4 and less K_2CO_3, etc.), followed by a subsequent heating in an inert atmosphere [25]. Further explanations about activated carbon could be found in our previous work [26]. Furthermore, the reported investigations have indicated potential of natural zeolites for the removal of pollutants [27–30]. Clinoptilolite is the most common natural zeolite which is an attractive alternative for the removal of pollutants [29,31]. For most catalytic applications, 'activated' zeolites, are required

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http://dx.doi.org/10.1016/j.jiec.2013.11.001

[31,32]. The modification of zeolites via acid can modify their adsorption capacity, porosity and the crystalline network [29]. Beside AC and zeolite, Ceria is an attractive component for mixed oxide catalysts due to its unique redox properties which can provide lattice oxygen and prevent the sintering of noble metals [33]. The reduction of Ce^{4+} to Ce^{3+} as shown below leads to oxygen defects that makes ceria active enough for catalytic applications [34,35]:

$$CeO_2 \overset{\text{Reducing/oxidizing}}{\longleftrightarrow} CeO_{2-y} + \frac{y}{2}O_2 (0 \leq y \leq 0.5)$$

The concentration of Ce^{3+} relative to Ce^{4+} increases by decreasing the particle size, and as a result more oxygen vacancies and more active sites are created [35–37]. The outcomes of Wang and Lin studies signified that highest activity could be achieved by utilizing redox reaction with H_2O_2 in preparing CeO_2 catalysts [38].

It is worth noting that the properties of ceria and zeolite could be enhanced by noble metals [35]. Also, supported noble metals are very active catalysts for hydrocarbons total oxidation [3]. Among these metals, Palladium was opted as the active phase in this work due to its high stability and economic considerations [39].

During recent decades, despite the wide use of various catalysts including activated carbon, zeolite and cerium oxide in abatement of VOCs, a catalyst with mixed supports is still not well understood and has not been examined yet. Hence, the objective of our current research is studying xylene removal using this novel catalyst (Pd/carbon-clinoptilolite-CeO_2: Pd/C-Z-CeO_2) with noble metal loading of 1%. XRD, FESEM, BET, FTIR and TG techniques were used to characterize the prepared nanocatalyst and a GC was applied to evaluate the pollutant removal of synthesized catalyst.

2. Materials and methods

2.1. Materials

In this work, pine cone, $ZnCl_2$ and H_3PO_4 (85%) were used in activated carbon preparation. Natural zeolite of clinoptilolite from Mianeh mine (East Azerbaijan, Iran) was received in powder form and modified by HCl acid (37%) treatment. Cerium oxide was synthesized via redox method using H_2O_2 (30%) and $Ce(NO_3)_3{\cdot}6H_2O$. $PdCl_2$ (59%) was applied as a precursor of precious metal in nanocatalyst and *p*-xylene was used as a VOC pollutant. All the materials were supplied from Merck.

2.2. Support preparation and procedures

The synthesis process of ceria nano particles through the redox method, preparation procedure of activated carbon, and modification steps of clinoptilolite by using acid treatment is demonstrated in Fig. 1(a)–(c), respectively. Besides, Fig. 2 represents the employed pilot for synthesis of AC. Supplementary details is reported in our prior studies [26,35,40–43].

2.3. Catalyst preparation and procedures

Fig. 1(d) illustrates the preparation steps of Pd/C-Z-CeO_2 nanocatalyst via impregnation method. Appropriate amounts of palladium chloride ($PdCl_2$) were dissolved in distilled water. Then, 25% synthesized nano ceria, 25% HCl treated clinoptilolite and 50% prepared activated carbon were added to the aqueous solution. The solution was stirred at 60 °C for 3 h, dried at 110 °C for 24 h and

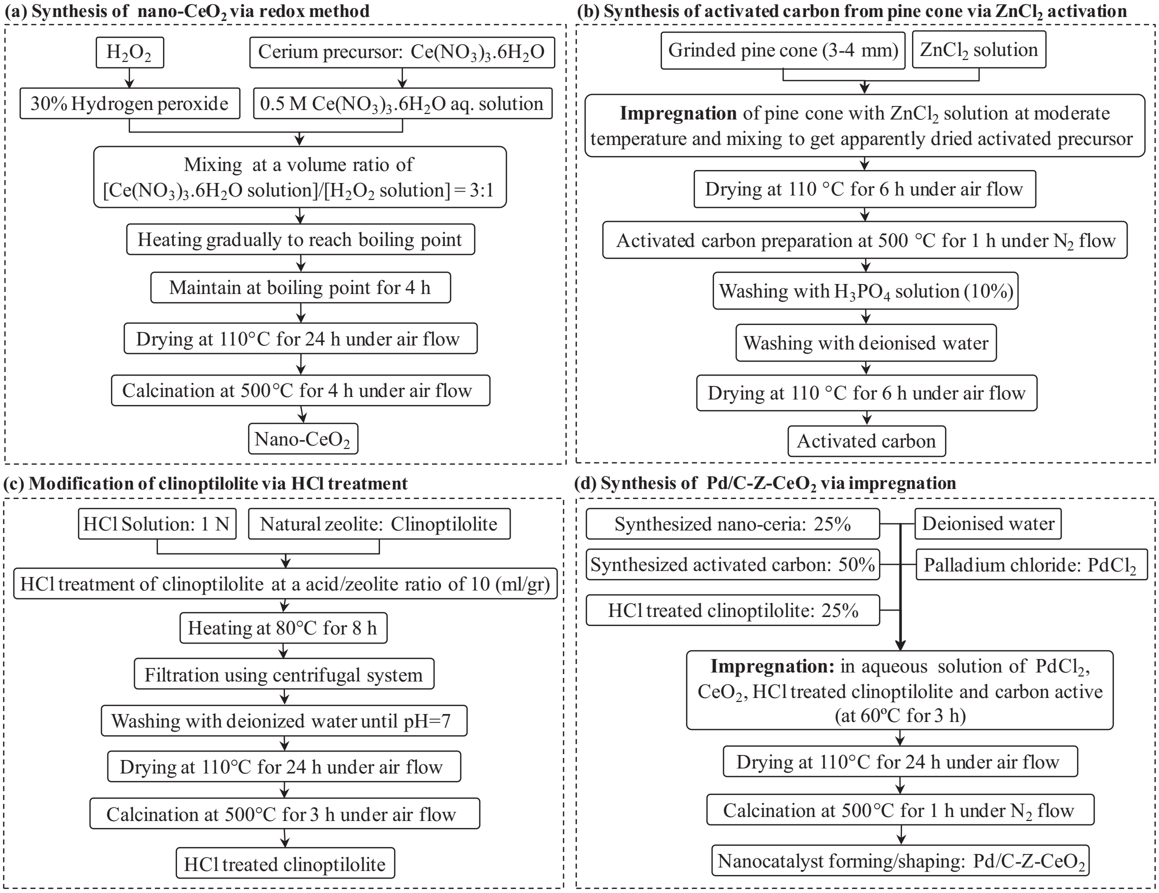

Fig. 1. Schematic flow chart for the preparation steps of nanostructured Pd/C-Z-CeO_2 catalyst: (a) synthesis of nano-CeO_2 via redox method, (b) synthesis of activated carbon from pine cone via $ZnCl_2$ activation, (c) modification of clinoptilolite via HCl treatment, and (d) synthesis of Pd/C-Z-CeO_2 via impregnation [25].