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Solvent-free selective aerobic oxidation of toluene by ultra fine nano-palladium catalyst

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ABSTRACT

High activity ultrafine Pd catalyst was synthesized by both functional polymer encapsulated and impregnation methods. Catalysts were characterized and used to catalyze solvent-free aerobic toluene oxidation. Reaction temperature, time, catalyst mass, air pressure and catalyst reusability were investigated. Catalyst synthesized by encapsulating and immobilizing Pd inside titanium oxide is more active and has a better reusability.

1. Background

Selective oxidation of toluene to produce its derivatives (such as benzyl alcohol, benzaldehyde, benzoic acid and benzyl benzoate) has been of great importance for the past decades. There has been a great increase in attraction towards how to convert this less valuable raw material, which is usually considered as volatile organic compounds (VOCs) liberated from industrial processes as higher-value chemical products instead of being fully combusted. Benzyl alcohol, benzaldehyde, benzoic acid and benzyl benzoate are commercially significant versatile intermediates in the manufacture of pharmaceuticals, dyes, solvents, perfumes, plasticizers and preservatives.

Pollutions and less efficient operation process usually come along with homogeneous catalysis reactions. Today, liquid phase toluene oxidation catalyzed by homogeneous metal salt catalyst using halogens or acidic acid as solvent to produce benzaldehyde, benzoic acid industrially is still the mainstream, employing oxygen or peroxide as the oxidant [1–3]. The use of solvent and homogeneous catalyst causes difficulties in catalyst–product separation and equipments. The process does not support green chemistry. Developing solvent-free toluene oxidation catalyzed by active heterogeneous catalyst to make production processes pollution free and easier has attracted special attention, and oxidation of organic compounds catalyzed by metal has already been widely applied [4]. Reports show that for aerobic toluene oxidation, many heterogeneous catalysts have been studied, including copper [5], silver [6], manganese [7,8], cobalt [9], chromium [10], iron [11], gold [12], palladium [13], platinum [14] and some bimetallic composition [15–18]. For the metal supported catalysts mentioned above, some of them are focused on the catalytic process of deep oxidation or combustion at relative high temperatures which causes a great loss of valuable carbon in aromatic compounds. While others tested for toluene selective oxidation at mild conditions, Shen et al. employed V–Ag–O/20% TiO_2 to convert toluene to benzaldehyde at 613 K with 7.3% of toluene conversion and 95% selectivity [6]. Suib et al. obtained the mixture of benzyl alcohol, benzaldehyde and benzoic acid at 110 °C by gamma-MnO_2 with 17.6% of toluene conversion [7]. Guo et al. used air to oxidize toluene catalyzed by cobalt in flow mode, recorded 8.9% of toluene conversion and 60% selectivity of both benzyl alcohol and benzaldehyde [9]. However, toluene catalyzed by the transition metal salts is usually accompanied by low selectivity or consumes large amounts of solvents or bromides [19,20]. Sometimes conversion needs to be sacrificed to prevent overoxidation [8].

In most of the studies, Pd catalyst has been used for toluene combustion [21–23] with only a few reports on its application for toluene selective oxidation. For instance, 50% conversion of toluene and 95% selectivity of benzyl benzoate were achieved by Hutchings group using synthesized Au/Pd alloy nanoparticles [15]. Others have also used Pd based nanoparticles as catalyst to oxidize toluene to benzyl acetate [24,25]. The solvent free toluene oxidation system catalyzed by single nano-size Pd catalyst was studied in this research. We investigated the efficiency of ultra fine supported Pd

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