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Hydro-purification of crude terephthalic acid using palladium catalyst supported on multi-wall carbon nanotubes

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ABSTRACT

Palladium catalysts supported on functionalized multi-wall carbon nanotubes were synthesized for hydro-purification of crude terephthalic acid containing 2100 ppm 4-carboxybenzaldehyde (4-CBA) as impurity. $PdCl_2$ and $Pd(OAc)_2$ were used as precursors. Palladium loadings were 0.05 to 0.6 wt.% with catalysts reduced at 200 to 400 °C. Catalysts prepared from both precursors with least 0.3 wt.% palladium resulted in 99%+ removal of 4-CBA. The most desired selectivity was obtained for the catalyst with $PdCl_2$ as precursor, reduction temperature of 300 °C, and palladium loading of 0.3 wt.%. This catalyst had slightly better performance than the commercial catalyst (0.5 wt.% of palladium on activated carbon).

Introduction

Purified terephthalic acid (PTA) is an important petrochemical product and the main raw material for polyethylene terephthalate (PET) which is extensively used in a variety of applications including polyester fibers, molded plastics, films, and blown beverage bottles [1]. The Amoco process is the most widely used industrial process for production of PTA that involves the oxidation of *p*-xylene (PX) by air at temperatures of about 200 °C and pressures of about 20 bar using soluble Co/Mn catalysts, acetic acid (AA) as solvent, and Br as a promoter [2]. The products from the oxidation reactor, after the required separation processes, include terephthalic acid (TA) as the major product with about 2000 to 5000 ppm of 4-carboxybenzaldehyde (4-CBA) and 200 to 500 ppm of *p*-toluic acid as the main impurities. When present as impurity, 4-CBA results in lower polymerization rates and a reduction in the average molecular weight of the resulting polymer. Furthermore, the presence of colored impurities results in a polymer color that is undesired for fiber manufacturing. Since the chemical structure and physical properties of TA and 4-CBA are quite similar, separation by adsorption, extraction, or membranes is not feasible. It is also hard to find a proper solvent that has a good selectivity to separate 4-CBA from TA using a crystallization process. The removal of 4-CBA from crude terephthalic acid (CTA), preferably to levels below 25 ppm, by hydrogenation over a suitable catalyst is the most practical route to achieve this goal [3]. Hydrogenation of 4-CBA to *p*-toluic acid is carried out over a noble metal catalyst [4]. The general chemistry [5–7] is presented in Fig. 1 where 4-CBA is hydrogenated to 4-hydroxymethylbenzoic acid (4-HMBA) that is subsequently converted to *p*-toluic acid (path 2). Simultaneously, 4-CBA is decarbonylated to benzoic acid (BA) (path 1) producing an equimolar amount of carbon monoxide which is a well-known poison for palladium hydrogenation catalysts. At the same time, yellow colored impurities are also hydrogenated to colorless compounds. The resulting products pass through a series of flash crystallizers where temperature and pressure are sequentially decreased. Hydrogenation products and *p*-toluic acid have a higher solubility than TA in water [8]. The solubility of 4-CBA and other compounds in water are reported in Table 1. All hydrogenation products therefore remain in the mother liquor while TA is crystallized out. The final PTA product has less than 25 ppm of 4-CBA as impurity [4].

Catalyst comprising of group VIII of the periodic table of elements supported on inert supports are well-known for various hydrogenation reactions. Supported precious metals including ruthenium, rhodium, platinum, and palladium have also been used extensively as monometallic catalysts [9]. From an industrial viewpoint, carbonaceous supports are preferable because of the facile recovery of the precious metals by burning off the support. Activated carbon supported palladium is the catalyst commonly

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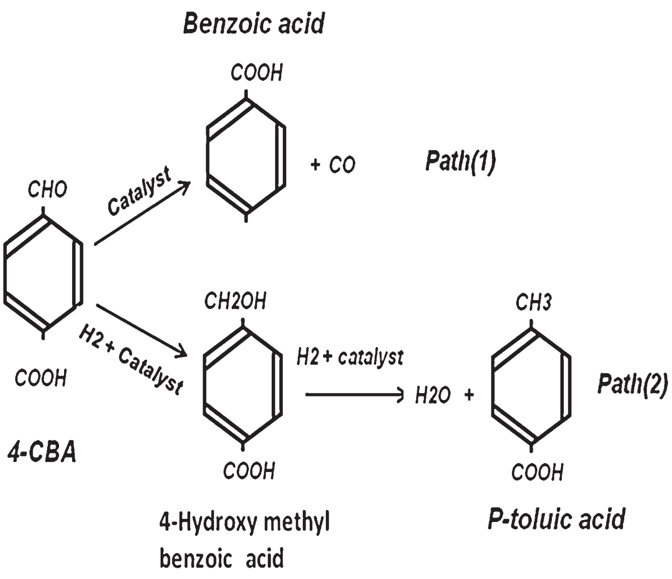

Fig. 1. Scheme of reactions in the hydro-purification of CTA.

used for CTA hydrogenation reactions [2,6–9]. Pellegrin et al. used 0.5 wt.% Pd/C catalyst for purification of terephthalic acid and investigated the effect of the main contaminants on catalyst deactivation [2]. Jhung et al. reported that the ruthenium-incorporated catalyst, (0.3% Pd–0.2% Ru)/CCM (carbonaceous composite material) was a suitable candidate to replace the existing 0.5% Pd/C commercial catalyst for hydropurification of crude terephthalic acid as it demonstrated a superior performance with higher stability under actual commercial conditions as well as under aging conditions in the lab compared with the commercial catalyst [6].

Activated carbon (AC) supports, however, are susceptible to deactivation and can result in the contamination of PTA. In order to overcome these shortcomings, there is a demand to focus research efforts on development of new nano-dimensional supports such as carbon nanotubes (CNTs) as alternative supports for the palladium catalysts. CNTs constitute a novel class of nano-materials with applications in catalysis and other areas [10]. CNTs have desirable properties including a high surface area, inertness to strong acids and bases, high electronic conductivity, a large fraction of graphite edge, and the possibility for their macronization and the use of non-traditional mode of heating such as μ-waves to allow for homogenizing the reaction temperature [11].

Several studies have focused on the application of CNTs as support for Pd and Pt catalysts for liquid phase oxidation of alcohols [12] and as electrocatalyst in proton exchange membrane fuel cells [13,14]. Zhang et al. used multiwall CNTs (MWCNT) with different Pd loadings for liquid phase hydrogenation of benzene [15]. They compared the results with those obtained from Pd/zeolite (SiO_2:Al_2O_3 = 5:1) and Pd/AC prepared under similar conditions and reported that benzene conversion to cyclohexane reached approximately 100% at the highest Pd loading of 12 wt.% for Pd/MWCNT. An intermediate loading of 8.0 wt.% Pd on MWCNT yielded nearly double the conversion of benzene compared with catalysts with similar Pd loading on AC or zeolite supports. Vu et al. also showed that Pd, Pt and Ru metal nanoparticles supported on CNTs had high catalytic activity in the liquid phase hydrogenation of cinnamaldehyde [16]. Esmaeili et al. synthesized Pd/MWCNTs with tin as a promoter for selective hydrogenation of highly concentrated acetylene feedstocks [17]. Cano et al. reported a high catalytic activity for palladium nanoparticles supported on MWCNT in alkene hydrogenation [18]. Corma et al. also reported that Pd nanoparticles supported on CNTs were more active than those supported on AC in the Heck reaction of styrene and iodobenzene and in the Suzuki coupling of phenylboronic acid and iodobenzene [19] while Karousis et al. reported a higher activity for CNT supported Pd catalysts compared with AC supported catalysts in the hydrogenation of methyl-9-octadecenoate and 2-methyl-2-pentenal and concluded that the high catalytic performance of CNT supported Pd was due to the large active surface of metallic palladium [20]. Villa and Wang also reported a higher activity for Pd nanoparticles supported on CNT compared with Pd nanoparticles supported on AC in the liquid phase oxidation of benzylic alcohol to benzaldehyde which was attributed to the differences in metal dispersion between Pd/AC and Pd/CNT resulting from textural, chemical, and physical differences between AC and CNTs [12]. Cornelio et al. also used Palladium nanoparticles on carbon nanotubes as catalysts of cross-coupling reactions. The decoration of multi-walled carbon nanotubes with preformed thiolate-stabilised palladium nanoparticles yielded the optimum catalyst, exhibiting high activity and stability towards carbon–carbon bond formation and excellent recyclability, retaining high activity from cycle to cycle [21]. Chen et al. used the structural and electronic promoting effect of nitrogen-doped carbon nanotubes on supported Pd nanoparticles for selective hydrogenation of olefins. The Pd on nitrogen-doped CNT catalyst showed excellent catalytic performance in terms of activity, selectivity, and stability in the selective hydrogenation of cyclooctadiene, which was related to the structural and electronic promoting effect of the NCNT support [22].

Table 1
Solubility (g/100 ml H_2O) of different compounds in water.

Compound	At 20 °C	At 100 °C
4-HMBA	0.5	10
BA	0.34	6.8
p-Toluic acid	0.2	0.22
4-CBA	0.005	0.25
TA	0.005	0.03

In the present investigation, we have developed a palladium on CNT catalyst for hydro-purification of CTA which, to the best of our knowledge, has not been reported in the open literature. Wet impregnation was used for preparation of Pd/CNT catalysts using two different Pd precursors. The influence of the reduction temperature and the effect of Pd loading on the activity and selectivity of the catalysts were investigated.

Experimental

Catalyst preparation and characterization

Purification and oxidation of CNT

The mutliwall carbon nanotube (MWCNT) employed in this study (96% purity, 10–30 nm in OD) was prepared in-house at the Research Institute of the Petroleum Industry (RIPI), Iran, by a special CVD method over a catalyst consisting of cobalt–molybdenum nanoparticles supported on nanoporous magnesium oxide (Co–Mo/MgO) [23]. The reaction of methane decomposition was conducted at atmospheric pressure with a retention time of 20–50 min. The purification procedure was as follows: a pristine MWCNT sample was added to 1:1 (v/v) solution of HCl (37%) and deionized (DI) water and mixed for about 16 h at 60 °C. The resulting mixture was filtered and washed several times with DI water until the pH of the filtrate was neutral. For further purification, the prepared materials were dissolved in 1:3 (v/v) solution of nitric acid (65%) and DI water for 3 h at 60 °C with the resulting mixture filtered and washed several times with DI water until the pH of the filtrate was neutral. The resulting cake was dried

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