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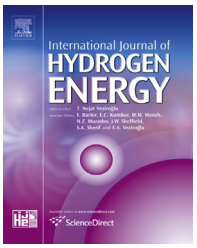

Selective hydrogenation of 4-carboxybenzaldehyde over palladium catalysts supported with different structural organization

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ABSTRACT

The palladium-incorporated catalyst, (0.5% Pd/C) (nanospace engineering KOH-activated carbon material) catalyst with macro-structured carbon nanofibers aggregates and micro-nano-porous activated carbons, has been studied as a candidate for hydro-purification of crude terephthalic acid containing of 4- carboxybenzaldehyde (4-CBA) as an impurity. The efficiency of different carbon structures (macro/micro) was investigated over selectivity catalyst. The reaction products were analyzed by HPLC to determine the amounts of 4-CBA, benzoic acid (BA), 4-Hydroxymethyl benzoic acid (4-HMBA) and para-toluic acid (p-tol). It has been confirmed that 0.5% Pd/microporous catalyst gave an excellent performance to catalyze the hydrogenation of 4-CBA to para-toluic acid due to high micro-porous surface area and the most desirable selectivity to 4-HMBA was obtained with macro-structured carbon nanofibers. Pd/AC catalyst with more micro surface area (85.26%) achieved a maximum yield to the intermediate product of 4-HMBA only 30% whereas the macro-structured CNFs achieved typically 66%. The desired selectivity to para-toluic acid was found to be deep dependent on the micro-porous structure.

Introduction

Purified terephthalic acid (PTA) is the important industrial chemical [1], which is used as a raw material for producing saturated polyester – mainly polyethylene terephthalate as PET [2]. In the process of company, i.e. Shahid Tondgooyan Petrochemical Co [3], theterephthalic acid (TA) production is based on the liquid-phase oxidation of p-xylene (PX) using a homogeneous catalyst $Co(OAc)_2$, HBr, and a co catalyst $Mn(OAc)_2$. The obtained crude terephthalic acid (CTA) usually contains approximately 2000–3000 ppm of 4-carboxybenzaldehyde (4-CBA) as the main impurity, which would decrease the polymerization rate during the production of PET, PBT and PTT [4]. The crude terephthalic acid (CTA) produced from PX oxidation contains a by-product, 4-carboxybenzaldehyde (4-CBA), which causes discoloration of

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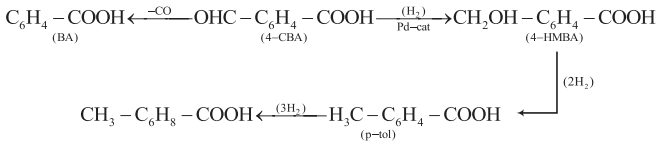
the CTA. The main upgrading step in refining purified terephthalic acid (PTA) is the catalytic hydrogenation of 4-CBA to 4-hydroxymethylbenzoic acid (4-HMBA) that is subsequently converted to p-toluic acid. Simultaneously, 4-CBA is decarbonylated to benzoic acid (BA) producing an equimolar amount of carbon monoxide, which is a well-known poison for palladium hydrogenation catalysts (shown in Eq. (1)) [4,5].



(1)

The unfavorable hydrogenation reaction, however, can occur over Pd catalysts [6–9]. The catalyst selectivity toward each hydrogenation path is affected by many factors, including the interaction between active phase and support, the cluster size of active sites, and the type of support. Activated carbon supported palladium is the catalyst commonly used for 4-CBA hydrogenation [10]. However, palladium particles on the carbon carrier have a sintering problem which results in catalyst deactivation. It has been reported that bimetallic Pd–Ru catalysts could increase the sintering resistance of Pd metal particles [11]. Recently, Jei Zhu et al. [12] prepared Palladium over carbon nanofiber coated monolith for purification of CTA. They investigated the effect of mass transfer on the catalyst performance. In this study, we investigated the efficiency of different carbon structures (macro/micro) over selectivity of Pd-catalyst in hydrogenation of 4-CBA. The present work compares the performance and characterization of Pd/KOH-modified carbon nanofiber as macro-pore structures and Pd/KOH-activated carbon as micro-pore structure for selectivity of catalysts. The majority of this paper has been focused on the KOH-treatment of carbon nanofiber optimization, factors affecting activation carbon production and performance of catalyst. Carbon nanofibers (CNFs) are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates.

Table 2 – The derived experimental parameters for optimal modified activation carbons during KOH agent –group 2.

Sample ID	PH/char ratio (w/w)	KOH/PH-AC ratio (w/w)	Activation temperature (°C)
KOH-PH-AC1	0.90	2.50	700
KOH-PH-AC2	0.90	2.50	800
KOH-PH-AC3	0.90	2.50	900
KOH-PH-AC4	0.90	3.50	700
KOH-PH-AC5	0.90	3.50	800
KOH-PH-AC6	0.90	3.50	900
KOH-PH-AC7	1.20	2.50	700
KOH-PH-AC8	1.90	2.50	700
KOH-PH-AC9	2.50	2.50	700

Chemical vapor deposition is the dominant commercial technique for the fabrication of CNFs. Thermal catalytic decomposition (TCD) of methane for simultaneous production of CO_x-free hydrogen and carbon nano-fibers over Ni–Co–Al, Ni–Fe/Al_2O_3 and Ni–Pd/Al_2O_3 catalysts has been studied in many researchers [13–16]. In previous paper [17], we synthesized carbon nanofibers with average 25 nm diameters by decomposition of methane over Ni–MgO catalyst. Thus in this paper, the role of KOH as an agent was analyzed in the macro-high surface area evolution and the properties of the performance of catalysts. Seong-Ho Yoon [18] reported that the increase of surface area in KOH activation of carbon nanofiber is first ascribed to local broadening of graghene interstices or local burn-off of graghenes, which limit the surface area increase of CNF with the fiber structure maintained. J Romanos et al. [19] in their paper demonstrate that nanospace engineering of KOH activated carbon is possible by controlling the degree of carbon consumption and metallic potassium intercalation into the carbon lattice during the activation process. High specific surface areas, porosities, sub-nanometer (<1 nm) and supra-nanometer (1–5 nm) pore volumes are quantitatively controlled by a combination of KOH concentration and activation temperature. Controlling the pore network is

Table 1 – The derived experimental parameters for optimal activation carbons during phosphoric acid –group 1.

Sample ID	PH/char ratio (w/w)	Carbonization time (h)	Carbonization temperature (°C)	Activation temperature (°C)
PH-C1	0.75	12	150	550
PH-C2	0.90	12	150	550
PH-C3	1.05	12	150	550
PH-C4	1.20	12	150	550
PH-C5	0.90	6	150	550
PH-C6	0.90	12	150	550
PH-C7	0.90	24	150	550
PH-C8	0.90	48	150	550
PH-C9	0.90	24	50	550
PH-C10	0.90	24	100	550
PH-C11	0.90	24	150	550
PH-C12	0.90	24	200	550
PH-C13	0.90	24	150	500
PH-C14	0.90	24	150	550
PH-C15	0.90	24	150	600
PH-C16	0.90	24	150	650

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