



Influence of internal diffusion on selective hydrogenation of 4-carboxybenzaldehyde over palladium catalysts supported on carbon nanofiber coated monolith

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ABSTRACT

In this study, a macro-structured Pd catalyst supported on carbon nanofiber coated on cordierite monolith (Pd/CNF/TiO₂/monolith) was employed for hydrogenation of 4-CBA. The effect of mass transfer on the catalyst performance was studied experimentally and the results are described using a simple kinetic model. The results were compared to Pd catalysts supported on activated carbon (Pd/AC) and on carbon nanofibers aggregates (Pd/CNF). Catalytic performance of the Pd/CNF/TiO₂/monolith is similar to Pd/CNF and the Pd/AC with particles as small as 50 μm (Pd/AC50), whereas Pd/AC with larger support particles revealed a lower activity per Pd active surface site, due to internal mass transfer limitation. Also the selectivity to the intermediate hydrogenation product (4-HMBA), versus deep hydrogenation to *p*-TA, is clearly affected by internal mass transfer. Pd/AC with large particles (3000 μm) achieves a maximum yield to the intermediate product of only 35%, whereas all the other catalysts achieve typically 70%. Remarkably, the conversion level at which the maximum yield of the intermediate product is achieved is highest for the Pd/CNF/TiO₂/monolith. This advantage is assigned to superior internal mass transfer properties, thanks to high porosity, low tortuosity and short diffusion length of the CNF layer. Clearly, the CNF/TiO₂/monolith applied as a fixed bed outperforms slurry phase catalysts, abandoning the need of a filtration section.

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1. Introduction

Activated carbon (AC) is commonly used as a catalyst support in chemical industry due to its advantages including high surface area and resistance to acid [1–3]. However, like two sides of a coin, its high micro-porosity, the main contributor to its high surface area, can also be the origin of significant internal mass transfer limitation in the catalyst. This effect might be reduced by decreasing the particle size, at the expense of increasing the costs for catalyst filtration as well as catalyst loss [4]. For the purpose of preventing these disadvantages, many attempts have been made to develop mesoporous structured supports, allowing operation in a fixed-bed reactor without significant internal diffusion limitation.

Macro-structured carbon nanofibers, which could be prepared by depositing carbon nanofibers (CNFs) on the surface of a pre-formed base material, is a candidate to substitute activated carbon.

CNFs possess exceptional properties including its open structure, high external surface area and high pore volume in absence of any micro porosity [5–7]. For example, macro-structured CNFs supports were developed on metal foam [8–11] and carbon felt [6,12] in recent years. Pd catalysts on these supports were reported to exhibit a high catalytic activity in selective hydrogenation of nitrite and oxidative dehydrogenation of ethylbenzene.

Cordierite monoliths are widely used in new reactor applications in chemical and petro-chemical processing, as well as catalytic combustion and cleaning of exhaust gases [13–15]. It offers several advantages such as a high geometric external surface, short diffusion lengths, structural durability, a low pressure drop and a low thermal expansion coefficient and mechanical stability [16,17]. These features also make monolithic structures suitable for three-phase catalytic reactions because it combines the advantages of slurry reactors and trickle-bed ones, while eliminating their disadvantages [18,19].

However, its small surface area (<1 m²/g) limits its direct applications in catalysis. Therefore, a coating with high specific surface area is usually deposited, covering the surface of monolith, in

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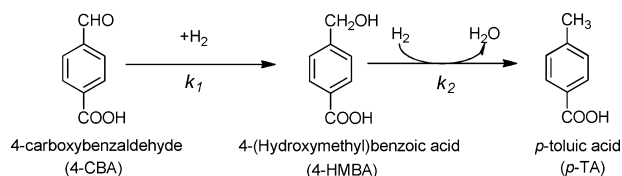


Fig. 1. Pathway of 4-carboxybenzaldehyde hydrogenation.

order to increase its effective surface area, facilitating high metal dispersions. Such thin washcoated layers are usually made by depositing an oxide layer (alumina, silica, etc.) with texture and porosity similar to traditional catalyst support particles. Different parameters can be adjusted, such as thickness of the layer, governing the diffusion length and porosity of the layer. But the porous washcoated layers generally suffer from relatively low pore volume and high tortuosity, hampering internal mass transfer. It urges the use of alternative thin layers such as entangled carbon nanofibers (CNFs) or nanotubes (CNTs) as support to satisfy the demands (high pore volume, high surface area and low tortuosity) for effective internal mass transfer [18,20]. In our previous work [17], we prepared a CNF coated cordierite monolith support (CNF/TiO₂/monolith) with a “sandwich” structure, where the CNFs layer was grown on the titania (TiO₂) film coated monolith. Results showed that after the CNF coating, its textural and acid-resistant properties improved greatly, compared with the bare monolith, while the CNFs are strongly anchored to the monolith. Moreover, CNF/TiO₂/monolith supported Pd catalyst (Pd/CNF/TiO₂/monolith) exhibited a high selectivity to the intermediate product in cinnamaldehyde hydrogenation, which was attributed to elimination of internal diffusion limitation in the catalyst. This confirmed the potential of CNF/TiO₂/monolith support in three-phase catalysis.

Purified terephthalic acid (PTA) is an important industrial raw material used for the manufacture of polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and polytrimethylene terephthalate (PTT), which are mainly applied in the production of fibers, resins, films and fabrics [21,22]. In the process of two companies, i.e. Scientific Design and Amoco MC [23,24], the terephthalic acid (TA) production is based on the liquid-phase oxidation of *p*-xylene (PX) using a homogeneous catalyst Co(OAc)₂, HBr, and a cocatalyst Mn(OAc)₂. The obtained crude terephthalic acid (CTA) usually contains approximately 2000–6000 μg/g of 4-carboxybenzaldehyde (4-CBA) as the main impurity, which would decrease the polymerization rate during the production of PET, PBT and PTT [25]. Therefore, the main upgrading step in refining CTA to PTA is the catalytic hydrogenation of 4-CBA to 4-(hydroxymethyl)benzoic acid (4-HMBA) and further to *p*-toluic acid (*p*-TA) in water (Fig. 1) [26,27]. 4-HMBA and *p*-TA are more soluble than 4-CBA and are thus much easier removed during PTA-crystallization, staying behind in the liquid. An activated carbon supported palladium catalyst (Pd/AC) is commonly used for PTA refinement [28], leading to the main product of *p*-TA due to the serious mass transfer limitation in Pd/AC. Nevertheless, only a few reports have focused on the product distribution, i.e. 4-HMBA and *p*-TA [29,30].

The formation of 4-HMBA is preferred over *p*-TA because 4-HMBA is better soluble in water, simplifying the separation. Furthermore, formation of 4-HMBA requires less hydrogen than *p*-TA. In addition, 4-HMBA is also an important monomer for the synthesis of the corresponding homopolymers, poly(*p*-methylenebenzoate) and its corresponding ester, methyl *p*-hydroxymethylbenzoate (mep-HMB) [31].

In this study, a macro-structured Pd/CNF/TiO₂/monolith catalyst was employed for the hydrogenation of 4-CBA. The effect of mass transfer on the catalyst performance was studied experimentally and the results are described using a simple kinetic model. For comparison, Pd catalysts supported on activated carbon (Pd/AC) and

carbon nanofiber agglomerates (Pd/CNF) with the same Pd loading as that of Pd/CNF/TiO₂/monolith were investigated under the same working conditions.

2. Experimental

2.1. Preparation of CNF/TiO₂/monolith support

A cordierite monolith with the total BET surface area of less than 1 m²/g, cell density of 62 cells/cm² (400 cps) and a wall thickness of 0.18 mm was purchased from Nanjing Gaochun ceramic company. The preparation procedure of CNF/monolith is described in detail in our previous publication [17]. In summary, bare monolith was first coated with a TiO₂ layer using a dip coating method. A Ni precursor was then introduced by impregnating TiO₂ coated monolith with a Ni(NO₃)₂ solution. The samples were dried overnight prior to calcination. After that, the samples were reduced in a gas mixture of N₂ and H₂, followed by CNF synthesis in methane resulting in 18.7 wt.% CNFs on the monolith. Finally, the exposed nickel metal particles were removed by leaching in HNO₃.

2.2. Pd deposition

A 0.5 wt% Pd catalyst was prepared by the adsorption method. Specifically, CNF agglomerates (diameter of CNFs in a range of 20–40 nm, BET surface area 180 m²/g, Chengdu Organic chemical, China) with the size of 177–149 μm were selected using 80 and 100 mesh sieves. The CNFs agglomerates were dispersed directly in a hydrochloric acid (HCl) solution (0.2 M) of palladium (II) chloride (PdCl₂, Sinopharm, China). CNF/TiO₂/monolith were placed in a home-made small basket with the size of φ 25 mm × 40 mm and the mean opening of the basket screen of 1.19 mm (16 mesh), which was fixed to the axle of a stirrer, and the stirrer was immersed in the PdCl₂ solution. The CNFs agglomerates and the CNF/TiO₂/monolith were stirred continuously for 4 h. After that, the CNF/monolith was removed from the solution and the CNF agglomerates were filtered off, followed by drying overnight at 393 K. Finally the samples were reduced in a quartz tube at 493 K at a heating rate of 2 K/min in a stream of N₂/H₂ (80:20) for 2 h. The catalysts prepared were named Pd/CNF/TiO₂/monolith and Pd/CNF160, respectively.

2.3. Selection to a series of Pd/AC catalysts with different particle size

The commercial Pd/AC3000 pellets (Pd loading 0.5 wt%, homogeneous distribution, irregular particles, φ ≈ 3 mm, 810 m²/g, Sinopec Yangzi, China) were crushed to small particles with different sizes of 177–149 μm and 53–44 μm, using sieves of 80 and 100 mesh, 270 and 325 mesh (Shanghai Fengxing Sieve Manufacturing Co., Ltd.), respectively. The resulting samples were hence named Pd/AC160 and Pd/AC50. These Pd/AC catalysts were employed to study the effect of internal diffusion limitation in the particles.

2.4. Characterizations of Pd catalysts

The Pd/CNF/TiO₂/monolith, the Pd/CNF prepared in Section 2.2 and the Pd/AC3000 were characterized in detail. The BET specific surface areas were determined with a Micromeritics ASAP 2010 apparatus. Scanning electron images and elemental distributions were recorded using a JEOL JSM-6360 LA scanning electron microscope. The Pd particle sizes were obtained with a JEM-2100 transmission electron microscopy (TEM). Average Pd particle size of each catalyst was statistically measured by 2 TEM images with at least 50 particles. The Pd loading was determined by Vista-AX inductively coupled plasma atomic emission spectrometry (ICP-AES). The Pd dispersions were calculated using hemispherical

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