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A highly active and chemoselective assembled Pt/C(Fe) catalyst for hydrogenation of *o*-chloronitrobenzene

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ABSTRACT

A highly active and chemoselective assembled Pt/C(Fe) catalyst was prepared by an adsorption protocol. Pt nanoparticles (~2.4 nm) in a Pt colloid solution obtained from the decomposition of $Pt_2(dba)_3$ (dba = dibenzalacetone) were utilized as Pt precursors and adsorbed by Fe-modified active carbon (AC). The adsorption method makes Pt nanoparticles enriched on the surface of the catalyst, and the enrichment was further enhanced due to the presence of Fe in the active carbon, leading to the formation of more active sites exposed on the surface. XPS analysis revealed that a much more electron-deficient state of the Pt nanoparticles was existed due to the electron transfer between Pt nanoparticles and Fe_2O_3. This catalyst was used for the liquid phase hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) with the highest turnover frequencies (TOF) of 78 ($mol_{o\text{-}CNB}/(mol_{Pt}\ s)$) and a selectivity of 99.5% at complete conversion of *o*-CNB. The catalyst was also recycled for five times and the total turnover number was more than 625,000 ($mol_{o\text{-}CNB}/mol_{Pt}$).

1. Introduction

Catalytic hydrogenation of chloro–nitro-aromatics has attracted great interest during the past decades, since the resultant chloroanilines (CAN) are important intermediates in the chemistry of dyes, drugs, herbicides, and pesticides [1–5]. This transformation has been well studied over Pt [6–15], Ru [16–18], Au [19,20], Pd [21–24], Ni [25–31], and Ag [32,33] catalysts. However, selective hydrogenation in the transformation still represents a challenge due to the low catalytic activity and high hydrodechlorination rate of the metal catalysts. To solve these problems, nanosized metal catalysts have become the focus of many researches because they generally exhibited superior activity, selectivity, or stability in comparison to conventional (bulk) metal catalysts [34–43]. Although several techniques for the preparation of various transition metal nano-catalysts have been developed, the prepared catalysts were found difficult to maintain a high uniformity of activity, selectivity, and stability [44,45]. In additional, many procedures involved in these techniques were not environmental-friendly [46].

Recently, our group developed a novel adsorption protocol which could produce very active Pt/C nano-catalyst for catalytic hydrogenation of halogenated nitrobenzene to homologus amine as compared to traditional nano-catalysts. In this protocol, Pt nanoparticles in a Pt colloid solution were utilized as Pt precursors and adsorbed by active carbons (ACs). Though the novel method was thought to be an important factor in explaining the excellent catalytic activity of the resulting Pt/C catalyst, the underlying mechanism remained unclear. To further improve the activity and selectivity of the nano-catalyst and develop more efficient methods to prepare the nano-catalyst, we herein report the synthesis and characterization of a new assembled Pt nano-catalyst by the adsorption method using Fe-modified AC as a carrier. The relationship between the adsorption method and the catalytic properties was also discussed in this work.

2. Experimental

2.1. Preparation of catalyst

2.1.1. Preparation of AC support

AC (specific area = 987 m^2/g, Hangzhou of China Timber Co., Ltd.) was selected as the catalyst support after proper processing. The AC was immersed in a nitric acid solution (3 mol/L) for 6 h, and then washed thoroughly by deionized water until the pH value of filtrate was 7. The wet AC was calcined for 2 h at 900 °C under N_2 atmosphere followed by grinding to ~100 meshes. 1 g of AC was further immersed in equal volume of $Fe(NO_3)_3{\cdot}9H_2O$ (Fe:C = 1 wt%) for overnight and finally dried at 60 °C and calcined at 200 °C. Similarly, ACs with different Fe-containing (Fe:C = *X* wt%, *X* = 2, 3, 4) were prepared by the same procedure. Hydrogen (99.9%) was supplied by Hangzhou Jingong Specialty Gases Co., Ltd. A commercial Pt/C catalyst was purchased from the Johnson Matthey Catalysts (Pt/C

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