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Selective hydrogenation of *o*-chloronitrobenzene using supported platinum nanoparticles without solvent

Manhong Liu[a,*], Xinxin Mo[a], Yanyan Liu[a], Hailian Xiao[a], Yu Zhang[b], Jieying Jing[c], Vicki L. Colvin[c], William W. Yu[a,b,c,**]

[a] College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao, China
[b] College of Electronic Science and Engineering, Jilin University, Changchun, China
[c] Center for Biological and Environmental Nanotechnology, Department of Chemistry, Rice University, Houston, TX, USA

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ABSTRACT

Colloidal platinum nanoparticles with 2.2 nm were immobilized on γ-iron oxide (γ-Fe_2O_3) powder to make a supported catalyst (Pt/γ-Fe_2O_3) with controlled Pt nanoparticle size and size distribution. This catalyst was used to catalyze the selective hydrogenation of *o*-chlorobenzene to *o*-chloroaniline without using any solvent; 99.9% selectivity at 99.95% conversion was achieved.

1. Introduction

Solvents are widely used in various chemical reactions. They are used to dissolve reactants, to transport materials and heat, to mediate the reaction processes. However, solvents also bring about many extra issues such as their cost, energy consumption, operation safety (for combustible, explosive, and/or volatile solvents), operator's health (for toxic ones), and waste treatment and related environmental and ecologic problems. It is therefore desirable to develop new technologies in chemical reactions including catalysis without using undesirable solvents or even no solvents [1–3]. Solid–solid and solid–gas reactions are two examples for solventless chemistry processes. There are some recent examples for liquid–liquid reactions without solvents, for example, the synthesis of Hantzsch polyhydroquinoline [4], the aerial oxidation of aromatic aldehydes [5], the alcohol and aldehyde oxidation over Au/MgO [6], and the alkylation of amines with alcohols over organoiridium catalysts [7].

Aromatic chloroamines are important intermediates in the synthesis many fine chemicals, such as perfumes, organic dyes, medicines, pesticides, and herbicides [8,9]. Selective hydrogenation of the corresponding chloronitrobenzenes to aromatic chloroamines is a convenient method to produce those vital intermediates. Some hydrogenation reactions showed high selectivity to aromatic chloroamines (≥99%) at high conversion of chloronitrobenzenes (90–100%), but many of them were pretty low in the reaction activity [10–14]. Efforts have been applied to the reactions without using hydrogen gas (H_2), but alternate hydrogen sources such as 1,4-cyclohexadiene [15], N,N-dimethyl hydrazine [16], bioethanol [17], and formic acid [18]. Nontraditional solvents like ionic liquids [19,20] and supercritical CO_2 [21,22] have also been tested for those catalytic hydrogenation reactions. For solvent-free catalytic hydrogenation of *o*-chlorobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN), Wang et al. demonstrated a process over a Pt–Ru/Fe_3O_4/C catalyst [23], Wang and coworkers described a Pt/Fe_3O_4 catalyst [24], Wei and colleagues reported a method using a Pd particle catalyst trapped in an ionic liquid layer associated to SiO_2 support [25], and Sun et al. claimed high selectivity and activity for CeO_2 nanowires-supported Pt particles [26].

Nanosized materials often show chemical and physical properties other than their bulk and atomic/molecular counterparts [27,28]. Metal nanoparticles dispersed in solution (colloidal nanoparticles) have been used in catalytic reactions with good stability, activity and selectivity [29–39]. Once these free moving

* Corresponding author.
** Corresponding author at: College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao, China.
E-mail addresses: liumanhong68@126.com (M. Liu), wyu6000@gmail.com (W.W. Yu).

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