

Letter

## Reduction of nitroaromatics with a new heterogenised MCM–silylamine palladium (II) catalyst

M. Lakshmi Kantam<sup>\*</sup>, Tapasree Bandyopadhyay, Ateeq Rahman,  
N. Mahender Reddy, B.M. Choudary

*Indian Institute of Chemical Technology, Hyderabad 500 007, India*

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### Abstract

A heterogenised palladium complex on MCM-41 was prepared for the first time and found to be remarkably efficient in the reduction of aromatic nitro compounds to the corresponding amino compounds. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Nitroaromatics; MCM; Reduction; Amino compounds; Catalyst

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### 1. Introduction

The selective and rapid reduction of nitro compounds is of continued interest in view of extensive synthetic application. Reagents, homogeneous complexes and heterogenised catalysts have been widely explored for this reaction [1–6]. Baralt and Holy used high pressures in the range of 500 to 800 psi and temperatures of 70–100°C for the reduction of nitrobenzene to aniline with polymer-anchored anthranilic acid palladium complexes [1]. Palladium on charcoal catalyses the reduction of nitro compounds to the corresponding amino compounds, using triethyl ammonium formate as hydrogen source at reflux temperature [7]. Hydrogenation of mono-

and poly-nitroaromatics is realised in high yields by Pd/C catalyst via hydrogen transfer from cyclohexene in ethanol under reflux conditions [8]. Thus, high temperatures, pressures, longer reaction times or low turnover numbers preclude the wide use of these catalysts. The recently discovered family of mesoporous materials [9,10] such as MCM possesses conceivable industrial application in fine chemical synthesis due to their tunable larger pore size. This prompted us to design an anchored catalyst using MCM-41 as a support.

Herein we describe the preparation of a new heterogenised catalyst by functionalising MCM-41 with silylpropylamine and subsequent complexation with palladium and the reduction of nitroaromatics to amino compounds at room temperature and atmospheric pressure.

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<sup>\*</sup> Corresponding author.

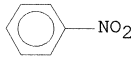
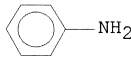


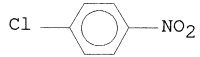
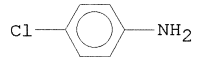
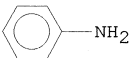
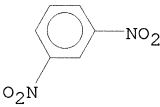
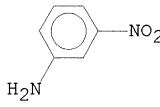
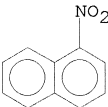
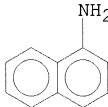
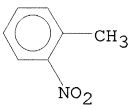
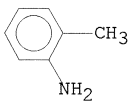
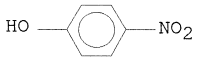
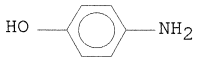
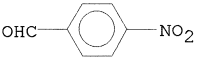
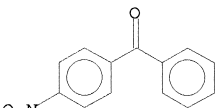
## 2. Experimental

### 2.1. Preparation of the catalyst

MCM-41 [11] was calcined at 550°C for overnight and refluxed with 3-triethoxysi-

lypropyl amine in dry toluene in inert atmosphere for 48 h. This was then complexed with dichlorobis(benzylcyano)palladium(II) in dry benzene under stirring at room temperature. The bright yellow coloured complex thus obtained was filtered, Soxhlet extracted with benzene for 8 h and dried under vacuum.

Table 1  
Reduction of nitroaromatics

S. No.	Substrate	Product	Time (h)	Yield (%) <sup>a</sup>
1			6	100 100 <sup>b</sup>
2			6	100
3		 48%  29%	6	77
4			6	58
5			3.5	100
6			6	41 <sup>c</sup>
7			6	26
8		--	6	No reaction
9		--	6	No reaction

<sup>a</sup>NMR yields based on the nitroaromatics.

<sup>b</sup>Recovered catalyst.

<sup>c</sup>40 mg of catalyst was used.

## 2.2. Hydrogenation reactions

In a typical run, the catalyst (25 mg, 0.0046 mmol of Pd) was suspended in dry THF (4 ml) and treated with molecular hydrogen for 20 min and then a solution of the nitro compound (1 mmol) dissolved in THF (4 ml) was added to it dropwise. A hydrogen balloon was fitted to the flask and the resultant solution was stirred at room temperature for the specified period. The progress of the reaction was monitored through TLC. The reaction mixture was filtered, the solvent evaporated and the reaction products analyzed by IR and  $^1\text{H}$  NMR.

## 3. Results and discussion

Pd content of the catalyst was determined by plasma analysis (1.99% Pd). The IR spectra of the ligand and the complex showed the silyl-propylamine bands. The complex showed an additional band at  $356\text{ cm}^{-1}$  indicating the presence of terminal Pd–Cl [12,13].

The reduction of nitroaromatics proceeded with high yield at atmospheric pressure and at room temperature (Table 1). The turnover frequencies (TOF) were in the range of  $37\text{--}63\text{ h}^{-1}$  (entry 1, 2 and 5). Dinitro compounds were reduced selectively (entry 4). The most important characteristic of our catalytic system is the reduction of the bulky molecule 1-nitronaphthalene in 100% yield within 3.5 h simply by stirring at room temperature with molecular hydrogen whereas Han and Jang [14] used montmorillonite clay (K-10) with anhydrous hydrazine (1:6 molar ratio) for the reduction of 1-nitronaphthalene in dry ethanol under reflux condition in nitrogen atmosphere for 2 h. It is observed that in case of *p*-nitrophenol, the yield was very poor (26%). Attempted reduction

of *p*-nitrobenzaldehyde and *p*-nitro benzo-phenone however resulted in recovery of the starting material. The catalyst was reused without any reactivation.

The advantages of our catalytic system over others are: (1) it is simple, (2) the reaction conditions are mild, i.e., atmospheric pressure and room temperature, (3) reduction of the bulky molecules was carried out simply eliminating the use of expensive reagents, (4) selective reduction of dinitro compounds and (5) reusability of the catalyst.

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