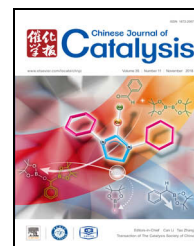


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Article

Unsupported nanoporous palladium-catalyzed chemoselective hydrogenation of quinolines: Heterolytic cleavage of H₂ molecule



Ye Lu^a, Yoshinori Yamamoto^{a,b,c}, Abdulrahman I. Almansour^d, Natarajan Arumugam^d, Raju Suresh Kumar^d, Ming Bao^{a,*}

^a State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116023, Liaoning, China

^b Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

^c Research Organization of Science and Technology, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

^d Department of Chemistry, College of Sciences, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

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ABSTRACT

An efficient and highly chemoselective heterogeneous catalyst system for quinoline hydrogenation was developed using unsupported nanoporous palladium (PdNPore). The PdNPore-catalyzed chemoselective hydrogenation of quinoline proceeded smoothly under mild reaction conditions (low H₂ pressure and temperature) to yield 1,2,3,4-tetrahydroquinolines (py-THQs) in satisfactory to excellent yields. Various synthetically useful functional groups, such as halogen, hydroxyl, formyl, ethoxycarbonyl, and aminocarbonyl groups, remained intact during the quinoline hydrogenation. No palladium was leached from PdNPore during the hydrogenation reaction. Moreover, the catalyst was easily recovered and reused without any loss of catalytic activity. The results of kinetic, deuterium-hydrogen exchange, and deuterium-labeling experiments indicated that the present hydrogenation involves heterolytic H₂ splitting on the surface of the catalyst.

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1. Introduction

Hydrogenation of unsaturated bonds is an important approach for molecular functionalization [1–5]. The hydrogenation of polar unsaturated bonds is often carried out using homogeneous catalysts; this process generates metal hydride (M–H) species in situ through the heterolysis of hydrogen molecules (H₂) [6,7]. Heterogeneous catalysts have been widely used in the industry because of their stability, reusability, and easy separation. The hydrogenation of nonpolar unsaturated bonds can be easily achieved on the surface of heterogeneous catalysts and involves the homolysis of H₂ [8]. However, the

hydrogenation of polar unsaturated bonds, which proceeds at mild conditions (low H₂ pressure and temperature) using a heterogeneous catalyst, remains challenging. Compared with heterolytic splitting, homolytic H₂ splitting can occur easily on the surface of heterogeneous catalysts.

The chemoselective hydrogenation of quinolines to obtain 1,2,3,4-tetrahydroquinolines (py-THQs), which is an important framework in numerous pharmaceuticals, agrochemicals, dyes, and biologically active natural products [9], has been demonstrated. This process is the most convenient and promising technique to produce py-THQs, because of its high atom utilization and the easy availability of the raw material [10]. Many

* Corresponding author. Tel: +86-411-84986180; Fax: +86-411-84986181; E-mail: mingbao@dlut.edu.cn

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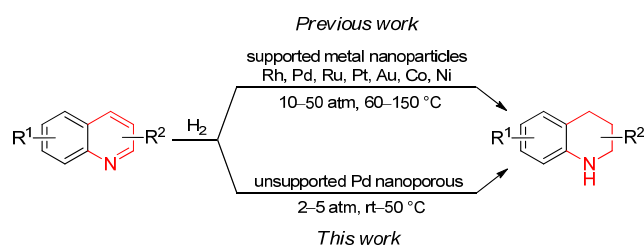
types of homogeneous [11–19] and heterogeneous [20–35] catalyst systems have been developed for the chemoselective hydrogenation of quinolines. Although heterogeneous catalyst systems have recently attracted considerable attention and are successfully employed in the chemoselective hydrogenation of quinolines (Scheme 1), relatively high H₂ pressures (10–50 atm) and high reaction temperatures (60–150 °C) are required. Therefore, hydrogenation under much milder conditions is highly desirable. In addition, no evidence was found for the heterolytic H₂ splitting on the surface of heterogeneous catalysts during the hydrogenation of quinolines.

Catalysts based on unsupported nanoporous metal materials are attracting considerable interest because of their “green” potential and sustainable catalytic properties [36,37]. Nanoporous metals are attractive as heterogeneous catalysts because of their nontoxicity, robustness, high recyclability, and easy recovery. We have previously demonstrated that nanoporous metals are promising green heterogeneous catalysts for liquid-phase organic synthesis [38–41]. In the present work, we investigated the hydrogenation of quinolines using PdNPore as a catalyst. The chemoselective hydrogenation of quinolines proceeded smoothly under relatively low H₂ pressures (2–5 atm) and temperatures (room temperature to 50 °C), to give py-THQs in satisfactory to excellent yields without leaching of palladium (Scheme 1). The results of a mechanistic analysis show that the chemoselective hydrogenation of quinolines involves heterolysis of H₂.

2. Experimental

2.1. General

The starting materials were purchased from Energy Chemicals Co., Ltd. Solvents were purified by standard techniques without special instructions. All other reagents were used as received. ¹H and ¹³C NMR spectra were recorded on either a Varian Inova-400 (400 MHz for ¹H, 100 MHz for ¹³C) or a Bruker Avance II-400 (400 MHz for ¹H, 100 MHz for ¹³C) spectrometer; CDCl₃ was used as a solvent, while tetramethylsilane (TMS) was used as an internal standard. In the following, chemical shifts are reported in ppm downfield (δ) from TMS, whereas the coupling constants *J* are expressed in Hz. The peak patterns are labeled as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Thin-layer chromatography (TLC) was carried out on SiO₂ (silica gel 60 F254, Merck), and the spots were located with UV light, iodoplatinate reagent, or 1% aque-



Scheme 1. PdNPore-catalyzed hydrogenation of nitrogen-containing heteroaromatic compounds.

ous KMnO₄. Flash chromatography was carried out on SiO₂ (silica gel 60, 200–300 mesh).

3. Results and discussion

The hydrogenation of quinoline (**1a**, Table 1) in the presence of PdNPore (5 mol%) was chosen as a model in preliminary tests aimed to optimize the reaction conditions. The results are shown in Table 1. It was expected that a polar and Lewis-basic solvent could assist the heterolytic cleavage of H–H bonds, facilitating the chemoselective hydrogenation of quinoline to py-THQ [24,42]. Accordingly, the reduction was initially tested in polar and Lewis-basic solvents, dimethylformamide (DMF), and 1,4-dioxane (Dioxane), under 5 atm H₂ at room temperature. As expected, **2a** was obtained as the sole product in moderate yields (entries 1 and 2, 55% and 51%, respectively). The yield of **2a** decreased when toluene, a nonpolar solvent, was used (entry 3, 30%). In contrast, the yield of **2a** increased to 72% by adding triethylamine (Et₃N), a polar and Lewis-basic additive, to toluene (entry 4). Thus, Et₃N was used as the solvent, and the yield of **2a** further increased (entry 5, 80%). The desired product **2a** was finally obtained in excellent yield (93%) when acetonitrile (CH₃CN) was used as a solvent (entry 6); in this case, ethylamine (1.5 mmol) was also obtained. These results indicate that CH₃CN was hydrogenated to the corresponding amine under the reaction conditions. The obtained ethylamine may act as a polar and Lewis-basic additive, in addition to CH₃CN itself. The yield decreased when the H₂

Table 1

Reaction conditions screening ^a.

Entry	Catalyst	Solvent	Yield ^b (%)
1	PdNPore	DMF	55
2	PdNPore	Dioxane	51
3	PdNPore	Toluene	30
4 ^c	PdNPore	Toluene	72
5	PdNPore	Et ₃ N	80
6 ^d	PdNPore	CH ₃ CN	93
7 ^e	PdNPore	CH ₃ CN	84
8 ^f	PdNPore	CH ₃ CN	76
9 ^g	PdNPore	CH ₃ CN	57
10	None	CH ₃ CN	NR ^h
11	Pd ₂₀ Al ₈₀ alloy	CH ₃ CN	NR ^h
12 ⁱ	Pd/C	CH ₃ CN	34
13 ^j	Lindlar Pd	CH ₃ CN	52

^a Reaction conditions: quinoline (**1a**, 0.5 mmol), PdNPore (5 mol%), H₂ (5 atm), and solvent (3 mL) at room temperature for 24 h. ^b Isolated yield. ^c Et₃N (2 equiv.) was used as additive. ^d The hydrogenation product of CH₃CN, ethylamine, was also obtained (1.5 mmol). ^e The hydrogenation reaction was performed under 4 atm of H₂. ^f 3.0 mol% of PdNPore was used. ^g The reaction mixture was treated for 18 h. ^h No reaction; the starting material **1a** was recovered. ⁱ Pd/C (5 wt%, 5 mol%) was used as the catalyst instead of PdNPore; *N*-ethyl-1,2,3,4-tetrahydroquinoline was obtained in 18% yield. ^j Lindlar palladium catalyst (5 wt%, 5 mol%) was used as the catalyst instead of PdNPore; *N*-ethyl-1,2,3,4-tetrahydroquinoline was obtained in 20% yield.

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