Published in final edited form as:

Catal Commun. 2007 December ; 8(12): 2115–2118.

Hydrogenation of quinoline by ruthenium nanoparticles immobilized on poly(4-vinylpyridine)

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Abstract

A series of catalysts composed of ruthenium nanoparticles immobilized on poly(4-vinylpyridine) was prepared by NaBH_4 reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in methanol in the presence of the polymer; TEM measurements of a 10 wt % Ru/P4VPy material indicate that ruthenium particles of 1–2 nm predominate. This catalyst is efficient for the selective hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline at 100–120 °C and 30–40 bar H_2 . The activity increases with hydrogen pressure up to 40 bar but is essentially independent of quinoline concentration. Polar solvents, triethylamine, and acetic acid enhance catalytic performance, suggesting an ionic mechanism involving heterolytic hydrogen activation.

1. Introduction

The hydrogenation of N-heteroaromatic compounds is of great importance in connection with hydrodenitrogenation (HDN), the process by which nitrogen is removed from fossil fuels. Commonly accepted HDN mechanisms involve hydrogenation of C=N and C=C bonds as key steps prior to C-N bond scission and nitrogen removal [1–3]. Reduction of N-heteroaromatics is also of interest as a synthetic method for valuable intermediates used in pharmaceutical developments [4].

Although hydrogenation by metals is a well-developed field [5], the use of nanostructured catalysts of well-defined structures is attracting increasing interest, since they can display unique properties including high catalytic activity [6–8]. However, in contrast with a good number of molecular systems based on ruthenium that are known to hydrogenate quinoline and related molecules [1,2,9–16], very few examples are available of the use of nanocatalysts for the hydrogenation of aromatics other than benzene and even fewer for N-heteroaromatics. Of relevance to our work, Ru nanoparticles prepared by calcination/reduction of silica-supported $\text{Ru}_3(\text{CO})_{12}$ catalyze the hydrogenation of both the carbocyclic and heterocyclic rings of quinoline, acridine, or indole at 100 °C and 30 bar H_2 [17], while Ru nanoparticles deposited on polyorganophosphazenes hydrogenate pyridine, and quinoline under 50 bar H_2 and 25–80 °C [18].

Functional polymers can be very efficient catalyst supports, since they provide the stabilizing steric bulk of their framework and several binding sites for simultaneous interactions with the particles and the substrates [19]. Poly(4-vinylpyridine) (P4VPy) is particularly attractive because of the strong affinity of the pyridyl group for metallic nanoparticles and because of its

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ability to interact with polar species like quinoline through hydrogen bonding. It is easily protonated (pK_a 7.4), thereby providing materials capable of undergoing strong electrostatic interactions with charged species, which may lead to an enhanced catalytic activity [20]. This polymer is also thermally stable and resistant to degradation by acids, bases, oxidizing and reducing agents. Immobilization of metal nanoparticles or Ru-NH₃ complexes in P4VPy has been reported for optical and magnetic applications [21–23]. Pd colloids stabilized on polystyrene-poly(4-vinylpyridine) block copolymers were used in the hydrogenation of C=C and C≡C bonds [24,25]; acetophenone hydrogenation by Pd/P4VPy catalysts was also described [27]. In this communication we report the synthesis of nanostructured materials composed of ruthenium particles immobilized on poly(4-vinylpyridine) and their catalytic properties in the hydrogenation of quinoline. To our knowledge, there are no prior examples of catalysis by Ru nanoparticles immobilized in P4VPy.

2. Experimental

Solvents (analytical grade, Aldrich) were purified in an Innovative Technology solvent purification unit. RuCl₃·3H₂O (Pressure Chemicals Inc.) and other reagents (Aldrich) were used as received, except for poly(4-vinylpyridine), which was dried under vacuum at 50 °C overnight. TEM measurements were carried out at The City College of New York using a Zeiss electron microscope EM 902.

2.1 Synthesis of Ru/P4VPy

Poly(4-vinylpyridine) (1.0 g) was suspended in dry deoxygenated methanol (20 ml) in a 3-neck round bottom flask and stirred for 1h under nitrogen at room temperature. Two pressure-equalizing dropping funnels were attached to the flask; a solution of RuCl₃·3H₂O (0.26 g, 1 mmol or 0.1g Ru) in dry deoxygenated methanol (10 ml) was placed in one and a solution of NaBH₄ (0.38 g, 10 mmol) in dry deoxygenated methanol (20 ml) was placed in the other. Approximately 50% of the NaBH₄ solution was quickly added to the polymer suspension and stirring was continued for 10 min, after which both the RuCl₃ and remaining NaBH₄ solutions were simultaneously added to the mixture at a rate of about one drop per second. After addition was complete, the solution was very lightly colored and the solid was dark brown; the suspension was further stirred at room temperature overnight, then filtered under nitrogen, washed with methanol, water, and methanol (10 ml each) and dried under vacuum for 2h at room temperature to afford a free flowing fine brown powder containing 10 wt % Ru. Other catalysts with different Ru loadings were prepared in a similar fashion by adjusting the required amount of the metal chloride and a 10-fold molar excess of NaBH₄.

2.2 Catalytic runs

Experiments were carried out using a 5513 Parr reactor (100 ml) fitted with internal stirring and thermocouple, sampling valve, and a high-pressure burette and coupled to a 4836 controller. The reactor was loaded with the catalyst (0.1 g) and the solvent (20 ml), flushed three times with H₂ at 20 bar and then the catalyst was incubated at 120 °C under a hydrogen pressure (30 bar) for 1h. The desired amount of quinoline dissolved in toluene (10 ml) was then added through the high-pressure burette and this was taken as the zero time for the reaction. Samples of the reaction mixture were periodically withdrawn through the sampling valve, the pressure was adjusted to maintain a constant value throughout the experiment, and the samples were immediately analyzed by gas chromatography using a Shimadzu 2010 chromatograph fitted with an FID detector. Each experiment was repeated at least twice in order to ensure reproducibility; average values of two or more experiments are reported in the figures. When toluene was used as the solvent, hydrogenation to methylcyclohexane was also observed during the incubation period. However, the presence of quinoline completely inhibited toluene hydrogenation.

3. Results and Discussion

The new nano-structured Ru/P4VPy catalysts were prepared by NaBH_4 reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in methanol under an inert atmosphere, in the presence of the polymer microbeads; the catalysts were obtained as dark brown to black free flowing solids. Although no signs of decomposition were evident upon exposure to air, the catalysts were stored under nitrogen. Most of the experiments described below were performed with a catalyst containing 10 wt % Ru. Preliminary TEM measurements indicate that metal particles of the order of 1–2 nm predominate (see Fig. 1a). The small particles remain unchanged after a catalytic run and no aggregation was apparent by TEM (Fig. 1b).

This catalyst is efficient for the selective hydrogenation of the heterocyclic ring of quinoline (Q) under moderate reaction conditions (50 turnovers per hour at 120 °C and 40 bar H_2) to yield 1,2,3,4-tetrahydroquinoline (1,2,3,4-THQ) almost exclusively (Fig. 2). The activity is low at room temperature but increases as expected with the reaction temperature in the range 50–150 °C, within which the catalyst is stable; at 150 °C, the TOF is 75 h^{-1} and only small amounts of 5,6,7,8-THQ (ca. 5%) and cis/trans-decahydroquinoline (DHQ) (ca. 2–3%) are detected in the product mixture. The dependence of the catalytic activity on the hydrogen pressure has a typical volcano shape shown in Fig. 3. Optimum results were obtained at 40 bar, while higher pressures resulted in lower reaction rates, possibly due to some aggregation of the ruthenium particles under harsher conditions. The metal loading did not have a marked effect on the activity for materials containing 2, 5, and 10 wt % Ru but the reproducibility of the results was compromised at low Ru content.

Interestingly, Fig. 4 shows that the use of highly polar solvents results in an enhancement of the catalytic activity with respect to low-polarity ones, with methanol producing the highest rate (TOF = 66 h^{-1} at 30 bar H_2). One of the reasons for employing PVPy as support is that it provides a unique opportunity to immobilize Ru nanoparticles in close proximity to quaternizable nitrogen atoms, thereby creating a nanostructure capable of promoting the heterolytic activation of hydrogen (Figure 5). Noyori [27] and others [28–32] have demonstrated that in the Ru-catalyzed homogeneous hydrogenation of polar molecules, substrate binding to the metal center is not required and hydrogen addition to unsaturated bonds takes place via simultaneous transfer of H^- from the metal and H^+ from a protonated nitrogen ligand. This type of ionic mechanism may be important also for metallic catalysts, since strong binding of substrates or products to active metal sites is commonly responsible for poisoning effects. The solvent effect observed in our case is consistent with a heterolytic splitting of H_2 by the Ru/P4VPy nanostructure. Further support for this idea was obtained by adding small amounts of a base or an acid to the reaction mixture, which also caused an increase in the activity (TOF = 120 h^{-1} for Et_3N and 180 h^{-1} for acetic acid). Triethylamine is a stronger base than P4VPy (pK_a 10.75 vs. 7.4) and therefore heterolytic hydrogen activation is favored by forming a metal hydride and a triethylammonium ion. Acetic acid, on the other hand, can protonate the pyridyl sites of the polymer, thereby providing a better site for interaction with quinoline through hydrogen bonding, which can also result in faster hydrogenation.

4. Conclusions

We have prepared a series of new nano-structured Ru/PVPy catalytic materials, which are active in the hydrogenation of quinoline and do not seem to be poisoned by the substrate or the products. The best catalyst contains 10 wt % of Ru and operates optimally under moderate reaction conditions in polar solvents. Preliminary evidence suggests the involvement of ionic pathways in this reaction. Further work is in progress in order to further explore the scope of these catalysts for the reduction of a variety of other N- and S-heteroaromatics, as well as of simple polynuclear aromatic hydrocarbons, and to shed more light on the reaction mechanism.

Acknowledgements

The authors thank Dr. Jorge Morales at City College of New York for the TEM measurements. This work has been supported by PSC-CUNY Grant # 60065-35 36 and NIH-MARC Grant # GM08078.

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Fig. 1. Transmission electron micrograph of : (a) A freshly prepared sample of 10 wt% Ru/P4VPy. (b) A sample of 10 wt% Ru/P4VPy after a quinoline hydrogenation run performed at 120 °C and 30 bar H₂.

Fig. 2. Hydrogenation of quinoline by 10% Ru/P4VPy. 120 °C, 40 bar H₂, [Q]:[Ru] = 84, in toluene. Δ: 1,2,3,4-Tetrahydroquinoline; X: 5,6,7,8-tetrahydroquinoline; □: cis/trans-decahydroquinoline.

Fig. 3. Effect of H₂ pressure on the hydrogenation of quinoline by 10% Ru/P4VPy. 120 °C, [Q]:[Ru] = 84, in toluene.

Fig. 4. Effect of the solvent on the hydrogenation of quinoline by 10% Ru/P4VPy. 120 °C, 30 bar H₂, [Q]:[Ru] = 84, in toluene.

Fig. 5.
Possible heterolytic splitting of H_2 on Ru/P4VPy catalysts.