Efficient Reductive Alkylation of Aniline with Acetone over Pt Nanoparticles Encapsulated in Hollow Porous Carbon

Takashi Harada,[1] Shigeru Ikeda,*[1] Natsumi Okamoto,[1] Yun Hau Ng,[1] Suguru Higashida,[2]
Tsukasa Torimoto,[3] and Michio Matsumura[1]
[1]*Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka 560-8531*
[2]*Department of Industrial Chemistry, Osaka Prefectural College of Technology, 26-12 Saiwai, Neyagawa 572-8572*
[3]*Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603*

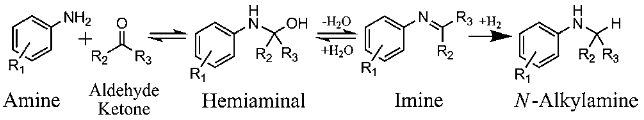
(Received May 15, 2008; CL-080500; E-mail: sikeda@chem.es.osaka-u.ac.jp)

Reductive alkylation of aniline with acetone over various Pt catalysts was studied under atmospheric pressure of hydrogen at room temperature. It was found that our newly designed Pt catalyst, i.e., Pt nanoparticles encapsulated in hollow porous carbon, showed excellent catalytic activity in comparison with activities of other Pt catalysts. Moreover, one-pot reductive alkylation of nitrobenzene with acetone proceeded smoothly over the catalyst.

Reductive alkylation of aromatic amine with carbonyl compounds (i.e., aldehyde or ketone) is a useful reaction for producing important amine compounds as intermediate chemicals for various industries. In general, the reaction is assumed to be started by addition of a carbonyl compound to aromatic amine. Then subsequent dehydration of an intermediate hemiaminal produces an imine. Finally, the C=N bond of the imine is hydrogenated with molecular hydrogen (H_2) or hydride compounds to yield the corresponding amine product (Scheme 1).

Stoichiometric reductants such as hydride compounds are the most widely employed reagents for this reaction. For example, a well-known Borch reduction which uses $NaBH_3CN$ as a reductant exhibits efficient activity.[1] However, the production of large amounts of toxic cyanide as a by-product greatly diminishes its applicability. Although other borohydride derivatives, including $NaBH_4(OAc)_3$,[2a] pyridine–borane,[2b] and $Ti(O\textit{i}\text{-}Pr)_4$/$NaBH_4$,[2c] have been developed to overcome the problem of toxic waste production, these systems often suffer from low atom efficiency, leading to the requirement of excessive amounts of hydrides.

An attractive alternative for reductive alkylation of amine is the use of a catalytic system based on molecular hydrogen (H_2) as a reductant because this only produces water as by-product. Actually, various efficient homogeneous metal complexes[3] and heterogeneously supported metals based on Pt, Pd, Ru, Rh, Ni, and Co have been reported.[4,5] However, the major drawback of these catalytic systems is the requirement of high pressure of H_2 and high temperature. Hence, the construction of an environmentally benign catalytic system having both high level of catalytic activity and sufficient reusability under mild conditions is strongly desired.



Scheme 1. Reductive alkylation of amine and carbonyl compound.

Recently, we have reported the fabrication of a Pt nanoparticle encapsulated in a hollow porous carbon (Pt@*hm*C) through a templating technique.[6] The rattle-like nanostructure is effective for preventing aggregation of Pt core particles. Moreover, the medial void space is suitable as a catalytic reaction site. Due to these specific properties, this material was proved to act as a highly active catalyst for hydrogenation of nitrobenzene and various olefins in comparison with several Pt catalysts. In this study, we investigated the applicability of Pt@*hm*C for the reductive alkylation of aniline, with a carbonyl compound of acetone using H_2 as a reductant. Moreover, one-pot reductive alkylation of nitrobenzene with acetone, i.e., hydrogenation of nitrobenzene followed by reductive alkylation of aniline, was also examined.

Pt@*hm*C was synthesized by a procedure similar to that reported previously using poly(*N*-vinyl-2-pyrrolidone)-protected Pt (Pt-PVP) as a starting material.[7] As determined from inductively coupled plasma (ICP) analysis, the content of Pt in Pt@*hm*C was 0.49 wt % in the present conditions. For comparison, Pt catalysts containing the same amount of Pt as that in Pt@*hm*C supported on activated carbon (AC) and alumina (Al_2O_3), labeled Pt/AC and Pt/Al_2O_3, respectively, were prepared by a conventional impregnation/H_2 reduction technique.[7]

For the evaluation of catalytic activity, room temperature reductive alkylation of aniline with acetone and atmospheric pressure of H_2 was performed as a model reaction. Table 1 summarizes the conversion of aniline and yield of the corresponding product, *N*-isopropylaniline (*N*-IPAN), using various Pt cata-

Table 1. Reductive alkylation of aniline with acetone catalyzed by various Pt catalysts[a]

Entry	Catalysts	Conversion /%	Yield /%	Pt size /nm[b]
1	Pt@*hm*C	93	75	3.1
2	Pt@*hm*C[c]	99	99	3.1
3	Pt-PVP	52	23	2.2
4	Pt/AC	33	3	4.5
5	Pt/Al_2O_3	30	18	3.1
6	Pt/AC (Wako)[d]	31	7	4.2
7	Pt/AC (N. E. Chem)[d]	40	23	3.4
8	Pt@*hm*C[e]	92	72	3.1
9	Pt@*hm*C[f]	96	77	3.3[g]

[a]Reaction conditions: Pt (0.25 μmol), aniline (1 mmol), acetone (1 cm^3), r.t., H_2 (balloon), 1 h. [b]Average Pt particles size. [c]2-h reaction time. [d]Commercial Pt/AC (Pt: 5 wt %) purchased from Wako pure chemical and N. E. Chemcat. [e]2nd run of Entry 1. [f]3rd run of Entry 1. [g]After reaction.

lysts. Among the catalysts examined, Pt@*hm*C showed the highest level of catalytic activity with aniline conversion of 99% and *N*-IPAN yield of 75% for 1 h (Entry 1). Turnover frequency (TOF) was estimated to be 3120 h^{-1}: this value is remarkably high among reported catalysts (e.g., TOF of 380 h^{-1} was achieved over Pd/Al_2O_3 at 393 K under 4 MPa H_2).[5] When the reaction was continued for 2 h, moreover, the remainder of imine was solely hydrogenated to *N*-IPAN without generating any by-products (Entry 2). Colloidal Pt-PVP, a source of Pt nanoparticles in Pt@*hm*C, exhibited a lower level of activity than that of Pt@*hm*C (Entry 3), though the Pt particle size in the Pt-PVP samples was smaller than that of Pt@*hm*C. All of the supported Pt catalysts were also found to be less effective (Entries 4–7). In addition, Pt@*hm*C was easily separated from the reaction solution by centrifugation. After drying the recovered Pt@*hm*C, the sample was shown to retain a high level of catalytic activity for at least 2 successive runs (Entries 8 and 9).

In separate experiments, nitrogen (N_2) was used as the gas medium instead of H_2. Due to the suppression of hydrogenation, the imine intermediate should be accumulated in this reaction condition.[8] As a result, the carbon-supported samples gave comparable amounts of imine, while the amount on the Pt/Al_2O_3 catalyst was significantly small. Thus, the low rate of conversion of aniline on Pt/Al_2O_3 can be explained, in part, by its poor activity for imine production. On the other hand, the formation of imine occurred in a similar manner on various carbon-supported catalysts regardless of their structure. The high yield of *N*-IPAN on Pt@*hm*C, as shown in Table 1, is therefore attributable to its high catalytic function for hydrogenation of the imine intermediate. In the Pt@*hm*C structure, the medial Pt nanoparticle in Pt@*hm*C is free from any surface-covered agents: instead, the particle is physically separated by the porous carbon shell. The carbon shell efficiently supplies the imine intermediate into the hydrophobic void space where an active “ligand-free” Pt nanoparticle is present. Due to the synergetic effect derived from this unique structure, Pt@*hm*C is likely to exhibit a high level of catalytic activity.

In our previous study, we found that the present Pt@*hm*C sample efficiently catalyzes hydrogenation of nitrobenzene into aniline. Hence, it is readily predicted that *N*-IPAN would be produced directly from a one-pot reductive alkylation of nitrobenzene with acetone. Based on this insight, reductive alkylation of nitrobenzene with acetone was conducted under the same conditions as those for the reaction of aniline. Table 2 shows the results together with the results on other Pt catalysts. Clearly, reductive alkylation smoothly proceeded only on the Pt@*hm*C catalyst, which achieved 99% conversion of nitrobenzene and *N*-IPAN yield of 42% for 3-h reaction duration (Entry 1): in contrast, there was almost no production of *N*-IPAN on the other catalysts (Entries 2–6). On some of the Pt catalysts, a low level of activity of reduction of nitrobenzene into aniline should affect the overall reaction (Entries 2, 3, and 6). On the other hand, Pt/Al_2O_3 and Pt/AC (Wako), were much less active for reductive alkylation of aniline than Pt@*hm*C (Entries 4 and 5), leading to their poor activity for the overall reaction, despite their efficient activity for reduction of nitrobenzene. Hence, as far as we examined, Pt@*hm*C is the sole Pt catalyst to induce this one-pot reaction efficiently.

Table 2. One-pot reductive alkylation of nitrobenzene with acetone catalyzed by various Pt catalysts[a]

Entry	Catalysts	Conversion/%	Yield/%
1	Pt@*hm*C	99	42
2	Pt-PVP	67	1
3	Pt/AC	69	2
4	Pt/Al_2O_3	99	3
5	Pt/AC (Wako)[b]	98	2
6	Pt/AC (N. E. Chem)[b]	64	4
7	Pt@*hm*C[c]	99	50

[a]Reaction conditions: Pt (0.25 µmol), nitrobenzene (0.5 mmol), acetone (1 cm^3), r.t., H_2 (balloon), 3 h. [b]Commercial Pt/AC (Pt: 5 wt %) purchased from Wako pure chemical and N. E. Chemcat. [c]18-h reaction time.

It should be noted that the yield of *N*-IPAN on Pt@*hm*C did not increase when the reaction time was extended to 18 h (Entry 7). Analysis of the reaction solution by GC-MS indicated the presence of a hemiaminal intermediate along with imine and *N*-IPAN. Since hemiaminal was not detected in the reductive alkylation of aniline, it was thought that the formation of water in the hydrogenation of nitrobenzene shifted the chemical equilibrium between imine and hemiaminal to the hemiaminal side. The restraint of the formation of imine resulted in suppression of the yield of *N*-IPAN to less than 50%. Therefore, removal of water formed in the first hydrogenation might be indispensable in order to improve the present one-pot reductive alkylation of the nitrocompound. Study along this line is now in progress.

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7 Experimental details are given in the Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

8 The same reaction mixture as that used in the reductive alkylation of aniline with acetone was stirred under N_2 at room temperature. Owing to the difficulty in obtaining the imine intermediate, we could not obtain quantitative data on imine production. Therefore, the amount of decrease in aniline, i.e., aniline conversion, was employed as the quantitative measure of imine production, for convenience. In consequence, we confirmed that carbon-supported samples gave ca. 30% conversion but that Pt/Al_2O_3 produced only 8% after for 1 h.