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Activated carbon as an efficient support for gold nanoparticles that catalyze the hydrogenation of nitro compounds with molecular hydrogen

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A catalyst based on activated carbon with deposited gold nanoparticles and impregnated with ethylenediamine for selective hydrogenation of nitroarenes has been suggested.

Nowadays gold nanoparticles (AuNPs) are widely used in organic reactions due to high catalytic activity comparable to that of homogeneous gold complexes, relative stability and selectivity to the substrate.[1] Naturally, the observed selectivity depends considerably on the size and morphology of AuNPs.[2,3] An advantage of these catalysts is the absence of ligands (especially toxic phosphine ones), easy separation from the product and the possibility of their reuse. As a rule, these advantages are achieved upon immobilization of AuNPs on inorganic or organic supports that allows one to avoid aggregation of NPs and to use simple separation methods, such as centrifugation or filtration. However, the immobilization process is often laborious.[4] Furthermore, the support is sometimes not inert, both to AuNPs and to the substrate.[5]

Reduction of nitrobenzene, a widely used industrial reaction, is often employed as a model process for studies on catalyst efficiency and recyclability. Previously, a number of systems based on AuNPs fixed on solid supports of SiO_2,[6] ZrO_2,[7] TiO_2,[8–13] Fe_2O_3,[9] Al_2O_3,[14] CeO_2 and other metal oxides[15,16] were suggested for hydrogenation of nitro compounds. In most cases, the target anilines were obtained in high yields and with good selectivity. In some cases, the smallest particles (up to 2 nm) had the highest activity,[12,13] in other cases 7–9 nm clusters were the most active,[6,16] and in some systems the reaction selectivity was affected by the solvent.[7] The catalyst activity depended on the methods of its preparation and deposition onto the support,[13] whereas the presence of oxide and hydroxy groups affected the formation of side azo and azoxy compounds.[16]

Currently, ecological standards and demands of chemical industry require a catalyst to be readily manufactured, inexpensive, easily utilized, and certainly well recyclable. Therefore, we paid attention to activated carbon (AC), a cheap and widely available inert support. Unique features of this support include a huge surface and polymodal size distribution of pores, ability to adsorb both large and small organic molecules, *e.g.*, gases and clusters of heavy metals with various sizes.[17] Meanwhile, gold nanoparticles fixed on AC were reported to be inefficient in hydrogenation of nitro compounds.[16,18]

In this study, we turned to the use of Au/C as the cheapest and most available catalyst for hydrogenation of nitroarenes. We developed a method of catalyst preparation preventing the adsorption of impurities by activated carbon that involves its impregnation with an $AuCl_3 \cdot 3H_2O$ solution in acetone followed by evaporation of the excess solvent and heating to 300 °C for 3 h in a stream of hydrogen. The material thus obtained was studied by scanning electron microscopy (SEM) and X-ray powder analysis (XRA).[†]

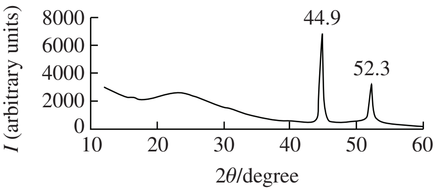


Figure 1 X-ray diagram of $Au/C_{BAU\text{-}A}$ catalyst.

Gold(III) was completely reduced with hydrogen under these conditions, as it is illustrated by the absence of characteristic peaks of gold cations in the XRA diagram exhibiting only signals at θ 44.9 and 52.3, which correspond to Au(0) (Figure 1). The particle size calculated by the Debye–Scherrer method based on XRA data was rather large, namely, 15±2 nm.

Furthermore, ordered gold clusters up to 50 nm in size were detected by means of SEM (Figure 2). Though the particles obtained were rather large, we decided to test them for hydrogenation of nitrobenzene. Such gold clusters should be more

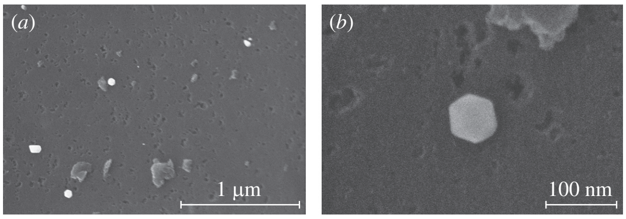


Figure 2 High resolution SEM picture of freshly prepared $Au/C_{BAU\text{-}A}$ catalyst. (*a*) General view of catalyst surface at 50000× magnification. (*b*) View of a part of catalyst surface with a hexagonal gold nanoparticle at 300000× magnification.

[†] *Preparation of 5 wt% Au/C catalyst*. Salt $AuCl_3 \cdot 3H_2O$ (0.052 g) was dissolved in acetone (5 ml). Pre-dried BAU-A activated carbon (0.544 g) was added to the solution. The mixture was stirred for 2.5 h until the solution discoloured, then the solvent was removed *in vacuo*. The dried catalyst was placed in a tube furnace and heated at 300 °C for 4 h in a stream of hydrogen (15–20 ml min^{-1}). The catalyst thus obtained was impregnated with ethylenediamine (En) using the technique known for Pd/C.[20] X-ray powder diffraction analysis was carried out on a DRON-3M diffractometer (CuKα irradiation, λ = 1.78896 Å). The microstructure of samples was studied by field emission scanning electron microscopy (FE-SEM) on a Hitachi SU8000 electron microscope. The catalyst was prepared from activated carbon, GOST (USSR State Standard) 6217-74. It is mostly manufactured from birch wood and has good mechanical strength characteristics, an average specific surface of 740–840 $m^2\ g^{-1}$ and a maximum adsorption pore volume of 0.33 $cm^3\ g^{-1}$ for benzene.[25]

Table 1 Optimization of conditions for hydrogenation of nitrobenzene with molecular hydrogen.[a]

Entry	AuNPs/support (mol%)	P/atm	T/°C	t/h	Yield[b] for cycle (%)				
					1	2	3	4	5
1	Au/C (1)	10	50	20	10				
2	Au/C (1)	20	50	8	43				
3	Au/C (1)	40	50	4	54				
4	Au/C (1)	40	20	20	52				
5	Au/C (1)	40	80	20	100	86	54		
6	Au/C (En) (1)	40	80	20	100	100			
7	Au/C (En) (1)	10	80	20	100	100	100	100	98

[a] *Reaction conditions*: 0.01 mmol of nitrobenzene, 1 mol% of the Au catalyst, 3 ml of EtOH, H_2. [b] The yield of aniline was determined by NMR spectroscopy.

stable during the reaction and in subsequent recycles than 1–3 nm nanoparticles that undergo leaching or coalescence with time. Moreover, 50 nm nanoparticles are safe for living organisms since they possess no genotoxic activity.[19]

As shown in Table 1, the first attempts to use the catalyst (1 mol%) in nitrobenzene hydrogenation showed poor efficiency: the yield of aniline after 20 h was only 10% (entry 1). We succeeded in raising the yield somewhat (43–54%) by varying hydrogen pressure, reaction time and temperature (entries 2–4). Finally, optimum conditions were found that allowed nitrobenzene to be quantitatively consumed in 20 h at 80 °C and a hydrogen pressure of 40 atm, however, the catalyst recyclization was insufficient (entry 5).

We solved the recyclization problem by modifying the catalyst by its treatment with ethylenediamine. Previously, this modification proved to be efficient in prolongation of activity and recyclization of palladium catalysts on carbon supports.[20,21] On the other hand, this treatment appears no less promising in the case of gold that forms stable complexes with various polyamines.[22] Furthermore, the amino group of ethylenediamine can interact with the nitro group of the substrate to give an adduct on the catalyst surface (Figure 3) that is analogous to the adduct identified previously in hydrogenation of nitrobenzene in the presence of Ru/CNT.[23] In fact, this treatment of the catalyst with ethylenediamine allowed us not only to perform successful recyclization and thus to increase the TON of the reaction at least fivefold but also to decrease hydrogen pressure to 10 atm (Table 1, entries 6, 7).

The AC surface stayed nearly unchanged after the treatment with ethylenediamine: gold nanoparticles of regular microcrystalline shape were observed in the catalyst (Figure 4).

Reduction of various nitroaromatic compounds was carried out using this catalytic system and the conditions identified previously (Scheme 1, Table 2).‡

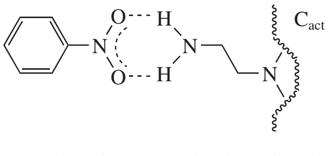


Figure 3 Reaction of ethylenediamine with nitrobenzene.

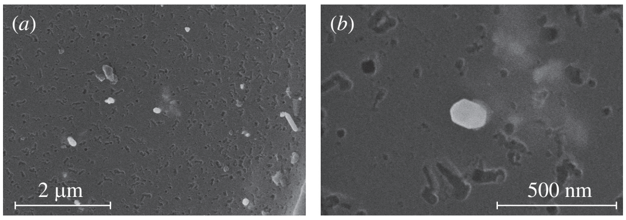
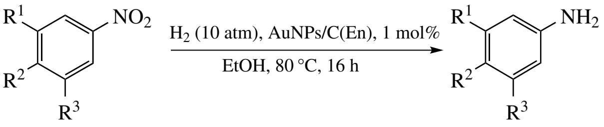


Figure 4 High resolution SEM image of an Au/C_{BAU-A} catalyst sample. (*a*) General view of catalyst surface at 20 000× magnification. (*b*) View of a part of catalyst surface with a hexagonal gold nanoparticle at 100 000× magnification.



1a–i **2a–i**

1a, **2a** $R^1 = R^2 = R^3 = H$
1b, **2b** $R^1 = R^3 = H$, $R^2 = Me$
1c, **2c** $R^1 = R^3 = H$, $R^2 = Br$
1d, **2d** $R^1 = R^2 = H$, $R^3 = Cl$
1e $R^1 = NO_2$, $R^2 = H$, $R^3 = Br$
2e $R^1 = NH_2$, $R^2 = H$, $R^3 = Br$
1f, **2f** $R^1 = R^3 = H$, $R^2 = OH$
1g, **2g** $R^1 = R^3 = H$, $R^2 = Ac$
1h $R^1 = NO_2$, $R^2 = R^3 = H$
2h $R^1 = NH_2$, $R^2 = R^3 = H$
1i, **2i** $R^1 = R^3 = H$,
$R^2 = CH{=}CHCO_2H$

Scheme 1

Table 2 Hydrogenation of nitroarenes using Au/C catalyst.

Entry	Substrate	Product	mol% Au	Yield[a] (%)
1	**1a**	**2a**	1	100
2	**1b**	**2b**	1	98
3	**1c**	**2c**	1	100
4	**1d**	**2d**	1	93
5	**1e**	**2e**	1	79[b]
6	**1e**	**2e**	2	100[b]
7	**1f**	**2f**	1	52
8	**1f**	**2f**	2	100
9	**1g**	**2g**	1	41
10	**1g**	**2g**	2	100
11	**1h**	**2h**	2	100[b,c]
12	**1i**	**2i**	2	98

[a] The yield was determined by NMR spectroscopy. The yield matches the conversion of the starting nitro compound in all cases. [b] The yield of the corresponding phenylenediamine is specified. [c] 60 atm H_2.

As shown in Table 2, hydrogenation with 1 mol% of the catalyst occurs rather smoothly both in the case of non-substituted nitrobenzene (entry 1) and in the case of compounds containing an electron-donating substituent, 4-nitrotoluene (entry 2) and 4-bromonitrobenzene (entry 3). In the case of 3-chloronitrobenzene, we managed to selectively hydrogenate only the nitro group (entry 4), avoiding dechlorination that is rather common in similar reactions.[24] Some substrates, namely, 5-bromo-1,3-dinitrobenzene (entries 5, 6), 4-nitrophenol (entries 7, 8) and 4-nitroacetophenone (entries 9, 10), require the catalyst amount to be increased to 2 mol%. In the case of 1,3-dinitrobenzene, hydrogen pressure had to be additionally increased to 60 atm (entry 11). If a readily reducible double bond is introduced into the molecule, only the nitro group is hydrogenated, as shown for 4-nitrocinnamic acid (entry 12). The selectivity was 100% in all cases. It should also be noted that when a starting molecule contains two nitro groups, only the corresponding phenylenediamine is formed even in the case of incomplete conversion (entries 5, 6, 11), *i.e.*, both nitro groups are reduced at once.

Thus, we suggested a simple modification of inexpensive and recyclable Au/C catalyst based on AC-supported gold nanoparticles

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‡ *General procedure for hydrogenation of nitroaromatic compounds.* Nitroarene **1** (0.1 mmol), anhydrous ethanol (3 ml) and the catalyst (3.9 mg or 7.9 mg, see Table 2) were placed in an RHP30ML high pressure reactor (www.openscience.ru) equipped with a magnetic stirrer. The reactor was purged with argon, purged and filled with hydrogen, then heated to 80 °C and its content was stirred for 20 h. After the reaction completion, the mixture was centrifuged for 10 min and the solution was decanted. The catalyst was washed with ethanol (2×5 ml) in the same manner. The combined centrifugate was concentrated in a rotary evaporator, the residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR (400 MHz).

and impregnated with ethylenediamine for selective hydrogenation of nitroarenes. Note that the rather considerable size of gold nanoparticles (15–50 nm) does not prevent catalyst recycling. Hydrogenation of dinitrobenzenes with molecular hydrogen on this catalyst results in total reduction of all nitro groups to exclusively give the target phenylenediamines. Functional groups such as halogen, ketone and olefin easily reduciable on Ni or Pd catalysts remain intact in our procedure, which makes it essentially prospective for fine organic synthesis.

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