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Mendeleev Commun., 2019, **29**, 553–555

Mendeleev
Communications

Chemoselective hydrogenation of 3-nitrostyrene over Ag/TiO_2-SiO_2 catalyst in a flow reactor

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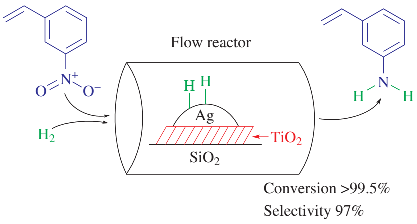
DOI: 10.1016/j.mencom.2019.09.025

Hydrogenation of 3-nitrostyrene in a flow reactor over silver nanoparticles on TiO_2-modified silica affords 3-vinylaniline with selectivity of 97% at the full conversion of the substrate.



Functionalized anilines are widely used in the manufacture of pharmaceuticals, agrochemicals, and fine chemicals. Conventional techniques for their production are based on the reduction of nitroaromatic compounds with stoichiometric amounts of reducing agents, such as iron in acid media, H_2S or NaHS. Hydrogenation of nitroarenes over heterogeneous catalysts is a more cost-effective and environmentally friendly alternative for the production of functionalized anilines.[1–3] However, chemoselective hydro-genation of the nitro moiety of a molecule that contains an easily reduced C=C bond (for example, 3-nitrostyrene) is a challenge.[3–5]

Several catalytic systems containing noble metals (Au,[4–10] Pt,[3,4,11] Ag,[12,13] Au–Pt[14] and Pt–Zn[15]), as well as Co or Fe particles embedded in mesoporous nitrogen-doped carbon,[16,17] were proposed for hydrogenation of nitrostyrenes to corresponding anilines. Silver catalysts such as the Al_2O_3- or TiO_2-supported silver nanoparticles[12] and Ag@CeO_2 core-shell nanocomposite[13] provide high selectivity in a batch reactor hydrogenation. Meanwhile, continuous flow synthesis is an attractive alternative to traditional batch protocols. Potential benefits of flow chemistry include excellent interfacial mass and energy transfer properties, suppression of by-product formation through a better control over reaction parameters, simplified scaling, and enhanced safety profile.[18–20] Here we report on the hydrogenation of 3-nitrostyrene **1** in a flow reactor over supported silver catalysts.

Previously, titania,[4–6,12,14] alumina,[6–9,12] and silica[21] were applied to the preparation of supported metal catalysts used for chemoselective hydrogenation of nitroarenes. However, it is difficult to form granules from individual titanium dioxide; therefore, we synthesized the TiO_2-modified silica (TiO_2-SiO_2) support containing 8.8 wt% TiO_2, with TiO_2 occupying approximately half of the silica surface.[22]

The catalysts containing approximately 2 wt% Ag were prepared by the incipient wetness impregnation of the support with an aqueous solution of silver nitrate with a subsequent drying and calcination in air[23] or in hydrogen flow.[†] The catalysts calcined in air and H_2 are denoted as Ag/support-A and Ag/support-H, respectively. The physico-chemical characteristics of the catalysts are given in Table 1.

According to transmission electron microscopy (TEM), the average diameter of silver nanoparticles in Ag/Al_2O_3-A and Ag/Al_2O_3-H samples was 3.7 and 2.9 nm, respectively. However, Ag/SiO_2-A, Ag/SiO_2-H and Ag/TiO_2-SiO_2-A samples comprised bigger Ag particles (see Table 1). This can be explained by a stronger interaction of silver(I) ions with the γ-Al_2O_3 surface, which contributes to a more uniform distribution of the active constituent.[22] The use of hydrogen for reduction of silver nitrate supported on TiO_2-SiO_2 allows one to decrease the calcination temperature from 500 to 300°C that provides smaller silver particles due to slower sintering.[8,12] The TEM data of Ag/TiO_2-SiO_2-H show mainly Ag particles of 1.5–9.5 nm in diameter (Figure 1).

The catalytic activity of the silver catalysts was evaluated in the hydrogenation of 3-nitrostyrene **1** in a packed-bed flow reactor using toluene as a solvent.[‡] In addition to 3-vinylaniline **2**, undesired 3-ethylaniline **3** and the derivatives of azobenzene **4a** and azoxybenzene **4b** were observed among the reaction products

Table 1 Physico-chemical properties of the catalysts.

Catalyst	Content of Ag (wt%)	T_{cal}/ °C[a]	S_{BET}/ m^2 g^{-1}	V_{pore}/ cm^3 g^{-1}	Particle size distribution/ nm
Ag/Al_2O_3-A	1.9	500 (air)	170	0.62	1.5–7.5 (3.7[b])
Ag/Al_2O_3-H	1.9	300 (H_2)	172	0.62	1–5 (2.9[b])
Ag/SiO_2-A	2.0	500 (air)	271	0.76	2–40
Ag/SiO_2-H	2.0	300 (H_2)	274	0.77	2–30
Ag/TiO_2-SiO_2-A	1.8	500 (air)	256	0.62	1–16
Ag/TiO_2-SiO_2-H	1.8	300 (H_2)	255	0.62	1.5–12 (4.2[b])

[a] Calcination temperature. [b] Average diameter of Ag nanoparticles.

[†] Supported silver catalysts were prepared by impregnating γ-Al_2O_3, SiO_2 and TiO_2-SiO_2 (grain size of 250–500 μm) with an aqueous solution of silver nitrate followed by drying at 60 °C *in vacuo* and calcination in air at 500 °C or in hydrogen flow at 300 °C for 3 h (for details, see refs. 12, 23 and 26). The solids were then cooled to room temperature, purged with N_2 and stored in a glass flask before being used.

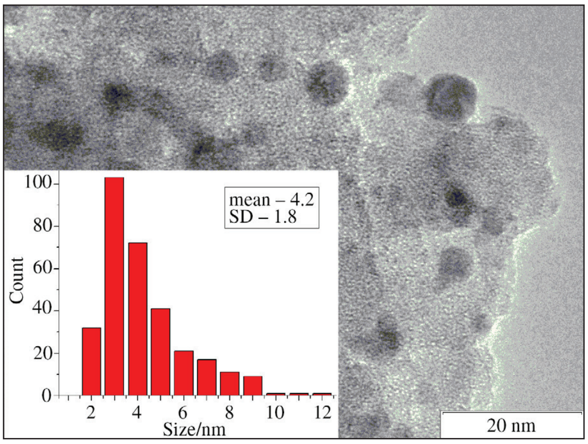
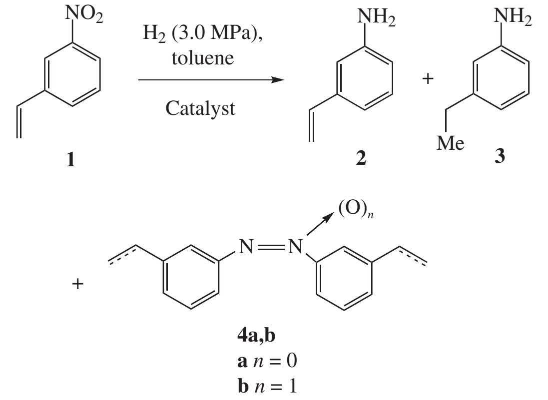


Figure 1 Transmission electron micrograph of the Ag/TiO_2-SiO_2-H catalyst.

(Scheme 1).[2–4] It was found that hydrogenation of substrate **1** over silver nanoparticles supported on γ-alumina and silica occurs with low selectivity towards **2** due to the formation of a large amount of diazenes **4a,b** and/or hydrogenation of **2** to **3** (Table 2, entries 1–6).

The modification of silica with titanium dioxide and the reduction of active component with hydrogen during the catalyst preparation ensure the better reaction selectivity. The Ag/TiO_2-SiO_2-A catalyst provides the formation of 3-vinylaniline with selectivity of 87% at substrate conversion of 98% (see Table 2, entry 7). At the same time, the Ag/TiO_2-SiO_2-H catalyst demonstrates excellent selectivity towards **2**, which is 96–97% at conversion of 99–100% (entries 8 and 9). Interestingly, the selectivity to the desired product is almost not affected by the conversion of substrate (entries 8–10). Consequently, the hydrogenation rate of the carbon–carbon double bond on Ag/TiO_2-SiO_2-H is very low under the reaction conditions. The observed chemoselectivity exceeds the results obtained both on the Au/Al_2O_3 catalysts in a flow reactor[7,8] and on Ag/Al_2O_3 catalyst in a batch reactor.[12] In addition, the reaction proceeds in a flow reactor at a much lower temperature than in a batch reactor.[12]



Scheme 1

Table 2 Hydrogenation of 3-nitrostyrene **1** over supported silver catalysts in a flow reactor. [a]

Entry	Catalyst	Mass of the catalyst/[b] mg	T/ °C	Conversion of **1** (%)	Selectivity (%)		
					2	**3**	**Σ4a,b**
1	Ag/Al_2O_3-A	190	80	88	50	8	42
2	Ag/Al_2O_3-A	190	90	99	59	18	23
3	Ag/Al_2O_3-H	195	80	89	59	3	38
4	Ag/Al_2O_3-H	195	90	100	70	10	20
5	Ag/SiO_2-A	162	120	97	71	28	1
6	Ag/SiO_2-H	163	120	99	76	23	1
7	Ag/TiO_2-SiO_2-A	170	120	98	87	12	1
8	Ag/TiO_2-SiO_2-H	170	120	99	96	3	1
9	Ag/TiO_2-SiO_2-H	170	125	>99.5	97	3	<0.5
10	Ag/TiO_2-SiO_2-H	170	110	69	97	1	2
11[c]	Ag/TiO_2-SiO_2-H	170	110	97	92	8	<0.5

[a] Reaction conditions: 3-nitrostyrene (0.025 M), toluene, $p(H_2)$ = 3.0 MPa, flow rates of the liquid phase and of H_2 were 0.5 and 60 ml min^{-1}, respectively. [b] For the complete filling of the reactor. [c] Reaction in methanol.

The use of methanol instead of toluene accelerated the hydrogenation, but the selectivity was low (see Table 2, entries 10 and 11). This can be explained by a decrease in the selectivity

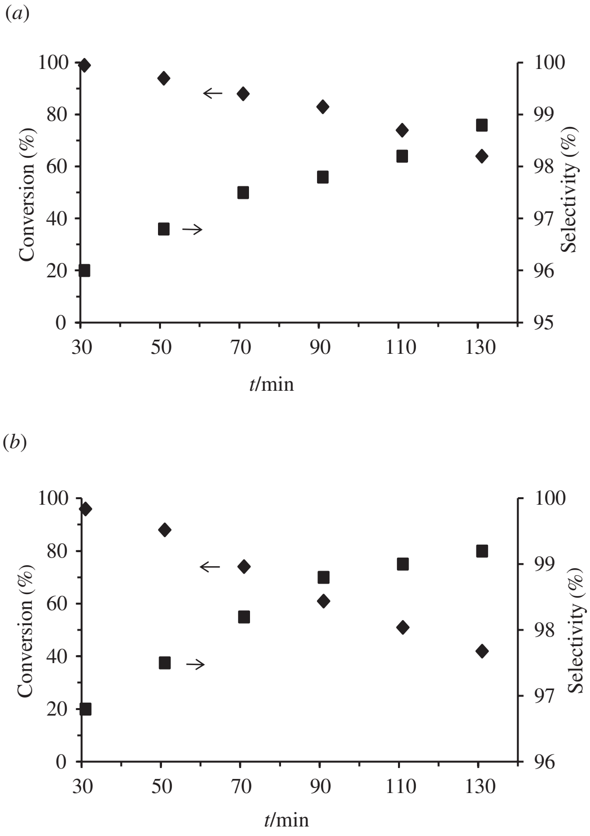


Figure 2 Time dependence of conversion and selectivity to 3-vinylaniline during hydrogenation of 3-nitrostyrene **1** at 120 °C over the Ag/TiO_2-SiO_2-H catalyst: (*a*) fresh sample and (*b*) regenerated sample.

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‡ The investigation of the catalytic properties was performed using continuous flow device H-Cube Pro™ (Thalesnano, Hungary) equipped with stainless-steel CatCart®30 reactors of 30 mm in length and 4.0 mm in inner diameter.[7,8] Before catalytic run, toluene was fed to the reactor loaded with catalyst (162–195 mg) until the required reaction parameters were reached. Afterwards, the inlet was switched to the flask filled with a 0.025 M solution of 3-nitrostyrene in toluene. This point in time was chosen as the starting point of the reaction. The catalytic tests were carried out within the 80–125 °C range with a hydrogen pressure of 3.0 MPa, where liquid and hydrogen feed rates were set to 0.5 and 60 ml min^{-1}, respectively. We found earlier that there was no influence of external or internal mass transfer limitations under the conditions used.[7] The performance of catalyst was evaluated by analysis of the samples taken 30–34 min after the start of the experiment. The reaction products were analyzed by GC (Agilent 6890N instrument with a capillary HP 5-MS column 60 m × 0.32 mm, 0.25 μm) using *n*-decane as the internal standard. Identification of the products was performed by GC–MS (Agilent 7000B Triple Quad System).

of 3-nitrostyrene **1** adsorption through nitro group on active sites[4,6,9,12] due to competition with methanol molecules. The active sites occupied by solvent molecules probably become available to the vinyl group of compound **2** that is hydrogenated yielding product **3**.

The evolution of the reaction products over the Ag/TiO_2-SiO_2-H catalyst in the course of hydrogenation of **1** showed a deactivation of the catalyst with time-on-stream [Figure 2(*a*)], which can be explained by the formation of carbonaceous deposits on the catalyst surface.[7,8,23,24] The rinsing of the spent catalyst by flowing methanol (1 ml min^{-1}) for 30 min results in the removal of these deposits[25] and restores the catalytic activity [Figure 2(*b*)]. The study of the regenerated catalyst by the methods of elemental analysis and TEM allows one to conclude that the leaching of Ag and Ti from this catalyst and the increase in silver particle size do not occur during the reaction and regeneration (see Online Supplementary Materials).

In summary, silver nanoparticles supported on TiO_2-modified silica catalyze highly chemoselective hydrogenation of 3-nitrostyrene in a flow reactor. Selectivity towards 3-vinylaniline is 97% at the full conversion of the substrate.

This study was conducted within the framework of the budget project no. AAAA-A17-117041710083-5 for G. K. Boreskov Institute of Catalysis.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.025.

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Received: 18th April 2018; Com. 19/5892