Supplementary Information

Ag/SiO₂: a novel catalyst with high activity and selectivity for hydrogenation of chloronitrobenzenes

Yangying Chen, a Chuang Wang, a Hongyang Liu, b Jieshan Qiu at and Xinhe Baob

^a State Key Lab of Fine Chemicals, Carbon Research Laboratory, Center for Nano Materials and Science, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, P.O. Box 49, Dalian 116012, China. E-mail: jqiu@dlut.edu.cn; Fax: +86-411-88993991

Preparation of Ag/SiO₂

The detailed procedure is as follows: first, 5.0 mL aminopropyltri-ethoxysilane (APTES) and 2.0 mL tetraethoxylsilicate (TEOS) were added into 10 mL of a mixture water solution of ammonia (27%) and 20 mL deionized water, and after stirring at room temperature for 24 h the solution was evaporated at 80 °C. The obtained solid was further dried in air at 120 °C for 12 h, leading to aminoproyl-functionalized silica (denoted as NH₂-SiO₂). 2.0 g of the NH₂-SiO₂ was added to 30 mL of an aqueous solution of HCHO (37%), which was stirred at 60 °C for 2h, filtered and dried in air at 120 °C for 3h, finally a white solid powder (denoted as CH₂O-SiO₂) was made. 1.0 g of CH₂O-SiO₂ was suspended in a solution of 0.063g AgNO₃ dissolved in 40 mL deionized water, after being stirred at 60 °C for 2h, and following filtering and drying in air at 120 °C for 12h, a yellow powder of the Ag/SiO₂ catalyst was obtained. The loading of silver was found to be *ca*. 4.0% in weight. The catalytic properties of these Ag catalysts were compared with a silver catalyst supported on SBA-15 with ordered mesostructure and high surface area (700m²/g) that was prepared by a conventional impregnation method and reduced at 500 °C in H₂ (denoted as Ag/SBA-15-imp).

b State Key Lab of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Test of Catalytic Properties

The catalytic reactions of CNBs were carried out in a Parr autoclave, of which the products were analyzed using a gas chromatography (Agilent 6890N) equipped with an SE-54 capillary column and an FID detector.

Table S1 The catalytic recycle properties of Ag/SiO₂-200 catalyst for selective hydrogenation of o-chloronitrobenzene

Cycle	Conversion (%)	Selectivity (%)	Cycle	Conversion (%)	Selectivity (%)
1	100	100	4	99.0	100
2	98.8	100	5	99.2	100
3	98.8	100	6	99.3	100

Reaction conditions: 0.1g of the catalyst, 0.5g of the substrate and 25 mL of ethanol, H_2 pressure 2.0MPa; reaction temperature 140° C; reaction time 3h.

 $\textbf{Table S2} \ \ \text{Selective hydrogenation of various chloronitrobenzens over} \ \ \text{Ag/SiO}_2\text{--}200$ catalyst

Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1	NO ₂	NH ₂	93.9	100
2	NO ₂	NH ₂	100	100
3	Cl—NO ₂	CI—NH ₂	100	100
4	Cl—NO ₂	CI———NH ₂	100	100
5	Cl NO ₂	Cl NH ₂	100	100
6	H ₃ C—NO ₂	H ₃ C—NH ₂	100	100
7	NO ₂ OH	NH ₂ OH	100	100

Reaction conditions: 0.1g of the catalyst, 0.5g of the substrate and 25 mL of ethanol, H_2 pressure 2.0MPa; reaction temperature 140°C; reaction time 3h.