ChemPubSoc Europe
DOI: 10.1002/cctc.201501265
CHEMCATCHEM
Full Papers

Recyclable and Selective Nitroarene Hydrogenation Catalysts Based on Carbon-Coated Cobalt Oxide Nanoparticles

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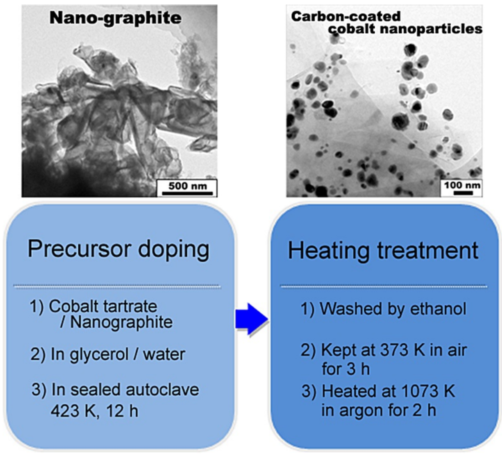
Co/CoO nanoparticles coated with graphene layers (Co/CoO@Carbon) have been developed through direct heating treatment of cobalt oxide precursors incipiently deposited over nanographite materials. Cobalt oxides are partially reduced to active zero-valent metal species and the simultaneous formation of carbon layers over the nanoparticles protects them from oxidation and deactivation. This nanocatalyst performs excellently in chemoselective hydrogenation of some challenging nitroarenes with reducible functionalities to the corresponding anilines. The catalyst is kept in active and selective performance in a ten-run recycling test.

Introduction

Many important industrial conversions of functional groups involve the use of molecular hydrogen.[1] If hydrogen is added across a π-bond, the process is typically called hydrogenation. It is generally defined as hydrogenolysis when hydrogen is added across a σ-bond. Homogeneous[1b] or heterogeneous[2] metal catalysts are crucial to the conversion efficiency of both processes. Homogeneous catalysis can lead to high selectivity of the targeted product through well-tailored ligands and metal complexes, but there are the inevitable drawbacks of recycling and recovering expensive ligands and metal species. Heterogeneous reaction systems with solid catalysts actually dominate practical operations in the petrochemical industry and other industrial organic conversions.

Hydroprocessing of petroleum includes hydrogenation (hydrodearomatization) and hydrogenolysis (hydrodesulfurization, hydrodenitrogenation, hydrocracking, hydrodeoxygenation, hydroisomerization). Hydroprocessing catalysts[3] are Mo (W)-containing supported catalysts promoted by Co or Ni, which work under relatively severe conditions (above 623 K). In organic synthesis, precious metals (Pt, Pd, Rh, Ru, Ir, Os, Re) in most cases show high activity and selectivity under mild conditions. However, they are very expensive because of the low abundance and substantial costs during the required recovery and recycle processes.[4] Nickel is the preferred catalyst for hydrotreatment of many functional groups under higher reaction temperature and hydrogen pressure,[5] but it shows poor selectivity and recyclability. Other base metals (Co, Cu, Fe) have the same drawbacks.[6] Great efforts have been put into replacing precious metal catalysts and this gives an impetus to developing base metal catalysts with improved selectivity and stability.[7] The development of nanoscience offers specific solutions to improve catalytic performances through harnessing nanostructured or nanoscale materials as catalysts.[8] Supported metal nanoparticles and metal species dispersed over nanomaterials are general nanocatalysts that afford specific properties from quantum size effect.[9] However, nanoparticles of base metals (Ni, Co, Cu, Fe) are not air-stable and fast deactivation takes place under the practical operation.[10] The group of Matthias Beller has reported the preparation of iron oxide and cobalt oxide nanoparticles coated by nitrogen-doped graphene layers though the pyrolysis of metal acetates and nitrogen ligands and the form of FeN_x or CoN_x centers gives the nanocatalysts high selectivity in nitroarene hydrogenation.[11]

In this work, cobalt oxide precursors are introduced onto nanographite materials prepared by a mechanical method (ball



Scheme 1. Preparation procedure of the Co/CoO@Carbon catalyst.

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/cctc.201501265.

milling). Through further heating treatment, carbon-coated nanoparticles are formed and cobalt oxides are partially reduced to zero-valent metal states (Co/CoO@Carbon) (as shown in Scheme 1). Nanographite layers are the carbon source for formation of graphene layers over nanoparticles and the reductant for cobalt oxide species. Coating of graphene layers leads to excellent recyclability. The formation of zero-valent cobalt centers and their synergistic effects with cobalt oxide species endow the supported nanoparticles with unexpected selectivity and activity in hydrogenation of nitroarenes to aromatic amines. Sustainability of chemical processes is readily improved through the development of this well-designed catalyst.

Results and Discussion

Development of Co/CoO@Carbon catalysts

Figure 1 shows transmission electron microscopic images of monodispersed supported nanoparticles. All nanoparticles are coated with several layers of graphene carbon (Figure 1 a, b), which provide protection against oxidation and deactivation. High-angle annular dark-field (HAADF) imaging is used to view the full-size spectra of the selected particle and the related element mapping shows that it has a core of cobalt species with some oxygen distributions and a carbon shell (Figure 1 c). The local energy dispersion X-ray (EDX) analysis reveals the same element mapping (Figure 1 d).

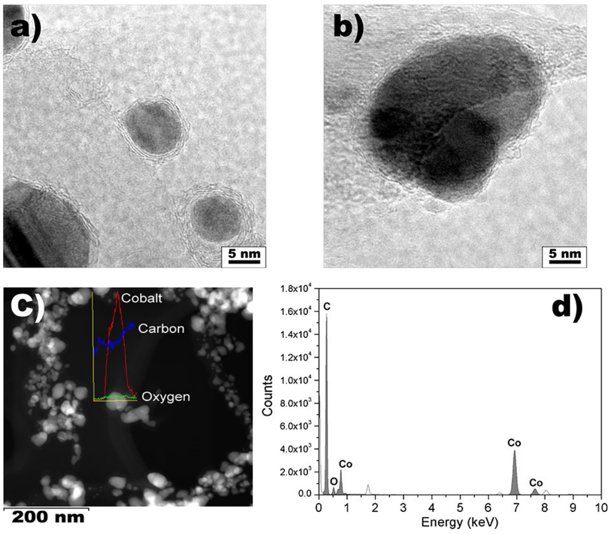


Figure 1. a, b) TEM images of supported Co/CoO nanoparticles coated with graphene carbon layers. c) HAADF image of the Co/CoO@Carbon catalyst particles with element mapping for the selected particle. d) EDX analysis of the element mapping.

X-ray photoelectron spectroscopy (XPS) measurement was performed to investigate the chemical state evolution of cobalt oxide nanoparticles during heating treatment (Figure 2). Cobalt oxide precursors are incipiently introduced onto nanographite materials and metallic cobalt species are gradually formed with the elevation of treatment temperature. The XPS-

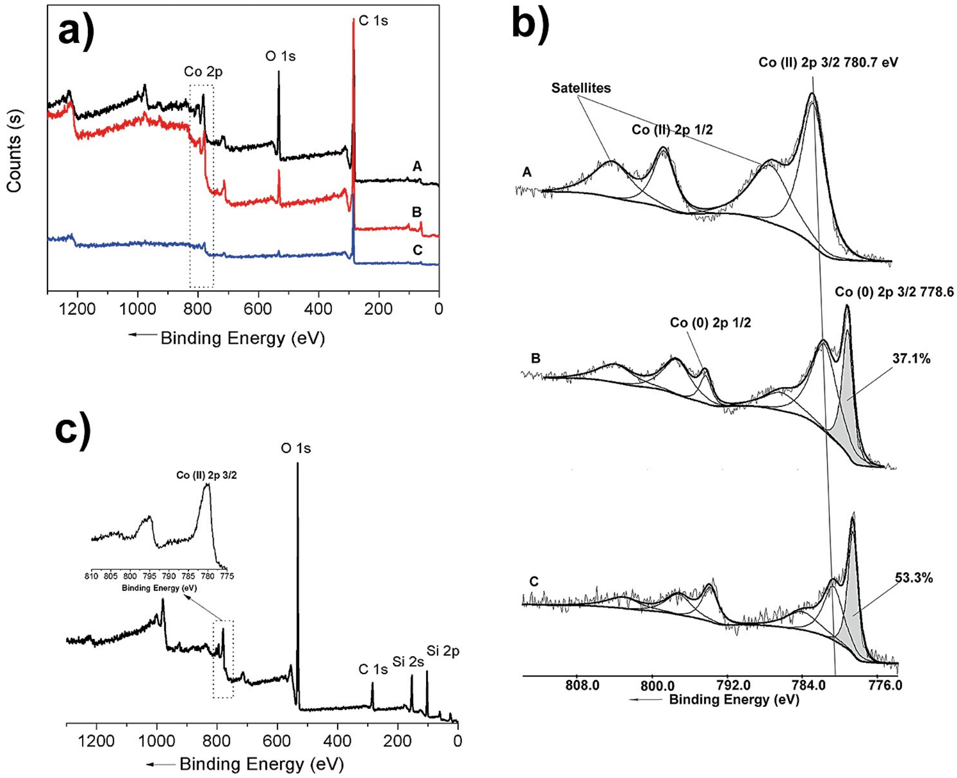


Figure 2. a) XPS survey spectra of the selected catalyst samples (A: nanographite deposited with cobalt oxide precursors; B: the sample treated at 873 K for 2.0 h in argon; C: the sample treated at 1073 K for 2.0 h in argon). b) Fitting of Co XPS peaks of A, B, and C samples. c) XPS survey spectra of the sample prepared by replacing nanographite with silica and treated at 1073 K for 2.0 h in argon (the inset shows the Co XPS peaks).

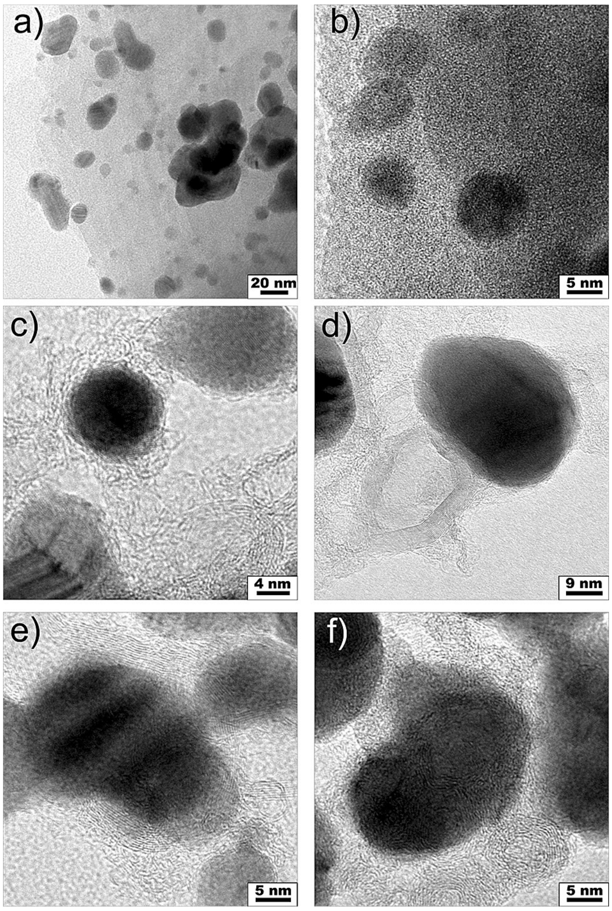


Figure 3. a, b) TEM images of the sample prepared by replacing nanographite with silica and treatment at 1073 K for 2.0 h in argon. c, d) TEM images of the sample treated at 873 K for 2.0 h in argon. e, f) TEM image of the sample treated at 1273 K for 2.0 h in argon.

determined atomic concentration of metallic cobalt reaches 37.1 % in the sample obtained at 873 K and the value increases to 53.3 % with the elevation of the treatment temperature to 1073 K (Figure 2 b). The control experiment was performed over fumed silica deposited with cobalt oxide precursors. No metallic species are detected by XPS measurement after heating treatment (Figure 2 c) and no carbon layers over supported nanoparticles are observed by TEM (Figure 3 a, b). Heat-driven transfer of carbon species form nanographite to cobalt oxide nanoparticles leads to the formation of carbon layers coating the particles (Figure 3 c, d). A further increase of treatment temperature to 1273 K causes the embedment of cobalt oxide nanoparticles in thick carbon layers (Figure 3 e, f).

Selective nitroarene hydrogenation over Co/CoO@Carbon

Nitrobenzene hydrogenation is the principal process for producing anilines and related derivatives, which are key building blocks for the synthesis of polyurethanes, rubber chemicals, agriculture products, dyestuffs, photographic chemicals, and drugs, as well as various other chemicals.[12] Industrial hydrogenation is performed in the vapor phase in tubular reactors over copper chromites, copper oxide, or nickel oxide supported on kieselguhr, Raney copper, and nickel sulfide supported by alumina.[13] These processes are generally operated at high temperature (> 523 K) and show poor chemoselectivity for producing substituted aromatic amines. Homogeneous complexes of platinum[14] or modified supported platinum[15] show improved performances in chemoselective hydrogenation of the nitro group in the presence of other sensitive moieties. However, they remain a great challenge. In Table 1, experimental results of the chemoselective hydrogenation of nitro groups over partially reduced cobalt oxide nanoparticles coated with carbon layers (Co/CoO@Carbon) are listed. The catalyst exhibits excellent performance in chemoselective hydrogenation of twenty nitroarenes with electron-withdrawing or electron-donating substituents. The substrates with methyl and methoxyl are converted with excellent yields. Nitroarenes with halogen substituents show good selectivity. Dehalogenation and coupling side reactions are avoided in the hydrogenation of nitroarenes with iodine and bromine (Table 1, entry 5, 6). Fluoroaniline is prepared with a yield of 99 % (entry 7). The presences of protic substituents (hydroxyl and amino) show no negative effects on the catalytic performances (entry 8–11). Carboxylic derivative substituents, nitrile, ester, and amide, are kept stable during the hydrogenation of the nitro group (entry 15–17). Supported gold catalysts[16] have been reported to show chemoselectivity in the presence of olefinic bonds. Some substrates with highly reducible moieties (entry 18–20) are converted to their corresponding aromatic amines with high yield (90–99 %).

The recyclability of Co/CoO@Carbon catalyst

The recyclability of the Co/CoO@Carbon catalyst was investigated through an eleven-run recycling test of nitrobenzene hydrogenation (Figure 4). After the ninth recycling batch, there is a tiny loss in the aniline yield. In the eleventh test, deactivation is observed and the aniline yield decreases to 44.2 %. As revealed by XPS measurements, the loss of catalytic activity is related to the gradual oxidation of active metallic cobalt species (Figure 5 a). Carbon layers over Co/CoO nanoparticles are gradually abraded by the inevitable intergranular friction, the colli-

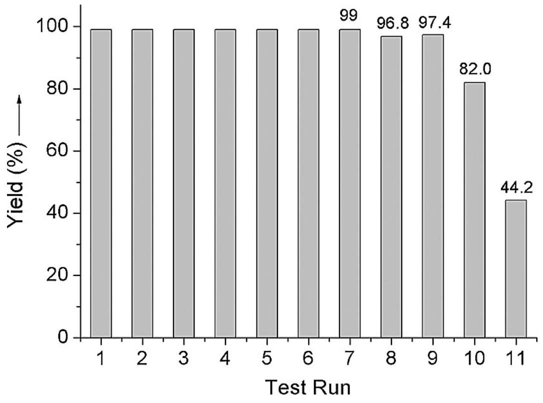
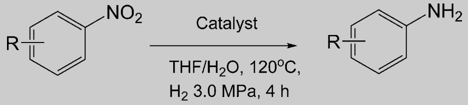
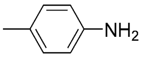
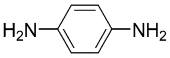
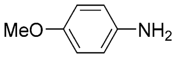
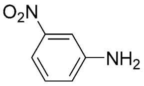
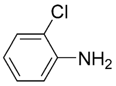
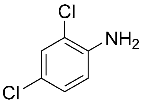
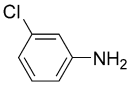
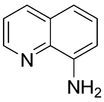
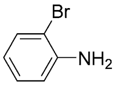
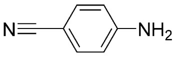
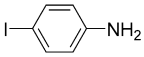
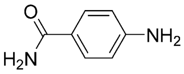
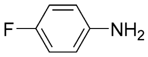
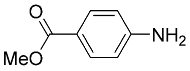
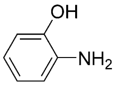
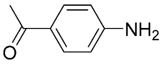
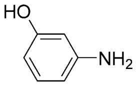
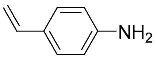
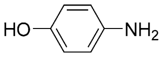
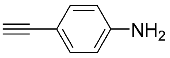


Figure 4. Recycling test of catalytic nitrobenzene hydrogenation over the Co/CoO@Carbon catalyst.

Table 1. Screening experiments of nitroarene hydrogenation over Co/CoO@Carbon.



Entry	Product	Yield [%] (*t* [h])	Entry	Product	Yield [%] (*t* [h])
1		>99 (4)	11		>99 (4)
2		>99 (4)	12		>99 (24)
3		97 (4)	13		>99 (4)
4		95 (4)	14		>99 (6)
5		>99 (4)	15		81 (4)
6		81 (24)	16		>99 (4)
7		>99 (4)	17		>99 (12)[a]
8		>99 (4)	18		>99 (4)
9		92 (4)	19		95 (4)
10		98 (4)	20		90 (4)[b]

Reaction conditions: 1.0 mmol substrate, 5.0 mL THF/0.2 mL H_2O, 393 K, 3.0 MPa Hydrogen. [a] The solvent is H_2O (5.0 mL). [b] 1.0 MPa hydrogen. Yields were determined by GC.

sion with the stirrer and autoclave wall, and the leaching effect of the solvent (Figure 5 b, c). The vanishing of protection coating directly leads to the oxidation of the active metallic cobalt species.

Carbon layers should be kept in appropriate thickness to balance protection coating and surface accessibility to the reactant molecules. Co/CoO nanoparticles can be overloaded with carbon layers through treatment at elevated temperatures (1273 K, see Figure 3 e, f) and the resulting materials show relatively poor catalytic activity (Figure 6 a). Typical oxides are used as the supports. The corresponding catalysts show very low yields of hydrogenation products. Other carbon supports, such as activated carbon and bulk graphite powder, seem not suitable for the formation of appropriate carbon-coating layers (Figure 6 b). Nanocarbon materials, such as nanotubes and graphene, are costly to prepare the practical catalysts and another drawback is the poor efficiency of depositing the metal precursors over them.

Conclusions

Co/CoO nanoparticles coated with appropriate carbon layers (Co/CoO@Carbon) were facilely developed though heating treatment of nanographite supports deposited with cobalt oxide precursors. Nanographite layers were the catalyst support, the carbon source for the formation of graphene layers over nanoparticles, and the reductant for cobalt oxide species. The Co/CoO@Carbon catalyst displayed excellent performance in the chemoselective hydrogenation of nitroarenes. Some most challenging nitroarenes with highly reducible functionalities are readily hydrogenated to the corresponding anilines with the yield above 90 %. The catalyst was kept in highly active and selective performance in a ten-run recycling test.

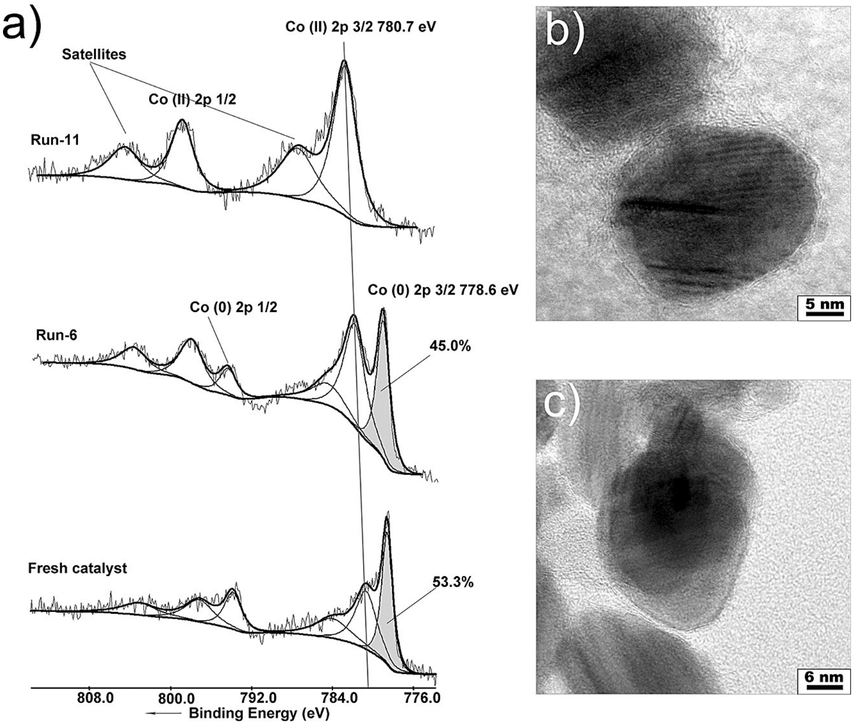


Figure 5. a) Fitting of Co XPS peaks of the catalyst during the recycling test. b) TEM image of the used catalyst after the sixth recycling test run. c) TEM image of the used catalyst after the eleventh recycling test run.

Experimental Section

Materials

Organic substrates were purchased from Acros Organics. Pd/C (Pd: 10 wt%), Pt/C (Pt: 5 wt%), Ru/C (Ru: 5 wt%), Rh/C (Rh: 5 wt%) and Raney Ni was obtained from Alfa Aesar. $Co(NO_3)_2 \cdot 6H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Nanographite powder (D50 < 600 nm, 99.95% metal basis, CAS: 7782-42-5) was purchased from Aladdin Reagent Limited Company (Shanghai, China).

Preparation of Co/CoO@Carbon catalyst

The Co/CoO@Carbon catalyst was prepared through a two-step method. Cobalt tartrate (6.25 mmol) was dissolved in 30 mL deionized water and then mixed with 50 mL glycerol. Nanographite materials (0.5 g) were added and dispersed by ultrasonic treatment for 1.0 h. The mixture was sealed in a hydrothermal kettle and kept at 423 K for 12 h. The solid was obtained by centrifugal separation, washed with ethanol three times, and dried at 373 K for 3.0 h. The resulting solids were further treated at 1073 K in pure argon for 2 h.

The resulting Co/CoO@Carbon catalyst (20 mg) was dissolved in a HNO_3/HCl mixture (4.0 mL, volume ratio = 1:3) and kept at 373 K for 30 min. Carbon solids were filtrated out and the aqueous solution was diluted to 500 mL. The Co concentration determined by inductively coupled plasma mass spectrometry is 11.66 mg L^{-1}. The load of cobalt was calculated to be 29.15 wt%.

Characterization methods

XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W $Al_{K\alpha}$ radiations. The base pressure was approximately 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. The Eclipse V2.1 data analysis software supplied by the VG ESCA-Lab200I-XL instrument manufacturer was used to manipulate the acquired spectra. TEM was performed on a JEOL 2010 TEM equipped with an attachment for local EDX analysis. The accelerating voltage was 200 kV, and the spot size was 1 nm. High-angle annular dark-field scanning transmission microscopy (HAADF–STEM) was performed on the carbon-coated Co bimetallic nanoparticles catalysts with JEOL JEM-2100F microscope in a scanning transmission electron microscopy (STEM) mode operated at 200 kV.

Catalytic hydrogenation test

In 100 mL stainless steel autoclave with Teflon liner were added nitroarene (1.0 mmol), solvent (5.0 mL THF/0.2 mL water), and Co/CoO@Carbon catalyst (20 mg). The sealed autoclave was flushed with hydrogen for four times. The reaction was performed under 3.0 MPa hydrogen at the selected temperature for the given time. After the reaction, the reaction mixture was analyzed by GC and GC–MS. In recycling tests, the Co/CoO@Carbon catalyst was collected by a magnet and washed by ethanol. After drying in air at 333 K, the catalyst was recycled into the next batch test.

The products were analyzed by GC and GC–MS. GC was performed by using a GC-2014 instrument (Shimadzu) with a high-temperature capillary column (MXT-1, 30 m, 0.25 mm ID) and flame ionization detector. GC–MS was performed by using a GCT Premier instrument (Waters) with a capillary column (DB-5MS/J&W Scientific, 30 m, 0.25 mm ID). NMR data of some new nitroarene hydrogenation products are listed in the Supporting Information.

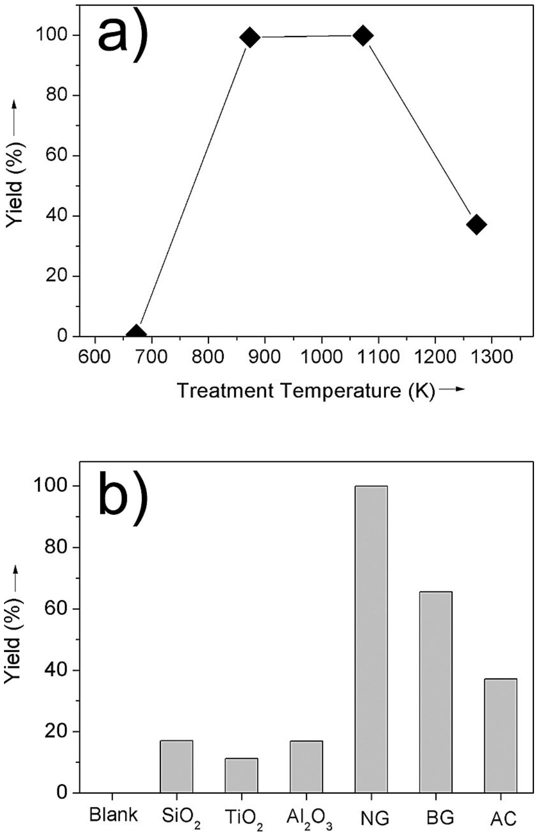


Figure 6. a) Catalytic activity of nitrobenzene hydrogenation over the Co/CoO@Carbon catalyst prepared at different treatment temperatures. b) Catalytic activity of nitrobenzene hydrogenation over the Co/CoO@Carbon catalyst prepared over various cobalt oxide depositing supports (NG: nanographite; BG: bulk graphite powder; AC: activated carbon).

Acknowledgements

This work was supported by the Natural Science Foundation of China (21403248, 21174148, 21101161, 21304101).

Keywords: cobalt · heterogeneous catalysis · graphene · hydrogenation · nanoparticles

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Received: November 17, 2015