Cobalt Graphitic Carbon Nanoparticles for Catalytic Hydrogenation of 2,4-Dinitrophenol

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Abstract

Cobalt carbon nanoparticles CoCNPs were prepared by pyrolysis of cobalt phenanthroline complex at different pyrolysis temperature and time of pyrolysis and used for the catalytic hydrogenation of 2,4-dinitrophenol. CoCNPs (1) and (3) were prepared by heating at 600 ºC and 800 ºC respectively, while (2) was prepared by heating at 600 ºC with an additional intermediate stage at 300 ºC. The structures and chemical properties of the three catalysts were correlated with their catalytic activities. Among the three studied catalysts, the highest rate constant was obtained for (2) while the highest conversion was achieved by (3). Our data show that an increase in oxygen content of the cobalt carbon nano-catalyst reduces the catalytic activity, while an increase in pyrolysis temperature improves the conversion yield.

Keywords: Cobalt nanocarbon, 2,4-dinitrophenol, catalytic hydrogenation, pyrolysis, cobalt phenanthroline complex.

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1. Introduction

Cobalt carbon nanostructures CoCNs are of great interest because of their wide important applications in batteries1, supercapacitors2, oxidation3 and hydrogenation4 catalysis and water treatment5,6.

Many methods have been developed so far in order to prepare CoCNs. For example, carbon nanotubes CNTs were prepared with cobalt catalyst by Arc discharge7, pulsed laser vaporization8 and chemical vapor deposition CVD9. However, these methods face the challenge to produce carbon nanostructures in large amount with a specific morphology that
serve a unique application. They are also sophisticated and expensive requiring catalyst and continuous flow of inert gas, carbon source gas like acetylene and reducing hydrogen gas. However, pyrolysis methods are simple and cheap. They involve pyrolysis in inert atmosphere of transition metal complexes which provide the metal catalyst for graphitization and carbon source from the ligands. Depending on precursors structures and heating conditions several nanostructures can be obtained. While pyrolysis of cobalt carbonyl phenyl-alkynes complexes gave carbon cobalt nanorods or nanospheres, pyrolysis of cobalt carbonyl graphene-alkyne complexes gave multi-walled carbon nanotubes MCNTs. Also, pyrolysis of polyphenylene dendrimer/cobalt complexes can produce CNTs, carbon cobalt nanorods, or carbon/cobalt nanospheres.

Nowadays, it is of great importance to find a suitable, abundant, and low-cost catalyst for reduction of nitrophenols into anilines. Since anilines have wide applications in industry such as preparation of pesticides, pharmaceuticals, dyes, pigments, agrochemicals, plastics, and rubbers. Palladium and gold-based catalysts were used for selective hydrogenation of nitrophenols, however they are expensive for industrial applications.

Cobalt oxide N-graphene/activated carbon nano-materials Co₃O₄-NGr@C prepared by pyrolysis of cobalt pyridines derivative acted as a selective catalyst for hydrogenation of nitroarene derivatives under demanding conditions (at 100 °C for 11-17 hours) in THF solvent using Triethylamine Et₃N and formic acid as hydrogen source. However, when hydrogen gas was used at high pressure 5 bar and temperature 110 °C, the reaction time was 4 to 12 hours in THF. Cobalt(0) nitrogen doped carbon Co@N-C 700 catalyst obtained by pyrolysis of Co metal organic framework showed remarkable performance for hydrogenation of p-nitrophenol to p-aminophenol using NaBH₄ as reducing agent in water.

Thus, there is still a need to seek nano-catalysts that can achieve hydrogenation of nitrophenol derivatives with high recyclability in short time at mild conditions. In the present study, we investigated the catalytic reduction of 2,4-dinitrophenol using cobalt carbon nanoparticles CoCNPs prepared by pyrolysis of cobalt phenanthroline complex under different pyrolysis temperature in presence of additional carbon source.

2. Experimental

- Preparation of cobalt carbon nanoparticles catalyst CoCNPs

Preparation of CoCNP (1)

\[\text{[Co(phen)₂Cl₂] } 1.5\text{CH₃CN} \text{ 0.2 g} \text{ and anthracene 0.064g, were mixed and placed in a crucible without lid cover. Then heated under reduced pressure of N₂ gas in a furnace for 2 hours to reach 600 °C. This was followed by pyrolysis at 600 °C for 8 hours. Porous silver black flakes were obtained with a yield of 0.05g.}\]
Co(phen)$_2$Cl$_2$ 1.5CH$_3$CN] 0.2 g and anthracene 0.3 g were heated in a crucible covered with lid for two hours to reach 300 °C. The mixture was left for 2 hours at 300 °C (intermediate stage). The heating was increased again for one hour to reach 600 °C. Finally, isothermal heat was used for 8 hours at 600 °C. Flaky silver black shiny foams (0.0737 g) were obtained after slow cooling.

Preparation of CoCNP (3)

[Co(phen)$_2$Cl$_2$ 1.5CH$_3$CN] 0.2 g and anthracene 0.064 g were mixed and heated in a crucible with lid. Two and a half hours of heating was used to reach 800 °C, then kept at 800 °C for 5 hours. After cooling 0.076 g of silver black flakes were obtained.

- Characterization of CoCNPs

The XRD patterns of CoCNPs were obtained on a Bruker AXS D8 Advance diffractometer (40 kV, 40 mA) employing a radiation source of Cu Kα in which λ equals 1.5418 Å. The 2θ range of diffractograms was recorded between 20° to 80° at a step size of 0.01° per minute.

Field-Emission Electron Microscope analysis FE-SEM images were measured by JSM 7600F, Jeol instrument, Japan.

High-resolution transmission electron microscopy (HRTEM) images were carried out on a Jeol JEM-2100F at an acceleration voltage of 200 kV using a tungsten field emission gun (FMG) as electron generator. A charge-coupled device was used (CCD) to collect the HRTEM images. Energy dispersive X-ray (EDX) was performed using an X-MaxN 80T detector that was attached to the JEM-2100F.

X-ray photoelectron spectroscopy (XPS) measurements were performed implanting a Kratos Axis Ultra DLD spectrometer at room temperature and under ultra-high vacuum (UHV) systems. The XPS was implemented with a monochromatic Al Kα (hv = 1486.7 eV) as an excitation light source in which the steps, collection time and pass energy were 0.1 eV, 0.5 s and 20 eV, respectively. The photoelectrons being detected at a 90° take-off angle. The spectra were referenced to the binding energy (BE) of the C 1s peaks (284.6 eV). The XPS data were fitted using the CasaXPS software.

- Kinetic studies

- Kinetic procedure of the reducing catalytic activity

Roughly 1 mg of nano-catalyst (1), (2) or (3) were dispersed in 5 ml of deionised water under sonication for 15 minutes. The dispersed mixture was used to record the baseline on the UV-Visible spectrophotometer before starting the catalytic activity measurements, in order to subtract the effect of the light scattering by the nanoparticles. On the other hand, a fresh solution of 2,4-Dinitrophenol (DNP), was prepared by dissolving 11.7 mg of DNP in 25 ml of deionised water. A 0.18 M fresh solution of sodium borohydride (NaBH$_4$) was also prepared for the reduction purpose.

3 ml of dispersed catalyst were introduced into a quartz cell (ℓ = 1 cm), followed by adding 100 µl of DNP solution and 50 µL of NaBH$_4$ solution. The UV-2600 spectrophotometer
(Shimadzu, Tokyo, Japan) was used to record the spectra range from 200 to 600 nm at defined times.

- Successive reduction of DNP

Nano-catalyst (2) was selected for the successive reduction study in the quartz cell. Briefly, 50 µl of DNP solution (4.4 × 10⁻³ M) were added into a quartz cell containing 3 ml (0.2 g/L) of dispersed catalyst by sonication. This is followed by adding 50 µL of fresh solution of NaBH₄ (1M). The rate constant was calculated from the decrease in intensity of the absorption peak at 358 nm (λ_max of DNP) over time for different experiments. At the end of each cycle of reduction, additional 50 µL of DNP were added to the solution and the reduction process was monitored as done in the previous cycle. After the sixth cycle the reduction started to be slow and the process was stopped.

- DNP reduction under sonication

1.3 mg of nano-catalyst (1), (2) or (3) were dispersed in 30 mL of deionised water under continuous sonication. For each cycle, 5.5 mg of DNP and 75 mg of NaBH₄ were used, and the reduction was monitored using the UV-Visible spectrophotometer and the percentage of reduction for each cycle was calculated. The average time for completion of each cycle is around 30 min.

3. Results and discussion

We have previously reported the preparation of porous cobalt carbon nanostructures and the study of their applications in water treatment. They were prepared by pyrolysis of cobalt phenanthroline chloride complex by pyrolysis at 600 °C in a quartz tube furnace under slow and continuous flow of nitrogen in presence and absence of anthracene⁶. The materials prepared in presence of carbon source gave a higher capacity for removing Malachite Green (492 mg/g). In a second study we have used silica as support in the pyrolysis experiment in a nitrogen box furnace at 850 °C and obtained cobalt carbon@silica nanostructures with durable and regenerative properties. The capacity for removing Crystal Violet was 214 mg/g¹⁹.

In the present study, we have focused on optimizing the experimental conditions in order to prepare cobalt carbon nanoparticles that can act as heterogenous catalysis for the hydrogenation of dinitrophenol at mild conditions, in short time and high recyclability.

- Material Preparation:

[Co(phen)₂Cl₂]1.5CH₃CN was prepared and used as a catalyst precursor for the pyrolytic synthesis of cobalt carbon nanoparticles. In addition to the phenanthroline ligands that acts a carbon source, anthracene was additionally used as an external source of carbon. Three experimental conditions were used for the pyrolysis of cobalt phen complex with anthracene under reduced nitrogen pressure of 0.02 atm.

(1) was obtained in an open crucible at 600 °C for 8 h, where the volatiles from decomposing materials have less chance to redeposit on the metal nanoparticles. (2) was prepared similarly to (1) by pyrolysis at 600 °C for 8 h, however after heating for 2 hours at intermediate stage of 300 °C in a cover crucible, so that decomposition of complex occurs at longer time and favors
cobalt nanoparticles formation. Finally, (3) was also prepared in a covered crucible but by heating at higher temperature 800 °C for only 5h, since higher temperature favors graphitic carbon formation.

The best method for catalyst preparation is the one that can generate highly active species of small size metal nanoparticles surrounded with well-developed graphitic structures [16]. This is supported by the catalytic hydrogenation results as can be seen in this work. Optimization of the pyrolysis step showed that the temperature gradient and the heating time at the maximum temperature significantly influence the activity and selectivity of the catalyst. All pyrolysis experimental conditions play a role in obtaining the best performing catalyst. These conditions include the presence of intermediate stage of heating necessary to prepare the metal nanoparticles which are the precursors for the formation of graphitic carbon, the time of heating and the value of maximum temperature in the final stage necessary to develop the graphitic carbon structures. Therefore, during pyrolysis, a part of the organic ligand decomposes and evaporates to the gas phase, whereas the other part becomes carbonized in the framework. The graphitic structure provides a robust shelter around metal nanoparticles and reduce their degradation during the catalytic process. Closed systems can ensure a long residence time of volatile carbons above the cobalt(0) nanoparticles which catalyses the graphitization surrounding carbon.

The graphitic shell can prevent cobalt nanoparticles from further agglomerations which reduce the catalytic efficiency. However, there is limitation for the use of catalysts with thick graphite shell which due to diffusion limitations render the active cobalt sites of nanoparticles hardly accessible by reactants.

In this work, the best catalyst structures were obtained by carrying out the pyrolysis at 800 °C or at 600 °C with an intermediate stage at 300 °C, as can be inferred from the following SEM and TEM results.

- **Materials Characterizations**
Fig. 1. Scanning electron microscopy SEM images of CoCNPs (1), (2) and (3).

As shown in SEM of CoCNPs, (Fig. 1), (1) consists of graphite sheets surrounding cobalt nanoparticles of size average in the range of hundreds of nanometers. While (2) and (3) showed cobalt nanoparticles of 20-200 nm embedded within porous hierarchical graphene sheets. Cobalt nanoparticles of 20 nm sizes were labeled in (2) but still there are larger particles up to 400 nm. While in the case of (3) the labeled particles were 30 nm in sizes. There are also smaller ones and the larger ones were up to 200 nm. The porous structure is ideal to attract analytes towards the cobalt nanoparticles and facilitate the catalytic process.
High resolution transmission electron microscopy HRTEM of CoCNPs are shown in Fig. 2. The catalyst (2) contains mainly small dark cobalt particles of 3-20 nm in size embedded in lighter graphitic web. The same nanostructure is found in (1), though the cobalt nanoparticles are clearly seen more blackish with well-defined interplanar lines and less surrounding graphitic carbon. This is expected because the pyrolysis was performed in an open flak that reduces the presence of gaseous carbon source. Regarding catalyst (3), it was prepared at higher temperature 850 °C. Thus, bamboo multiwall carbon nanotubes and graphitic onion like nanostructures were obtained along with cobalt nanoparticles of the same size as in the other nanostructures.

Energy dispersive X-ray EDX of CoCNPs indicates the spreading of cobalt, carbon and oxygen elements within the structure. EDX for (2) is shown in Fig. 3, while EDX for (1) and (3) are presented in supplementary figure SI. Fig. 1.

Fig. 3. Energy dispersive X-ray EDX of CoCNPs (2).
Fig. 4. Powder X-ray patterns (PXRD) of CoCNPs (1), (2) and (3).

The powder X-ray patterns of all CoCNPs show sharp peaks characteristic of metallic cobalt $\alpha$-Co (Fig. 4). The experimental 20 values for (1), (2) and (3) are very close to the theoretical 20 for $\alpha$-Co which are 44.098° and 51.376° and 75.617°. While $\beta$-cobalt metal is not present because of absence of its theoretical 20 peaks at 41.588, 44.262, 47.392, 62.349, 75.889 (International Centre for Diffraction Data 2020).
Fig. 5. Raman spectra of CoCNPs (1), (2) and (3).

Raman measurements were used to investigate the carbon defects and the degree of graphitization. In Fig. 5, two distinct peaks about 1350 and 1584 cm$^{-1}$ are associated with D and G bands, respectively. These are present in pyrolytic graphite and carbon nanotube. They are sharper in the case of nanotubes and broader in the case of graphite, while they merge into a single broad peak in the case of cobalt amorphous carbons$^{20}$. It can be inferred that (3) with sharper peaks contains more CNTs, than (1) and (2). This is expected since higher temperature of pyrolysis (850 $^\circ$C) was used in the preparation of (3). The area ratio between D and G bands ($S_D/S_G$) were calculated as 7.3, 3.43 and 4.17 for (1), (2), and (3) respectively. Two characteristic peaks of Co were observed around 477.85, and 687 cm$^{-1}$ by Raman spectroscopy, which correspond to classical vibration modes $E_g$, and $A_{1g}$ of Co, respectively$^{21}$.

XPS survey spectra show that nano-catalyst (1) contains more oxygen and less carbon atoms in its elemental composition compared with the two other nanomaterials (SI. Fig. 2, 3 and 4). Indeed catalyst (1) comprises 68% of carbon compared to 77% and 84% for catalysts (2) and (3) respectively. By comparing the nano-catalyst elemental composition and its catalytic
activity, one can suggest that there is an important role of the carbon skeleton in the catalytic reduction of DNP. The XPS survey and high-resolution spectra have shown the presence of cobalt in the composition of nano-catalysts, Fig. 6. The Co 2p spectrum could be fitted into two spin-orbit doublets, which are characteristic of Co$^{2+}$ and Co$^{3+}$, and two shake-up satellites. Only in the case of catalyst (1), a small quantity of metallic cobalt was observed represented by the additional peak of Co$^0$ in the cobalt 2P$_{3/2}$ spin orbit.

**Fig. 6.** XPS high resolution spectra of Co 2p in nano-catalysts (1), (2) and (3).

The XPS high resolution was also conducted on the elements C (1s), O (1s) and N (1s) existing in the three nanomaterials as shown in Fig. 7, 8, and 9. Evaluation of C 1s photoelectron spectrum of the three nanomaterials showed similar resolving into components for different carbon chemical forms (C sp$^2$, C sp$^3$, other oxygen groups like hydroxyl COH, carbonyl CO, carboxyl COOH and satellite). Regarding the peak of O 1s, we can observe that nano-catalyst (1) shows less oxygen bound to cobalt in its composition, which is in agreement with the presence of metallic cobalt in this material. Additionally, the examination of N 1s peak shows that nano-catalyst (3) contains more graphitic nitrogen compared with the two other nanomaterials which could have a role in enhancing the catalytic activity.
Fig. 7. XPS high resolution spectra of C (1s) in nano-catalysts (1), (2) and (3).
Fig. 8. XPS high resolution spectra of O (1s) in nano-catalysts (1), (2) and (3).
Fig. 9. XPS high resolution spectra of N (1s) in nano-catalysts (1), (2) and (3).

- **Kinetics**

The DNP reducing catalytic activity of nano-catalyst (2) was examined at room temperature (25 °C) by measuring the UV-vis spectrum of DNP in the presence of NaBH₄ in the range of 200-600 nm at various times, Fig. 10. The reduction of DNP occurs due to the self hydrolysis of NaBH₄ and hydrogen generation according to equation (1). In absence of catalyst, the reduction of DNP is very slow, however the presence of our carbon nanomaterial makes the reduction occur rapidly at room temperature.

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2(\text{g}) \quad (1)
\]

In the presence of catalyst, the peaks at 258 and 358 nm, significantly decrease, which is due to decreased DNP concentration and new peaks appeared at 275 and 437 nm indicating the formation of 2,4-dinitrophenolate ion in the solution. It is well known, that the reduction of nitrophenols with an excess of NaBH₄ in the presence of catalysts, undergoes via the formation of phenolate ions which will be transformed into aminophenols\(^{26}\). The color of the solution has changed from yellow to pale orange. These new peaks showed their maximum absorption after 4 minutes as shown in Fig. 10 (a).
Fig. 10. a) Time-dependent UV-visible absorption spectrum for the reduction of DNP with NaBH₄ in the presence of nanocatalyst (2); First 4 minutes. Solvent: Water, [DNP] = 8.5 ×10⁻⁵ M; [NaBH₄] = 0.003 M; ℓ = 1 cm; T = 25 °C; 0.18 mg/mL of catalyst was used. b) Time-dependent UV-visible absorption spectrum for the reduction of DNP with NaBH₄ in the presence of nanocatalyst (2); From 5 to 13 minutes. Solvent: Water, [DNP] = 8.5 ×10⁻⁵ M; [NaBH₄] = 0.003 M; ℓ = 1 cm; T = 25 °C; 0.18 mg/mL of catalyst was used.

However, after ~5 minutes from the beginning of the reduction process, the intensities of absorptions at 275 nm and 437 nm gradually decreased as the reduction proceeds in the presence of the carbon nanomaterial as shown in Fig. 10 (b). A new peak appears at 302 nm which is attributed to the formation of the reduced product 2,4-diaminophenolate.

Similarly, using the same experimental conditions, the catalytic activity of reduction of DNP was studied in presence of nano-catalysts (1) and (3) as shown in SI. Fig. 5 and 6, and in absence of catalysts SI. Fig. 7.

In order to compare the catalytic activity of the different nano-catalysts, the rate constant of the reduction process was calculated from the decrease in intensity of the absorption peak (A) at 358 nm over time for the different experiments. As the concentration of sodium borohydride can be considered constant, the reaction follows a pseudo first-order kinetic reaction. The apparent rate constants can be directly calculated from the linear relation between ln(A/A₀) and time, where A₀ represents the initial absorbance intensity of DNP at 358 nm.

Fig. shows the kinetic plot of the DNP reduction processes in presence and absence of catalysts.
From these kinetic linear variation, the apparent rate constants ($k_{\text{app}}$, min$^{-1}$) were calculated. The rate constants $k_{\text{app}}$ (min$^{-1}$) of DNP reduction were 0.34 for (2) > 0.17 for (3) > 0.04 for (1) > 0.005 (no catalyst). It can be noted that nano-catalyst (2) showed the faster catalytic activity among the tested catalysts.

In order to demonstrate the efficiency of our catalysts, we have initially conducted cyclic catalytic reduction of DNP by continuously adding DNP in the quartz cell in presence of nano-catalyst (2). The reaction was followed by UV-visible spectrophotometry, where the presence of only one peak in the spectra, centred at 300 nm, indicates the completion of the reaction (Fig. 12).
Fig. 12. Cyclic catalytic reduction of DNP in quartz cell in presence of nanocatalyst (2). Solvent: Water; [NaBH₄] = 0.017 M; l = 1cm; T = 25°C; 0.2 mg/ml of catalyst. 50 µl of 4.4×10⁻³ M of DNP are added in the cuvette in each cycle. The inset image shows the linear increase of absorbance at 300 nm with the number of cycles.

In our experimental conditions, six cycles of DNP reduction were completed with a 100% conversion rate in presence of nano-catalyst (2). After the sixth cycle, the reaction became much slower indicating the possible poisoning of the catalyst. After this reaction, the catalyst was recovered by centrifugation, washed with distilled water and was reused for a total of four successive reduction cycles before the start of catalyst inactivation.

On the other hand, the catalytic activities at larger scale, under continuous sonication, of the three nanomaterials (1), (2), and (3) were compared. Different cycles of DNP reduction were performed without any treatment of the nano-catalysts between cycles, and the yield of DNP conversion was determined each time (Fig. 13).

Fig. 13. Cyclic catalytic reduction of DNP in a flask containing 1.3 mg of nano-catalyst and 30 ml of water. 5.5 mg of DNP and 75 mg of NaBH₄ were added each cycle, average time for the cycle is 30 min.

Indeed, up to the sixth cycle, the conversion percentage of DNP by (3) was still more close to 70%. Starting the seventh cycle, the % conversion decreased until 30% indicating a significant poisoning of the catalyst. In these experimental conditions, nano catalyst (3) which was prepared at highest temperature 800 °C is more efficient in the reduction of DNP compared with the two other catalysts. Conversion percentage increased with pyrolysis temperature of
the complex, suggesting that the increase in graphitic structure formed at higher temperature played an important role in this catalytic system. The ratio of C=C to C-C in XPS is in the order of increase (1) < (2) < (3), beside that we have shown that (3) contains more graphitic nitrogen compared with the two other catalysts. It has been suggested that the presence of basic groups on CoCNP might facilitate the transfer of protons to Co nanoparticles to form Co metal hydride species, thus promoting the production of the desired hydrogenation products. The turn over number TON for (1), (2) and (3) was calculated to be 11.10, 21.68, and 25.41 mmol DNP per mmol cobalt. The best performance is for (3) which contains small size CoCNP dispersed uniformly with less agglomeration compared to other samples.

Conclusion

Novel cobalt carbon nanoparticles (1), (2), (3) were prepared by pyrolysis of cobalt phenanthroline chloride complex at different temperature and period of time. They were characterized using different techniques and applied as catalyst for hydrogenation of 2,4-dinitrophenol. Catalyst (3) showed a highest catalytic conversion, this can be attributed to its higher content of graphitic structures and more uniformly dispersed cobalt carbon nanoparticles compared to the other catalyst. Nano-catalyst (1) demonstrated less catalytic activity. It contains more oxygen and less carbon atoms in its elemental composition compared to the two other nanomaterials. The obtained results in this work have showed the effect of selected temperature for nano-catalysts’ preparations on the hydrogenation catalytic activities. These results should pave the road towards future discoveries of cheap and efficient metal carbon based nano-catalyst for different applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

The authors acknowledge the Deanship of Scientific Research at King Faisal University for the financial support under Research Group (Grant No. 1811029).

Author Contributions Statement

H.H. supervised the work and wrote the manuscript, H.T. assisted in writing the manuscript, R.K performed pyrolysis experiments, H.T. and R.K. performed catalysis experiments, M.K. and S.H performed nanomaterial analysis and characterizations, A.T. and E.B. assisted in discussing the paper. All authors reviewed the manuscript

References
Li-Jing Xie, Jun-Feng Wu, Cheng-Meng Chen, Chang-Ming Zhang, Liu Wan, Jian-Long Wang, Qing-Qiang Kong, Chun-Xiang Lv, Kai-Xi Li, Guo-Hua Sun, A novel asymmetric supercapacitor with an activated carbon cathode and a reduced graphene oxide-cobalt oxide nanocomposite anode, Journal of Power Sources 242 (2013) 148-156.

2 Jun Mei, Ting Liao, Godwin A. Ayoko, John Bell, Ziqi Sun*, Cobalt oxide-based nanoarchitectures for electrochemical energy applications, Progress in Materials Science 103 (2019) 596–677

3 Xiun Lin, Zhenzhen Nie, Liyun Zhang, Shuchuan Mei, Yuan Chen, Bingsen Zhang, Runliang Zhuc and Zhigang Liu, Nitrogen-doped carbon nanotubes encapsulate cobalt nanoparticles as efficient catalysts for aerobic and solvent-free selective oxidation of hydrocarbons, Green Chem., 2017, 19, 2164-2173

4 Tao Song, Peng Ren, Yanan Duan, Zhaozhan Wang, Xiufang Chen, and Yong Yang, Cobalt Nanocomposites on N-Doped Hierarchical Porous Carbon for Highly Selective Formation of Anilines and Imines from Nitroarenes, Green Chem., 2018, 20, 4629-4637

5 Weimo Zhu, Jiawen Ren, Xin Gu, Muhammad Usman Azmat, Guanzhong Lu, Yanqin Wang, Synthesis of hermetically-sealed graphite-encapsulated metallic cobalt (alloy) core/shell nanostructures, Carbon 49 (2011) 1462–1472

6 Hassan H. Hammud*, Bassem El Hamaoui, Nada H. Noubani, Xingliang Feng, Zhong-Shuai Wu, Klaus Müllen and Khurshid Ayub, Carbon-Cobalt Nanoarchitectures as an Efficient Adsorbent of Malachite Green, Nanoscience & Nanotechnology-Asia, 2018, 8(2), 263-280.

7 D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls, Nature, 363, 1993, 605-607

8 Nishide, D.; Kataura, H.; Suzuki, S.; Okubo, S.; Achiba, Y. Growth of single-wall carbon nanotubes from ethanol vapor on cobalt particles produced by pulsed laser vaporization. Chem. Phys. Lett. 2004, 392, 309–313

9 Terrado, E.; Redrado, M.; Munoz, E.; Maser, W.K.; Benito, A.M.; Martinez, M.T. Carbon nanotube growth on cobalt-sprayed substrates by thermal CVD. Mat. Sci. Eng. C 2006, 26, 1185–1188

10 B. E. Hamaoui, L. Zhi, J. Wu, J. Li, N. T. Lucas, Z. Tomovic*, U. Kolb, and K. Müllen, Solid-State Pyrolysis of Polyphenylene–Metal Complexes: A Facile Approach Toward Carbon Nanoparticles, Adv. Funct. Mater. 2007, 17, 1179–1187

11 B. E. Hamaoui, L. Zhi, J. Wu, U. Kolb, K. Müllen, Uniform Carbon and Carbon/Cobalt Nanoarchitectures by Solid-State Thermolysis of Polyphenylene Dendrimer/Cobalt Complexes, Adv. Mater. 2005, 17, 2957–2960.

12 Luciana Ribeiro Pereira, Pijush Kanti Mondal, Madalena S Alves, Aromatic amines: main sources, environmental impact and remediation In book: ENVIRONMENTAL CHEMISTRY FOR A SUSTAINABLE WORLD, December 2013, DOI: 10.1007/978-3-319-19276-5_7, Editors: Eric Lichtfouse, Jan Schwarzauer, Didier Robert, Publisher: Springer

13 Raja, R. et al. Highly efficient catalysts for the hydrogenation of nitro-substituted aromatics. Chem. Commun. 2026–2028 (2005).

14 Corma, A., Gona’lez-Arellano, C., Iglesias, M. & Sa’nchez, F. Gold complexes as catalysts: chemoselective hydrogenation of nitroarrenes. Appl. Catal. A 356, 99–102 (2009).

15 Rajenahally V. Jagadeesh, Debasis Banerjee, Percia Beatrice Arockiam, Henrik Junge, Kathrin Junge, Martina Pohl, Jörg Radnik, Angelika Brückner, and Matthias Beller, Highly Selective Transfer Hydrogenation of Functionalised Nitroarrenes Using Cobalt-based Nanocatalysts, Green Chem., 2015,17, 898-902.

16 Felix A. Westerhaus, Rajenahally V. Jagadeesh, Gerrit Wienen’fer, Marga-Martina Pohl, Jo’rg Radnik, Annette-Enrica Surkus, Jabor Rabeah, Kathrin Junge, Henrik Junge, Martin Nielsen, Angelika Brü’ckner and Matthias Beller, Heterogenized cobalt oxide catalysts for nitroarene reduction by pyrolysis of molecularly defined complexes, Nature chemistry, 5, 2013, 537-543.

17 Yusran Yusran, Dan Xu, Qianrong Fang, Daliang Zhang, Shilun Qiu, MOF-derived Co@N-C nanocatalyst for catalytic reduction of 4-nitrophenol to 4-aminophenol, Microporous and Mesoporous Materials 241 (2017) 346-354.

18 Hazell, A.; McKenzie, C.J. Dichlororob(1,10-phenanthrolineN,N’)-cobalt(II)-Acetonitrile (1/1,5), Acta Cryst., 1997, CS3, 723-725

19 Nusaybah Alotaibi, Hassan H. Hammud, Ranjith Kumar Karnati, Syed Ghazanfar Hussain, Javed Mazher and Thirumurugan Prakasam, Cobalt–carbon/silica nanocomposites prepared by pyrolysis of a cobalt 2,2’-bipyridine terephthalate complex for remediation of cationic dyes, RSC Adv., 2020, 10, 17660–17672.

20 Y.B. Zhang, S.P. Lau, L. Huang, B.K. Tay, Carbon nanotubes grown on cobalt-containing amorphous carbon composite films, Diamond & Related Materials 15 (2006) 171 – 175.
Yang Liu, Peng Dong, Mian Li, Hao Wu, Chengxu Zhang, Lina Han and Yingjie Zhang, Cobalt Nanoparticles Encapsulated in Nitrogen-Doped Carbon Nanotube as Bifunctional-Catalyst for Rechargeable Zn-Air Batteries, Front. Mater. 6(85) (2019) 1-10.

Damin Lee, Qi Xun Xia, Je Moon Yun, Kwang Ho Kim, High-performance cobalt carbonate hydroxide nanodot/NiCo\((\text{CO}_3)\)(OH)\(_2\) electrode for asymmetric supercapacitors Applied Surface Science, 2018, 433, 16-26.

B. Lesiak, L.Kövér, J.Tóth, J.Zemek, P.Jiricek, A.Kromka, N.Rangama, C sp2/sp3 hybridisations in carbon nanomaterials – XPS and (X)AES study Applied Surface Science., 2018, 452, 223-231.

Safia Benkoula, Olivier Sublemontier, Minna Patanen, Christophe Nicolas, Fausto Sirotti, Ahmed Naitabdi, François Gaie-Levrel, Egill Antonsson, Damien Aureau, François-Xavier Ouf, Shin-Ichi Wada, Arnaud Etcheberry, Kiyoshi Ueda, Catalin Miron Water adsorption on TiO2 surfaces probed by soft X-ray spectroscopies: bulk materials vs. isolated nanoparticles., Scientific Reports., 2015, 5:10588.

Rongrong Jia, Jiazang Chen, Jianghong Zhao, Jianfeng Zheng, Chang Song, Li Lia, Zhenping Zhu J. Mater. Chem., 2010, 20, 10829-10834.

Kadir Karakas, Asli Celebioglu, Metin Celebi, Tamer Uyar, Mehmet Zahmakiran, Nickel nanoparticles decorated on electrospun polycaprolactone/chitosan nanofibers as flexible, highly active and reusable nanocatalyst in the reduction of nitrophenols under mild conditions Applied Catalysis B: Environmental 203 (2017) 549–562.

Khalida Naseem, Robina Begum, Zahoor H. Farooqi, Weitai Wu, Ahmad Irfan Core-shell microgel stabilized silver nanoparticles for catalytic reduction of aryl nitro compounds. Applied Organomettalic Chemistry., 2020, 34, e5742.

Lide Oar-Arteta, Tim Wezendonk, Xiaohui Sun, Freek Kapteijn and Jorge Gascon, Metal organic frameworks as precursors for the manufacture of advanced catalytic materials Mater. Chem. Front., 2017, 1, 1709