COBALT CATALYZED REDUCTION OF AROMATIC NITRO COMPOUNDS VIA HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

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Abstract

Catalytic reduction of aromatic nitro compounds to amines via homogeneous and heterogeneous approaches was performed. For homogeneous catalysis the combination of commercially available Co(acac)$_2$ and dpephos ligand (dpephos = bis[(2-diphenylphosphino)phenyl]ether) was effectively employed showing the full conversion of the substrate at room temperature using PhSiH$_3$ and HBPin as reductants. For heterogeneous catalysis, two approaches were used, such as generation of free cobalt nanoparticles from Co(OAc)$_2$ and preparation of three composites derived from commercially available Co(OAc)$_2$ and CoCl$_2$ and surface modified silica. The application of free cobalt nanoparticles showed reduction of nitro compounds with full conversion at room temperature within 20 h. The synthesized cobalt composite materials were subjected to reduction of 2-nitrophenol with NaBH$_4$ in water. Comparative kinetic studies indicated that the composite catalyst derived from Co(OAc)$_2$ has the highest catalytic activity in reduction of 2-nitrophenol with the rate constant of 6.72×10^{-2} min^{-1}. The transition from homogenous catalysis to heterogeneous approach for an effective reduction of aromatic nitro compounds to amines as well as removal of nitro compounds from aqueous solutions were articulated in the present thesis work.

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List of Abbreviations & Symbols

2-NPh	2-nitrophenol
acac	acetylacetonate
As	arsenic
Cat	Catechol
DME	1,2-dimethoxyethane
dpephos	bis[(2-diphenylphosphino)phenyl]ether
GC-MS	Gas Chromatography - Mass Spectroscopy
G-CNT	Graphene/(carbon nanotube)
MeCN	acetonitrile
MeOH	methanol
OAc	acetate
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
NP	nanoparticle
Pc	Phthalocyanine
PCy_3	tricyclohexyl phosphine
phen	1,10-phenanthroline
Pin	pinacol
PMHS	polymethylhydrosiloxane
PPh_3	triphenyl phosphine
SEM-EDS	Scanning Electron Microscope – Energy Dispersive Spectroscopy
TEOS	tetraethyl orthosilicate
THF	tetrahydrofuran
TMDS	1,1,3,3-tetramethyl disiloxane
tris-trz-PEG	tris(triazolyl)-polyethylene glycol
UV-vis	Ultraviolet-visible
XRD	X-ray diffraction
XRF	X-ray fluorescence

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Chapter 1 - Introduction

1.1 Amines and their production

Amines are among the most important organic compounds that are widely used for production of commodity and fine chemicals, including natural products, agrochemicals, pharmaceuticals, polymers and functional materials [1-4]. They play a significant role as structural motifs of many biologically active molecules [5]. Aniline was first isolated in 1926 and it constitutes a huge portion of the worldwide market in chemical industries up to these days [6].

There are a numerous conventional ways to obtain amines and their derivatives, namely stoichiometric reduction of nitriles [7], imines [8], amides [9] and nitro compounds [10]; decarboxylation of carbamic acids [11]; reductive amination of compounds bearing carbonyl group [12]; hydroamination of alkenes and alkynes, etc. [13]. For example, one of the most acknowledged laboratory approaches to amines is N-H alkylation with alkyl halides and/or alcohols [14]. However, such reactions often suffer from lack of control and selectivity resulting in mixtures of products with different alkylation degree [15]. Alternative methods, the reductive amination and stoichiometric reduction of nitriles, amides, imines, etc. require the use of metal hydride reagents and suffer from functional group tolerance and lead to formation of large amounts of byproducts [16]. Analogous problems are found in industrial preparation of amines, which mostly rely on reduction of organic nitriles and nitro compounds to the corresponding amine products [1, 3]. Current technologies based on either stoichiometric transformations or heterogeneous catalytic systems (for example, RANEY® nickel and RANEY® cobalt are commonly used in industry for reduction of nitriles to amines [17] come along with limited reactions control, product selectivity and low functional group tolerance. Another problem is that many nitroaromatic compounds, which serve as precursors for most industrial aromatic amines, are toxic. Considering their incomplete conversion to aromatic amines and aqueous workup procedures for isolation of amine products, nitroaromatic compounds can be present in small amounts in industrial waste waters. Thus, nitrophenols belong to the list of emerging pollutants and their effective removal from waste waters plays an important role in environmental chemistry [18]. These issues prompted chemists around the world to work on effective and “greener” alternative ways for production of amines.

The application of transition metals in the catalytic reduction reactions of nitriles and nitro compounds (e.g. hydrogenation, hydrosilylation and hydroboration) to amines provides promising results in molecular synthesis [19]. The use of homogeneous catalytic systems results in enhanced selectivity and reproducibility of such reduction reactions, whereas heterogeneous catalysis allows for better separation of product(s)/catalyst mixtures and catalyst recovery [20-25]. Among all catalytic reduction methods, hydrogenation of organic nitriles and nitro compounds to the corresponding amines represents the most atom-economical approach; however, the reactions usually require precious metal catalysts and harsh conditions [20-25] and are often non-selective, affording mixtures of aldimines and primary, secondary and tertiary amines [26-31].

During the last decade, hydrosilative and hydroborative reduction of nitriles and nitro compounds to amines have attracted significant attention [9, 32]. This is mainly because compared to H_2, hydrosilanes and hydroboranes are easy to handle and most importantly, can be activated under mild conditions [33]. Moreover, due to the mild reaction conditions the use of hydrosilanes and hydroboranes as reductants often results in increased selectivity of the reactions towards the desired amine product [34].

The conventional catalytic systems for hydrosilylation and hydroboration catalysis are based on precious metals, such as 2nd and 3rd row transition metals of groups 8-10 of the Periodic Table [14, 35-42]. Due to the skyrocketing prices of these elements one of the attractive research venues in this area is transferring the reactivity of such catalysts to more economical and "greener" first-row metal surrogates, those involving so called base metals: Fe, Co, Ni [10, 14, 32, 37, 43]. However, the examples of base metal systems for mild and selective catalytic hydrosilylation and hydroboration of nitriles and nitro compounds to amines are still scarce [10, 14, 32, 35]. The reported few examples of homogeneous base metal catalysts for hydroborative and hydrosilative reduction of nitriles and nitro compounds to amines require the use of rather sophisticated ligands and/or elevated temperatures [14]. Similarly, only a handful of heterogeneous base-metal catalysts for hydrosilylation and hydroboration of nitriles and nitro compounds have been reported with only few examples of such systems operating under mild reaction conditions [11, 14].

Recent developments in base metal-catalyzed homogeneous reduction of nitroaromatic compounds to the corresponding amines show promising results since the catalysts based on Fe, Co and Ni were able to effectively reduce the toxic substrates with high conversions under mild conditions [14]. The main problem associated with homogenous systems is that the majority of the reduction reactions are performed in organic solvents [14]. In the literature, there are no examples of these systems performing the reduction in water due to water sensitivity of the proposed catalysts. In this regard, heterogeneous catalysts would be more advantageous over the homogenous ones since the former catalysts are water tolerant and can potentially perform the reduction in an aqueous media [10]. On the other hand, compared to homogeneous systems, heterogeneous reduction of nitro compounds often requires rather under harsh reaction conditions, such as high temperatures and pressures and long reaction times [10].

1.2 Nitrophenols

Among a variety of aromatic nitro compounds, catalytic reduction of nitrophenols in water received special attention due to their hazardous/pollutant nature. Thus, 4-nitrophenol and 2-nitrophenol are toxic, anthropogenic and considered as emerging pollutants due to their reasonably high solubility in water. The consequences of the release of wastewater containing nitrophenols into receiving water are severe since it may damage the ecosystem and human health [74].

1.3 Thesis aims and objectives

The objective of this thesis is twofold. Firstly, the project aims at the design of simple and effective base metal catalysts for selective reduction of aromatic nitro compounds to amines and then to apply this strategy to the development of heterogeneous base metal catalytic systems for effective removal of nitrophenols from waste waters.

This work presents the results of cobalt-catalyzed hydrosilylation and hydroboration of aromatic nitro compounds, such as nitrobenzene, 2-nitrophenol and 4-nitrophenol to the corresponding amines, using homogeneous and heterogeneous catalytic systems. For homogeneous catalysis we employed the combination of commercially available $Co(acac)_2$ (acac = acetylacetonate) and dpephos (dpephos = bis[(2-diphenylphosphino)phenyl]ether). For heterogeneous catalysis, two approaches were used, such as generation of free cobalt nanoparticles generated from $Co(OAc)_2$ (OAc = acetate) and preparation of three composites derived from commercially available cobalt salts and surface modified silica. These both homogeneous and heterogeneous systems were subjected to reduction of nitrobenzene, 2-nitrophenol and 4-nitrophenol in both organic solvents and water. The obtained amine products were isolated and analyzed using NMR spectroscopy and ultraviolet-visible (UV-vis) spectrophotometry. In order to compare the activity of the developed catalytic systems, kinetics studies of the reduction of 2-nitrophenol with $NaBH_4$ in water were performed for these three Co-Silica composites (derived from $CoCl_2$ and $Co(OAc)_2$) using UV-vis NanoDrop microvolume spectrophotometer.

The thesis aims to apply the knowledge acquired for homogeneously catalyzed reduction of nitro compounds to the design of an applicable heterogeneous catalytic system for effective removal of nitroaromatic pollutants form waste waters. Therefore, the project described in this thesis shows the transition from homogenous catalysis to heterogeneous catalysis for reduction of nitroaromatic compounds to aromatic amines. Although, the developed homogeneous catalysts show promising activity and selectivity in the reduction of aromatic nitro compounds, the use of heterogeneous composite materials as catalysts in such transformations potentially allows for effective catalyst separation and catalyst recovery, which is essential for wastewater treatment to avoid further contamination of water with catalyst material.

1.4 Thesis organization

This thesis work consists of five chapters. The first chapter is an introduction, where in the first part the importance of amines, methodologies for their synthesis and environmental issues associated with their industrial production are discussed. The second part summarizes the major aims and objectives of the thesis work, such as finding effective and selective methodology of obtaining amines from nitro compounds, making a transition from homogeneous catalysts to heterogeneous ones due to separation issues and effective removal of nitroaromatic compounds from waste waters. And at the end of the introduction, there is an overall structure of this thesis work.

The literature review is presented in the second chapter, where background information regarding the reduction of nitro compounds is given. In addition to this, the most recent findings in the field of catalytic reduction using transition metals in both homogeneous and heterogeneous catalysis are reported.

Chapter three describes all materials, reagents and methodology used to implement the project. All experimental procedures and laboratory equipment used for the synthesis and characterization of the catalysts and the products of catalytic reactions are described thoroughly.

In the next chapter called results and discussion, all results are summarized and a comprehensive description of the obtained results is shown. In addition, kinetic studies of the reduction of 2-nitrophenol with $NaBH_4$ in water catalyzed by heterogeneous Co-silica composite systems and $Co(OAc)_2$ and $CoCl_2$ reported in this chapter.

Finally, all findings are summarized in the conclusion section. The recommendations for further work are also given.

Chapter 2 - Literature review

Literature review mainly focuses on the reduction of aromatic nitro compounds to the corresponding amine products using silanes and boranes as reductants in homogenous catalysis, whereas $NaBH_4$ is used as reductant in heterogeneous catalysis.

2.1 Homogeneous catalysis

Almost all industrially used catalytic reduction reactions of unfunctionalized nitro compounds to the corresponding amines make use of the heterogeneous catalysts [10]. At the same time, some homogenous systems show promising results in chemoselective reduction of more challenging substrates having different functional groups other than nitro group. Despite the advantages of homogeneous catalysts over heterogeneous systems in selectivity and activity, the difficulty of the recovery of the former systems makes them less industrially attractive over heterogeneous materials. Moreover, common sensitivity of homogeneous transition metal catalysts to water makes them almost futile in transformation in aqueous media. Despite this, the present review will discuss both homogeneous and heterogeneous catalysis approaches since knowledge of the mechanisms of the reduction of nitro compounds as well as molecular chemistry behind these processes provided from homogeneously catalyzed reactions is essential for the design of an efficient heterogeneous catalytic system for reduction of nitroarenes in water.

Historically, the majority of the effective catalysts for the production of aromatic amines from the corresponding nitro aromatic compounds are based on late transition (precious) metals, such as Ru [35-36], Pd [14] and Rh [14, 38], which despite their high catalytic activity are limited in supply and expensive. Therefore, in recent years, there is a huge demand for the development of more economical and efficient non-noble transition metal-based catalysts. In this regard, earth-abundant first-row transition metals (such as Mn, Ni, Fe, Co) have become an alternative to conventional precious metals systems for the reduction of aromatic nitro compounds to the corresponding amines [14]. In the following sub chapters, the most significant findings for both precious metal-based and earth abundant metal-based catalysts will be reported.

For homogeneous transition metal catalysts, a special attention is paid to chemoselectivity of the reduction of nitroarenes in the presence of other potent reductive functional groups. For heterogeneous catalysis, this review covers the reduction of aromatic nitro compounds only with molecular hydrogen and $NaBH_4$ since heterogeneous hydrosilylation and hydroboration reactions are a lot less important and less studied compared to homogeneous systems.

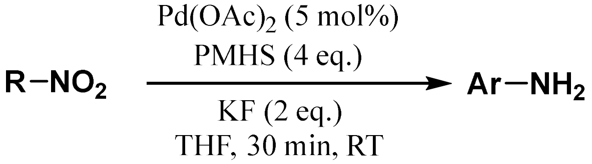
2.1.1 Hydrosilative reduction reactions

2.1.1.1 Precious metals based homogeneous catalysts

For years, the precious-metal-based catalysts were extensively studied in homogenous catalysis for the reduction of various unsaturated organic compounds leading to the production of amines [14]. Catalytic reduction of nitro compounds is not an exception.

In 2006, Rahaim and Maleczka reported the Pd-based catalyst for the reduction of nitrobenzene [44]. This work describes the use of $Pd(OAc)_2$ for effective hydrosilative reduction of nitroarenes. Thus, reduction of nitrobenzene to aniline was performed within 30 min at room temperature using 2 equivalents of an aqueous solution of KF, 5 mol% of $Pd(OAc)_2$ and 4 equivalents of PMHS as reductant in THF (Scheme 1) [44]. The same system was also applied for chemoselective hydrosilative reduction of nitroarenes bearing such functional groups as nitriles, esters, amides and aldehydes. However, no chemoselectivity was observed for $Pd(OAc)_2$-catalyzed hydrosilative reduction of alkynyl and alkenyl substrates resulting in complete reduction of alkynyl and alkenyl groups together with the nitro group [44].

Scheme 1. Hydrosilative reduction of nitro compounds based on Pd [44]



$$R{-}NO_2 \xrightarrow[\text{KF (2 eq.)}\;\text{THF, 30 min, RT}]{Pd(OAc)_2\text{ (5 mol\%)}\;\text{PMHS (4 eq.)}} Ar{-}NH_2$$

Moving beyond platinum group metals, Wilkinson's catalyst $RhCl(PPh_3)_3$ was also demonstrated as an effective catalyst for the reduction of aromatic nitro compounds with triethylsilane in toluene [45]. The reaction resulted in the formation of silylamines, which after acidic treatment of the reaction mixture were converted to the corresponding aniline derivatives in good yields (73-89%) [45]. Although the reduction of nitroarenes proved non-selective in the presence of ketone and aldehyde functionalities, ester groups were tolerated under the reaction conditions [45].

Hydrosilative reduction of aromatic nitro compounds to aromatic amines has been also reported for rhenium oxohalide complexes, $ReOCl_3(PPh_3)_2$ and $ReIO_2(PPh_3)_2$ [46]. Using 5 mol% of rhenium catalyst and excess $PhMe_2SiH$ (3.6 mol%) in toluene under reflux, a series of nitroarenes were reduced to the corresponding aromatic amines within 1-45 h with 31-96% product yields [46]. Notably, rhenium oxohalide catalytic systems were found to tolerate such functional groups, as nitriles, amides, esters and halides.

2.1.1.2 Iron based catalysts

Iron catalyzed reduction of aromatic nitro compounds using silanes as a reductant was firstly reported by Nagashima and co-workers in 2009 [47]. Thus, using 10 mol% of [$Fe_3(CO)_{12}$] catalyst, *N,N*-dimethyl-4-nitrobenzamide was chemoselectively reduced to *N,N*-dimethyl-4-aminobenzamide with 5 equivalents of 1,1,3,3-tetramethyl disiloxane (TMDS) with 77% yield [47]. Interestingly, applying the same reaction conditions for reduction of *N,N*-dimethyl-4-nitrobenzamide and replacing [$Fe_3(CO)_{12}$] with noble metal complexes ([(μ^3, η^2, η^3, η^5-acenaphthylene)$Ru_3(CO)_{12}$] and $H_2PtCl_6{\cdot}6H_2O$) resulted in selective reduction of carboxamide moiety instead of the nitro group (Scheme 2) [37, 47]. [$Fe_3(CO)_{12}$] was also used for chemoselective reduction of halogenated and methoxy-substituted nitro aromatic compounds. Thus, using 10 mol% of [$Fe_3(CO)_{12}$] catalyst with 10 equivalents of TMDS, the reduction of the halogenated nitro aromatic compounds was performed in toluene at 100 ^oC within 24 h to give 73-93% yields of the corresponding halogenated amine products (Table 1) [47].

Scheme 2. Chemoselectivity upon reaction of N,N-dimethyl-4-nitrobenzamide with TMDS using iron and noble metal complexes as catalysts [37]

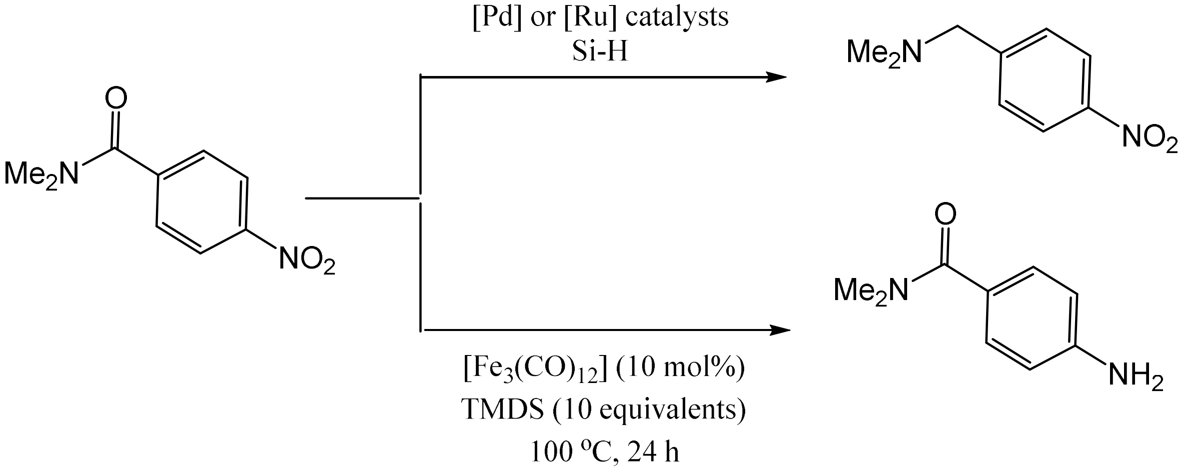
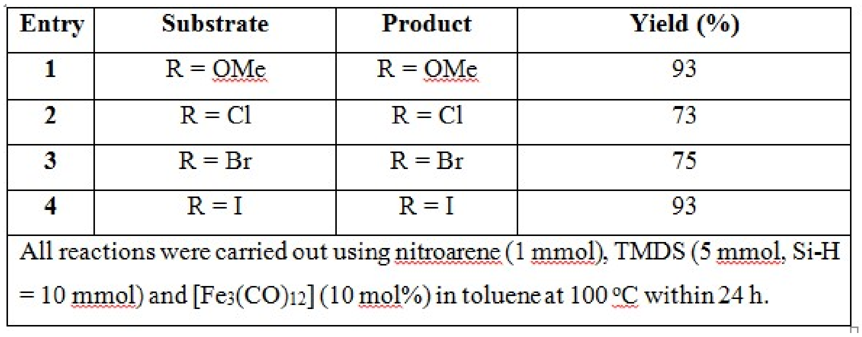
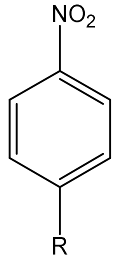


Table 1. Reduction of nitro aromatic compounds with TMDS using iron complex (e.g. [$Fe_3(CO)_{12}$]) as the catalyst [37]



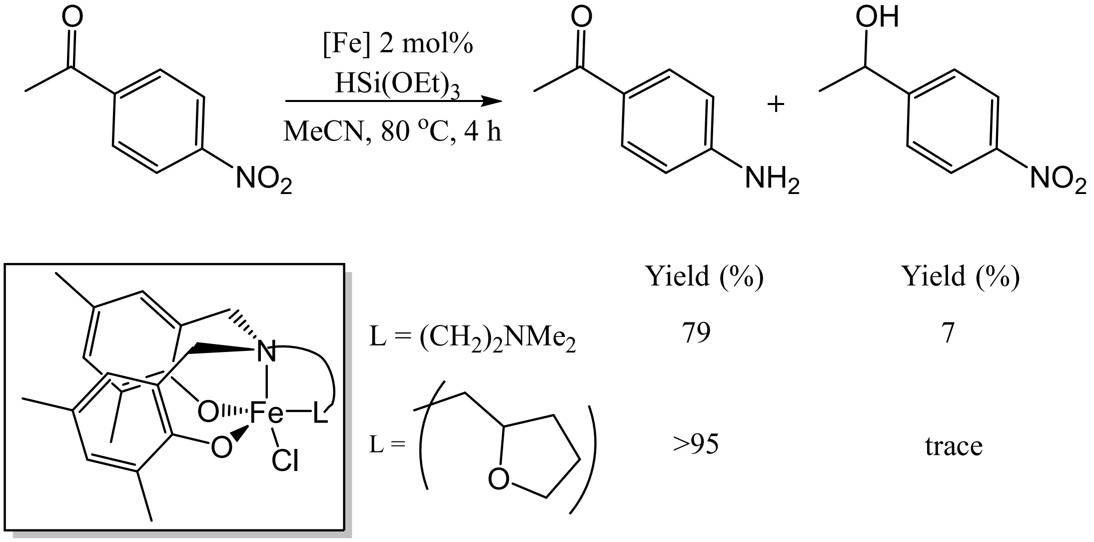
Entry	Substrate	Product	Yield (%)
1	R = OMe	R = OMe	93
2	R = Cl	R = Cl	73
3	R = Br	R = Br	75
4	R = I	R = I	93
All reactions were carried out using nitroarene (1 mmol), TMDS (5 mmol, Si-H = 10 mmol) and [$Fe_3(CO)_{12}$] (10 mol%) in toluene at 100 °C within 24 h.			



In 2010, Junge et al. applied iron salts ($FeBr_2$, FeI_2) in combination with tricyclohexyl phosphine (PCy_3) and triphenylphosphine ligands (PPh_3) for hydrosilylation of nitroarenes with phenylsilane ($PhSiH_3$) in toluene at 110 °C [48]. The best results, namely hydrosilylation of halogenated and methoxy nitro compounds (89-99% yields within 16 h) were achieved using 12 mol% of PPh_3 and 10 mol% of $FeBr_2$ in the presence of 2.5 equivalents of $PhSiH_3$ [48]. The presence of the phosphine ligands was found to be essential as the control experiments with 1-bromo-4-nitrobenzene in the absence of PPh_3 showed negligible conversion of 1-bromo-4-nitrobenzene to *p*-bromoaniline [48]. Besides halogenated nitroarenes, these systems proved effective in the reduction of nitroarenes with other functional groups, such as cyano, carboxylic groups, hydroxyl and etc. [48]. Very similar results were obtained in $Fe(acac)_3$-catalyzed (10 mol%) reduction of nitroarenes with an excess of TMDS, which at 60 °C required 24-48 hours [49-50].

Chemoselective reduction of nitroarenes having carbonyl functional groups was shown for iron(III)-amine-bis(phenolate)-catalyzed reduction of *p*-nitroacetophenone with triethyoxysilane $(EtO)_3SiH$ (Scheme 3) [51]. The reaction times and the selectivity were highly affected by the nature of different donor groups attached to the iron center and the nitrogen atom of the ligand (Scheme 3). For instance, when tetrahydro-2-furanyl group was present in the iron catalyst, the reduction proceeded faster and resulted in only trace amount of product derived from the reduction of carbonyl group (Scheme 3). Chemoselective reduction of nitro group was also observed for substrates bearing other potent reductive functional groups, such as nitriles, chloro, bromo, esters. Using 2 mol% of the catalyst in the presence of $(EtO)_3SiH$ in acetonitrile at 80 °C the reaction proceeded within 8 h [51].

Scheme 3. Effect of the ligand for iron(III)-amine-bis(phenolate) system [51]

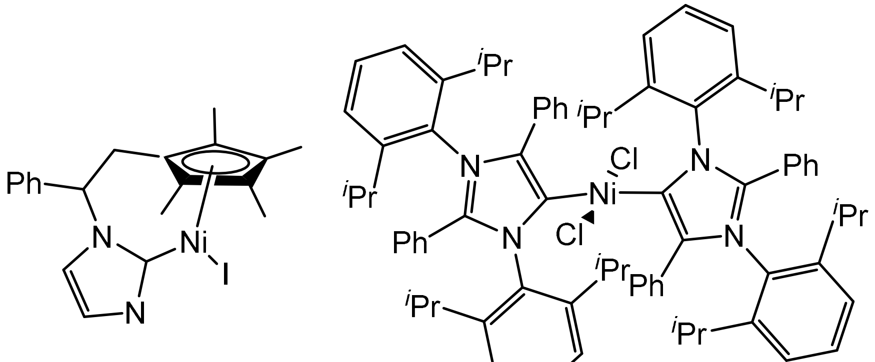


	Yield (%)	Yield (%)
L = $(CH_2)_2NMe_2$	79	7
L =	>95	trace

2.1.1.3 Nickel based catalysts

The application of nickel based homogenous catalysts for the reduction of nitro compounds is scarce. Unlike iron complexes, in the presence of PMHS (polymethylhydrosiloxane) using combination of Ni(acac)$_2$ with PPh$_3$ showed no reactivity towards the hydrosilative reduction of nitro compounds. Interestingly, without PPh$_3$ added Ni(acac)$_2$ showed an increased activity in hydrosilylation of nitroarenes [43]. Thus, with 10 mol% of Ni(acac)$_2$ and PMHS as the reductant resulted in the reduction of a series of nitro compounds to the corresponding amines within 3-5 h at 110 °C with the yields varying from 60% to 80%. In contrast, much longer reduction reaction times (12-16 h) were observed for FeBr$_2$/PR$_3$ (R = PCy$_3$, PPh$_3$ and MePPh$_2$) systems [48].

Introduction of N-heterocyclic carbenes as ligands for Ni catalysts (Figure 1) also proved effective and resulted in fast hydrosilative reduction of nitroarenes to the corresponding amines with PhSiH$_3$ [52-53].



1a **1b**

Figure 1. Ni-NHC complexes [10]

Using the compounds represented in Figure 1 as catalysts a series of iodine- and nitrile- containing aromatic nitro compounds were effectively and selectively reduced to the corresponding amines within 3 h in the presence of PhSiH$_3$ at 60 °C [52-53].

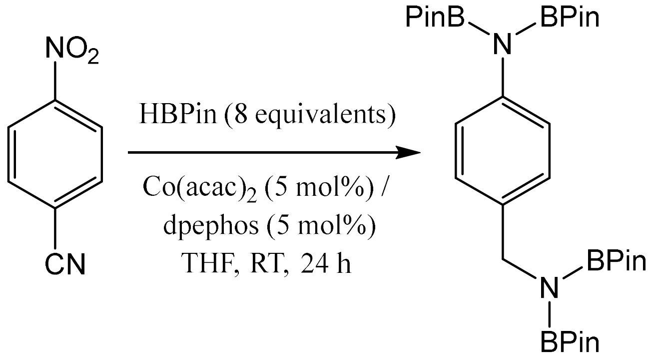
2.1.1.4 Cobalt based catalysts

Co-catalyzed hydrosilylation of nitro compounds to amines is unprecedented in the literature, however, Co systems find widespread applications in catalytic hydrosilylation of other classes of unsaturated organic molecules, such as alkenes [9, 54], alkynes [9, 55], aldehydes [56], ketones [56], nitriles [14] carboxamides [9], etc. Co-catalyzed hydrosilative reduction of carboxamides to amines was also previously studied in our laboratory and will be mentioned in the results and discussion part of this thesis.

2.1.2 Hydroborative reduction reactions

Hydroboration is another type of reduction reactions involving hydroboranes as reductants to perform the same catalytic transformations as reported above. Similarly to hydrosilative reductions, catalytic hydroborative reduction has attracted attention of the scientists and may serve as an alternative route to stoichiometric reactions for the production of amines [32]. However, compared to hydrosilylation, hydroboration of nitro compounds is underdeveloped. The only example of homogeneous transition metal catalyzed hydroboration of nitroarenes has been recently reported by our group for hydroboration of 4-nitrobenzonitrile with HBPin (Pin = pinacol) (8.0 equivalents) using 5 mol% of Co(acac)$_2$ in combination with dpephos (dpephos = bis[(2-diphenylphosphino)phenyl] ether) (5 mol%) [23]. The reaction resulted in reduction of both nitrile and nitro groups and proceeded to full conversion at room temperature within 24 hours (Scheme 4) [32].

Scheme 4. Cobalt-catalyzed hydroboration of 4-nitrobenzonitrile with HBPin [32]



2.1.3 Hydrogenation reactions

An effective methodology for ruthenium-catalyzed homogeneous hydrogenation of nitrobenzene to aniline was developed almost 45 years ago by Knifton (1976) [57]. Three different Ru-based catalysts, such as $RuCl_2(PPh_3)_3$, $[RuCl_2(CO)_3]_2$ and $RuCl_2(CO)_2(PPh_3)_2$ (1.6 mM of [Ru] catalyst) showed effective hydrogenation of nitrobenzene having >99% conversion within 7 h in benzene-ethanol mixture at 125 °C under 80 atm of molecular hydrogen [57]. In the same work, iron-catalyzed hydrogenation reactions were presented. Using the same reaction conditions as for Ru-catalyzed systems, the best results in hydrogenation of nitrobenzene (>99% conversions) were obtained for $Fe(CO)_3(PPh_3)_2$ and $Fe(CO)_3(AsPh_3)_2$ catalysts (1.6 mM of [Fe] catalyst) [57].

2.2 Heterogeneous catalysis

2.2.1 Catalytic hydrogenation of aromatic nitro compounds

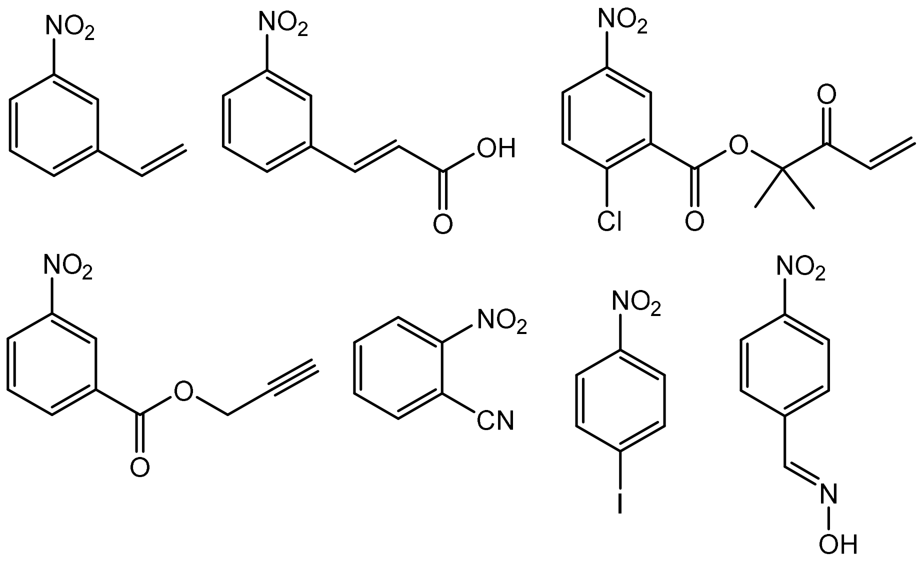
Historically, the reduction of nitro compounds with the aid of hydrogenation reactions has been studied extensively and these types of transformations are considered to be the most atom efficient and, therefore, more advantageous among all others methods for production of amines [10]. Beller and co-workers (2019) in their recent work summarized the most frequently applied methodologies in the industry for the production of aniline from the corresponding nitrobenzene (Table 2) [10]. However, the exact structure of the catalysts proposed by various chemical companies as well as the exact reaction conditions for these transformations are unknown since this information is hidden in patents [10].

Table 2. Reduction of aniline in industry [10]

catalyst	company	reaction conditions
Ni sulfides	Bayer, Allied	300-475 °C
Cu, Mn, Fe	ICI	300-475 °C
Pd/Al_2O_3	Bayer	250-350 °C; 7 bar
Cu/SiO_2 (Cr, Ba and Zn as promoters)	BASF, Cynamide	270-290 °C; 5 bar
Pd-Pt/C (Fe as modifier)	DuPont	90-200 °C; 6 bar

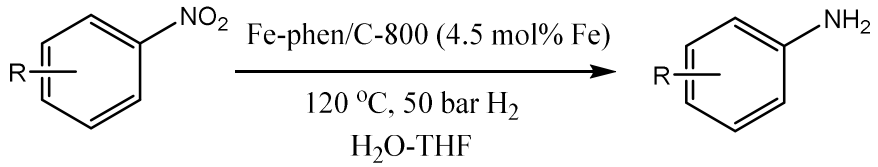
Table 2 shows some representative examples of such systems and illustrates that most of them require rather high temperature. Another problem associated with heterogeneously catalyzed hydrogenation of nitro compounds is the selectivity issues. For example, the hydrogenation of nitroarenes using well-known Pd/C and RANEY® nickel catalysts shows the lack of selectivity in the presence of heterocyclic substrates, halide and carboxylic acid functional groups [58]. Blaser et al. (2009) reported a numerous examples of industrially important and challenging nitro compounds that are not easily reduced due to selectivity issues associated with industrially applied heterogeneous catalytic hydrogenation systems (Scheme 5) [59]. Only a few catalytic systems, such as $Pd-Pb/CaCO_3$, $Fe-Pt/TiO_2$ and platinum colloids with nickel showed promising results to perform chemoselective hydrogenation of nitro groups of the substrates depicted in Scheme 5 [59]. The examples of efficient and selective base metal heterogeneous systems for hydrogenation of nitro compounds are still rather scarce [10].

Scheme 5. Examples of nitrocompounds reported by Blaser et al. [59]



Probably the first example of heterogeneous Fe-catalyzed hydrogenation of aromatic nitro compounds to amines was reported by Jagadeesh and co-workers in 2013 [60]. Firstly, the iron complex was synthesized using $Fe(OAc)_2$ ligated to 1,10-phenanthroline (phen). Then, the deposition of this complex was performed on the surface of carbon, followed by further pyrolysis at 800 °C to obtain catalytic active iron catalyst, namely Fe-phen/C [60-61]. The hydrogenation of various nitro compounds using 4.5 mol% of Fe-phen/C catalyst showed >99 % conversion of the substrates at 120 °C in H_2O-THF mixtures (Scheme 6) [60].

Scheme 6. Fe-phen/C-catalyzed hydrogenation of nitro compounds [60]



Wang et al. (2016) demonstrated one-pot synthesis of iron carbide embedded in graphene, which in turn was inserted into carbon nanotubes to obtain iron-based catalyst (Fe_3C@G-CNT) [62]. The schematic representation for the production of this catalyst initially derived from $FeCl_3$ is shown in Figure 2. 1 mol% of Fe_3C@G-CNT catalyst showed an excellent catalytic activity in the hydrogenation reactions of different aromatic nitro compounds with bromide, chloride, methoxy and methyl functionalities. The hydrogenation of the above-mentioned substrates led to the full conversion of the substrates within 3-8 h at 40-60 °C using 20 bar of molecular hydrogen [62].

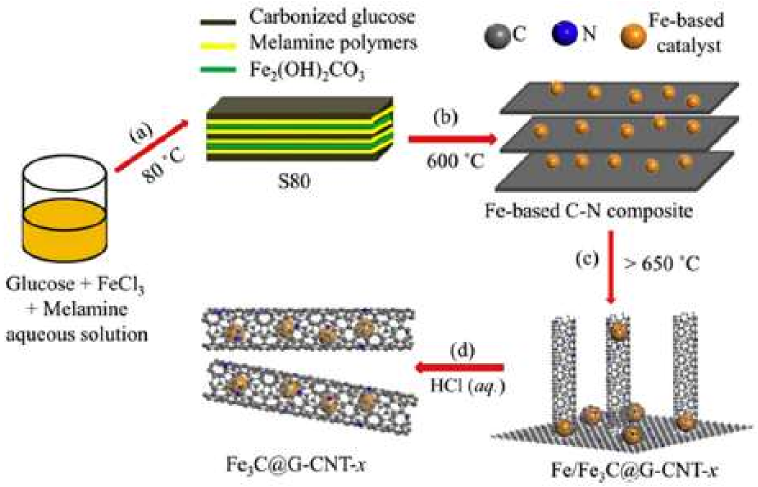


Figure 2. Fe_3C-based catalyst developed by Wang and co-workers (2016) [62]

Johnson and co-workers (2005) presented the application of metallic cobalt nanoparticles adsorbed on the surface of silica (SiO_2) for the hydrogenation of aromatic nitro compounds to the corresponding amines [63]. Using this cobalt colloidal catalyst, the hydrogenation of aromatic nitroarenes resulted in conversions of the substrates at 80-100 ^oC with 25 bar of H_2 [63]. This catalytic system provides the highest efficiency among other reported heterogeneous cobalt catalysts for the hydrogenation of nitro compounds to amines up to these days [10].

Recently, a novel nickel-based heterogeneous catalyst that can compete with RANEY$^{®}$ nickel for the reduction of aromatic nitro compounds in terms of hydrogenation reactions was suggested by Ryabchuk and co-workers (2018) [64]. Mixing commercially available $Ni(OAc)_2$ and 1,10-phenanthroline (phen) and treating this pre-catalyst on the surface of the support (silicide) with further pyrolysis at 1000 ^oC led to the formation of the nickel-based catalyst [64]. This nickel catalyst (4 mol%) was highly catalytically active in hydrogenation of 10 different aromatic nitroarenes in H_2O/MeOH resulting in excellent conversions varying from 93-99% within 20 h at 60 ^oC and 10 bar of H_2 [64].

Although hydrogenation methodologies described above are considered to be the most atom economic and are commonly used on industrial scale for production of amines there are still some challenging issues associated with them, such as harsh reaction conditions (e.g. high pressure, elevated temperatures), sophisticated experimental setup, long reaction times and difficulties with handling the molecular hydrogen [10]. Many of these issues can be resolved by implementing an alternative hydrogen source, such as metal hydrides [65] (e.g. $NaBH_4$ [66] and $LiAlH_4$ [67]) and hydrazine [68].

2.2.2 Reduction of nitroarenes with $NaBH_4$ by precious metal systems

Similarly to other reduction reactions, the reactions of nitro compounds with $NaBH_4$ are mostly catalyzed by precious metals [69]. Such catalytic systems are well studied and there is a plethora of precious metal systems that proved effective in reduction of nitroarenes with $NaBH_4$ [70]. Since this thesis focuses on development of base metal systems, only a few examples of catalysts based on precious metals are discussed below. Special attention is paid to the systems that catalyze reduction of nitrophenols in water.

Thus in 1970s, Lipowitz and co-workers presented an example of the reduction of nitrobenzene using 5 mol% of Pd/C system and 3 equivalents of PMHS as reductant in ethanol at 60 ^{o}C within 1 h [71].

Xu and co-workers (2013) developed a novel system based on platinum nanoparticles for an effective reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$ in water, showing full conversion of nitrophenol within 15 min at room temperature [72].

In 2015, Goksu proposed a catalyst based on Pd for an effective reduction of aromatic nitro compounds to the corresponding aromatic amines using $NaBH_4$ as the reductant [73]. This catalyst was supported on aluminum oxy-hydroxide (AlO(OH)). Thus, by using 25 mg of this catalyst and 3 equivalents of $NaBH_4$, the hydrogenation of various aromatic nitroarenes was achieved with 99% conversions at room temperature [73].

The example of heterogeneous noble metal catalyzed reduction of 2-nitrophenol in an aqueous media has been recently reported by Inglezakis and co-workers (2018) [74]. The most catalytically active catalyst was found to be Pd nanoparticles on the surface of modified silica (TEOS-SiO_2) (TEOS = tetraethyl orthosilicate) compared to other systems based on gold, platinum and ruthenium [74]. Thus, by using 5 mg of Pd/SiO_2 nanocomposite and excess of $NaBH_4$, the reduction of 2-nitrophenol to 2-aminophenol was achieved with full conversion of the substrate at room temperature within 15 min [74].

2.2.3 Reduction of nitroarenes with $NaBH_4$ catalyzed by Earth abundant metal systems

2.2.3.1 Cobalt based catalysts

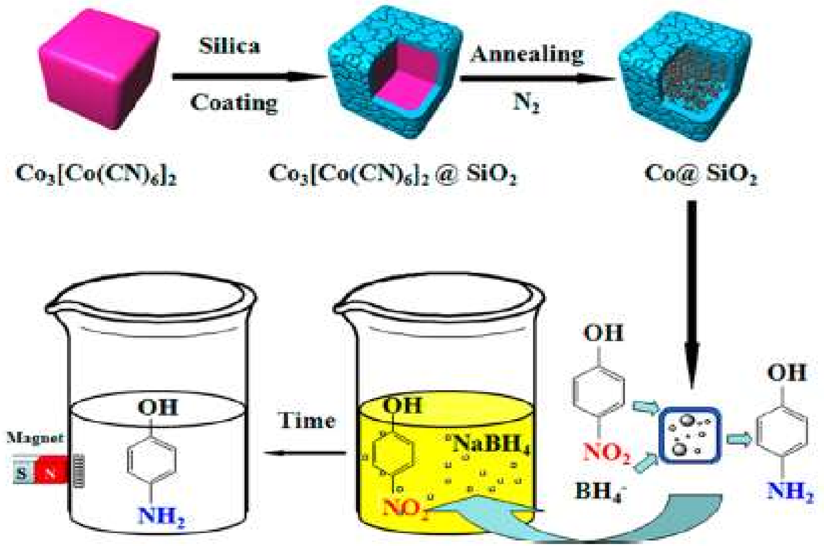
In the transition metal catalyzed heterogeneous reduction reactions involving $NaBH_4$, 4-nitrophenol is commonly used as the model substrate [10]. The commercially available mixed cobalt (II/III) oxide (Co_3O_4) (100 mg) showed the effective reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$ in water at 30 ^{o}C in 2 minutes with full conversion of the substrate [75]. Interestingly, mesoporous Co_3O_4 provided even greater catalytic activity for the same transformation than the regular Co_3O_4 [76]. Thus, 2 mg of mesoporous Co_3O_4 was effective in reduction of 4-nitrophenol in water with $NaBH_4$ within 70 minutes at room temperature [76]. With the aim to improve the catalyst activity, Meziane et al. (2017) applied cobalt nanoparticles derived from Co_3O_4 on silica for reduction of nitrophenols with aqueous solution of $NaBH_4$ but no improvement of catalytic activity was observed [77].

Pina et al. (2014) have reported that enhanced (compared to Co_3O_4) activity in reduction of nitrobenzene in water at room temperature with $NaBH_4$ in 1 h was observed for Co_3S_4 (99.9% conversion), which also showed greater catalytic activity among other base metal sulfides, Fe_3S_4 (9.3% conversion), CuS (11.2% conversion), ZnS (10.9% conversion) and NiS (96.3% conversion) [78].

The same year, Yan et al. (2014) applied silica-supported Co nanoparticles (Co NPs) (1 mg), derived from $Co_3[Co(CN)_6]_2$ via sol-gel technique, for the reduction of 4-nitrophenol with $NaBH_4$ at room temperature in water with full conversion of the substrate within 5 minutes [79].

Few years later, Li et al. (2016) developed cobalt nanoparticles on graphene using cobalt-metal organic frameworks and tested the reactivity of this catalyst in the reduction of nitrophenol to aminophenol [80]. The effective reduction of 4-nitrophenol to 4-aminophenol showing full conversion of the substrate in an aqueous media at room temperature was performed using (0.06 mg) Co@graphene catalyst and an excess amount of $NaBH_4$ in 4 minutes [80]. Interestingly, comparative analysis of the kinetics of this reaction vs. the reduction of 4-nitrophenol catalyzed by silica-supported cobalt nanocomposites reported by Yan et al. (2014) revealed similar catalytic activity of Co@graphene and Co@silica systems, as indicated by almost identical rate constant for both transformations (about 10^{-2} s^{-1}) [79-80]. As indicated in Scheme 7, the advantage of this system is that the catalyst material can be easily separated from the mixture using magnetic field.

Scheme 7. Cobalt nanoparticle on the surface of silica for further reduction reactions [79]

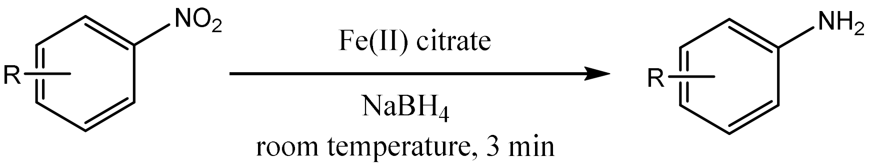


Promising results in reduction of 4-nitrophenol with aqueous $NaBH_4$ were also reported by Zhan et al. (2016) [81] using Co-N-C catalytic system, which was obtained by high temperature pyrolysis of cobalt cobalt complexes ligated to the nitrogen-containing ligand, such as histidine [81]. This material composite (50 mg) was used to obtain composite with silica with pore size <1 nm, which showed excellent catalytic activity in the production of 4-aminohenol from 4-nitrophenol at room temperature in water within 3 min [81].

2.2.3.2 Iron based catalysts

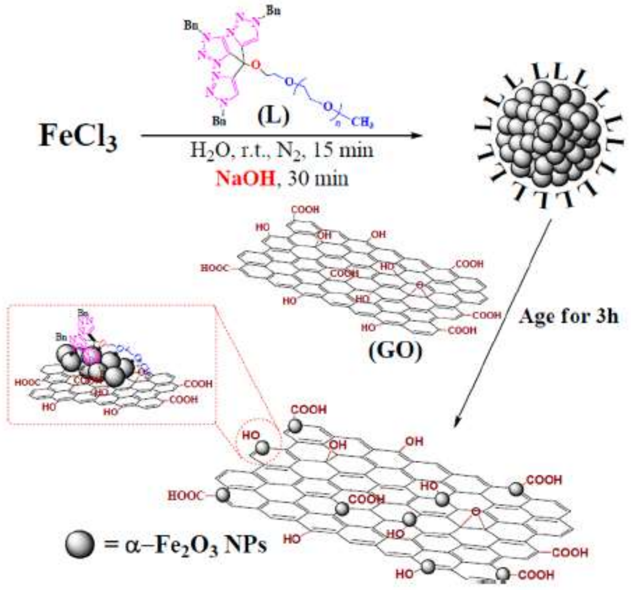
During the last decade, the reduction of nitro compounds with $NaBH_4$ in water has been demonstrated using heterogeneous iron based catalytic systems [10]. Thus, He et al. (2016) and Bae et al. (2016) both reported the application of iron nanoparticles for the reduction of the nitroarenes to corresponding amines group in the presence of $NaBH_4$ [82-83]. The catalyst presented by He and co-workers was obtained by reduction of commercially available $FeCl_2$ with excess $NaBH_4$ to obtain metallic Fe NPs. Recovering the catalyst material after the reduction reaction and subjecting it to the second reduction cycle showed significant reduction of the catalyst activity [83]. In contrast, effective and recyclable catalytic iron based system was reported using Fe(II) citrate / $NaBH_4$ (Scheme 8) [82]. The complete reduction of 4-nitrophenol to 4-aminophenol in water with $NaBH_4$ was achieved at room temperature within 3 min using the Fe(II) citrate catalyst ($[Fe^{2+}] = 0.8$ mmol L^{-1} and [citrate] $= 0.013$ mmol L^{-1}) [82]. The catalyst was used five times without any activity loss; however, a decrease of the catalytic activity of this system was evident since the sixth catalytic run [82].

Scheme 8. Iron catalyst proposed by He and co-workers [82]

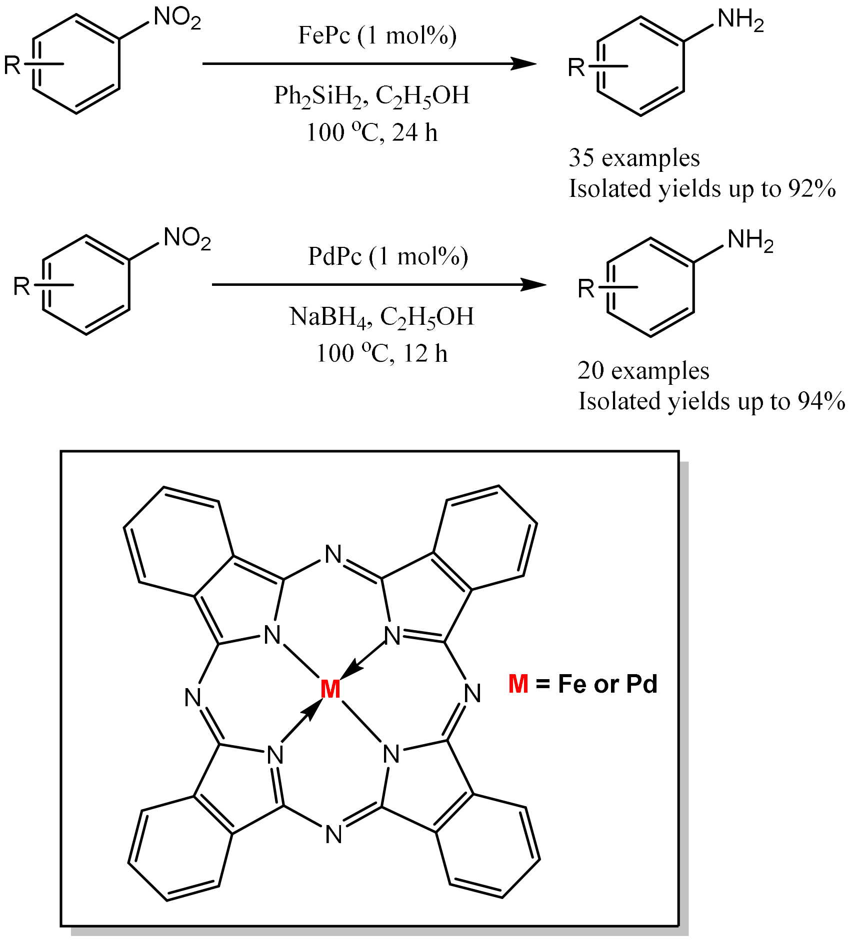


In 2017, Wang and co-workers disclosed another effective and recyclable iron-based catalytic system for reduction of nitro compounds with $NaBH_4$ in an aqueous media [84]. The catalyst material consists of α-iron(III) oxide nanoparticles on the surface of graphene oxide and was prepared in an aqueous solution by mixing commercially available $FeCl_3$ with tris(triazolyl)-polyethylene glycol (tris-trz-PEG) followed by reduction with NaOH [84]. The resulting material was deposited on the surface of graphene oxide (Scheme 9) and subjected to reduction of 4-nitrophenol with $NaBH_4$ in water, showing no loss of the catalytic activity even during the fourth catalytic run [84].

Scheme 9. Iron catalyst proposed by Wang and co-workers [84]



Scheme 10. Fe-phen-catalyzed reduction using Ph2SiH2 [85]



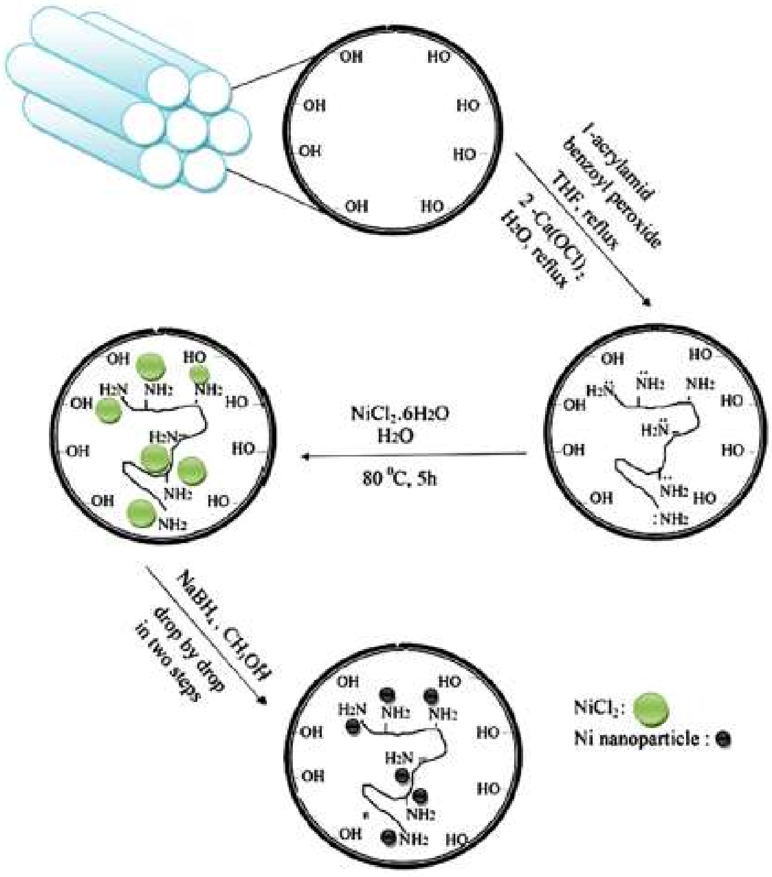
Application of 10 mol% of heterogeneous Fe(II) phthalocyanine catalyst for the same type of reduction in the presence of diphenylsilane (Ph_2SiH_2) showed high yields (Scheme 10) [85]. Moreover, the selective reduction of dinitrocompounds in order to obtain monoaminobenzenes and diaminobenzenes was achieved by varying the amount of Ph_2SiH_2 [85]. However, they also reported that the reduction of aldehydes proceeded much faster compared to nitroarenes [85].

2.2.3.3 Nickel based catalysts

Reduction of nitroarenes with $NaBH_4$ was also achieved using heterogeneous nickel catalysts. Similarly to other base metals, the best results were shown for systems with zero valent nickel. Thus, the well-known RANEY® nickel (10 mol%) was found to mediate the reduction of various aromatic nitro compounds with $NaBH_4$ [86]. High substrate conversions (10 examples of nitro compounds with 85-99% product yields) were observed in methanol at 40 ^oC within 20 min [86]. Inspired by these results, Rahman and Jonnalagadda (2008) prepared various nickel catalysts supported on TiO_2 and SiO_2 and studied the effect of the loading of the nickel for the reduction of aromatic nitro compounds [87]. According to these studies, the most effective was found the catalyst material having 5 mol% of Ni on silica, which resulted in full reduction of nitroarenes with $NaBH_4$ at 5 ^oC within 20 min [87].

Reduction of aromatic nitro compounds with $NaBH_4$ using nickel nanoparticles was also reported by Babaknezhad and co-workers (2011) [88]. The schematic representation of the method for production of this catalyst material is depicted in Scheme 11. Thus, the polymerization reaction of acrylamide on the surface of modified silica SBA-15 was carried out by benzoyl peroxide in THF. The product of the polymerization reaction is the polyacrylamide, which upon the addition of the calcium hypochlorite ($Ca(OCl)_2$) in aqueous solution led to the formation of polyvinylamine (PVAm) [88]. This was followed by addition of nickel(II) chloride hydrate in water and further reduction with $NaBH_4$ resulting in formation of anchored nickel nanoparticles [88]. Babaknezhad et al. (2011) reported the effective application of this system in the reduction of various nitro compounds with the obtained yields greater than 98% within 2-85 min at room temperature. The reduction reactions were carried out in water using excess amount of $NaBH_4$ under pseudo-first order regime [88].

Scheme 11. Preparation of Ni-based catalyst [88]



Chapter 3 – Materials and Methods

3.1 Materials

$CoCl_2$, $Co(OAc)_2*4H_2O$, $Co(acac)_2$, bis[(2-diphenylphosphino)phenyl] ether (dpephos), $PhSiH_3$, $(EtO)_3SiH$, Na_2SO_4, NaOH, HCl, $NaBH_4$, $LiHBEt_3$ (1.0 M in THF), hydrogen chloride solution (4.0 M in dioxane), nitrobenzene, 2-nitrophenol, 4-nitrophenol were purchased from Sigma-Aldrich and used without any additional purification. All solvents (tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), diethyl ether (Et_2O) and dichloromethane (DCM)) were dried using appropriate drying agents. All aqueous solutions were made using ultrapure water.

3.2 Equipment

The instrumentations used during this work include JEOL JNM-ECA 500 MHz for nuclear magnetic resonance (NMR) analysis; Evolution 300 UV-Vis Spectrophotometer for catalytic reduction reactions analysis; TSQ 8000 Evo Triple Quadrupole GC-MS/MS for product analysis; NanoDrop 2000C Spectrophotometer for kinetics studies; both Scanning Electron Microscope JSM-IT200(LA) and Scanning Electron Microscope Crossbeam 540 to obtain SEM images of the composites with EDS maps; Rigaku SmartLab® X-ray diffraction (XRD), XRF Axios Max PANalytical and Raman Spectroscopy (The Horiba LabRam Evolution) for characterization analysis**.**

3.3 Experimental procedure

3.3.1 Homogeneous catalytic hydrosilative reduction of amides

To the mixture of bis[(2-diphenylphosphino)phenyl] ether (13.2 μmol) and either $Co(acac)_2$ (12 μmol) or $Co(OAc)_2$ (12 μmol), amide substrate (0.24 mmol), followed by $PhSiH_3$ (44.4 μl, 0.36 mmol) were added in 0.5 ml of THF in an NMR tube. The NMR tube was sealed and, depending on the amide substrate, was left at either room temperature or 60 ^oC or 100 ^oC and the reaction was monitored by NMR spectroscopy.

3.3.2 Homogeneous NMR scale catalytic hydrosilative reduction of nitrobenzene and nitrophenols with $PhSiH_3$ and $(EtO)_3SiH$

A. To the mixture of bis[(2-diphenylphosphino)phenyl] ether (42.8 μmol) and $Co(acac)_2$ (38.9 μmol), nitrobenzene (0.78 mmol), followed by $PhSiH_3$ (143.8 μl, 1.16 mmol) were added in 0.5 ml of THF in NMR tube. The tube was sealed and left at room temperature for 5 h and then, at 60 ^oC for an additional 5 h. The reaction was monitored by NMR spectroscopy.

B. To the mixture of bis[(2-diphenylphosphino)phenyl] ether (42.8 μmol) and Co(acac)$_2$ (38.9 μmol), either 4-nitrophenol or 2-nitrophenol (0.78 mmol), followed by PhSiH$_3$ (532 μl, 2.33 mmol) were added in 0.5 mL of THF in NMR tube. The tube was sealed and left at room temperature with monitoring of the reaction by NMR spectroscopy.

C. To the mixture of bis[(2-diphenylphosphino)phenyl] ether (42.8 μmol) and Co(acac)$_2$ (38.9 μmol), 2-nitrophenol (0.78 mmol), followed by (EtO)$_3$SiH (663.4 μl, 1.94 mmol) were added in 0.5 mL of THF in NMR tube. The tube was sealed and left at room temperature with monitoring of the reaction by NMR spectroscopy.

3.3.3 Homogeneous catalytic hydroborative reduction of nitro compound

To the mixture of bis[(2-diphenylphosphino)phenyl] ether (5 mol%) and Co(acac)$_2$ (5 mol%), nitro compound (1 mmol), followed by HBPin (5-8 equivalents) were added in 0.5 mL of THF in NMR tube. The tube was sealed and left at room temperature with monitoring of the reaction by NMR spectroscopy.

3.3.4 Heterogeneous reduction with free cobalt nanoparticles

The experimental procedure to generate free cobalt nanoparticles to catalyze the reduction of nitro compounds was done in analogy with recent article published by Michon and co-workers (2018) [94].

In a Schlenk tube, Co(OAc)$_2$*4H$_2$O (12.45 mg, 0.05 mmol) was weighed and dried in vacuo at 80 °C oil bath for 1 h. Then, 7 ml of 1,2-dimethoxyethane was added and the Schlenk tube was placed on pre-heated oil bath at 60 °C for 40 min, followed by addition of LiHBEt$_3$ (100 μl, 0.1 mmol, 1.0 M in THF). After 5 min, PhSiH$_3$ (616.3 μl, 5 mmol) and substrate (either nitrobenzene or 4-nitrophenol) (1 mmol) were added under inert atmosphere. The reaction was left stirring at room temperature for 20 h.

To isolate the product, initially, upon the reaction completion, the contents of the Schlenk tube was gone through Celite and washed several times with dichloromethane. After, the acid-based extraction was performed. 10 ml of HCl (2 M) was added to the flask and the reaction mixture was extracted with water (2 x 10 ml), then, after collecting the aqueous layer, NaOH (2 M) was added to this layer. Finally, the product was extracted using Et$_2$O, the organic layer was collected and dried over Na$_2$SO$_4$.

Later, the procedure for product isolation was optimized. Thus, hydrogen chloride solution in dioxane (4.0 M) was used to convert the obtained amine to the corresponding ammonium salt, [Ph(NH$_3$)]Cl.

The reaction was also repeated using Co(acac)$_2$ (0.05 mmol) instead of Co(OAc)$_2$*4H$_2$O (0.05 mmol).

3.3.5 Heterogeneous reduction with silica supported composites

The synthesis of Co-SiO_2 composites was performed in analogy with the procedure reported by Inglezakis and co-workers (2018) [74]. Three composites derived from aqueous solutions of $Co(OAc)_2$ (9.77×10^{-3} M) and CoCl2 (1.26×10^{-2} M and 1.00×10^{-2} M) were synthesized using modified silica with two different concentrations of activated Si-H bonds per gram of silica ((0.9 mmol of Si-H)/g and (1.2 mmol of Si-H)/g). The experimental procedure is depicted below. The silica (SiO_2) was modified with tetraethyl orthosilicate (TEOS) according to the procedure reported by Katok (2012) [89] and Inglezakis and co-workers (2018) [90].

108.63 mg of TEOS-SiO_2 (0.9 mmol of activated Si-H / 1 g of silica) was placed in a vial containing 12.17 mg of $Co(OAc)_2$*$4H_2O$ and 5 ml of ultrapure water. The vial was left stirring overnight at room temperature in the dark. The centrifugation of the reaction mixture was done, the aqueous solution was carefully decanted and the composite was washed with fresh ultrapure water several times and dried in an oven at 80 ^{o}C overnight.

100.15 mg of TEOS-SiO_2 (1.2 mmol of activated Si-H / 1 g of silica) was placed in a vial containing 8.18 mg of $CoCl_2$ and 5 ml of ultrapure water. The vial was left stirring overnight at room temperature in the dark. After that, the centrifugation of the reaction mixture was done, the aqueous solution was carefully decanted and the composite was washed with fresh ultrapure water several times and dried in an oven at 80 ^{o}C overnight.

200.03 mg of TEOS-SiO_2 (1.2 mmol of activated Si-H / 1 g of silica) was placed in a vial containing 5.20 mg of $CoCl_2$ and 4 ml of ultrapure water. The vial was left stirring overnight at room temperature in the dark. After that, the centrifugation of the reaction mixture was done, the aqueous solution was carefully decanted and the composite was washed with fresh ultrapure water several times and dried in an oven at 80 ^{o}C overnight.

3.3.6 Heterogeneous catalytic reduction of 2-nitrophenol with $NaBH_4$ using Co-SiO_2 composites

The reduction of 2-nitrophenol was performed in a quartz cuvette and the reaction was analyzed with UV-Vis spectrophotometer every 2.5 min. 5 mg of composite was placed into a cuvette already containing 2-nitrophenol (1.5 ml, 0.0003M) and aqueous solution of $NaBH_4$ (1.5 ml, 0.3 M).

3.3.7 Kinetics studies procedure

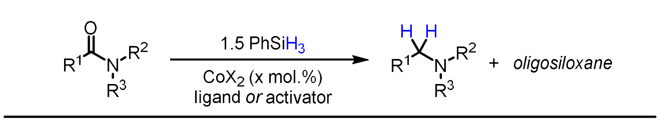
The reduction of 2-nitrophenol was carried out using three different Co-SiO_2 composites derived from $Co(OAc)_2$ and $CoCl_2$. Additionally, two control experiments for reduction of 2-nitrophenol were performed using $Co(OAc)_2$ and $CoCl_2$ in order to compare the activity of composites with cobalt salts. In addition, the kinetics studies were performed using the aliquots from the reaction mixture at specified times and the reaction product was analyzed with UV-vis NanoDrop apparatus at room temperature.

The reduction of 2-nitrophenol (1.5 ml, 0.0003 M) was performed using either 2 mg of composite material (0.34 μmol%, 1.01 μmol% and 0.356 μmol% of cobalt) or aqueous solution of cobalt salts ($Co(OAc)_2$ (4 μl, $8.47x10^{-2}$ M, 0.34 μmol%), $CoCl_2$, (4 μl, $8.47x10^{-2}$ M, 0.34 μmol%)) and aqueous solution of $NaBH_4$ (1.5 ml, 0.15 M). The reactions were analyzed with UV-Vis spectrophotometer.

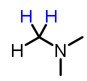
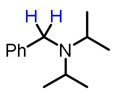
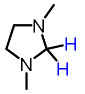
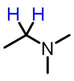
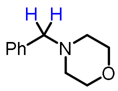
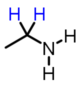
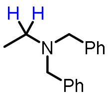
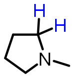
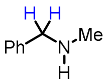
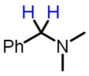
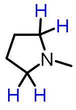
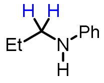
Chapter 4 – Results and Discussion

Based on literature review, cobalt based catalysts for the hydrosilative reduction of nitro compounds are limited. However, somewhat related Co-catalyzed mild deoxygenative hydrosilative reduction of tertiary carboxamides to the corresponding amines has been recently developed in our research group using commercially available $Co(acac)_2$, $Co(OAc)_2$ and $CoCl_2$ and bis[(2-diphenylphosphino)phenyl] ether (dpephos) and PPh_3 ligands [9]. For $Co(OAc)_2$ and $Co(acac)_2$ (OAc = acetate; acac = acetylacetonate) the reactions were activated by $PhSiH_3$ reductant, whereas in the presence of $(dpephos)CoCl_2$ (5 mol%) 10 mol% of $LiBHEt_3$ was used as an external activator (Table 3) [9]. All systems, $Co(OAc)_2$, $Co(acac)_2$ and $CoCl_2$, were found effective for mild reduction of cyclic, aromatic and aliphatic tertiary carboxamides to the corresponding tertiary amines in the presence of $PhSiH_3$ with many examples of room temperature transformations (Table 3) [9]. Our mechanistic studies by variable-temperature nuclear magnetic resonance (NMR) spectroscopy indicated that the reactions start with the reduction of Co(II) pre-catalysts to catalytically active Co(I) hydride species [9].

Table 3. Cobalt based hydrosilative reduction of amides [9]



A = $(dpephos)CoCl_2$ / $LiBHEt_3$ (5/10 mol.%)
B = $Co(acac)_2$ / dpephos (5/5.5 mol.%)
C = $Co(OAc)_2$ / dpephos (5/5.5 mol.%)
D = $Co(acac)_2$ / PPh_3 (5/10 mol.%)
E = $Co(acac)_2$ / dpephos (0.5/0.55 mol.%)
F = $Co(OAc)_2$ / PPh_3 (5/10 mol.%)

Product	Catalytic system	T, °C / *t*, h	Conv., %	Product	Catalytic system	T, °C / *t*, h	Conv., %	Product	Catalytic system	T, °C / *t*, h	Conv., %
	**A-F** **A-C, F** **E** **D**	60 / 5 25 / 5 25 / 6.5 25 / 24	>99 >99 >99 79		**A** **B** **B** **E**	60 / 5 25 / 17 60 / 5 60 / 24	>99 >99 >99 72		**A** **A** **B**	60 / 5 65 / 16 100 / 24	28 44 15
	**A** **B** **E** **E**	60 / 5 25 / 17 60 / 5 60 / 24	>99 >99 82 94		**A** **B** **B** **E**	60 / 5 25 / 17 60 / 5 60 / 24	>99 87 85 87		**B** **B** **B**	75 / 24 75 / 48 75 / 72	45 73 >99
	**A** **B** **D** **E** **E**	60 / 5 25 / 3 25 / 24 25 / 32 60 / 5	>99 >99 80 68 >99		**A** **B** **E**	60 / 5 25 / 17 60 / 24	>99 >99 61		**B** **B**	75 / 24 75 / 48	89 >99
	**A** **B** **E** **E**	60 / 16 60 / 24 60 / 24 60 / 48	91 >99 28 37		**A** **A** **B** **E**	60 / 5 65 / 16 25 / 24 60 / 24	>99 96 90 43		**B**	60 / 60	>99

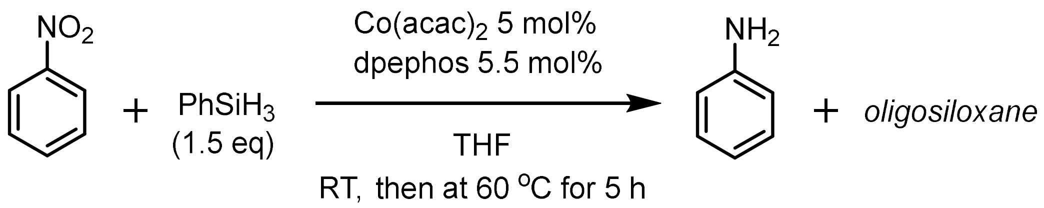
According to Table 3 (entry 1), it can be seen that the reduction of dimethylformamide showed conversion of >99 % at 60 °C within 5 h for all the applied cobalt pre-catalysts even upon the substitution of the dpephos ligand with PPh_3. With dpephos as ligand the reactions can be conducted even at room temperature, showing full conversion of dimethylformamide in 5 hours.

High conversions to amines were also found for aromatic carboxamides (Table 3). For instance, the reduction of *N,N*-dibenzylacetamide at room temperature using $Co(acac)_2/PPh_3$ and $Co(acac)_2$/dpephos systems resulted in 80% in 24 h and >99 % in 3 h conversions, respectively [9]. By comparing the proposed three pre-catalysts, the most active cobalt pre-catalyst for the reduction of tertiary amides to the corresponding amine derivatives is found to be $Co(acac)_2$/dpephos system. This system has shown excellent reduction reactions at room temperature with the conversions starting from 90% up to >99% using 1.5 eq. of $PhSiH_3$ for the eight different amides [9]. In addition, while performing the reduction of amides using the previously mentioned system, the compounds bearing ester, nitrile and alkene functional groups were tolerated [9]. Overall, the developed Co system represents only the second example of mild (<100 °C) base metal catalyzed hydrosilative reduction of tertiary amides to amines. The first example was based on manganese and was shown by Turculet and co-workers in 2017 [91-92].

4.1 Homogeneous hydrosilative reduction of nitro compounds with $Co(acac)_2$/dpephos system

Inspired by the successful reduction of tertiary amides under mild conditions, we turned our attention towards the reduction of aromatic nitroarenes using the most active pre-catalyst among others from previously reported work, namely $Co(acac)_2$ / dpephos system. The experimental procedure for the hydrosilative reduction of nitrobenzene was performed in analogy with amides previously reported by our research group (Khalimon and co-workers (2018)) [9] (Scheme 12).

Scheme 12. Hydrosilative reduction of nitrobenzene

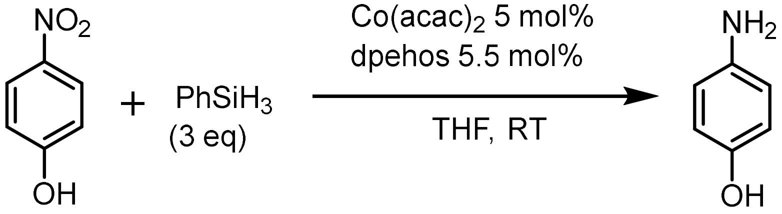


Using $Co(acac)_2$ (5 mol%), dpephos (5.5 mol%) and $PhSiH_3$ (1.5 equivalents), the successful reduction of nitrobenzene in THF was accomplished at 60 °C within 5 h showing full conversion of the substrate. Initially, the reaction was attempted at room temperature but did not show any significant conversion of nitrobenzene within 5 h. Additionally, the formation of oligosiloxanes was also observed during the reaction. We assume, that similar to deoxygenative hydrosilative reduction of carboxamides [9], the reduction of nitro compounds mediated by $Co(acac)_2$/dpephos proceeds via intermediacy of the Co(I) hydride species, akin to (dpephos)Co-

H. After the reaction, aniline was converted to hydrochloride salt, which was isolated in 30% yield. We assume that such low yield of the isolated product is associated with partial solubility of $[PhNH_3]Cl$ in THF/Et_2O solutions since almost full conversion of the starting nitrobenzene and no formation of by products were observed by NMR spectroscopy during the reaction. ^1H NMR spectra of aniline and $[Ph(NH_3)]Cl$ are shown in Figures 3 and 4 respectively (refer to Appendix A).

The same catalytic transformation using 4-nitrophenol as the substrate was accomplished as depicted in Scheme 13. Interestingly, as can be seen from the ^1H NMR spectrum for this reaction (Figure 5 in Appendix A), full conversion of 4-nitrophenol was observed; however, both ^1H NMR and GC-MS spectra were inconclusive. Repeating the experiment on a larger scale using the same reaction conditions with further treatment of the reaction mixture with hydrogen chloride solution in dioxane (4.0 M) to isolate the product led to the formation of a hydrochloride salt of 4-aminophenol. The ^1H and ^{13}C NMR spectra of the reaction product are shown in Figures 6-8 (Appendix A).

Scheme 13. Hydrosilative reduction of 4-nitrophenol



4.2 Homogeneous hydroborative reduction of nitro compounds with $Co(acac)_2$/(dpephos) system

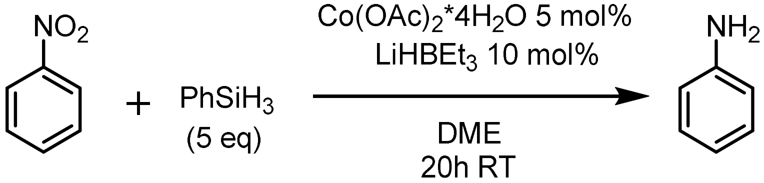
As previously stated in the literature review, hydroborative reduction of nitro compounds is underdeveloped. Considering our results in Co-catalyzed hydrosilative reduction of nitrobenzene and nitrophenols and believing that compared to hydrosilanes hydroboranes, such as HBPin (Pin = pinacol) and HBCat (Cat = catechol), might show excellent reactivity due to B-H bond possessing more hydridic character in comparison with Si-H bond in hydrosilanes; and the increased Lewis acidity of boron center compared to silicon center, we elected to study the hydroborative reduction of aromatic nitro compounds. Prior to this research, the only example of homogeneous transition metal catalyzed hydroboration of nitroarenes has been recently reported by our group for hydroboration of 4-nitrobenzonitrile with HBPin (Pin = pinacol) (8.0 equivalents) using 5 mol% of $Co(acac)_2$ in combination with dpephos (dpephos = bis[(2-diphenylphosphino)phenyl] ether) (5 mol%) [32]. The reaction resulted in reduction of both nitrile and nitro groups and proceeded to full conversion at room temperature within 24 hours (Scheme 4) [32].

As expected, using only 0.5 mol % of both Co(acac)$_2$ and dpephos, nitrobenzene was fully converted to monoboryl amine derivative PhN(H)BPin within only 1 hour at room temperature. Increasing the catalyst loading to 1-5 mol% results in almost instantaneous conversion of nitrobenzene to PhN(H)BPin. After the completion of the reaction was confirmed by NMR spectroscopy, the reaction mixture was treated with exess HCl in dioxane (4.0 M) and the product was isolated in the form of hydrochloride salt, [Ph(NH$_3$)]Cl in 46% yield (Figure 9 in Appendix A).

4.3 Reduction of aromatic nitro compounds using free cobalt nanoparticles

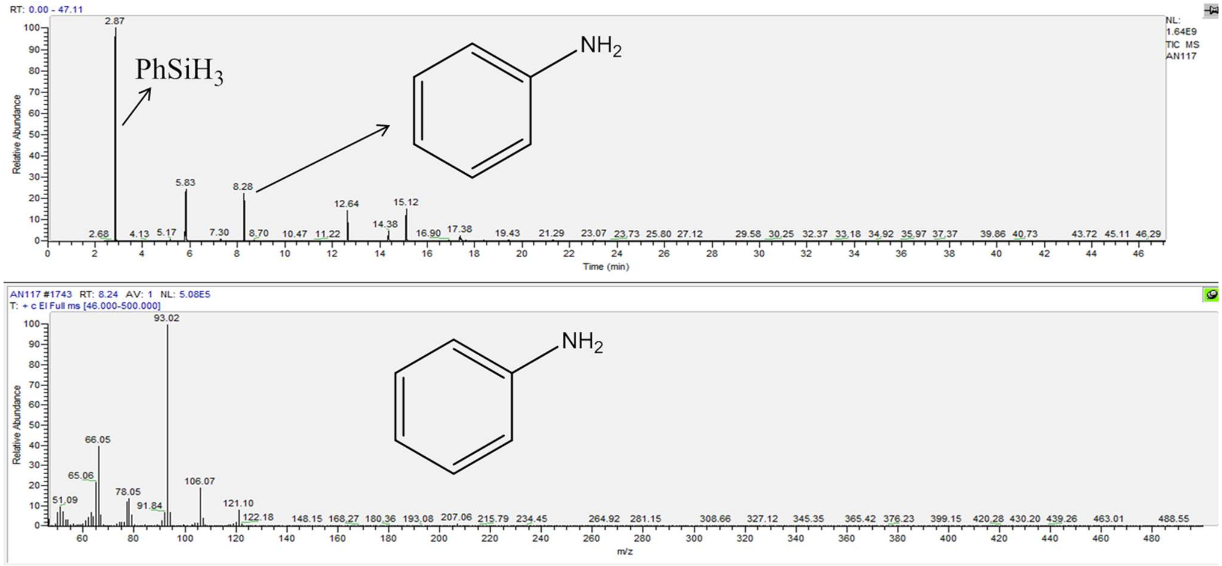
Using the procedure, reported previously by Michon and co-workers (2018) [94], free cobalt nanoparticles generated in situ by reaction of Co(OAc)$_2$ with LiHBEt$_3$ in 1,2-dimethoxyethane. These nanoparticles (5 mol% of Co) were subjected to catalytic reduction of nitrobenzene with PhSiH$_3$ in DME at room temperature (Scheme 14). Within 20 h of reaction, ^{1}H NMR analysis of the reaction mixture showed full conversion of the substrate. Full conversion of nitrobenzene was also confirmed by GC-MS, which also showed the presence of the desired product of this reduction, aniline, with retention time of 8.28 min (Figure 10).

Scheme 14. Heterogeneous reduction of nitrobenzene with free cobalt nanoparticles



The reaction product was then treated with hydrogen chloride solution in dioxane (4.0 M) to successfully obtain the corresponding hydrochloride salt [Ph(NH$_3$)]Cl, which was analyzed by NMR spectroscopy (Figure 11 in Appendix A).

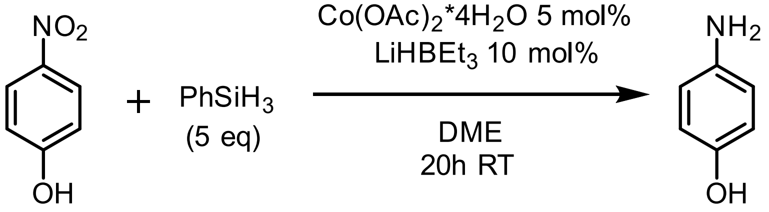
Figure 10. GC-MS spectrum of the reaction mixture catalyzed by heterogeneous free cobalt nanoparticles



Applying the same system and reaction conditions, 4-nitrophenol was also succesfully reduced to 4-aminophenol showing full conversion of the substrate within 20 h at room temperature (Scheme 15). The product of the reaction, 4-aminophenol was converted to the corresponding ammonium salt using hydrogen chloride solution in dioxane (4.0 M) (40% isolated yield) and analyzed by NMR (Figure 12 in Appendix A).

Interestingly, application of Co(acac)$_2$ instead of Co(OAc)$_2$ to perform the same catalytic transformation has failed since no reduction of 4-nitrophenol was observed. Both ^{1}H NMR and GC-MS spectra were inconclusive.

Scheme 15. Heterogeneous reduction of 4-nitrophenol with free cobalt nanoparticles



4.4 Characterization of silica-supported cobalt composites

Three cobalt-silica composites supported on Si-H modified silica (TEOS-SiO$_2$) were prepared analogously to procedure recently reported by Inglezakis and co-workers (2018) for metal-silica nanocomposites with precious metals (Ru, Au, Pd and Pt) [74]. TEOS-SiO$_2$ was prepared in analogy with the procedure reported by Katok (2012) [89] and Inglezakis and co-workers (2018) [90]. The first composite material was derived from $Co(OAc)_2$ (composite **1** hereafter); second one was derived from $CoCl_2$ (composite **2** hereafter) and the other also derived from $CoCl_2$ (composite **3** hereafter) but with different cobalt precursor loadings (0.048 mmol, 0.063 mmol and 0.04 mmol respectively). The prepared composite materials were analyzed by X-ray fluorescence (XRF), X-ray diffractometer (XRD), Raman spectroscopy, Scanning Electron Microscope – Energy Dispersive Spectroscopy (SEM-EDS).

The idea for application of TEOS-SiO_2 in the heterogeneous catalysis lays behind its potential ability to reduce the M(II) to M(0) (where M = metal). Inglezakis and co-workers (2018) reported that the reduction of noble metal ions was accomplished by TEOS-SiO_2 since the modified silica contains Si-H groups and act as the reductant [74]. In this regard, analogously, we attempted to reduce the cobalt(II) salts with TEOS-SiO_2 to obtain metallic cobalt on the surface of the modified silica for further catalytic reduction of 2-nitrophenol in an aqueous media.

Although X-ray fluorescence analysis could not provide the exact information regarding the precise percentage value of cobalt present within analyzed composite, it still can present valid information about the composition and relative percentage of each component. According to XRF data, the compositions of cobalt in these three composites were found to be 1.25 wt% (for composite **1**), 2.99 wt% (for composite **2**) and 1.05 wt% (for composite **3**) (Appendix B: Figures 13-15).

The attempted XRD analysis of the prepared composite materials and its comparison with XRD of the parent Co salts ($Co(OAc)_2$ and $CoCl_2$) showed inconclusive results (Appendix B: Figures 22-27) due to low concentration of cobalt in all three composite materials However, successful formation of Co-SiO_2 composites **1** and **2** was confirmed by Raman spectroscopy, showing a significant shift of the peaks corresponding to TEOS-SiO_2 (Appendix B: Figures 28-34). Interestingly, the composite **3** showed no change in the Raman spectrum upon treatment of TEOS-SiO_2 with $CoCl_2$.

Formation of Co-SiO_2 composites is further supported with Scanning Electron Microscope – Energy Dispersive Spectroscopy (SEM-EDS) results, which confirm the presence of cobalt metal in all synthesized composites (Appendix B: Figures 16-17). SEM images at high magnifications show the change of the silica surface of the composites compared to pure TEOS-SiO_2. At this point it remains unclear whether the reduction of Co(II) to Co(0) with TOES-SiO_2 takes place, as it was observed in the case of noble metals nanocomposites reported by Inglezakis et al. [92], SEM shows that upon treatment of TEOS-SiO_2 with $Co(OAc)_2$ and $CoCl_2$, the surface of the silica becomes fluffy possibly indicating that cobalt might reside in the form of cobalt(II) salt adsorbed on the surface of TEOS-SiO_2 (Appendix B: Figures 18-21). To elucidate this more detailed analysis distinguishing between Co(II) and Co(0) states is necessary. However, considering our intent to use $NaBH_4$ as the reductant in Co-catalyzed deoxygenative reduction of aromatic nitro compounds and the well-known ability of $NaBH_4$ to reduce M(II) salts to M(0) [82, 85, 88], even the composite materials having Co(II) salts adsorbed on silica should perform well in the reduction of nitroarenes with $NaBH_4$. Upon addition of $NaBH_4$ all Co(II) centers should be converted to Co(0) active in reduction catalysis [82, 85, 88].

4.5 Heterogeneous reduction of 2-nitrophenol with $NaBH_4$ using Co-SiO_2 composites 1, 2 and 3

The effective reduction of 0.0003 M of 2-nitrophenol (1.5 ml) (2-NPh) with 0.3 M of $NaBH_4$ (1.5 ml) using 5 mg of composite **1** (derived from $Co(OAc)_2$) was performed in water at room temperature. The reaction was monitored by UV-vis showing full conversion of the substrate to 2-aminophenol within 3 minutes at room temperature. Upon **1**-catalyzed reaction of 2-nitrophenol with $NaBH_4$, the UV-vis spectra showed disappearance of the peak at 350 nm, which correspond to the nitro group (Figure 35). In addition, the peak at 279 nm in the UV-vis spectrum of 2-aminophenol shifts to 291 nm due to formation of 2-aminophenol (Figure 35).

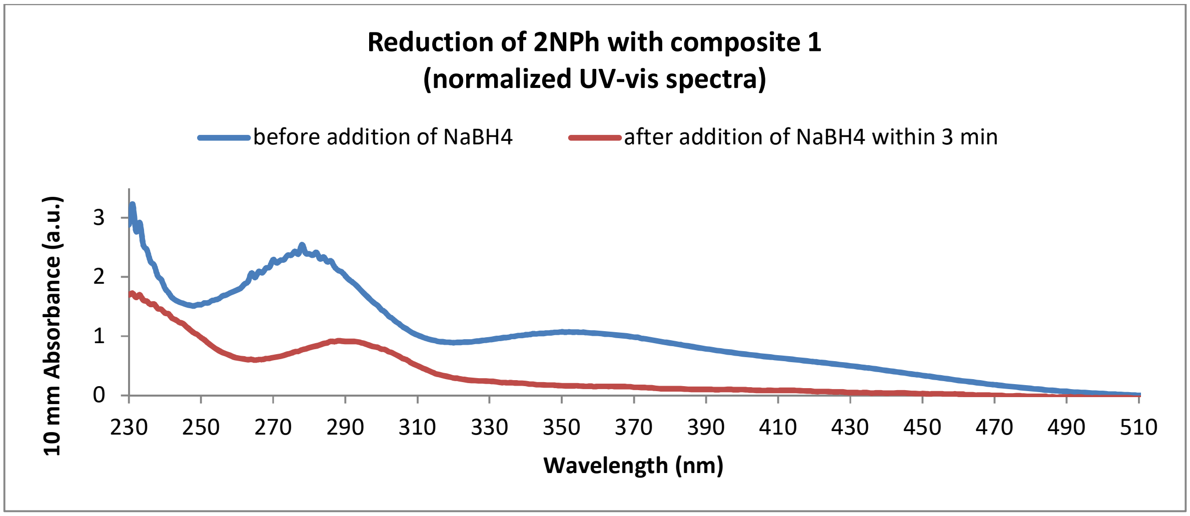


Figure 35. UV-Vis spectra for the reduction of 2-NPh with $NaBH_4$ using composite 1

Similarly, composite **2** was also found to be catalytically active in reduction of 2-nitrophenol with $NaBH_4$ in water (Figure 36). Thus, using 0.0003 M (1.5 ml) of aqueous solution of 2-nitrophenol, 0.3 M (1.5 ml) of aqueous solution of $NaBH_4$ and 5 mg of composite **2**, the reaction was completed within 3 minutes at room temperature to form 2-aminophenol. Similar to composite **1**, the UV-vis spectrum of the reaction catalyzed by composite **2** showed disappearance of absorbance at 350 nm (nitro group of 2-nitrophenol) and appearance of absorbance at 291 nm, corresponding to 2-aminophenol (Figure 36). The fact that the spectrum baseline does not approach zero absorbance is attributed to the presence of composite dispersion in the cuvette. Some time is needed for the composite dispersion to settle down and only then baseline would approach zero.

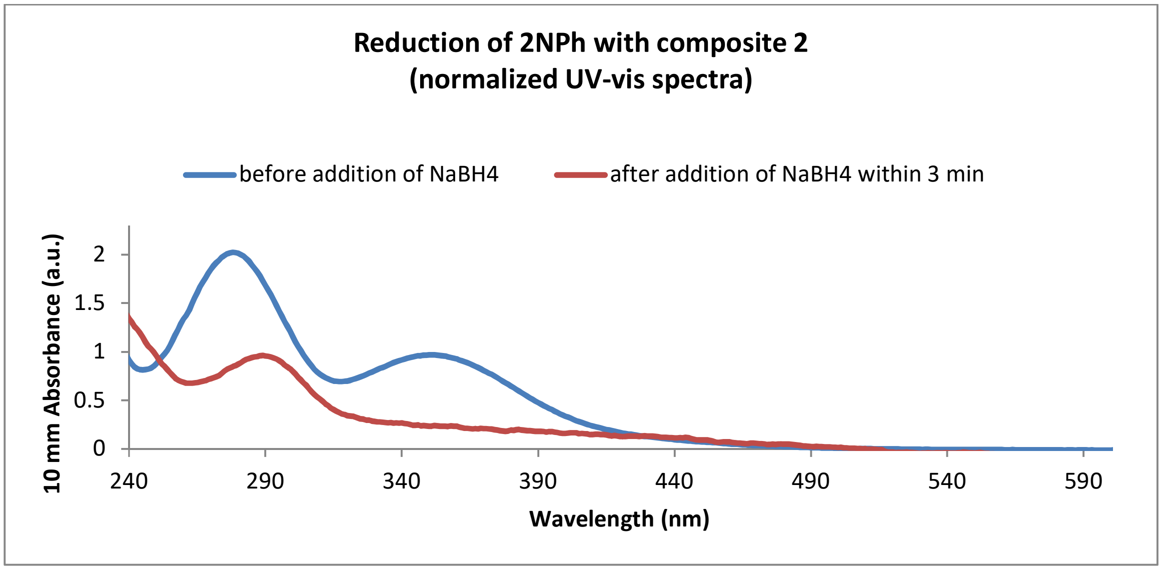


Figure 36. UV-Vis spectra for the reduction of 2-NPh with NaBH4 using composite 2

Compared to composite materials **1** and **2**, somewhat reduced catalytic activity in deoxygenative reduction of 2-nitrophenol to 2-aminophenol with $NaBH_4$ in water was observed for Co-SiO_2 composite **3**. Applying the reaction conditions identical to **1** and **2**-catalyzed reactions, Co-SiO_2 composite **3** was able to convert 2-nitrophenol to 2-aminophenol only in 10 minutes at room temperature (Figure 37).

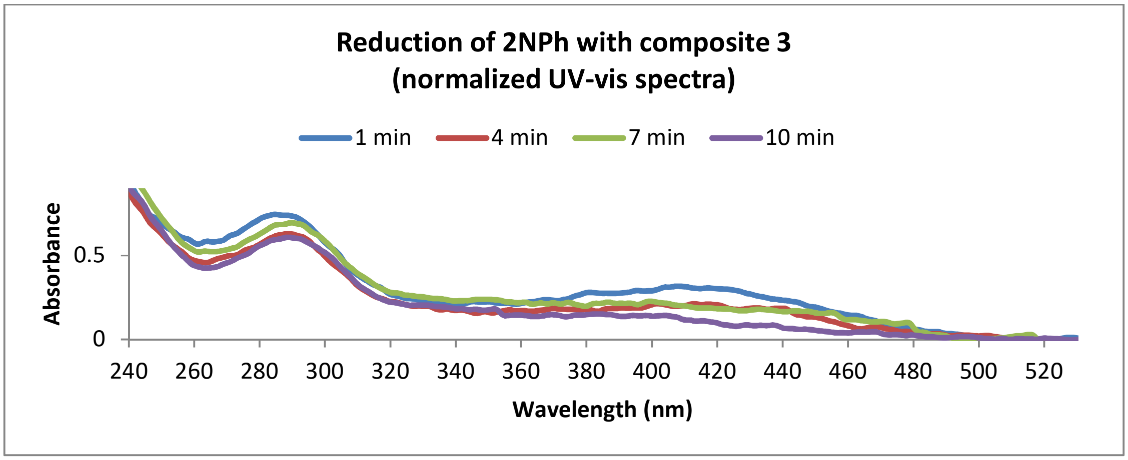


Figure 37. UV-Vis spectra for the reduction of 2-NPh with $NaBH_4$ using composite 3

To elucidate the role of cobalt in the reduction catalysis by Co-SiO_2 composites we performed a control experiment for the reduction of 2-nitrophenol with $NaBH_4$ in water in the presence of TEOS-SiO_2 without cobalt additives. Thus, using 0.00025 M (1.5 ml) aqueous solution of 2-nitrophenol and 0.3 M aqueous NaBH4 in the presence of 4.5 mg of TEOS-SiO_2 showed no reduction of 2-nitrophenol to 2-aminophenol within 19 minutes at room temperature (Figure 38). Analogously, no reaction was observed upon mixing aqueous 2-nitrophenol with aqueous $NaBH_4$ in the absence of TEOS-SiO_2. In contrast, starting Co(II) salts, $Co(OAc)_2$ and $CoCl_2$, were both found to catalyze the reduction of 2-nitrophenol with $NaBH_4$ in water in the absence of TEOS-SiO_2, indirectly confirming the in situ formation of catalytically active Co(0) species from Co(II) precursors upon reaction with $NaBH_4$. The details of these findings are described below under kinetic studies of reduction of 2-nitrophenol. Moreover, the discoloration of the solution was observed due to full conversion of 2-nitrophenol to 2-aminophenol (Figure 39).

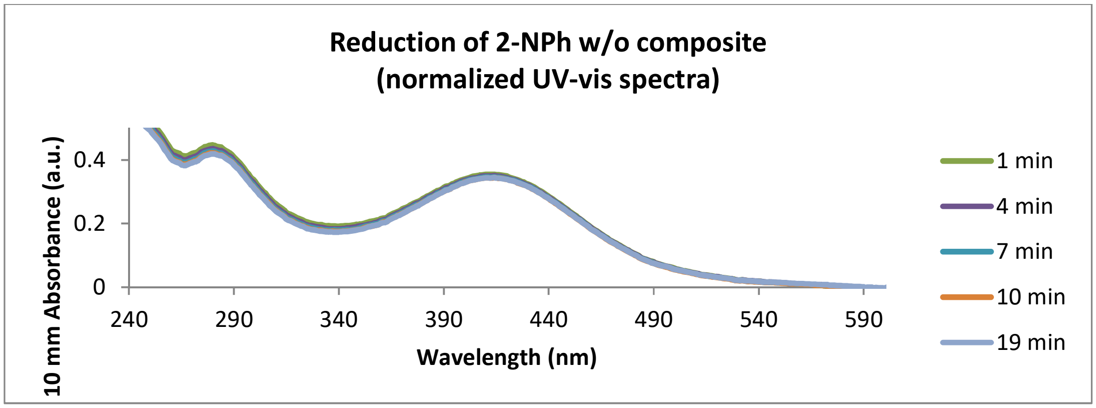


Figure 38. UV-Vis spectra for the reduction of 2-NPh with $NaBH_4$ using TEOS-SiO_2

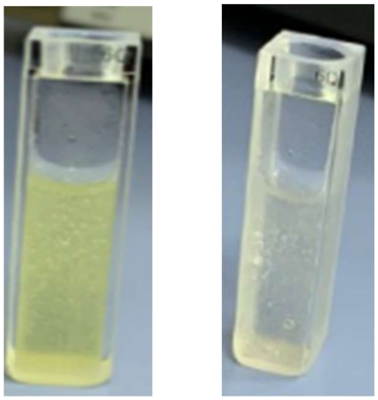


Figure 39. Discoloration of the solution representing the complete conversion of the substrate

4.6 Kinetics studies for the reduction of 2-nitrophenol with $NaBH_4$ using Co-SiO_2 composites, $CoCl_2$ and $Co(OAc)_2$

In order to quantitatively compare the catalytic activity of the prepared Co-SiO_2 composites, we performed kinetic studies of the reduction of 2-nitrophenol with $NaBH_4$ in water, catalyzed by three composite materials derived from $Co(OAc)_2$ and $CoCl_2$ (composites **1**, **2** and **3** respectively). Thus, 2 mg of composites **1**, **2** and **3** were used to catalyze the reduction of 2-nitrophenol (0.0003 M). For control experiments, the reduction of 2-nitrophenol (0.0003M) with $NaBH_4$ was also performed in the presence of $Co(OAc)_2$ (0.34 µmol%) and $CoCl_2$ (0.34 µmol%). The reactions were monitored using UV-Vis NanoDrop spectrophotometry. The UV-vis spectra were taken every 2 minutes to monitor the progress of the reactions. These spectra are depicted in Figures 41-49.

First it should be noted that upon addition of $NaBH_4$ to aqueous solution of 2-nitrophenol the shift of absorbance spectra was observed due to change in pH of the resulting solution. Thus, the absorbance corresponding to the nitro group of 2-nitrophenol in water was shifted from 357 nm to 415 nm upon addition of $NaBH_4$ and then disappearance of the absorbance at 415 nm was monitored indicating the conversion of nitrophenol to aniline (Figure 40).

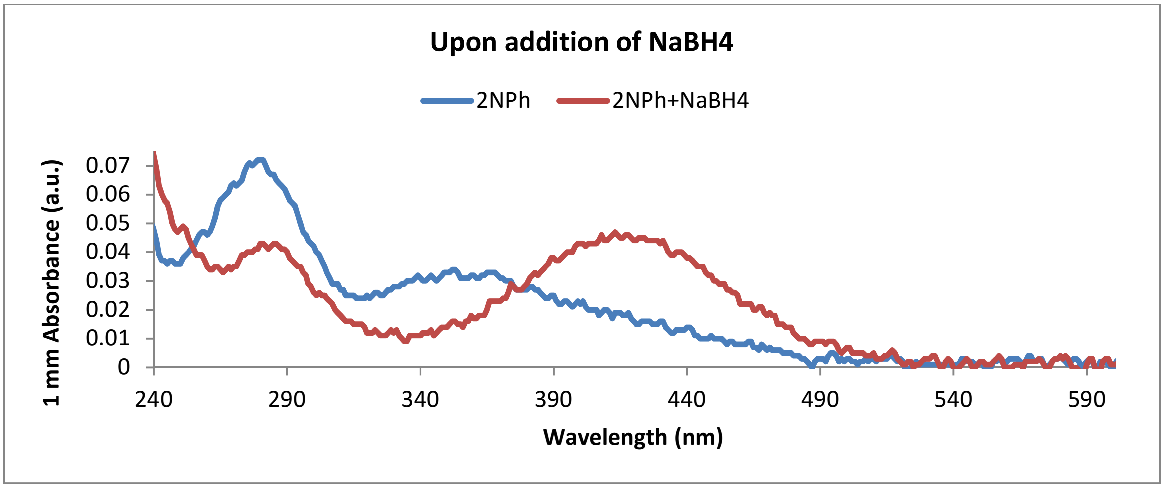


Figure 40. UV-Vis spectra of peak shifting due to change in pH

Since in the presence of Co-SiO_2 very fast reduction of 2-nitrophenol was observed using 0.3 M $NaBH_4$ solution, the concentration of $NaBH_4$ had to be reduced twice to achieve the reaction rates suitable for kinetic studies. Thus, the overall reaction conditions applied for kinetic studies of the reduction of 2-nitrophenol with $NaBH_4$ were: 2-nitrophenol (0.0003 M, 1.5 ml), $NaBH_4$ (0.15 m, 0.5 ml) and 2 mg of Co-SiO_2 composite material. The reactions were carried out at room temperature and analyzed by NanoDrop UV-vis spectrophotometry.

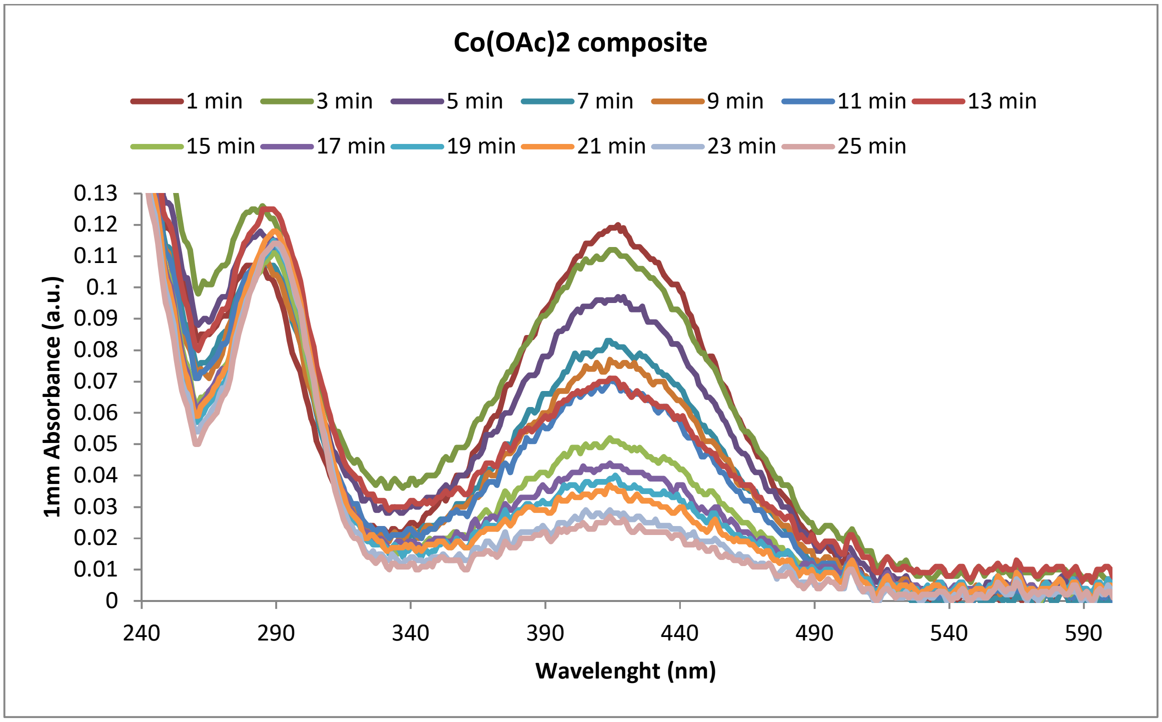


Figure 41. UV-Vis spectra for reduction of 2-nitrophenol with NaBH$_4$ with composite 1

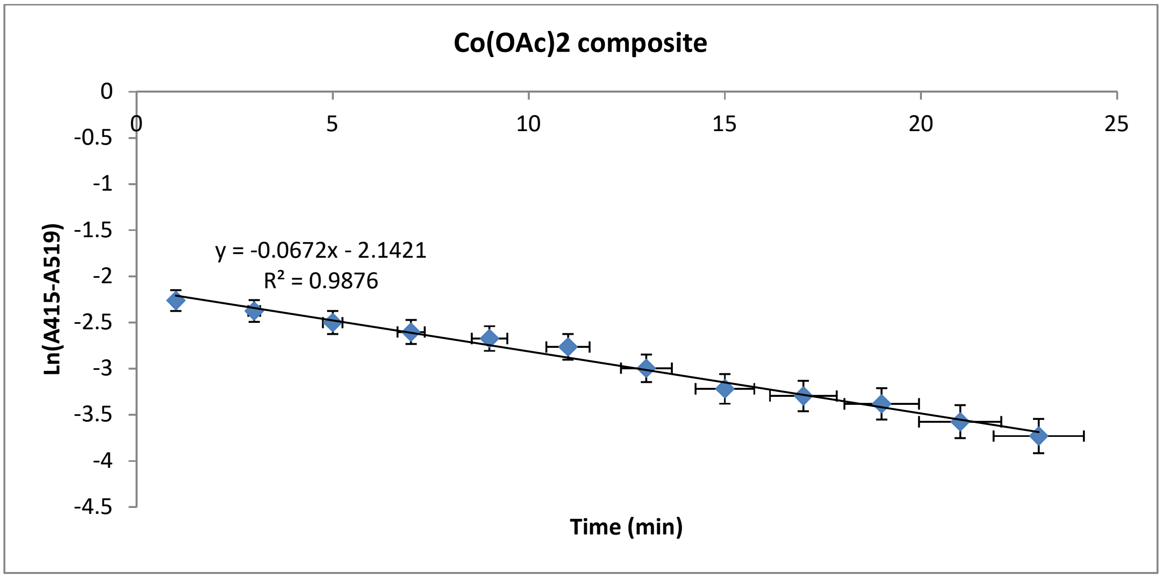


Figure 42. Reaction kinetics for composite 1 catalyzed reduction of 2-NPh

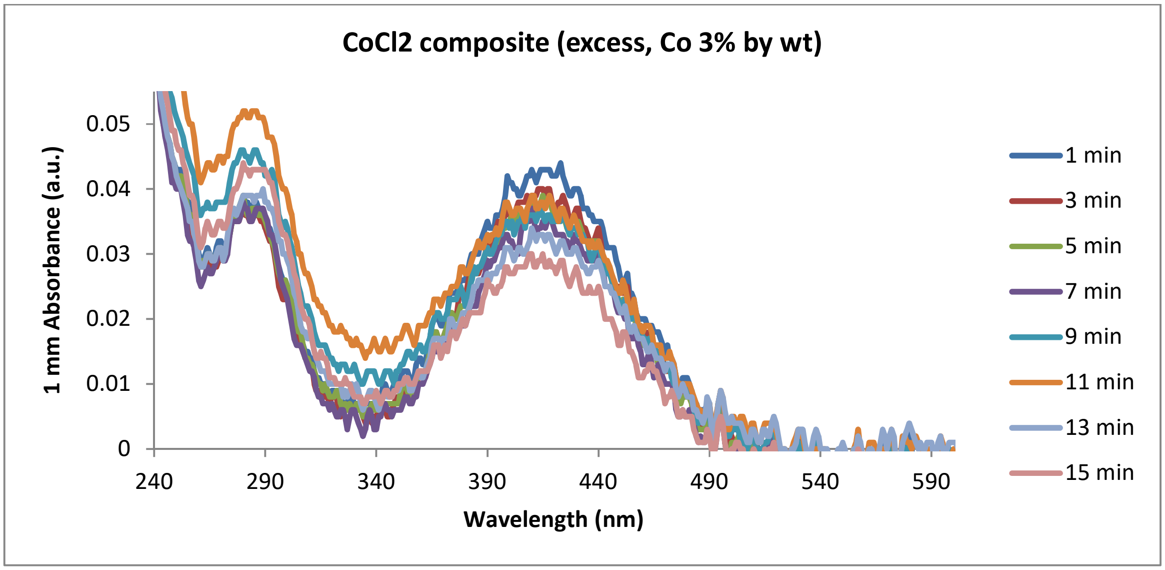


Figure 43. UV-Vis spectra for reduction of 2-nitrophenol with NaBH4 with composite 2

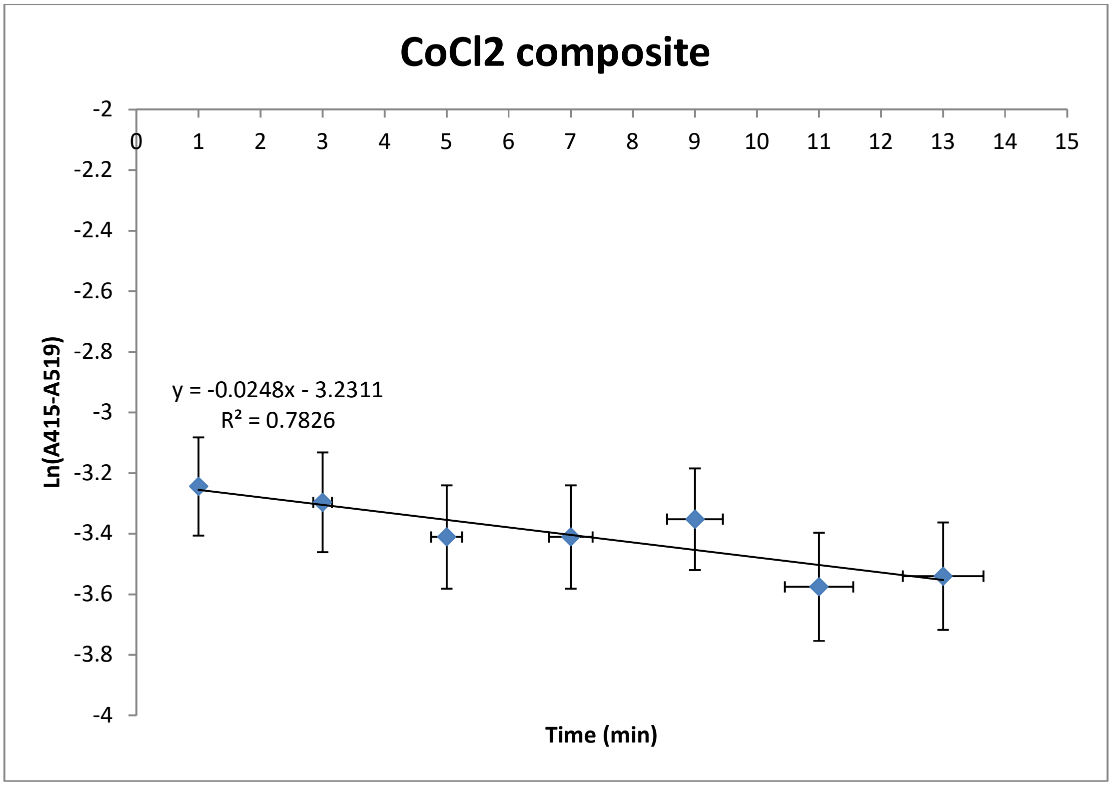


Figure 44. Reaction kinetics for composite 2 catalyzed reduction of 2-NPh

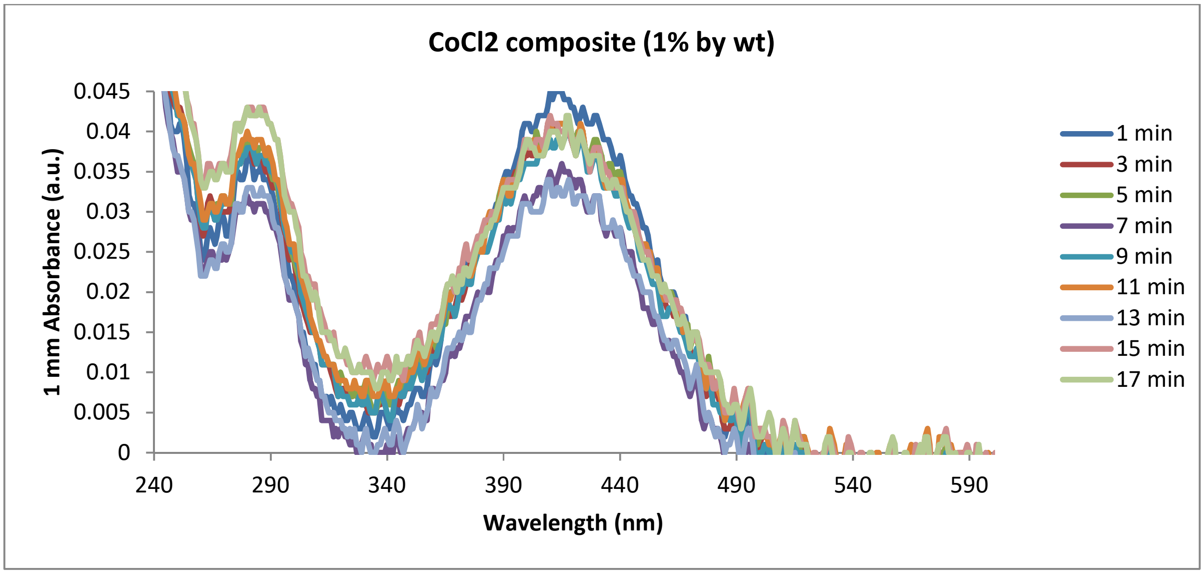


Figure 45. Reaction kinetics for composite 3 catalyzed reduction of 2-NPh

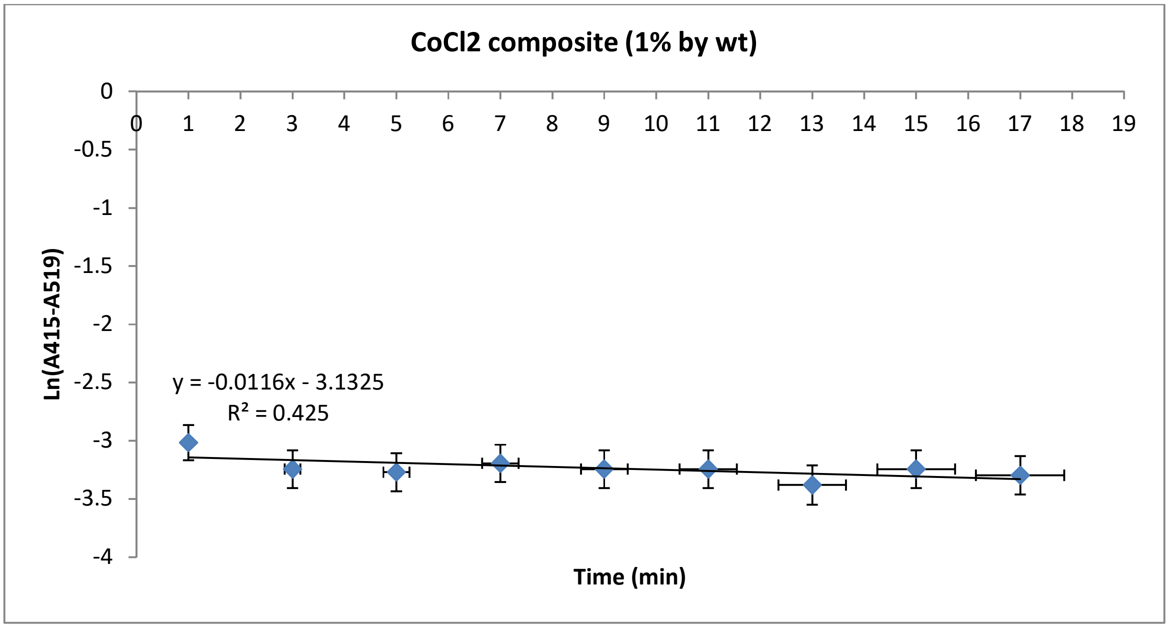


Figure 46. Reaction kinetics for composite 3 catalyzed reduction of 2-NPh

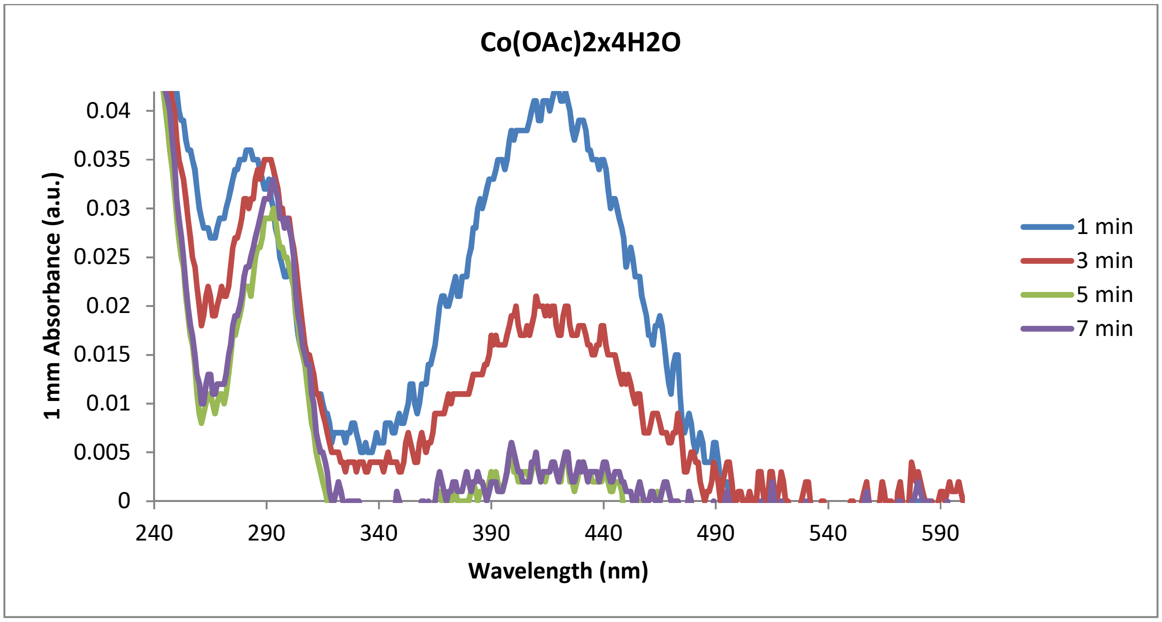


Figure 47. UV-Vis spectra for reduction of 2-nitrophenol with $NaBH_4$ with $Co(OAc)_2$

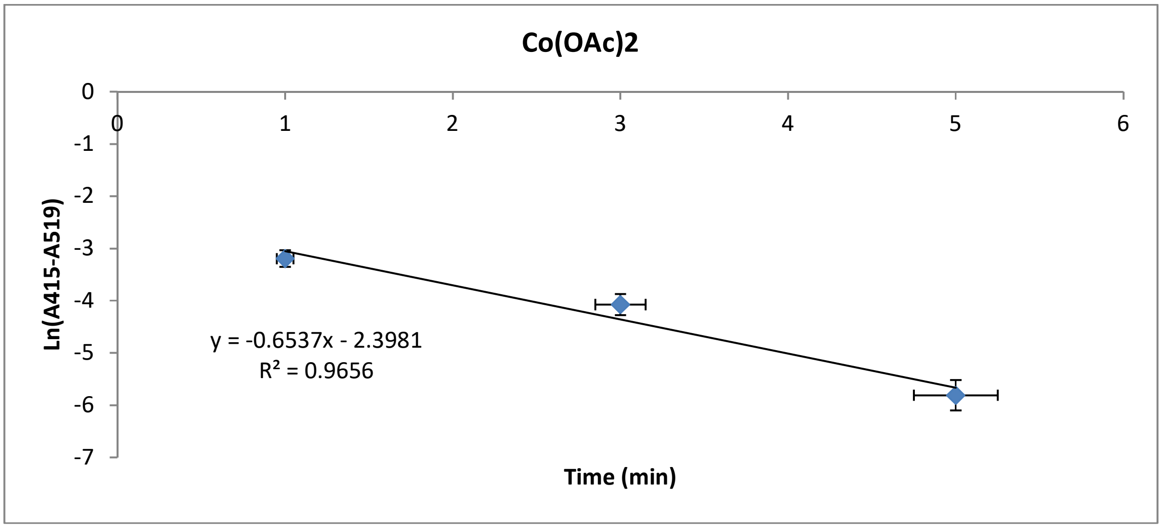


Figure 48. Reaction kinetics for $Co(OAc)_2$ catalyzed reduction of 2-NPh

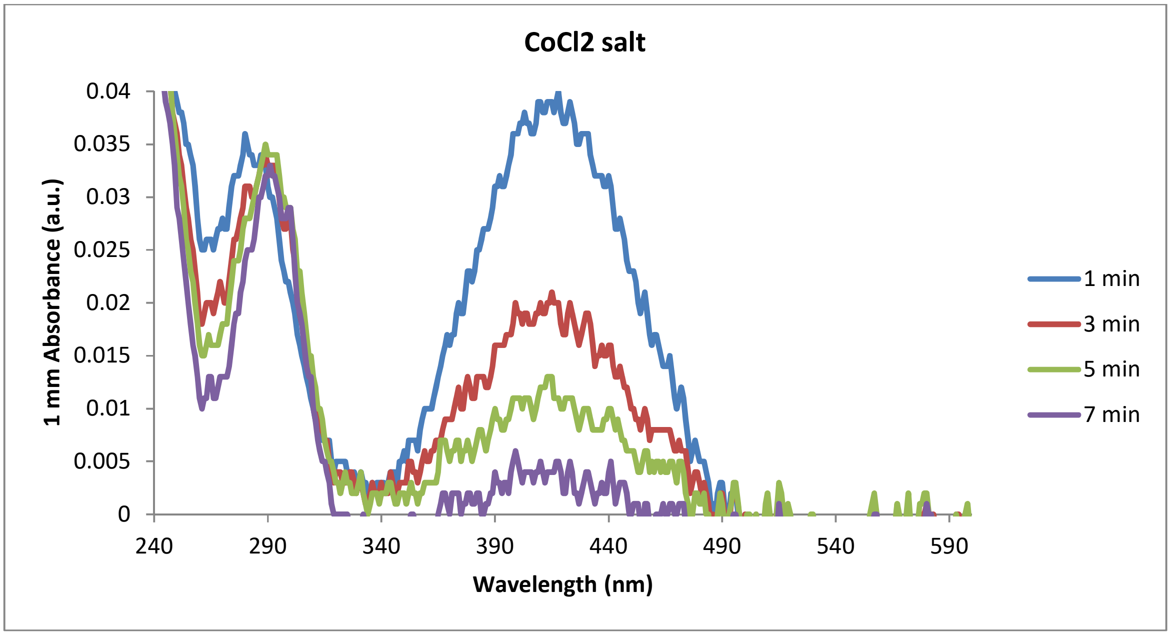


Figure 49. UV-Vis spectra for reduction of 2-nitrophenol with $NaBH_4$ *with* $CoCl_2$

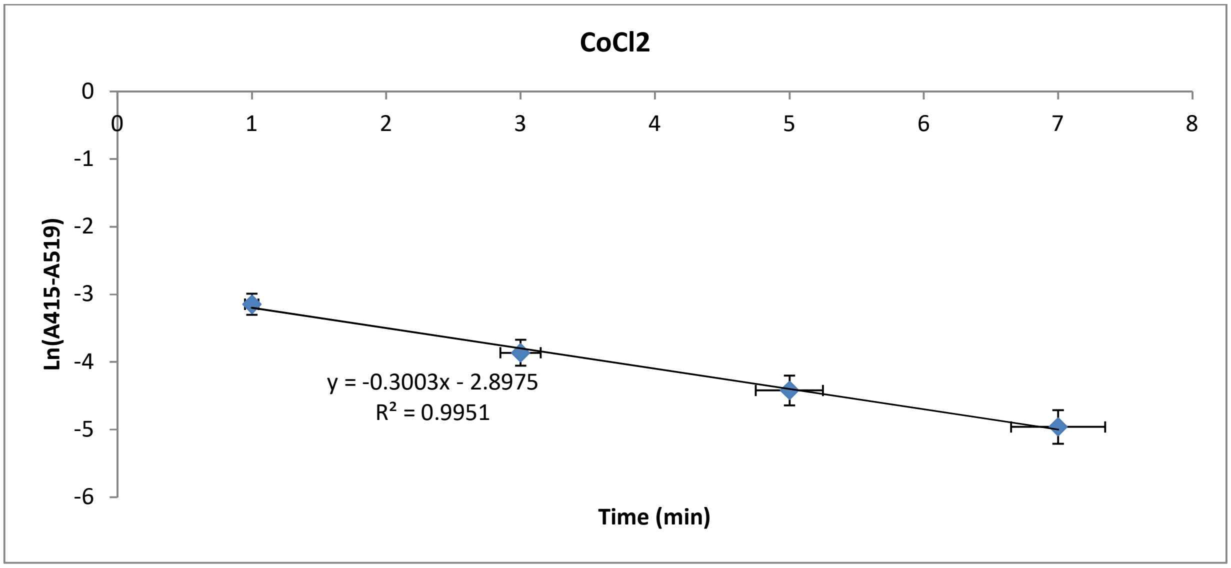


Figure 50. Reaction kinetics for CoCl2 catalyzed reduction of 2-NPh

Additionally, to measure the kinetics and be able to quantitatively compare the catalytic activity of the prepared Co-SiO_2 composites **1**, **2** and **3** as well as parent cobalt(II) salts, $Co(OAc)_2$ and $CoCl_2$, plots showing the change in absorbance unit, indicated as $\ln(A_{415} - A_{519})$ as a function of time of the reaction were drawn (Figures 42, 44, 46, 48 and 50). Thus, linear correlation between change in absorbance unit and time shows the pseudo-first order reaction with respect to 2-nitrophenol. The pseudo-first order reaction rates are summarized in Table 4.

Table 4. Overview of the obtained rate constants

Catalyst	**Rate constant, k (min^{-1})**
$Co(OAc)_2$ composite 1	$6.72 x 10^{-2}$
$CoCl_2$ composite 2	$2.48 x 10^{-2}$
$CoCl_2$ composite 3	$1.16 x 10^{-2}$
$Co(OAc)_2$ salt	$6.54 x 10^{-1}$
$CoCl_2$ salt	$3.00 x 10^{-1}$

According to the obtained results, the highest catalytic activity among three composites was found to be composite **1** (with approx.. 1.3 wt% of Co) derived from $Co(OAc)_2$ having rate constant of $6.72 x 10^{-2}$ min^{-1} (Table 4, entry 1). The reduction of 2-nitrophenol using composite **2**, which has approx.. 3 wt% of cobalt, was found to be almost twice slower with the rate constant of $2.48 x 10^{-2}$ min^{-1} (Table 4, entry 2). And the slowest transformation with the rate constant of 1.16 $x 10^{-2}$ min^{-1} was determined in the case of composite **3** having approx. 1 wt% of Co (Table 4, entry 3). Interestingly, the reaction rates for the parent cobalt(II) salts, $Co(OAc)_2$ and $CoCl_2$, under the same reaction conditions and catalyst loadings were found to be an order of magnitude higher compared to the reaction rates observed for the Co-SiO_2 composites derived from these salts, composites **1** and **2**, respectively (compare entries 1 and 4, entries 2 and 5, Table 4). This difference can be explained be different surface area and completely different mechanism of the reduction reaction while comparing the cobalt salts and composite materials. The advantages of the use of Co-SiO_2 composite materials **1** and **2** vs. $Co(OAc)_2$ and $CoCl_2$ as catalysts for deoxygenative reduction of 2-nitrophenol could be attributed to easier separation of insoluble composite materials from the reaction mixtures. Catalyst recovery and reuse as well as the experiments directed towards better understanding of the nature of cobalt species incorporated into Co-SiO_2 composites will be the subject of further studies within this project.

Chapter 5 - Conclusion

In the course of this thesis work, the design of simple and effective cobalt catalyzed system ($Co(acac)_2$/dpephos) for selective reduction of aromatic nitro compounds to the corresponding amines in terms of homogeneous catalysis and implementation of this system in heterogeneous catalysis, namely cobalt-catalyzed effective removal of nitrophenols from waste waters were achieved and reported. $Co(acac)_2$/dpephos system was effective in hydrosilative and hydroborative reduction of aromatic nitro compounds with $PhSiH_3$ and HBPin under mild conditions. In addition, cobalt nanoparticles were generated to perform the heterogeneous reduction of nitro compounds showing full conversion of the substrate. Moreover, three cobalt-silica composite materials were synthesized. These composite materials derived from commercially available cobalt salts ($Co(OAc)_2$ and $CoCl_2$) and TEOS modified silica were found to effectively reduce nitroarenes to the corresponding amines in an aqueous media at room temperature within several minutes. The most catalytically active composite material was derived from $Co(OAc)_2$ having the rate constant of 6.72×10^{-2} min^{-1}. Overall, the transition from homogenous catalysis to heterogeneous approach for an effective reduction of aromatic nitro compounds to amines as well as removal of nitro compounds from aqueous solutions were articulated in the present thesis work.

As for the future recommendations, additional characterization of cobalt-silica composite materials as well as cobalt-silica catalyst recovery and catalyst reuse experiments should be performed for better understanding of the nature of silica-supported cobalt species.

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Appendices

Appendix A:

Figure 3. ^{1}H NMR spectrum of aniline in $CDCl_3$ (product was obtained from hydrosilative reduction of nitrobenzene with $PhSiH_3$ and $Co(acac)_2$ / (dpephos) system).

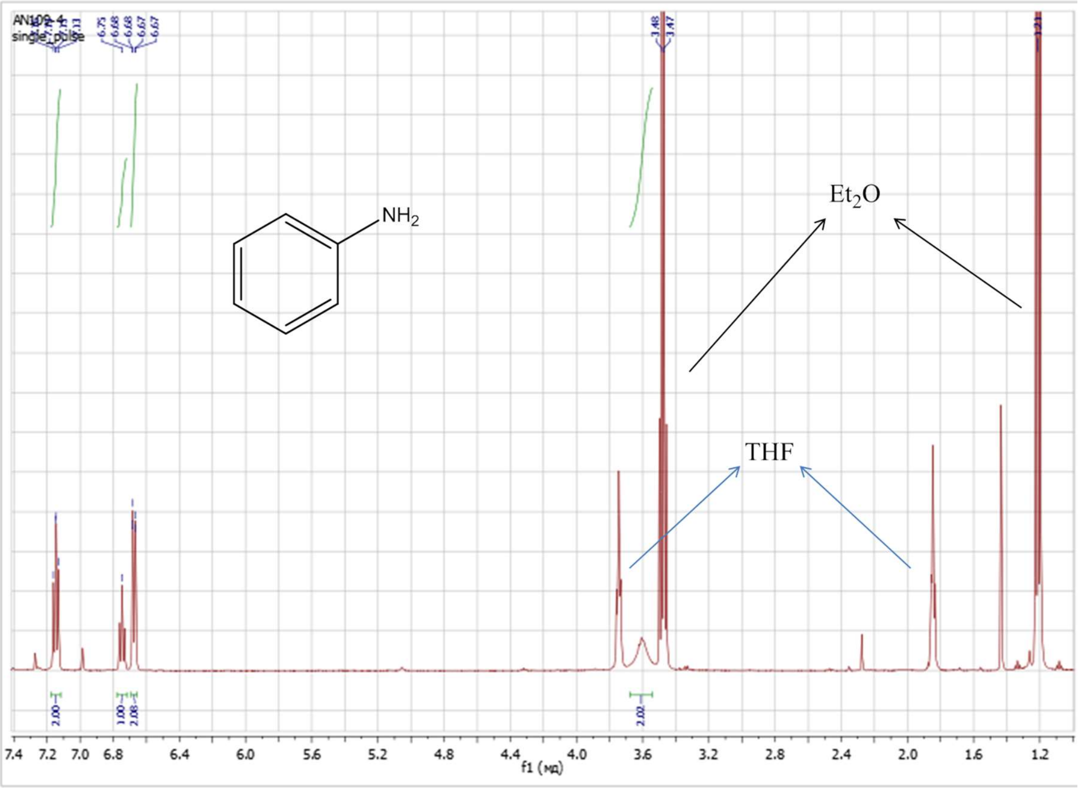


Figure 4. ^1H NMR spectrum of $[Ph(NH_3)]Cl$ in D_2O

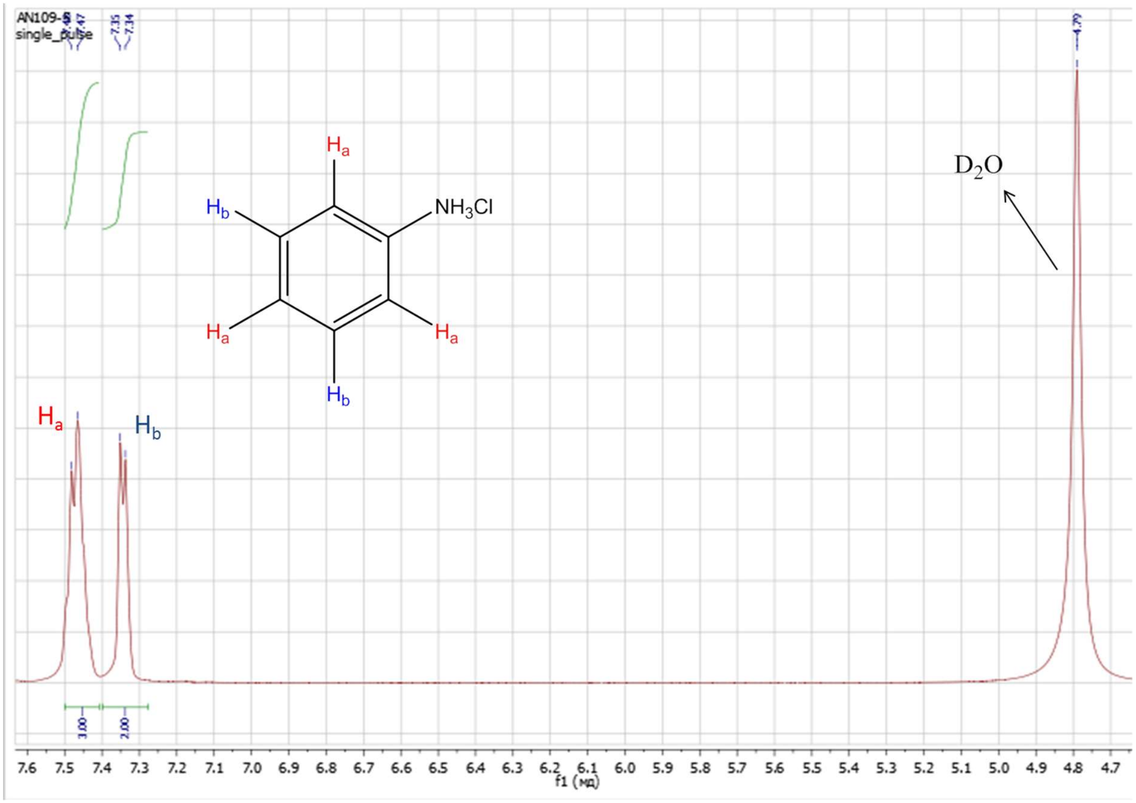


Figure 5. ^1H NMR spectra for of the product in $CDCl_3$ obtained from hydrosilative reduction of 4-nitrophenol using $Co(acac)_2$/(dpephos). (bottom spectrum shows the reaction mixture after the reaction; top spectrum shows the reaction mixture after the reaction to which additional small amount of 4-NPh was added, indicating full conversion of 4-NPh during the reaction)

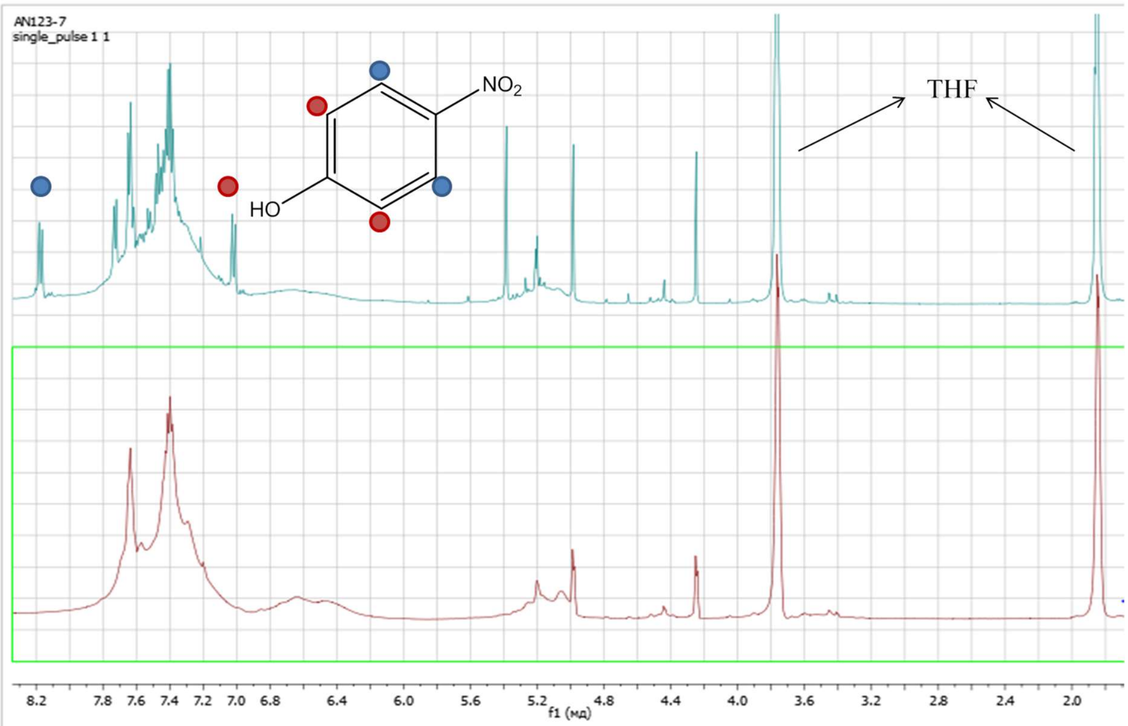


Figure 6. ***^{1}H NMR spectrum of [Ph(OH)(NH_3)]Cl in D_2O obtained from hydrosilative reduction of 4-nitrophenol using Co(acac)$_2$/(dpephos).***

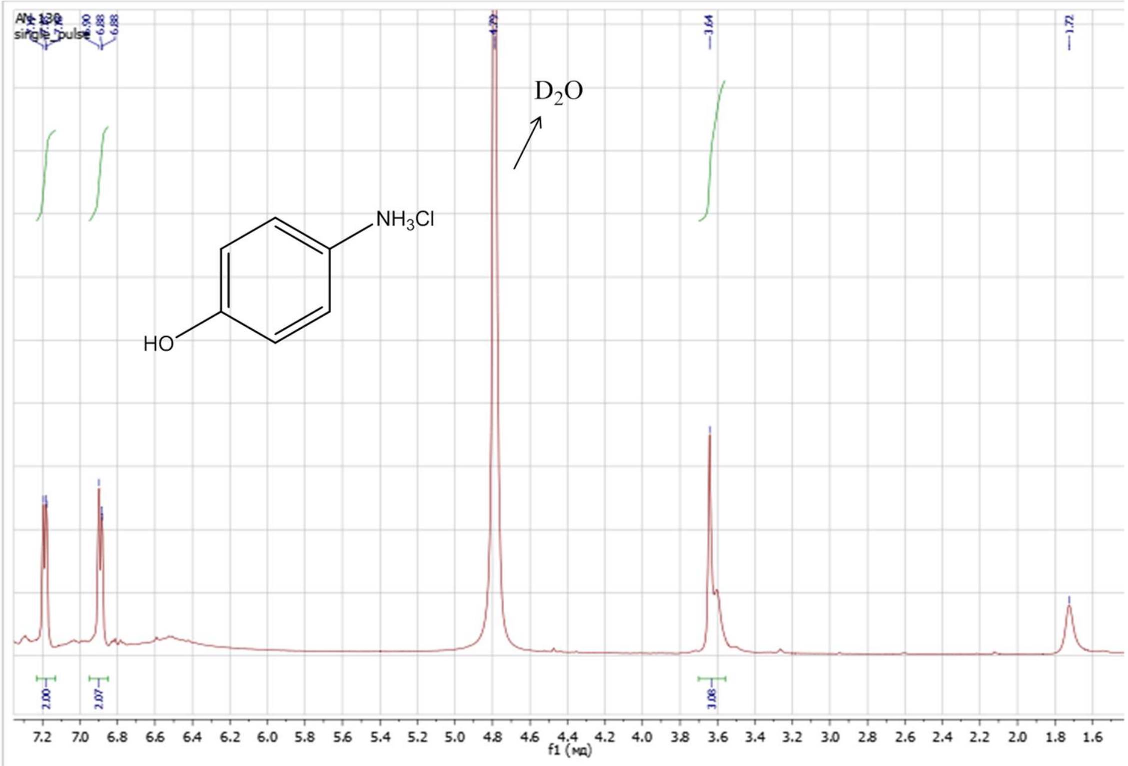


Figure 7. ***^{1}H NMR spectrum of [Ph(OH)(NH_3)]Cl in DMSO-d_6 obtained from hydrosilative reduction of 4-nitrophenol using Co(acac)$_2$/(dpephos).***

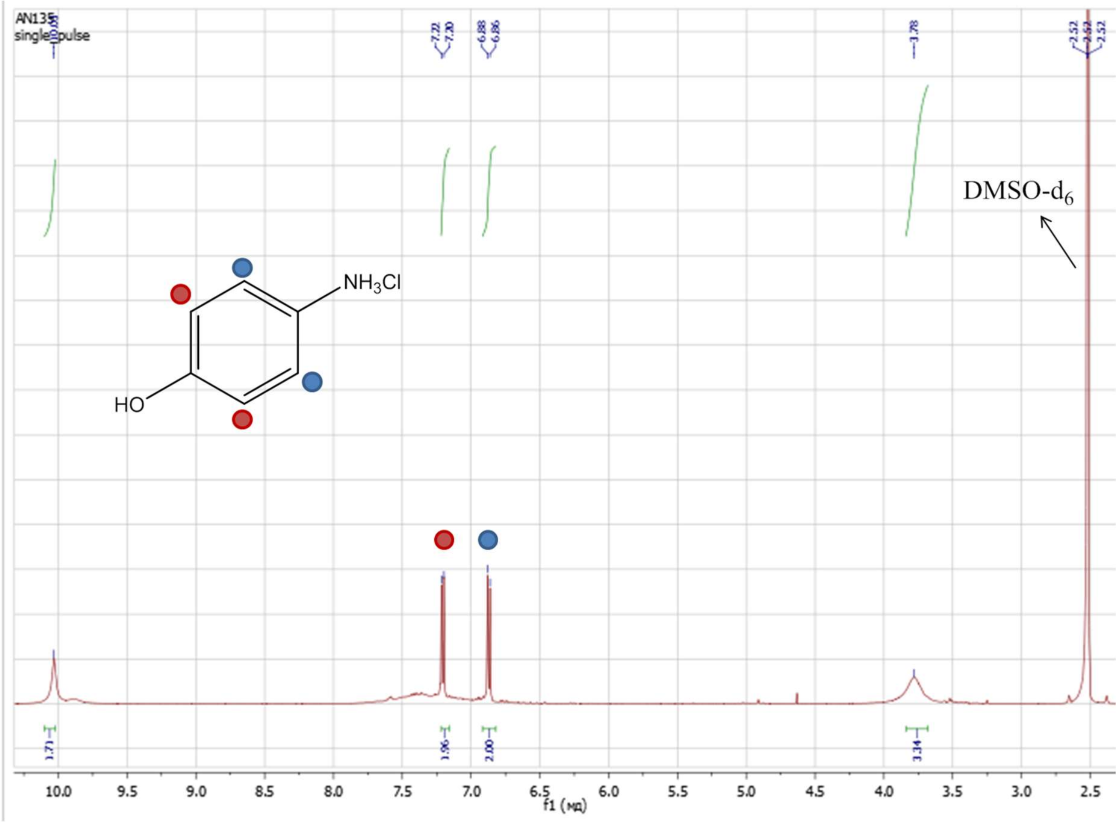


Figure 8. ***^{13}C NMR spectrum of [Ph(OH)(NH$_3$)]Cl in DMSO-d$_6$ obtained from hydrosilative reduction of 4-nitrophenol using Co(acac)$_2$/(dpephos).***

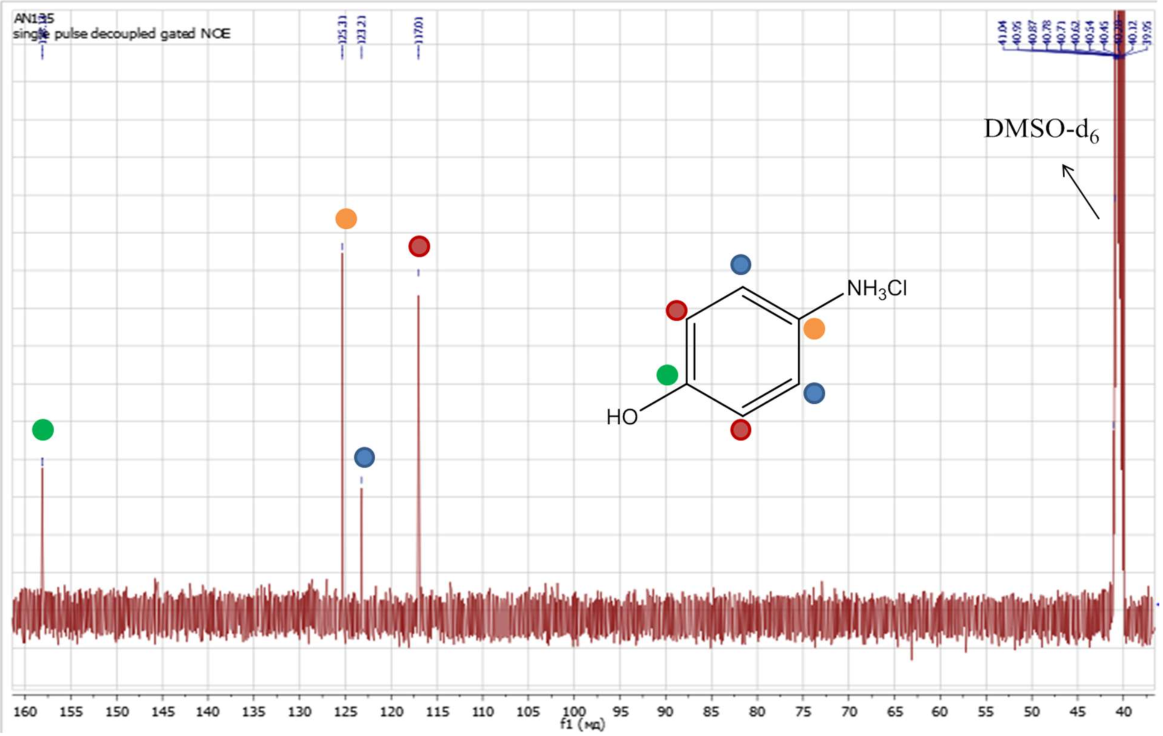


Figure 9. ***^{1}H NMR spectrum of [Ph(NH$_3$)]Cl in DMSO-d$_6$ obtained from hydroborative reduction of nitrobenzene with HBPin using Co(acac)$_2$/(dpephos).***

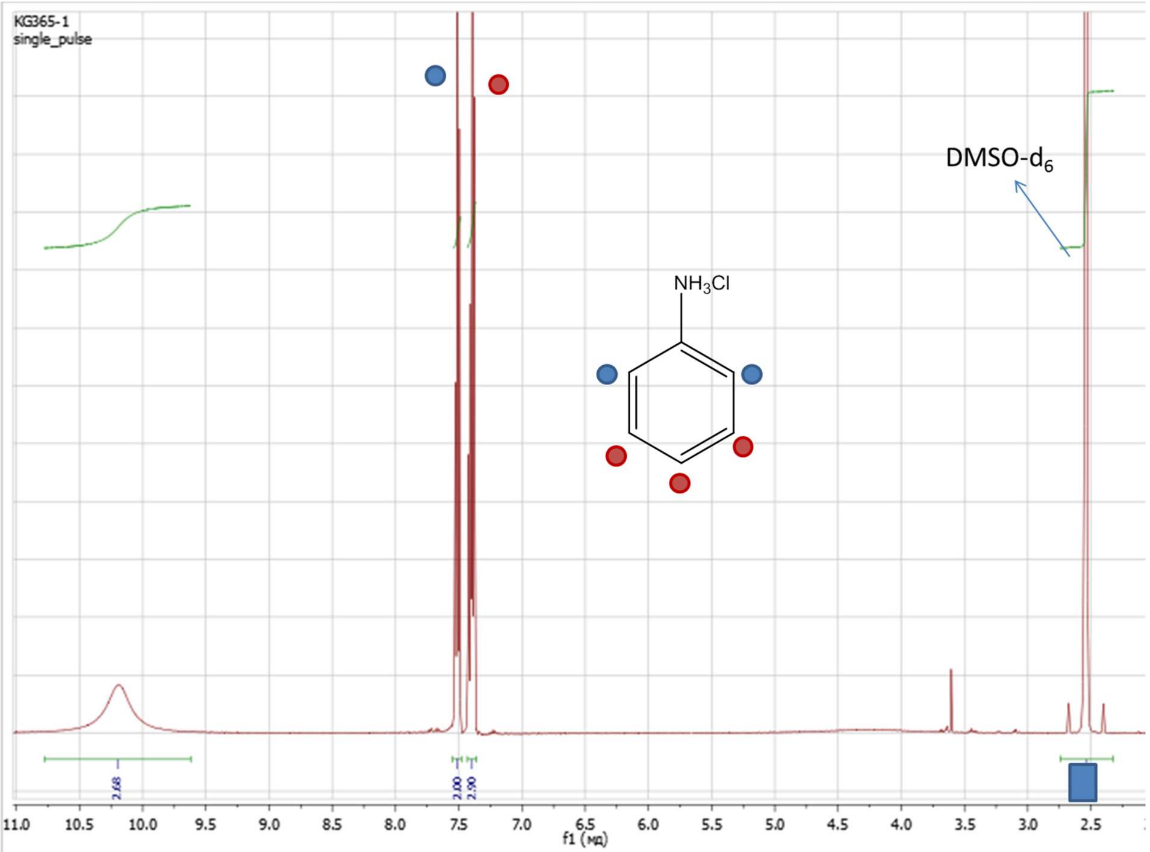


Figure 11. ^{1}H NMR spectrum of [Ph(NH$_3$)]Cl in D$_2$O obtained from heterogeneous reduction of nitrobenzene using free cobalt nanoparticles

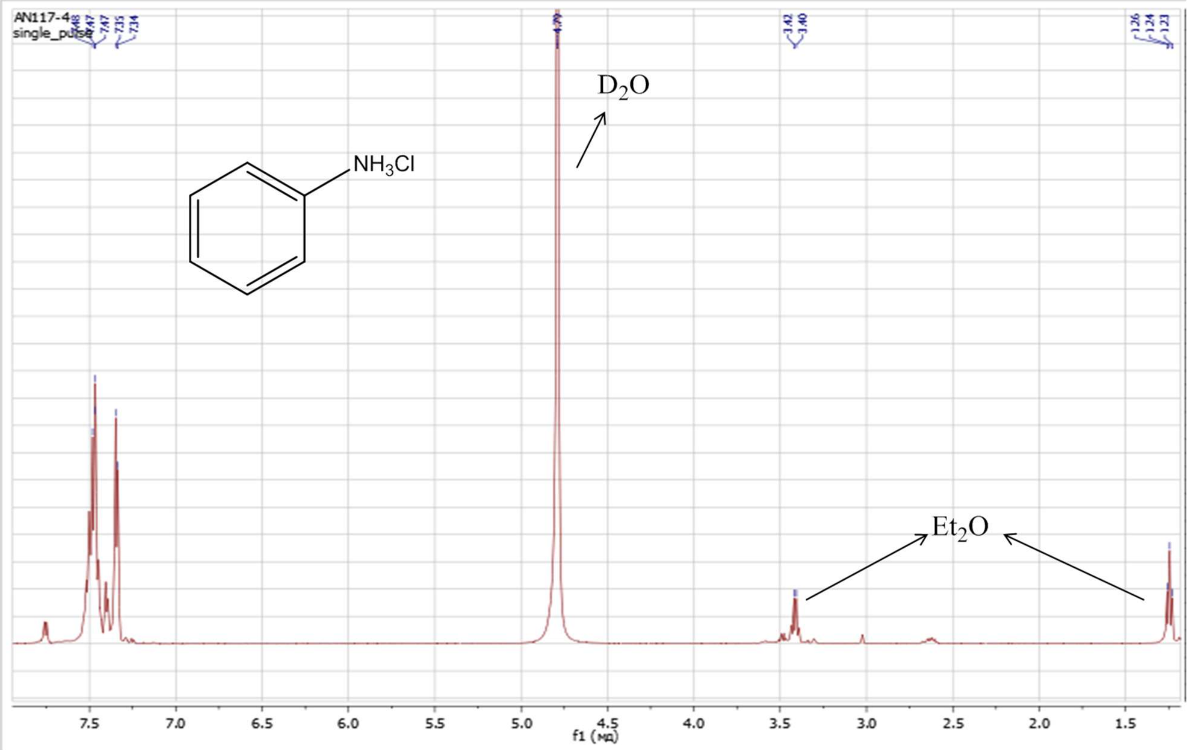
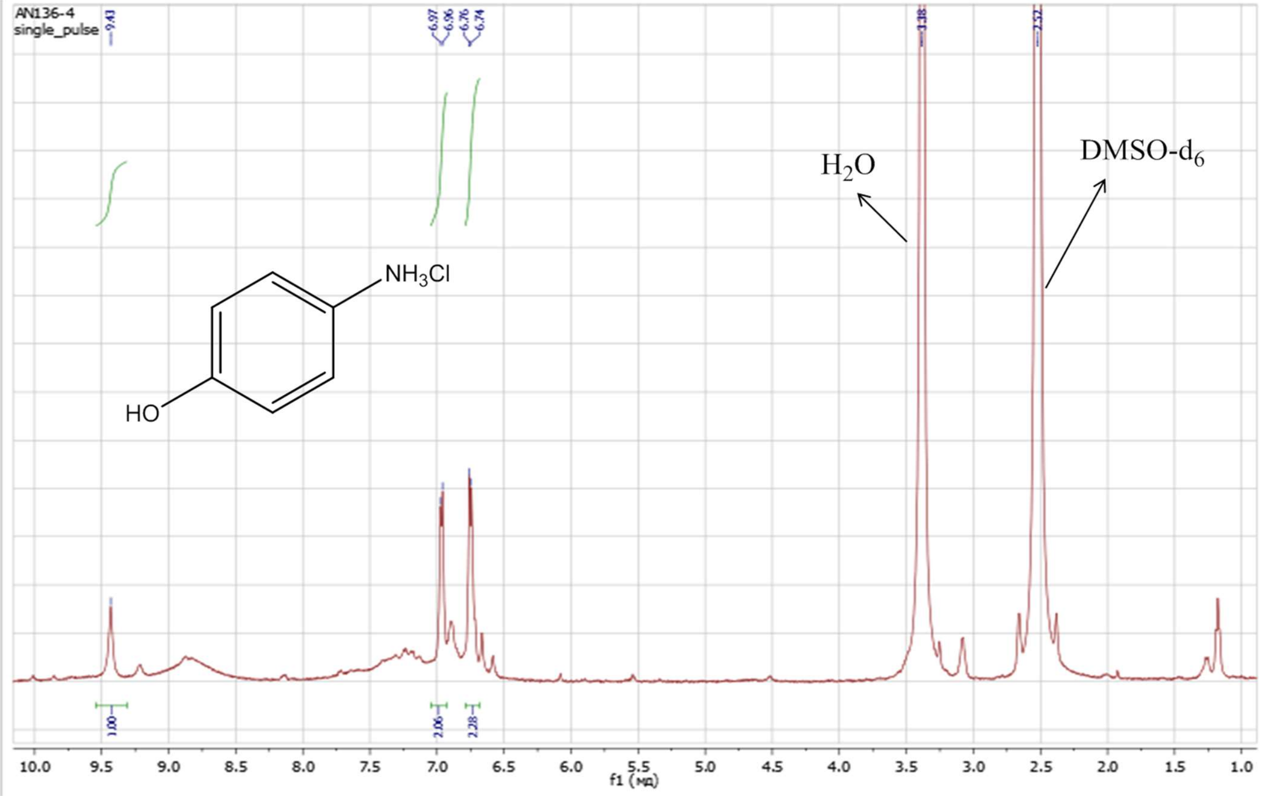
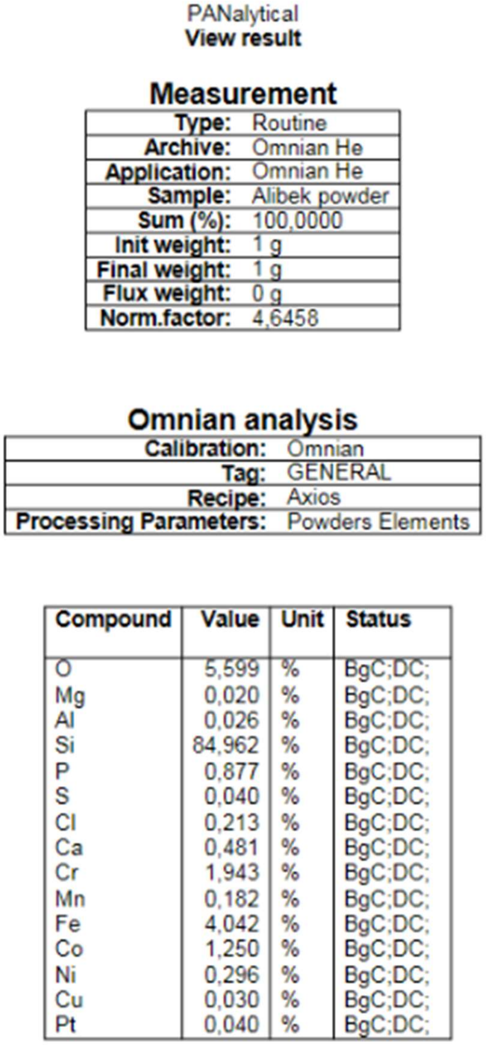


Figure 12. ^{1}H NMR spectrum of [Ph(OH)(NH$_3$)]Cl in DMSO-d$_6$ obtained from heterogeneous reduction of 4-nitrophenol using free cobalt nanoparticles



Appendix B:

Figure 13. XRF data for Co(OAc)$_2$ composite (1)



PANalytical
View result

Measurement

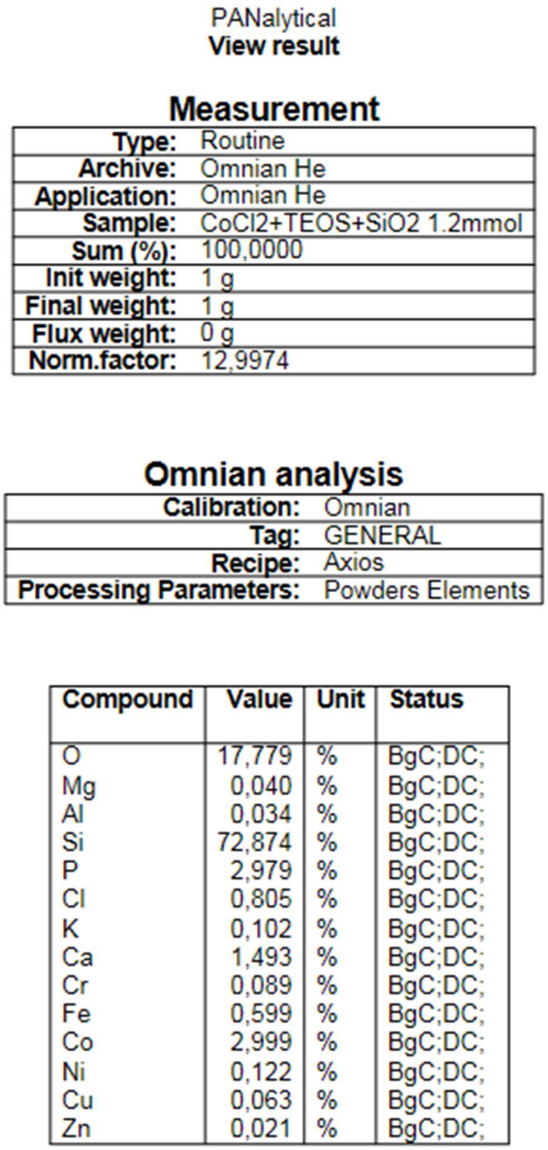
Type:	Routine
Archive:	Omnian He
Application:	Omnian He
Sample:	Alibek powder
Sum (%):	100,0000
Init weight:	1 g
Final weight:	1 g
Flux weight:	0 g
Norm.factor:	4,6458

Omnian analysis

Calibration:	Omnian
Tag:	GENERAL
Recipe:	Axios
Processing Parameters:	Powders Elements

Compound	Value	Unit	Status
O	5,599	%	BgC;DC;
Mg	0,020	%	BgC;DC;
Al	0,026	%	BgC;DC;
Si	84,962	%	BgC;DC;
P	0,877	%	BgC;DC;
S	0,040	%	BgC;DC;
Cl	0,213	%	BgC;DC;
Ca	0,481	%	BgC;DC;
Cr	1,943	%	BgC;DC;
Mn	0,182	%	BgC;DC;
Fe	4,042	%	BgC;DC;
Co	1,250	%	BgC;DC;
Ni	0,296	%	BgC;DC;
Cu	0,030	%	BgC;DC;
Pt	0,040	%	BgC;DC;

Figure 14. XRF data for $CoCl_2$ composite (2)



PANalytical
View result

Measurement

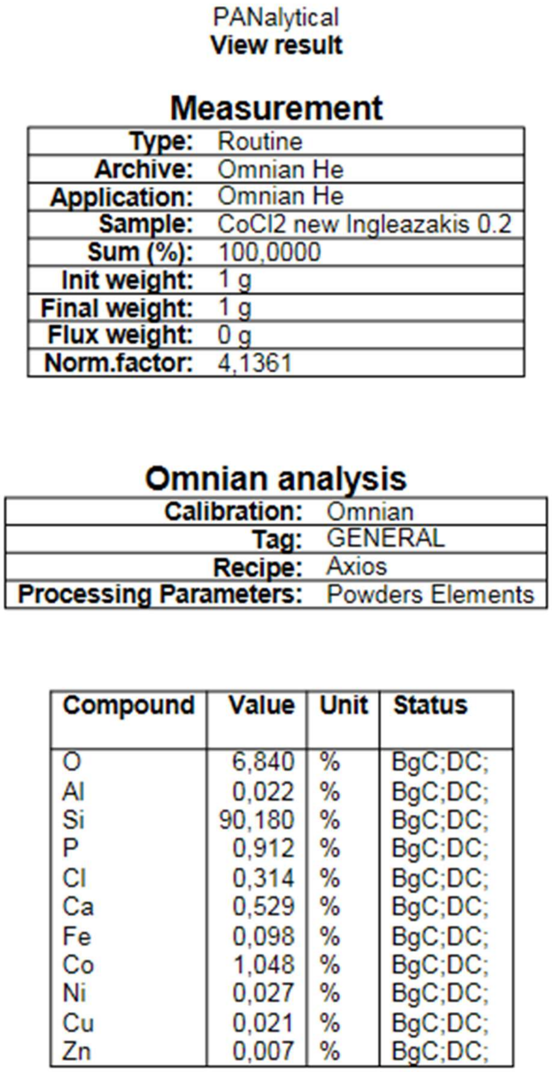
Type:	Routine
Archive:	Omnian He
Application:	Omnian He
Sample:	CoCl2+TEOS+SiO2 1.2mmol
Sum (%):	100,0000
Init weight:	1 g
Final weight:	1 g
Flux weight:	0 g
Norm.factor:	12,9974

Omnian analysis

Calibration:	Omnian
Tag:	GENERAL
Recipe:	Axios
Processing Parameters:	Powders Elements

Compound	Value	Unit	Status
O	17,779	%	BgC;DC;
Mg	0,040	%	BgC;DC;
Al	0,034	%	BgC;DC;
Si	72,874	%	BgC;DC;
P	2,979	%	BgC;DC;
Cl	0,805	%	BgC;DC;
K	0,102	%	BgC;DC;
Ca	1,493	%	BgC;DC;
Cr	0,089	%	BgC;DC;
Fe	0,599	%	BgC;DC;
Co	2,999	%	BgC;DC;
Ni	0,122	%	BgC;DC;
Cu	0,063	%	BgC;DC;
Zn	0,021	%	BgC;DC;

Figure 15. XRF data for $CoCl_2$ composite (3)



PANalytical
View result

Measurement

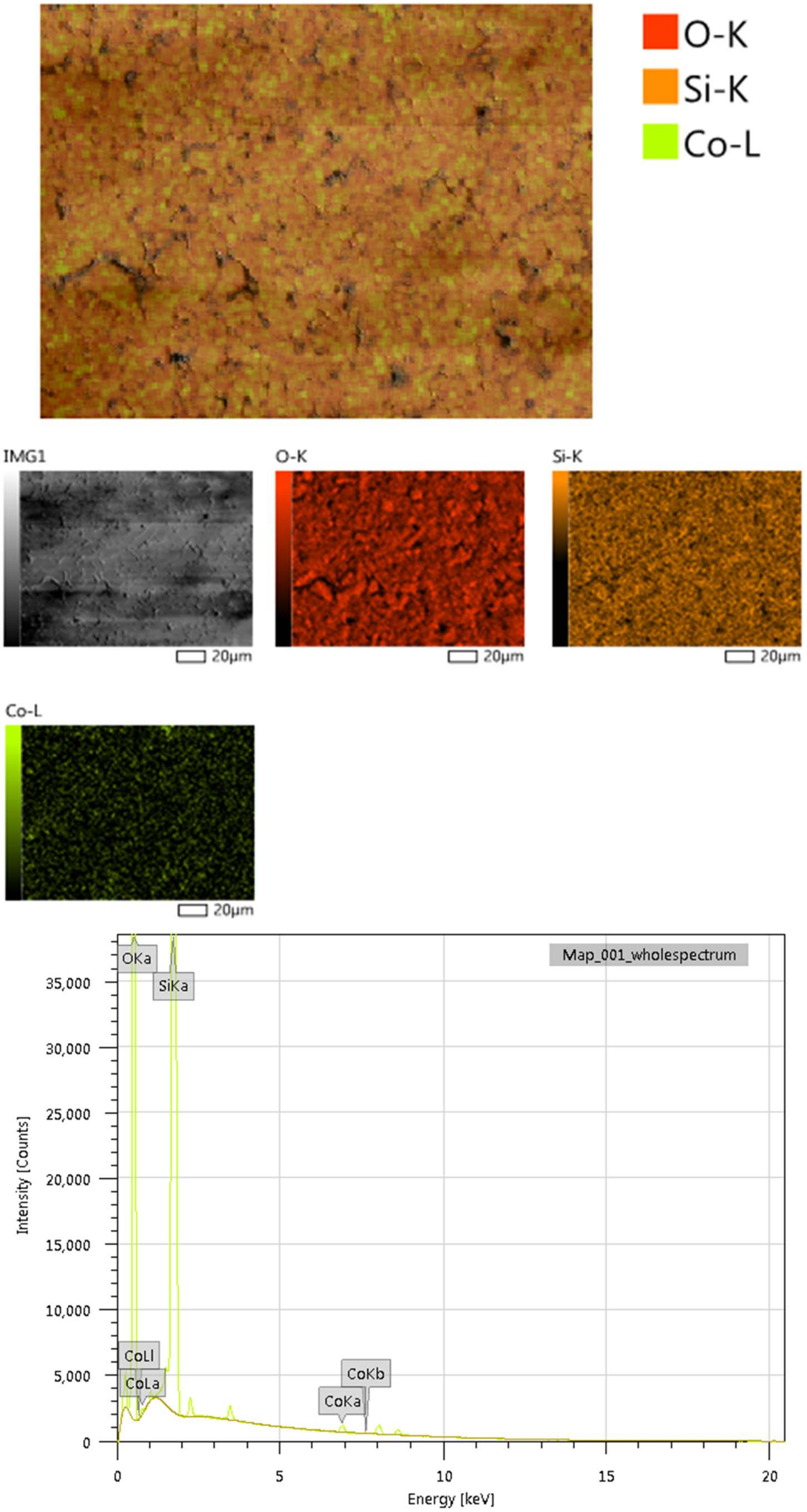
Type:	Routine
Archive:	Omnian He
Application:	Omnian He
Sample:	CoCl2 new Ingleazakis 0.2
Sum (%):	100,0000
Init weight:	1 g
Final weight:	1 g
Flux weight:	0 g
Norm.factor:	4,1361

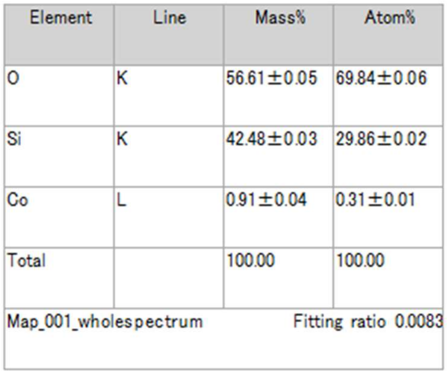
Omnian analysis

Calibration:	Omnian
Tag:	GENERAL
Recipe:	Axios
Processing Parameters:	Powders Elements

Compound	Value	Unit	Status
O	6,840	%	BgC;DC;
Al	0,022	%	BgC;DC;
Si	90,180	%	BgC;DC;
P	0,912	%	BgC;DC;
Cl	0,314	%	BgC;DC;
Ca	0,529	%	BgC;DC;
Fe	0,098	%	BgC;DC;
Co	1,048	%	BgC;DC;
Ni	0,027	%	BgC;DC;
Cu	0,021	%	BgC;DC;
Zn	0,007	%	BgC;DC;

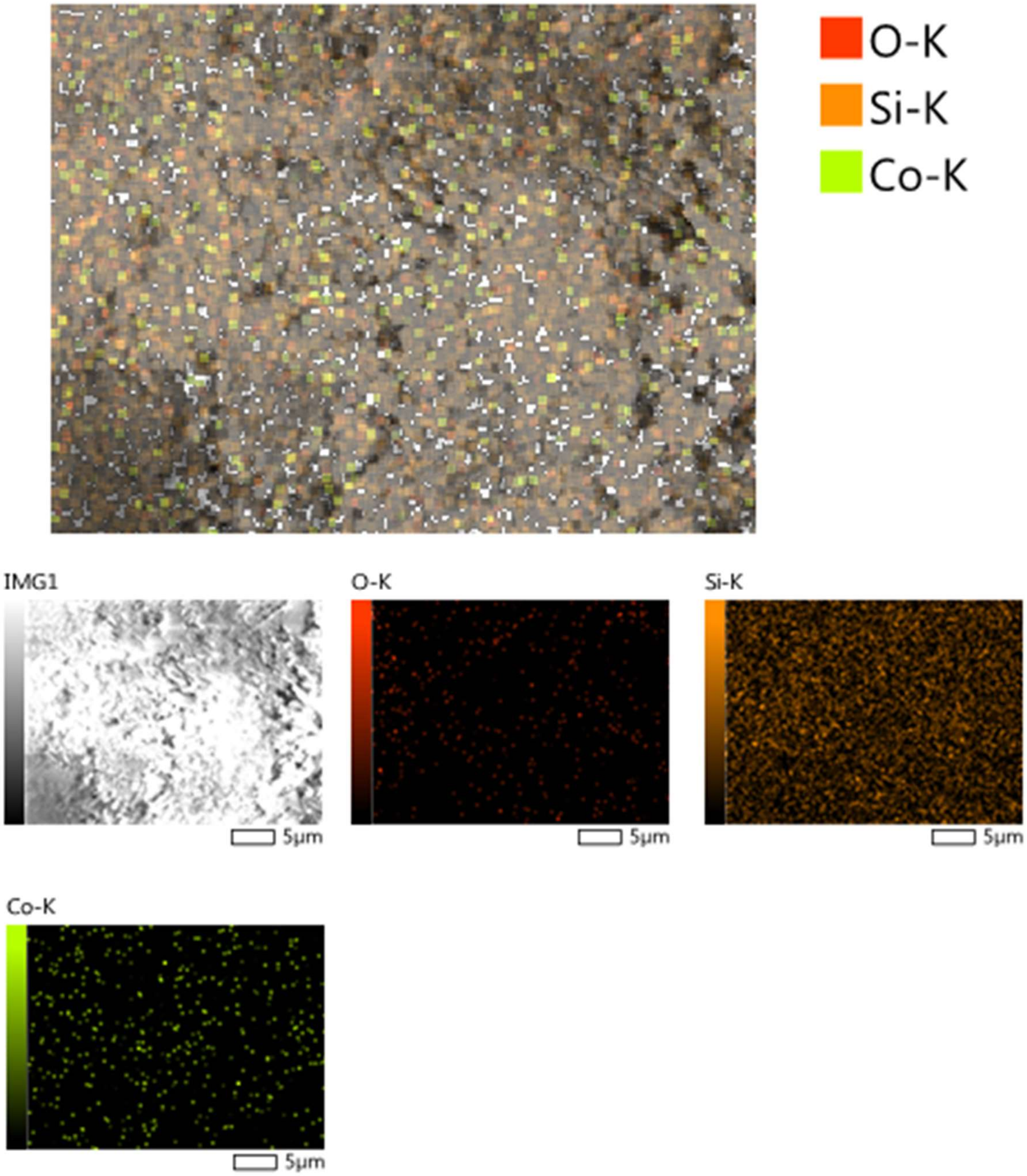
Figure 16. SEM-EDS map for the composite 1 (derived from $Co(OAc)_2$)

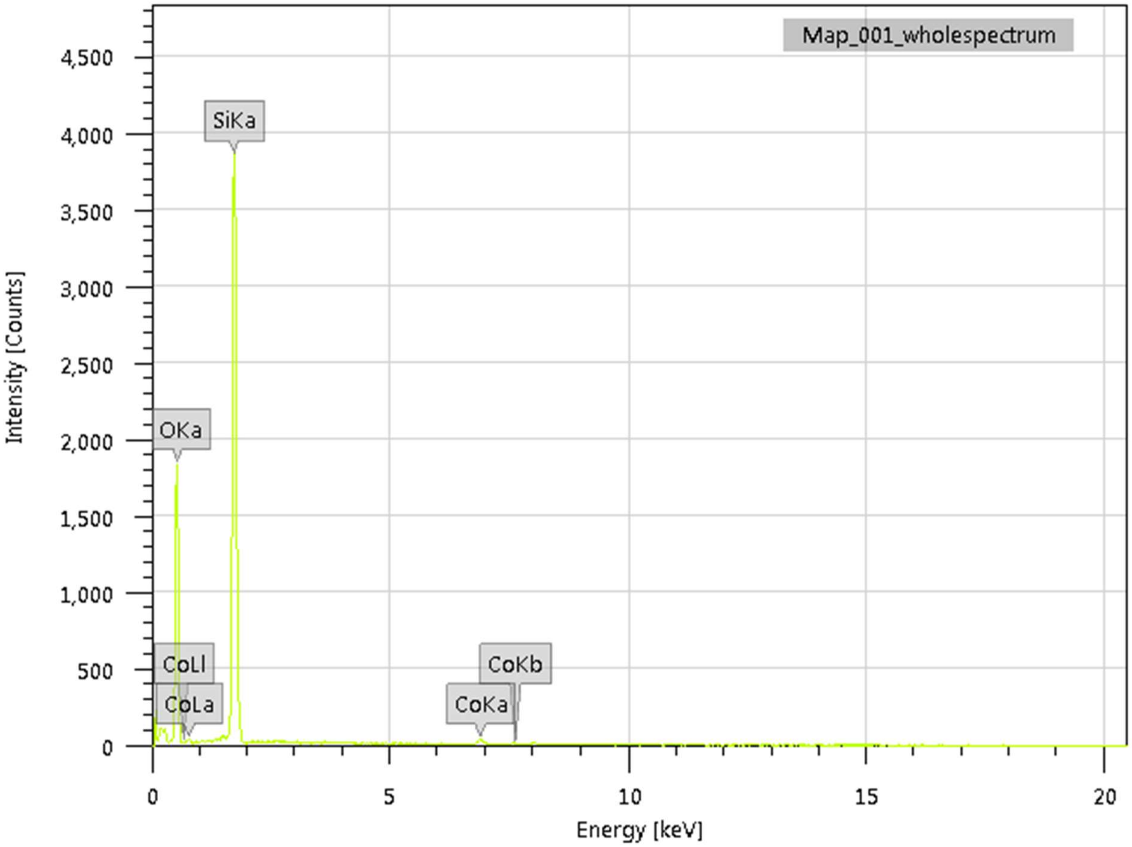


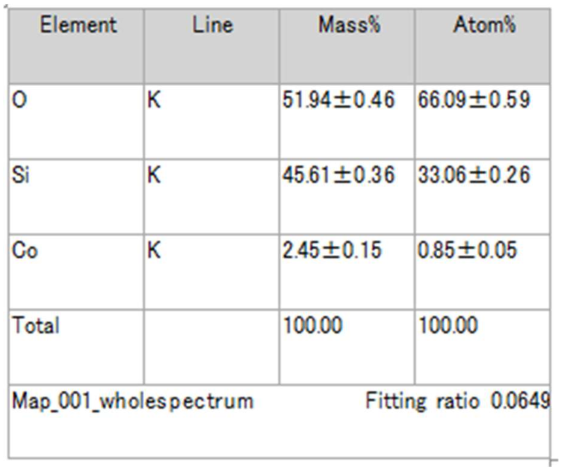


Element	Line	Mass%	Atom%
O	K	56.61±0.05	69.84±0.06
Si	K	42.48±0.03	29.86±0.02
Co	L	0.91±0.04	0.31±0.01
Total		100.00	100.00
Map_001_wholespectrum		Fitting ratio 0.0083	

Figure 17. SEM-EDS map for the composite 2 (derived from CoCl₂)







Element	Line	Mass%	Atom%
O	K	51.94±0.46	66.09±0.59
Si	K	45.61±0.36	33.06±0.26
Co	K	2.45±0.15	0.85±0.05
Total		100.00	100.00

Map_001_wholespectrum Fitting ratio 0.0649

Figure 18. SEM image of composite 1 (derived from Co(OAc)$_2$)

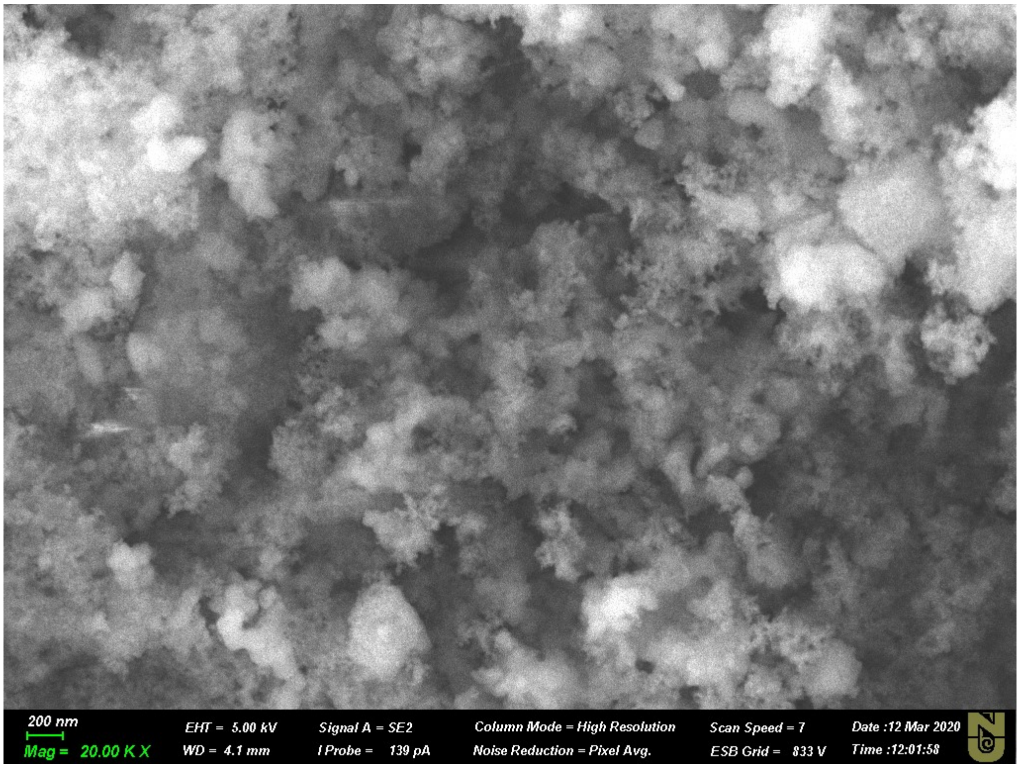


Figure 19. SEM image of composite 2 (derived from CoCl$_2$)

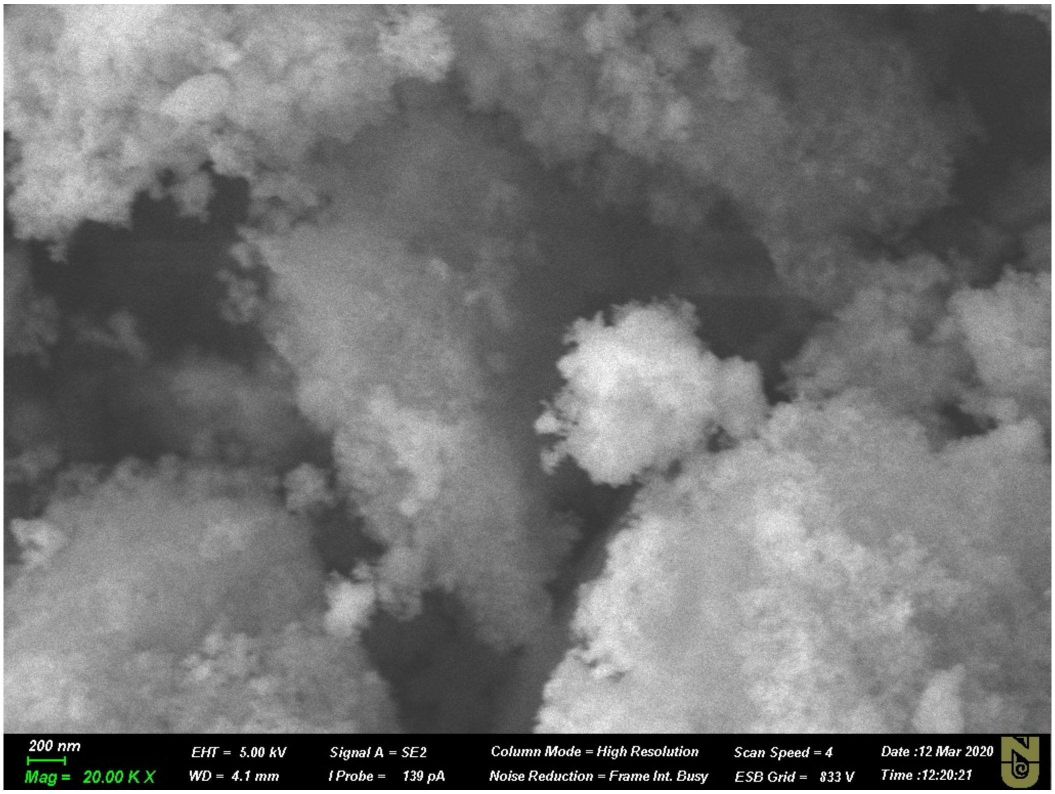


Figure 20. SEM image of composite 3 (derived from $CoCl_2$)

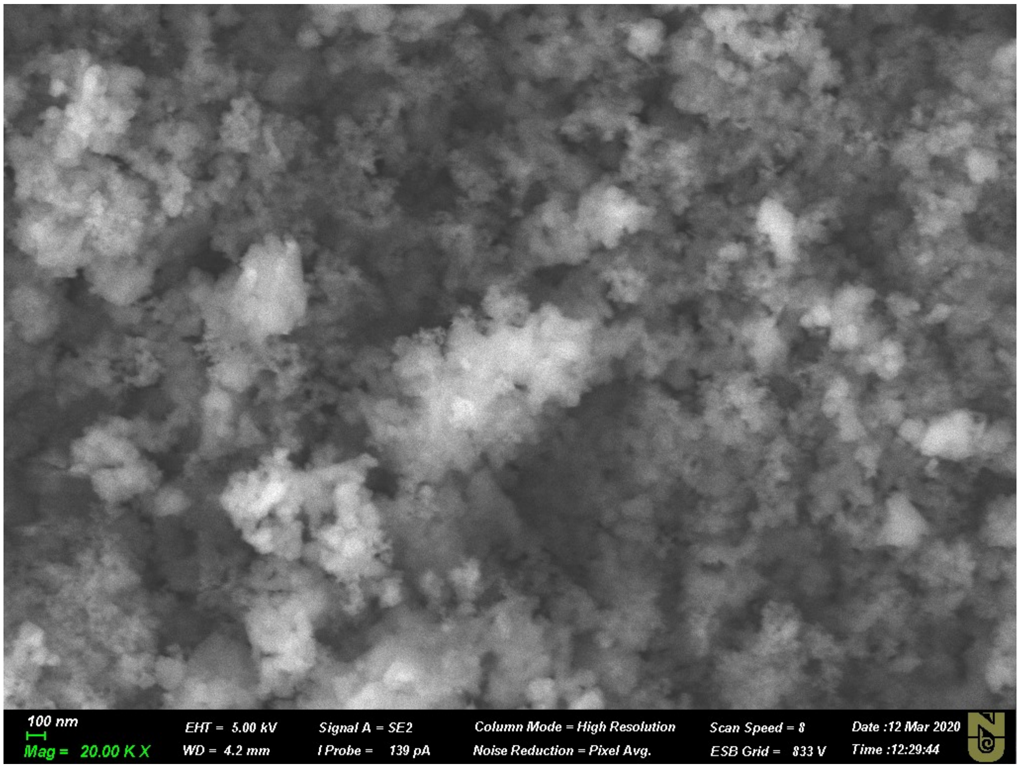


Figure 21. SEM image of pure TEOS-SiO_2 (1.2 mmol of activated Si-H)

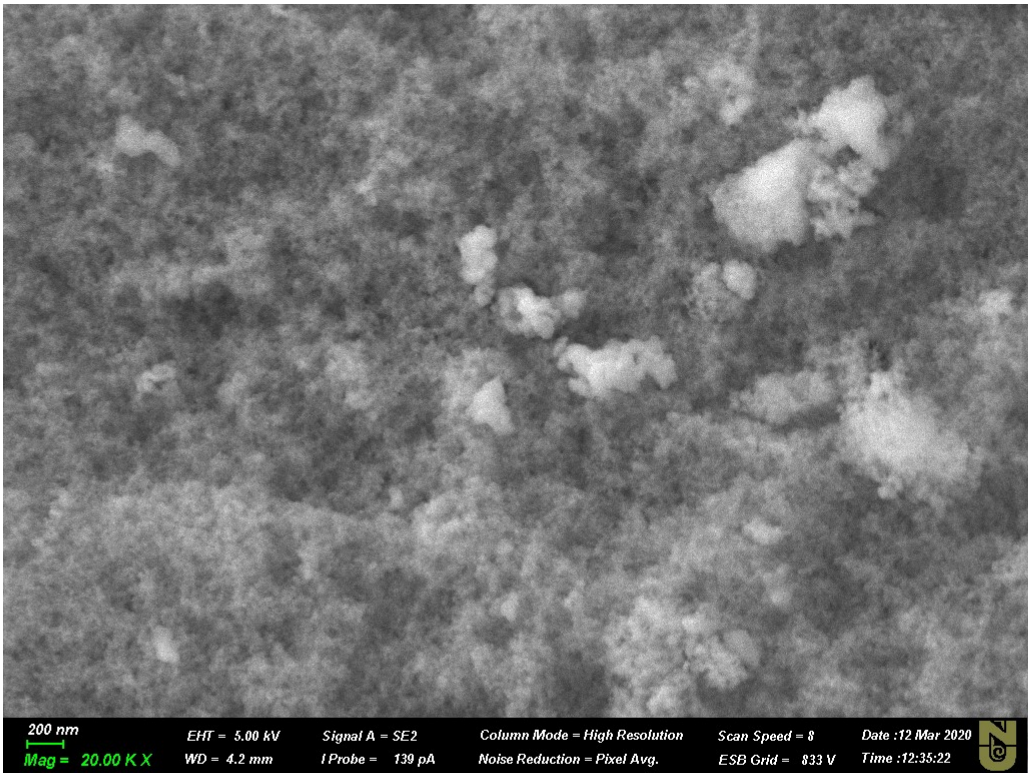


Figure 22. XRD spectrum of composite 1 (derived from $Co(OAc)_2$)

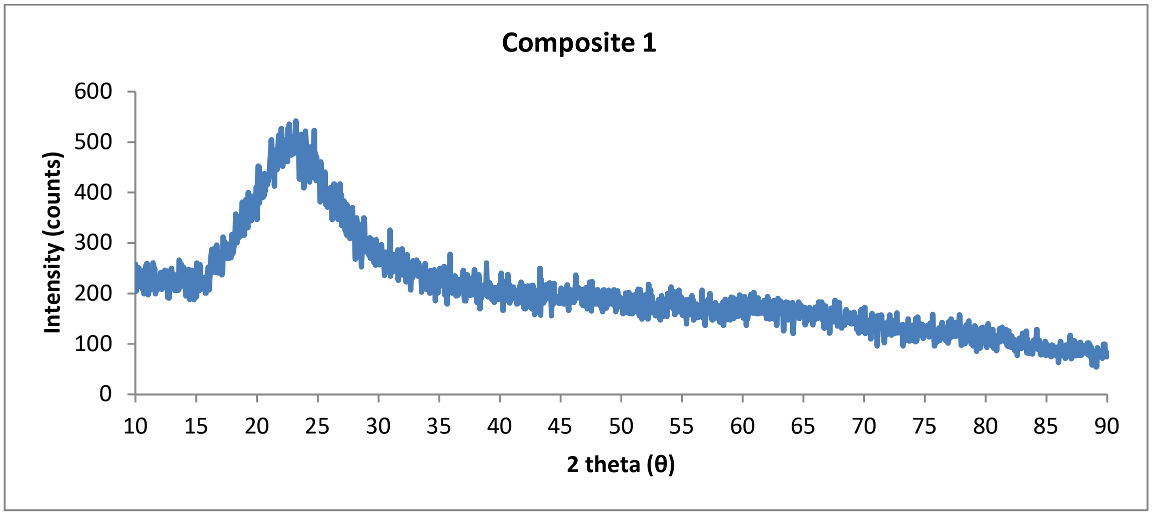


Figure 23. XRD spectrum of composite 2 (derived from $CoCl_2$)

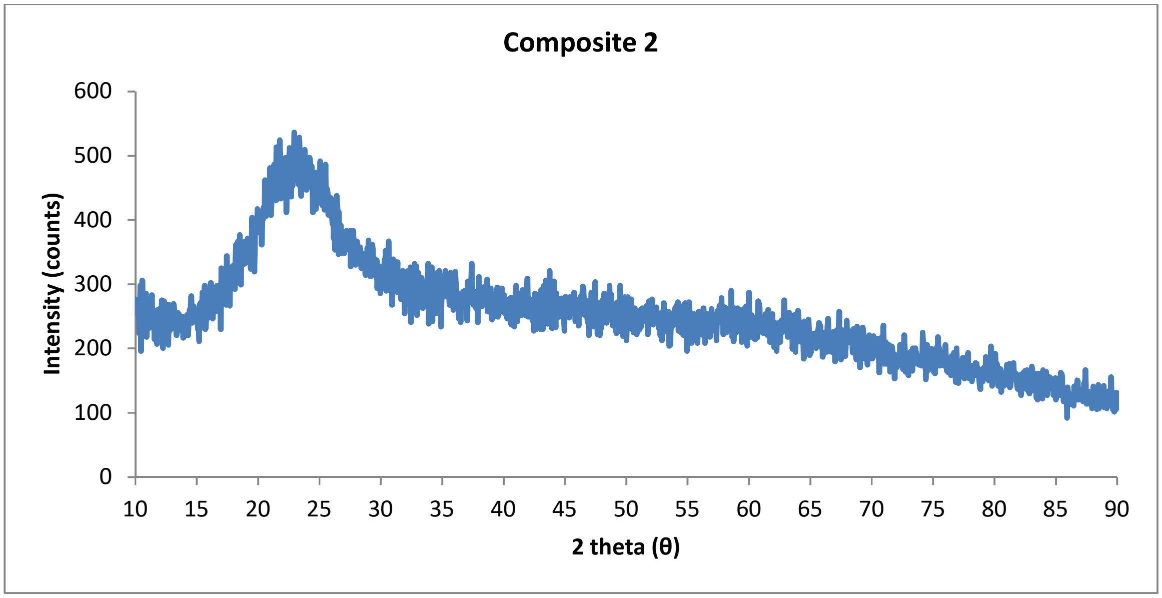


Figure 24. XRD spectrum of composite 3 (derived from $CoCl_2$)

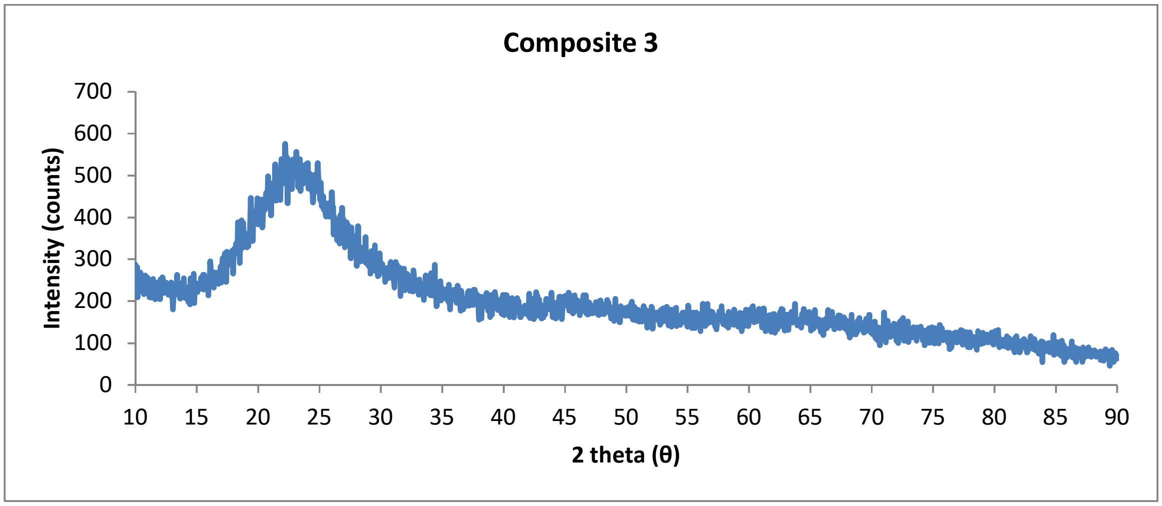


Figure 25. XRD spectrum of pure modified silica (TEOS-SiO_2, 1.2 mmol Si-H/1g)

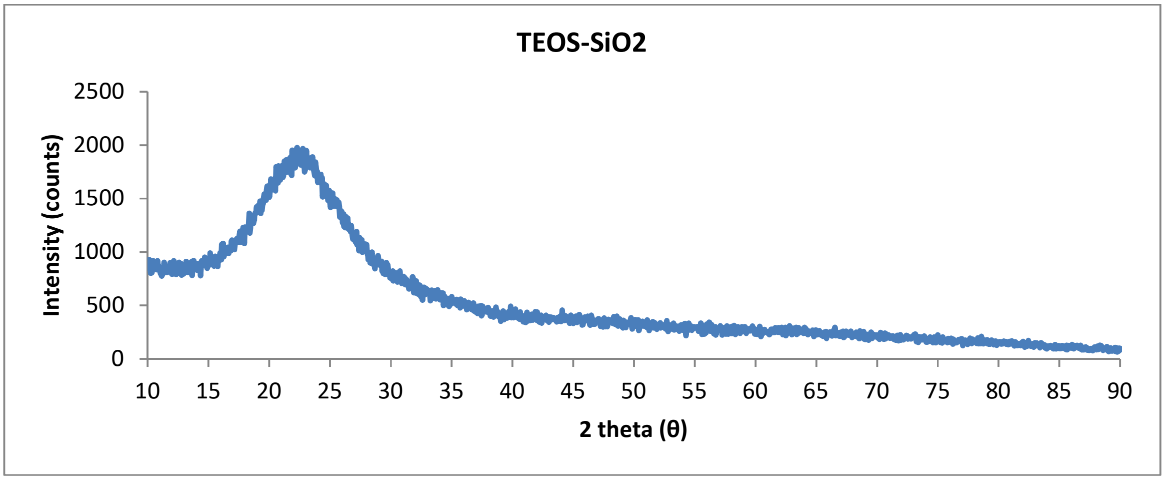


Figure 26. XRD spectrum of $Co(OAc)_2$

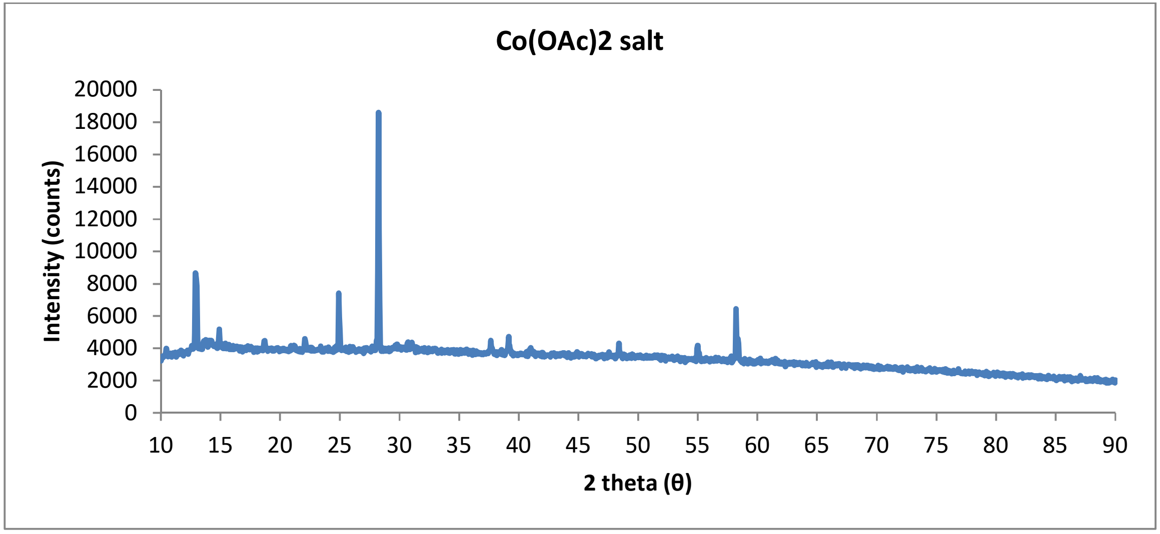


Figure 27. XRD spectrum of $CoCl_2$

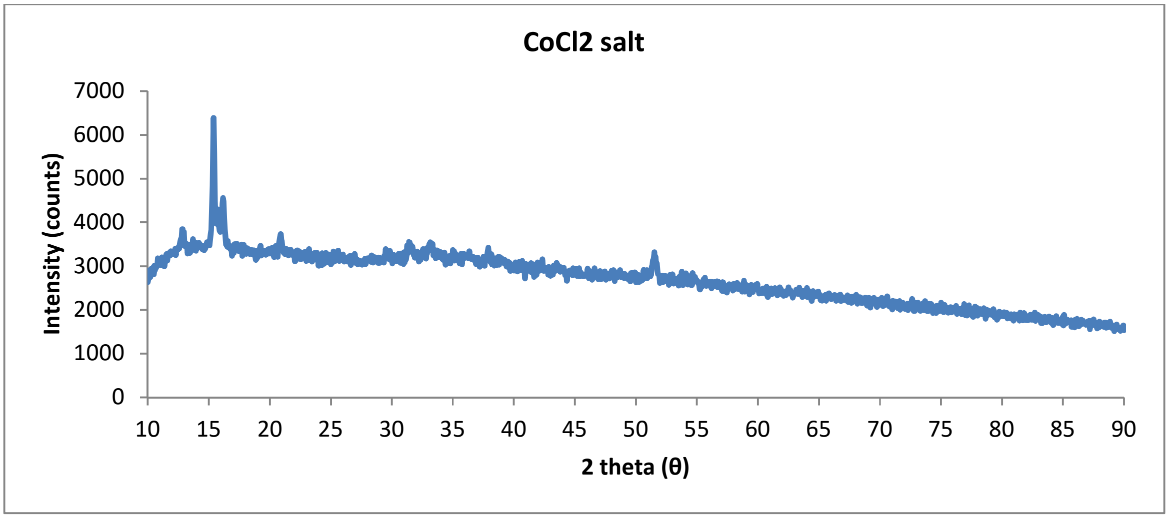


Figure 28. Raman spectrum of composite 1 (derived from Co(OAc)₂)

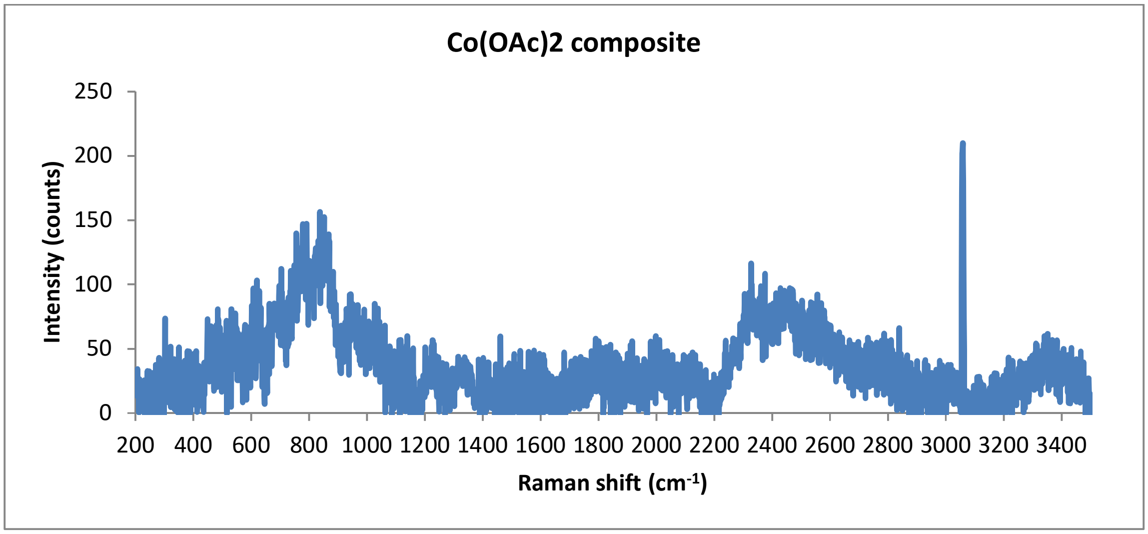


Figure 29. Raman spectrum of composite 2 (derived from $CoCl_2$)

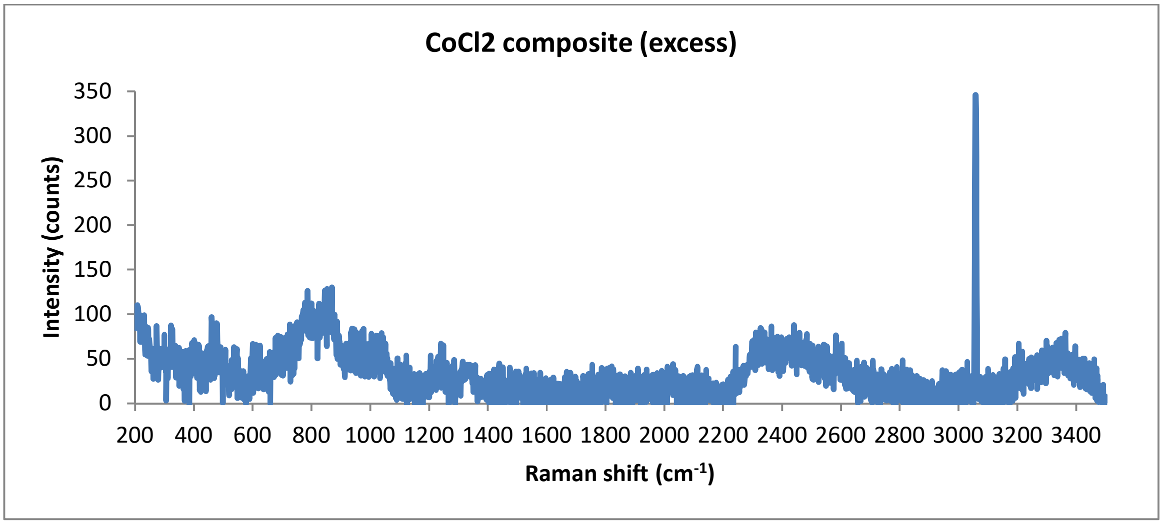


Figure 30. Raman spectrum of composite 3 (derived from $CoCl_2$)

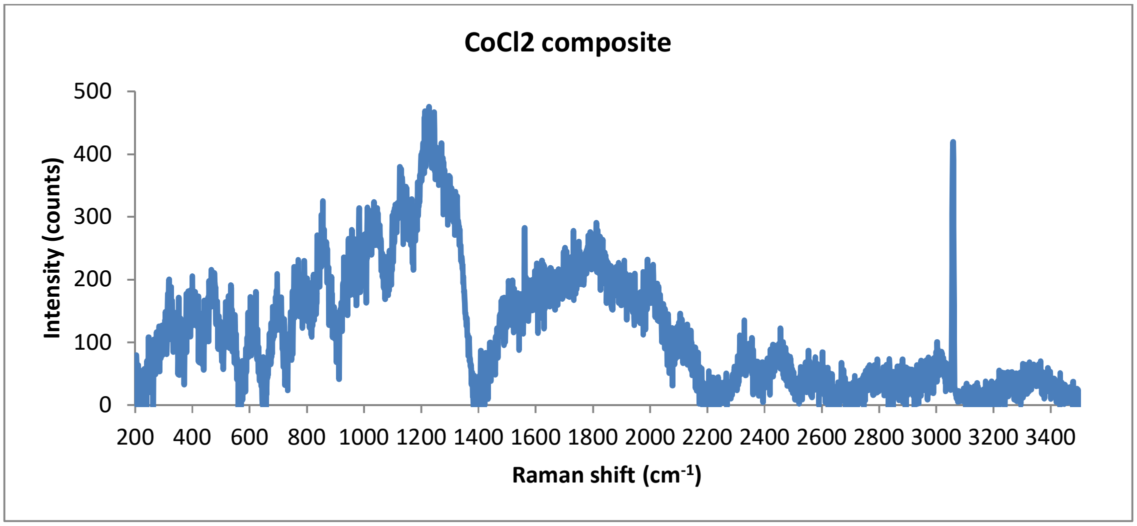


Figure 31. Raman spectrum of pure modified silica (TEOS-SiO₂, 1.2 mmol Si-H/1g)

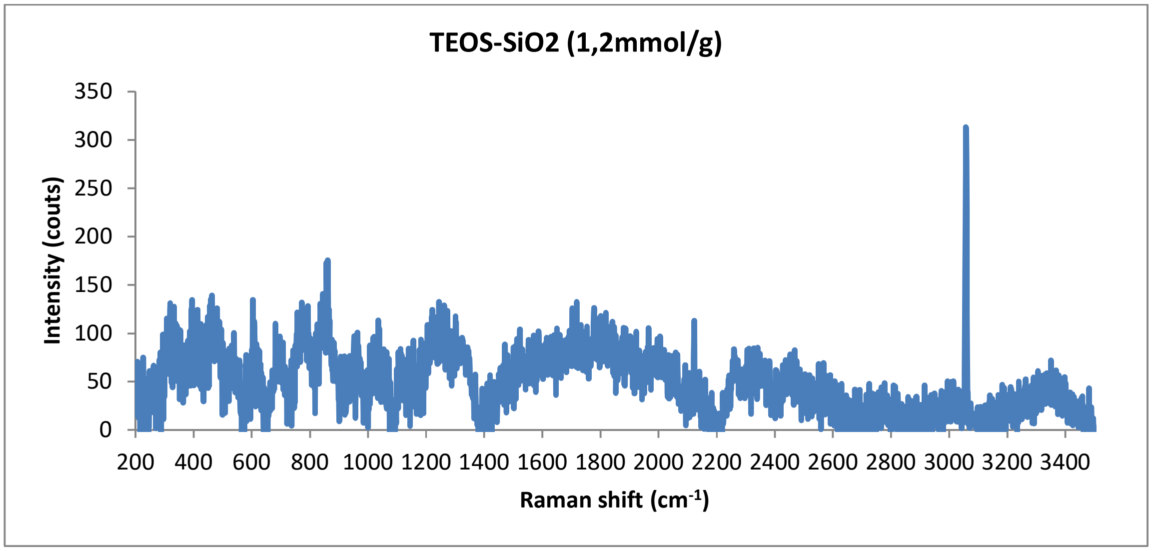


Figure 32. Raman spectrum of pure modified silica (TEOS-SiO₂, 0.9 mmol Si-H/1g)

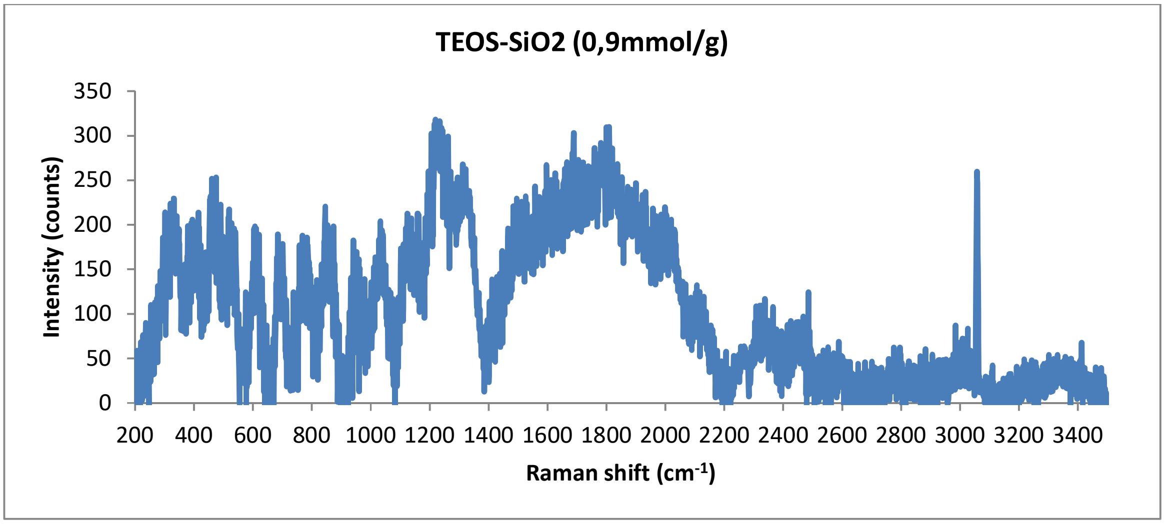


*Figure 33. Raman spectrum of Co(OAc)₂*4H₂O*

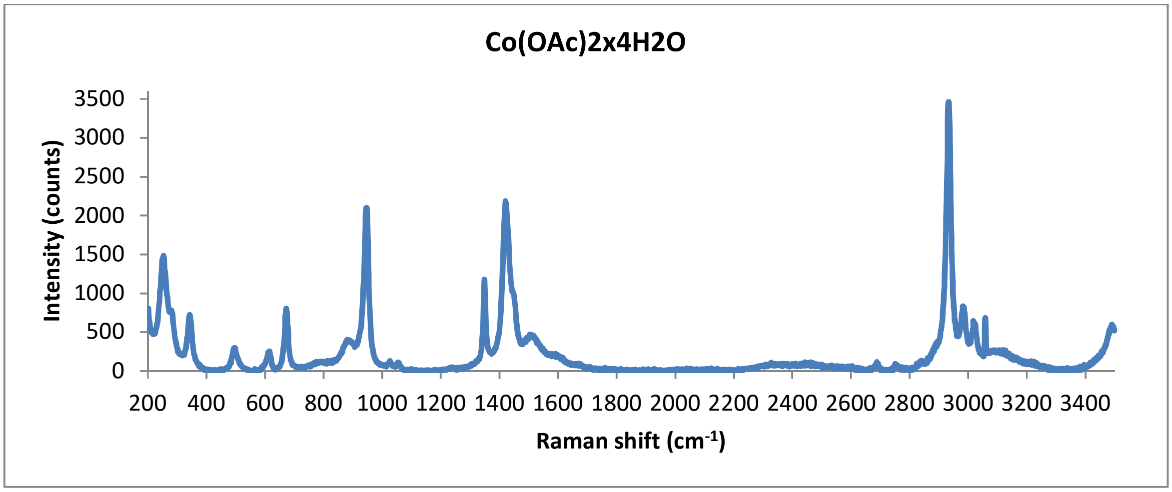


Figure 34. Raman spectrum of $CoCl_2$