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Synthesis of cobalt oxide nanoparticles coated with carbon and its catalytic applications in organic reactions

Sachin Kharat [a,b], Shailendra Dahiwale [a], Shaukatali N. Inamdar [c,*], Mahadev P. Shinde [a,b,c,*]

[a] Department of Chemistry & Central Research Laboratory, ASC College Indapur, dist-Pune 413 106, India
[b] Department of Chemistry, PDEA's Baburaoji Gholap College, Sangvi, Pune 411027, India
[c] Department of Pharmaceutical Chemistry, College of Health Sciences, University of KwaZulu-Natal, Westville, Durban 4000, South Africa

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ABSTRACT

Cobalt oxide nanoparticles coated with carbon were prepared by the modified flame pyrolysis method. The preparation was carried out by simply exposing the cobalt nitrate salt onto a spatula to gas flame, the flame temperature converted the cobalt nitrate into cobalt oxide, which further get coated by carbon produced from the combustion of fuel gas. The obtained product from the flame pyrolysis was characterized using techniques viz. XRD, FTIR and SEM. SEM data show that the short length rod shaped nanoparticles coated with carbon ranging from 0.3 to 1 μm μm formed during the process. XRD and FTIR data also support the formation of cobalt oxide nanoparticles coated with carbon particles. Cobalt oxide NPs were utilized for the catalytic N-formylation reaction of amines at 70–80 °C. The optimization of the catalyst as well as temperature have been done carefully. The product of the reaction were characterized by various techniques viz. FTIR, HRMS and ^{1}H NMR which confirmed the formation of the product.

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1. Introduction

Metal oxide demonstrates wide range of applications. Cobalt oxide here is the most stable phase in the Co-O system [1–4]. Cobalt oxide has been reported demonstrating wide range of applications viz. in lithium-ion batteries, heterogeneous catalysts, gas sensing, ceramic pigments, electrochemical devices etc. [5–9]. Co_3O_4 reportedly plays a vital role as selective coating material for the high-temperature solar collectors [10]. Supercapacitors are responsible for the advancement of mobile phones, digital cameras and solar cell power storage. Some electrode material which can be used in the supercapacitors is made up of metal oxides, metal sulfides etc. Co_3O_4 nanoparticles as electrode material for supercapacitors were also reported in the literature [11]. Cobalt oxide also gained very much attention in supercapacitors applications in the worldwide researchers, as it has capability to impart higher power density than normal batteries.

Various methods like sol–gel, surfactant-mediated synthesis, thermal decomposition, polymer-matrix assisted synthesis and spray-pyrolysis are well known for the synthesis of Co_3O_4 nanoparticles [12–14].

Applications of transition metal-oxide nanoparticles especially cobalt oxide are also well known in the organic reactions. Various reactions of N-formylation of aliphatic and aromatic amines have been reported. Reactions were carried out either in the broad range of solvents or under solvent free condition. Application of cobalt oxide NPs on growth of various parts of the plants are also reported in the literature [15–21]. Various biological applications of cobalt oxide have been found [22–26].

N-Formyl compounds are the main precursors as protecting groups for amines and an ideal starting material for isocynide compounds. [2–3] These compounds can also act as an intermediate for mono methylated amines from primary amines [4].

Many reports on the formylation reactions are available such as chloral,[27] activated formic acid using DCC [28] or EDCI,[29] formic esters [30–33] and ammonium formate [34]. Although these strategies have their own advantages high yield, mild reaction conditions but they are expensive and may be toxic to use. The green approach for such reactions has great importance concerning to the 'save environment campaign' run all over the world.

Here, we report a modified flame pyrolysis method to synthesis cobalt oxide nanomaterial from cobalt nitrate. We used modified

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* Corresponding authors.

E-mail addresses: saliinamdar@gmail.com (S.N. Inamdar), mahadevs07@gmail.com (M.P. Shinde).

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method developed by Inamdar *et al.* [35–40]. In short, the cobalt oxide nanomaterial prepared using cobalt nitrate salt directly burned in the ordinary gas flame. It's very simple, facile, easy to operate and economical method which yielded rod shaped nanoparticles ranging from 0.3 to 1 µm. The prepared product is utilized directly as catalyst for the N-formylation reaction. In this strategy we first optimized the quantity of catalyst required for the completion of the reaction. The temperature optimization was also done under the solvent free condition. Overall, we report here very simple and solvent free approach for the preparation of N-formyl amines using cobalt oxide nanoparticles (Co_3O_4) as catalyst.

2. Experimental

AR grade materials were used for the preparation of cobalt oxide nanoparticles. A civil gas was used to produce the flame which is employed for the heating the material to get nanosized Co-O material. The resulting product was characterized by using various techniques such as XRD, EDS, FTIR, SEM, UV–Visible etc. Reactions were monitored by the silica coated alumina TLC plates. The resulting organic products were isolated and purified by appropriate chromatographic methods. The characterization of the N-formylated products have been done using FTIR, ^{1}H NMR, and mass spectrometry.

2.1. Preparation of cobalt oxide nanoparticles

AR grade 0.50 g (2.7 mM) cobalt nitrate was taken into the spatula and heated over ordinary gas flame for about 15 to 20 min. The sample first was melted and then transformed in to solid dark brown colored material and finally converted into black colored material. The product was collected and weighed. 0.45 g (2.4 mM) product was obtained. The black powder of the product was characterized by SEM, XRD, UV, and IR and confirmed the formation of rod-shaped cobalt oxide nanoparticles. The resulting product showed magnetic property checked by ordinary magnet.

3. Result and discussion

3.1. FTIR of Cobalt-Oxide nanoparticles:

FT-IR spectrum of Co_3O_4 nanoparticles (Fig. 1) depict prominent absorption peaks at 655 and 540 cm^{-1}. The Co—O stretching frequency was assigned to 540 cm^{-1}and absorption band at 655 cm^{-1} was assigned to bridging vibrations of O—Co—O bond [17]. The octahedral site of Co^{3+}–O vibrations were observed at 655 cm^{-1} band and tetrahedral site Co^{3+}–O of the Co_3O_4 lattice were attributed to 540 cm^{-1}[18].

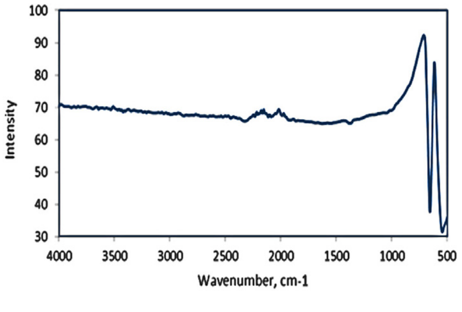

Fig. 1. FT-IR spectrum of cobalt oxide NPs.

3.2. XRD of Cobalt-Oxide nanoparticles:

XRD pattern of as prepared catalyst is shown in Fig. 2. The formation of Co_3O_4 nanoparticles from the cobalt nitrate can be seen in the pattern. The sharp peaks at 2θ values are indexed as 220 (31.92°), 311 (37.44°), 511 (59.92°) & 440 (65.76°) to the characteristic (JCPDS file no. 42–1467) peaks of the Co_3O_4 [41].

3.3. SEM of Cobalt-Oxide nanoparticles:

SEM image of the prepared catalyst Co_3O_4 nanoparticles is given in Fig. 3. The image clearly shows formation of rod like structure. The length of the rod is observed ranging from 0.3 to 1 µm. the structure of the prepared catalyst seen uniform throughout in the form of rods.

3.4. EDS of Cobalt-Oxide nanoparticles

EDS of the prepared catalyst Co_3O_4 nanoparticles is given in Fig. 4. The EDS showed major composition of the catalyst as Co, O and C. traces of Zn are observed may be due to impurities either from spatula or in the cobalt salt itself.

4. Applications of cobalt oxide nanoparticles in organic reactions

There are very few reports available on use of cobalt oxide NPs in the organic reactions. N-formylation of amines have been achieved using different metal oxide catalysts [19–25]. However, heterogeneous catalysts have more advantages over homogenous catalysts due to their recovery at the end of the reaction without major loss of activity and ease of handling, despite the merit homogeneous catalyst it is difficult to recover and reuse.

The scope of N-formylation reaction was demonstrated by the reaction of diverse amines with formic acid. The use of aromatic amines having various substituents like nitro, chloro, alkyl, methyl etc. On aromatic ring resulted into the formation of desired products.

4.1. Optimization of cobalt oxide NPs in the organic reactions

Optimization of the cobalt oxide NPs was done at various quantities and is tabulated as shown in Table 1. Finally, it's concluded that 5 mg catalyst was sufficient to achieve the conversion at set temperature of 80 °C. The yield of the reaction was found to be 92 % (Table 1: entry 7). These reaction conditions were applied for further reactions (Fig. 5 and Fig. 6).

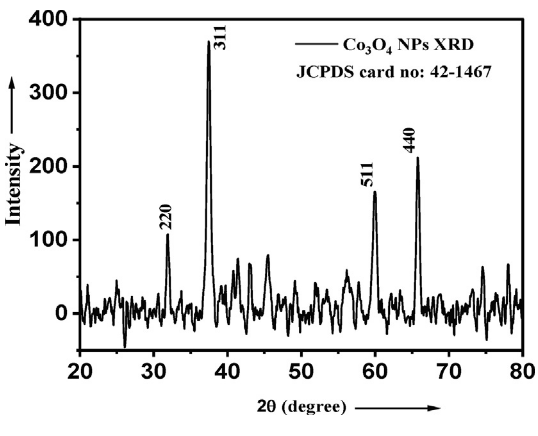

Fig. 2. XRD pattern of the catalyst cobalt oxide NPs.

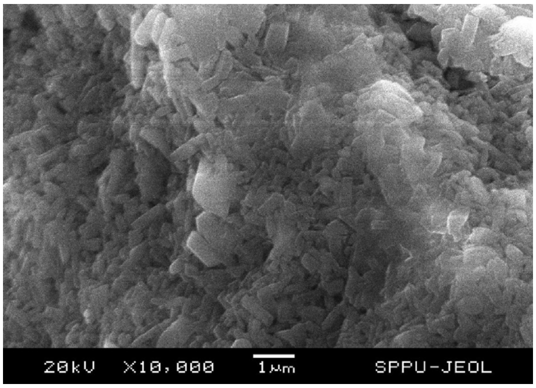

Fig. 3. SEM spectrum of cobalt oxide NPs.

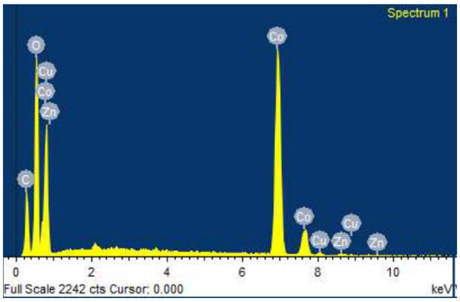

Fig. 4. EDS spectrum of cobalt oxide NPs.

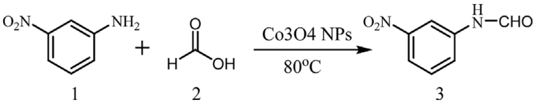

Fig. 5. Solvent free N-formylation of m-nitroaniline using formic acid and Co_3O_4 NPs.

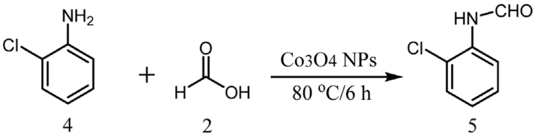

Fig. 6. Solvent free N-formylation of o-chloroaniline using formic acid and Co_3O_4 NPs.

We have successively achieved solvent free N-formylation of aromatic amines using formic acid and catalytic amount of cobalt-oxide nanoparticles. The temperature range of 70–80 °C was employed for the period of 3–4 h under nitrogen atmosphere. Before that optimization of catalyst was done at the same reaction condition. Here formic acid reagent was acting as solvent for the reaction. This green reaction was monitored by TLC and the resulting product was characterized by NMR, mass spectra (HRMS) and FTIR (Fig. 7).

In second example we use o-chloroanilin precursor for N-formylation reaction under identical reaction conditions (Fig. 6). The product in excellent amount was obtained from this reaction and subsequent purification provide bright pale yellow-colored crystals. The confirmation of the product o-chloro N-formyl amine done was using FTIR, ^{1}H NMR and LCMS (refer Fig. 8).

4.2. Experimental procedure

4.2.1. Preparation of N-formyl m-nitroaniline ***3***

A mixture of 0.5 g (0.0036 mol) of amine, Cobalt oxide NPs in catalytic amount (0.005 g) and about 3 equiv. of formic acid (0.5 g, 0.0106 mol) was heated at 80 °C for about 6 hrs. The progress of reaction was monitored by TLC, and after starting material was disappeared, the reaction mixture was allowed to cool at room temperature and ether (20 ml) was added in the reaction flask and filtered. Finally, after washing with 1 N $NaHCO_3$ and treatment with sodium sulphate, the solvent gets evaporated and collected the crude product quantitatively. The reaction product was recrystallized in DCM solvent to get pale yellowish 0.55 g product in almost 92% yield.

FTIR: 3258 cm^{-1} (N–H stretch), 1689 cm^{-1} (-C = O stretch), 1392–1518.62 cm^{-1}(N = O stretch).

^{1}H NMR: δ 10.70 (S, 1H, **H**-CO), δ 8.86 (t, 1H, J = 2.0 Hz, Ar-**H**), δ 8.39 (d, 1H, J = 1.2 Hz, N–**H**), δ 7.95 (dd, J = 8 Hz & 2 Hz, Ar-**H**), δ 7.89 (dd, J = 8 Hz & 2 Hz, Ar-**H**), δ 7.61 (dd, J = 8.4 Hz & 8.4 Hz, Ar-**H**).

Table 1
Optimization of cobalt oxide NPs in the organic reactions.

Entry	Substrate	Amount of catalyst (Co_3O_4)	Reaction temperature	Yield in %
1	m-nitroaniline	100 mg	80 ℃	85
2	m-nitroaniline	75 mg	80 ℃	86
3	m-nitroaniline	50 mg	80 ℃	90
4	m-nitroaniline	25 mg	80 ℃	91
5	m-nitroaniline	10 mg	80 ℃	90
6	m-nitroaniline	5 mg	80 ℃	92

LCMS: M/Z, [M^+] 166, 165.

4.2.2. Preparation of N-formyl o-chloroaniline ***5:***

A 0.5 g (0.0039 mol) of o-chloroaniline was added to the flask containing cobalt oxide NPs in catalytic amount (0.005 g) and formic acid (0.5 g, 0.0106 mol). The resulting mixture was heated at 80 °C for the period of 6 hrs. After TLC check the reaction mixture was cooled to room temperature and ether (20 ml) was added to the reaction flask, filtered and finally washed with 1 N $NaHCO_3$ followed by treatment with sodium sulphate. Solvent from the reaction mixture evaporated off and crude product was collected quantitatively. The obtained product was recrystallized in DCM solvent to get bright pale yellow product in 0.52 g. The confirmation of the product as follows.

FTIR: 3244 cm^{-1} (N–H stretch); 2898 cm^{-1}(H-C = O, C–H stretch); 734.39 cm^{-1} (C-Cl stretch).

^{1}H NMR: δ 9.86 (S, 1H, **H**-C = O); δ 8.85 (d, 1H, J = 0.8 Hz,N–**H**); δ 8.09 (dd, J = 9.2 & 1.2 Hz, Ar-**H**); δ 7.51 (dt, J = 1.2 & 1.2 Hz, Ar-**H**); δ 7.35 (dt, J = 1.2 & 1.2 Hz, Ar-**H**); δ 7.15 (dd, J = 1.6 & 1.6 Hz, Ar-**H**).

LCMS: M/Z, [M^+] 155, 153.99.

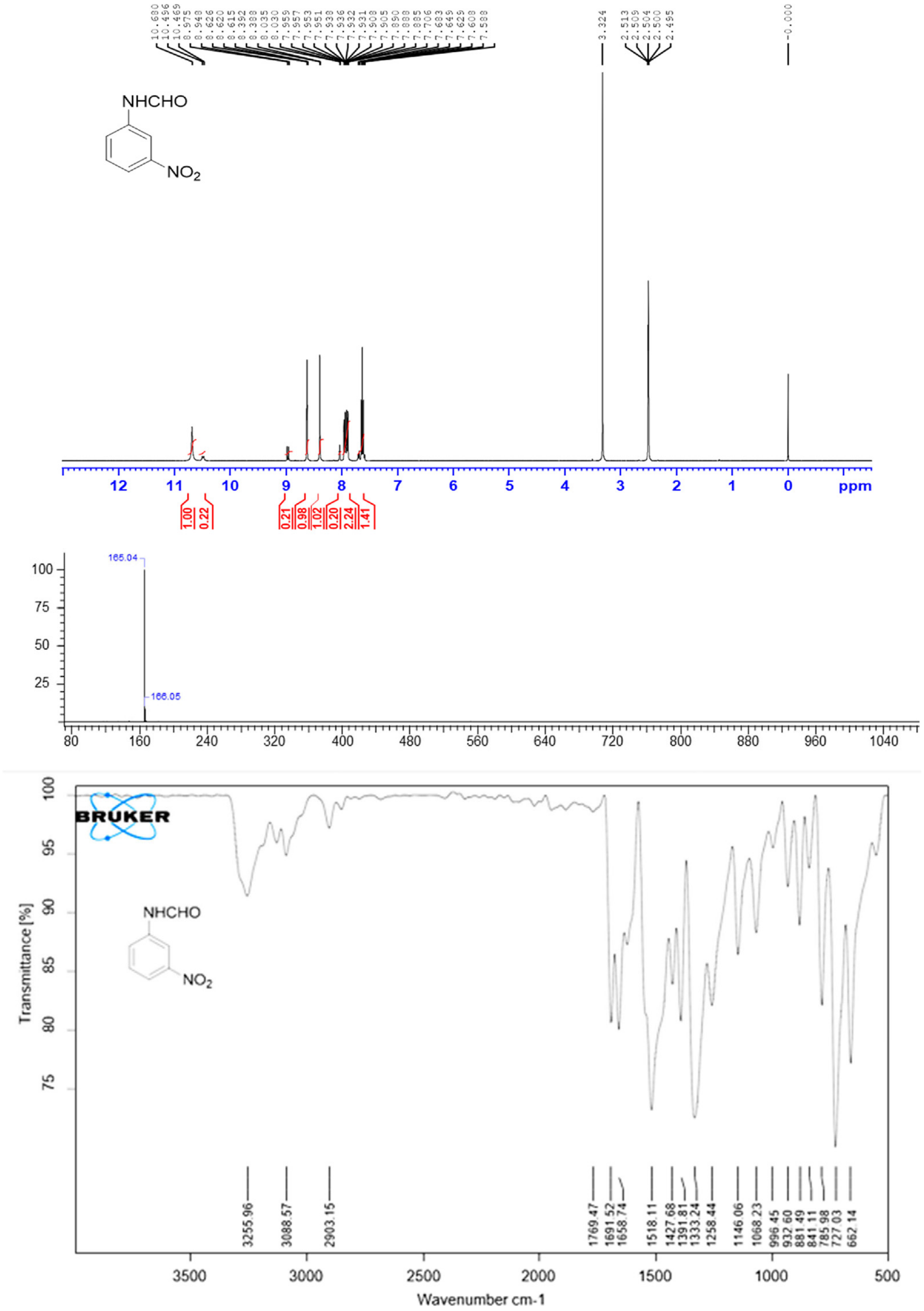

Fig. 7. NMR, HRMS and FTIR of m-nitroaniline synthesized using Co_3O_4 NPs.

5. Conclusion

In conclusion we can say that cobalt oxide nanoparticles coated with carbon particles have been prepared by the exposure of cobalt nitrate to ordinary gas flame in excellent yield. SEM, UV, XRD and EDS data support the formation of short length ranging from 0.3 to 1 µm rod shaped nanoparticles coated with carbon. Optimization showed that catalytic amount of catalyst is required to complete the reaction. Therefore, catalytic amount of cobalt oxide NPs were employed for the N-formylation of amines. The products of the reaction were characterized by various techniques viz. FTIR, ^{1}H NMR, which confirmed the formation of the product in excellent yield.

CRediT authorship contribution statement

Sachin Kharat: Conceptualization, Investigation. **Shailendra Dahiwale:** Data curation, Formal analysis. **Shaukatali N. Inamdar:** Formal analysis, Writing – review & editing. **Mahadev P. Shinde:** Conceptualization, Supervision, Writing – original draft.

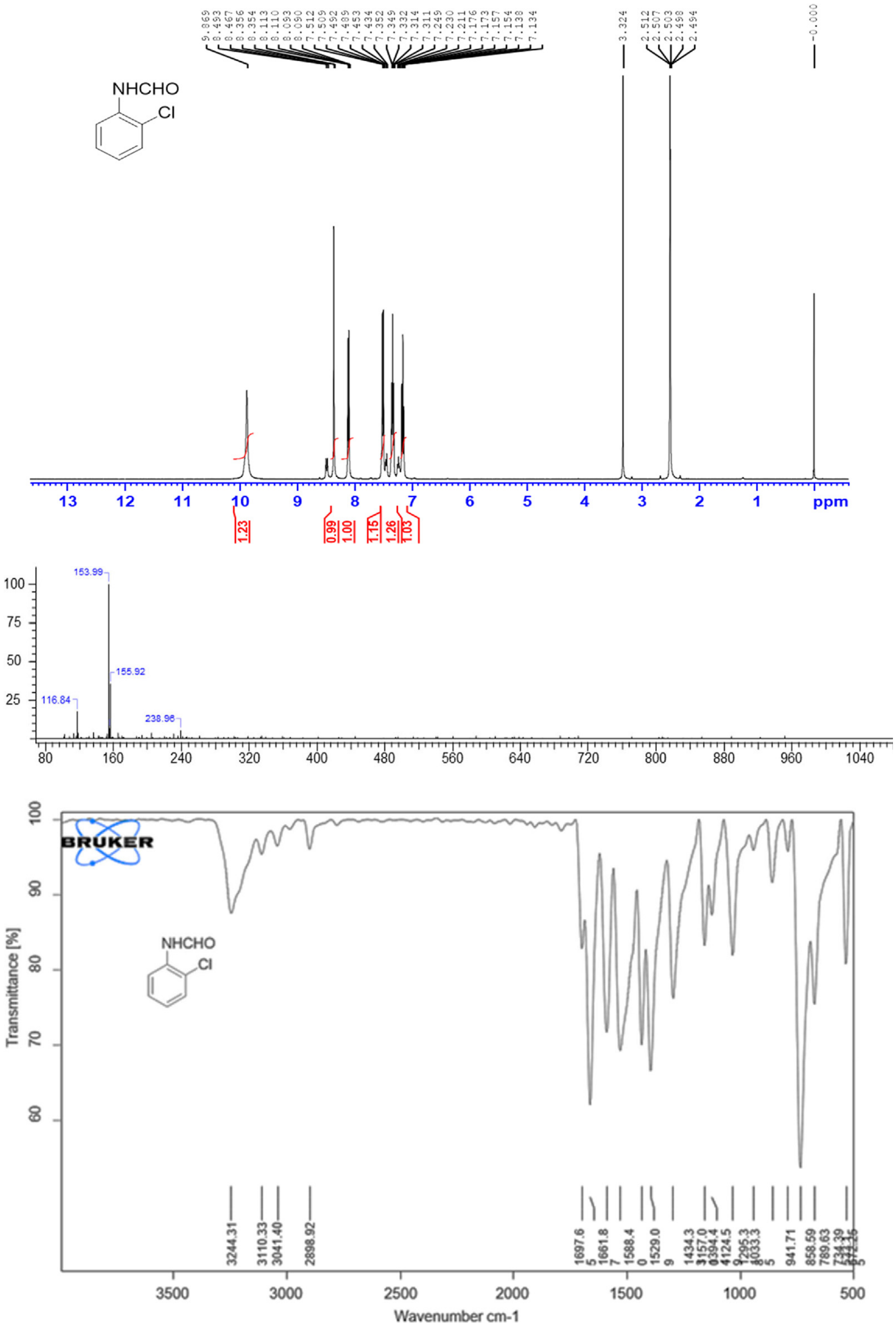

Fig. 8. NMR, HRMS and FTIR of o-chloroaniline synthesized using Co_3O_4 NPs.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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