Original Article

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The green synthesis of pyranopyrazole derivatives by silica supported cobalt chloride and cobalt nitrate as nanocatalysts

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Abstract

In this work, anhydrous cobalt salts of cobalt chloride and cobalt nitrate ($CoCl_2$ and $Co(NO_3)_2$) were stabilized on the silica gel surface. Characterization of these nanoparticles was investigated by the FT-IR (Fourier Transform Infrared Spectroscopy), FE-SEM (Field Emission Scanning Electron Microscope), EDS (Energy -Dispersive X-Ray Spectroscopy), XRD (X-ray Diffraction), and ICO-OES (Inductively Coupled Plasma Optical Emission Spectroscopy). Furthermore, the efficiency of these nanoparticles was investigated for one-pot synthesis of pyranopyrazole and spiropyranopyrazole derivatives via a four-component reaction of hydrazines, ethyl acetoacetate, aldehyde or isatine derivatives, and malononitrile or ethyl cyanoacetate under green media. The obtained data from EDX and ICO-OES analyses confirm the amount of cobalt metal in SiO_2@$CoCl_2$ is more than that in SiO_2@$Co(NO_3)_2$. The availability and reusability of SiO_2@$CoCl_2$ catalyst without its significant reduction in catalytic efficiency during six runs, suitable reaction times, easy workup procedure and good efficiency are some advantages of this green procedure.

Keywords: Pyranopyrazoles; Spiropyranopyrazoles; Silica gel@Co salts; One-pot synthesis; Nanocatalyst

1. Introduction

Among organic reactions, multi-component reactions are extremely important in pharmaceutical and industrial chemistry because of many advantages such as short reaction time, high degree of atom economy, convergence, and easy workup [1-3]. These advantages are in line with the principle of green chemistry [4-6]. Pyranopyrazoles are an important class of heterocyclic compounds due to their biological activities such as anti-cancer, anti-microbial, anti-tubercular, and anti-inflammatory [7-11]. In recent decades, several methods have been reported for one-pot synthesis of pyranopyrazoles due to their importance in pharmaceutical researches. These compounds have been prepared via a multi-component reaction of the related materials in the presence of different catalysts such as ZnO nanoparticles [12], $[(CH_2)_4SO_3HMIM][HSO_4]$ [13], Cu (II)- β- cyclodextrin complex stabilized on magnetic nanoparticles [14], nano-SiO_2 /HMTA [15], Fe-CaO_X [16], and $InCl_3$ [17]. Despite their advantages, some of these methods have certain restrictions such as use of force reaction conditions and low product yields. Therefore, development of a facile and mild general method based on green chemistry to overcome these restrictions for the synthesis of pyranopyrazoles is a challenge for organic chemists.

The use of nanoparticles as a catalyst in organic reactions have attracted many attentions due to the unique properties of nanoparticles (large surface-to-volume ratio and more surface sites compare to the bulk materials). Nanoparticles have the unique properties due to a strong interplay between elastic, geometric, and electronic parameters, as well as interactions with the support [18] . Among various nanoparticles (NPs), silica nanoparticles have found considerable attention in science due to their various applications including absorbent [19], substrate for catalysts [20, 21], drug delivery systems [22, 23], anti-corrosion agent [24, 25] and filler in rubber and plastics [26, 27]. Inorganic supports such as silica gel as a catalyst in organic reactions have received considerable attention in recent years due to many properties such as enhanced reaction rate, high selectivity, easy workup, recoverability, and reusability of catalysts [28-30]. There are many advantages for silica gel coated with metal salts such as low cost, ease of preparation, and catalyst recycling [31, 32].

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In view of this report and also due to continuation of our efforts for development of efficient and new green synthetic procedures for design and synthesis of heterocyclic compounds [33], we wish to report the multi-component synthesis of pyranopyrazole and spiropyranopyrazole derivatives in the presence of silica coated nanoparticles (SiO_2: Co).

2. Experimental

2.1. Materials and instruments

All chemicals were purchased from Merck or Aldrich chemical companies and used without further purification. Melting points were measured in open capillary tubes by electrothermal digital apparatus and are uncorrected. Progress reaction was followed by TLC using aluminum backed plates of silica gel 60F 254. The FT-IR spectra were recorded by Aapha-Bruker spectrophotometer using KBr pellets. NMR spectra were recorded at room temperature on a 300 MHz Brucker-Avance spectrometer using TMS as an internal standard.

2.2. Preparation of silica supported cobalt salts [SiO_2@Co]

2.2.1. Preparation of the activated silica gel

SiO_2@Co particles were prepared by the reported method in literature [34]. Initially, 10 g of silica gel (K100) was added to a 200 mL solution of HCl: H_2O (1:1) in a round-bottom flask, and the mixture was stirred at 120 °C for 12 h. The result was filtered by vacuum filter pump and washed with deionized water, and dried at 110 °C for 7 h.

2.2.2. The cobalt complexed on the activated silica gel

The mixture of activated silica (5 g) and dry diethyl ether (25 mL) was stirred for 10 min and anhydrous cobalt salts (2.5 mmol) ($Co(NO_3)_2$ (0.457 g) or $CoCl_2$ (0.324 g) was added to this suspension and stirred at room temperature for 5 h. The catalyst was filtered and washed with deionized water several times until the filtered solution became colourless. Finally, the catalyst was dried in oven at 80 °C for 7 h.

2.2.3. Synthesis of pyranopyrazole and spiropyranopyrazole derivatives in the presence of SiO_2@$CoCl_2$ particles as catalyst (5a-g)

A mixture of ethyl acetoacetate (1 mmol, 0.1 mL), hydrazine derivatives (1.5 mmol), ethanol (6 mL), and 0.02 g SiO_2@$CoCl_2$ in a round-bottom flask was stirred for 5 min under reflux conditions. Then, aldehyde or isatin derivatives (1mmol) and malononitrile (1 mmol, 0.066 g) or ethylcyanoacetate (1mmol, 0.1 mL) were added. After the completion of the reaction (the progress was controlled by TLC) the catalyst was separated by filtration and the solvent evaporated to give the desired products (5a-g) and **(7a-d)**, which then recrystallized from ethanol.

2.2.4. Characterization

All products were identified by comparing their physical constants as well as their IR and NMR data with those reported in literature. The crystal structure of SiO_2@$CoCl_2$ and SiO_2@$Co(NO_3)_2$ were performed by Philips Xray powder diffraction (XRD) diffract meter (Cu-Kα radiation and λ= 0.15406) in range of Bragg angle of 10-80 using 0.05 as the step length. The morphology and size of nanoparticles were investigated by a Tescan mira Π field emission scanning electron microscope (FE- SEM). For recognition of chemical elements of the SiO_2@Co particles, elemental chemical analysis and energy- dispersive X-ray spectroscopy (EDS)] coupled with SEM were used. Also, the loading amount of Co on silica gel was measured by an inductively coupled plasma- optical emission spectrometer (ICP/OES).

2.2.5. Selected data

6-amino-4-(4-hydroxy-3-nitrophenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-arbonitrile (5g). mp: 223-225 °C. IR (KBr) ῡ (cm^{-1}): 3480, 3230, 3119, 2190, 1646, 1598, 1489, ^{1}H NMR (300 MHz, DMSO-d_6) δ_H: 1.61 (s, 3H, CH_3), 4.44 (s, 1H, CH), 6.79-7.50 (m, 5H, H_{Ar} and NH_2), 10.76 (br s, 1H, OH), 11.98 (s, 1H, NH) ppm. ^{13}C NMR δ: 10.1, 56.9, 98.3, 120.2, 121.3, 123.9, 135.0, 136.0, 151.5, 155.3, 162.4 ppm. Anal. Calcd for $C_{14}H_{11}N_5O_4$: C, 53.68; H, 3.54; N, 22.36%. Found: C, 53.47; H, 3.76; N, 22.09%.

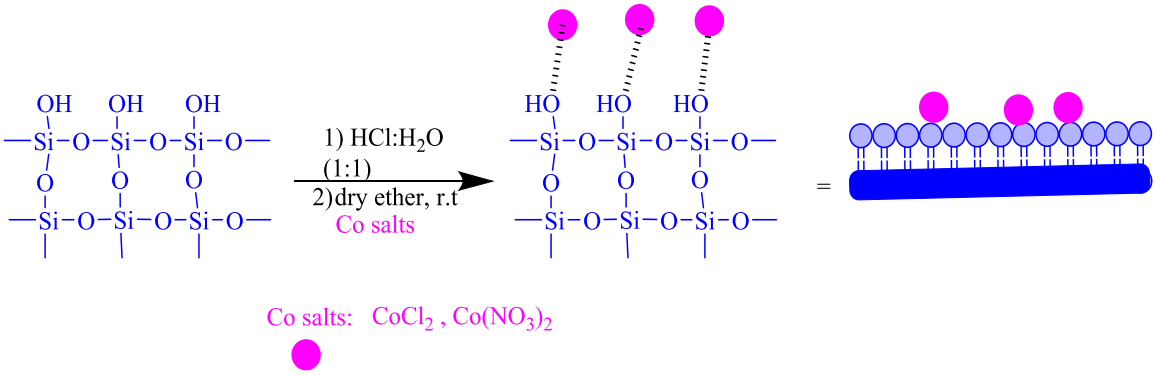
6'-amino-3'-methyl-2-oxo-1'H-spiro [indoline-3, 4'-pyrano [2, 3-c] pyrazole]-5'-carbonitrile (7a). mp: 289-

290 °C. IR (KBr) ῡ (cm^{-1}): 3340, 3130, 2183, 1710, 1651, 1582, 1496, ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 1.63 (s, 3H, CH_3), 7.02-7.37 (m, 4H, H_{Ar}) 7.31 (s, 2H, NH_2), 10.75 (s, 1H, NH), 12.38 (s, 1H, NH) ppm. Anal. Calcd for $C_{15}H_{11}N_5O_2$: C, 61.43; H, 3.78; N, 23.88%. Found: C, 61.65; H, 3.98; N, 23.61%.

6'-amino-1-benzyl-3'-methyl-2-oxo-1'H-spiro [indoline-3, 4'-pyrano [2, 3-c] pyrazole]-5'-carbonitrile (7c). mp: 263-264 °C. IR (KBr) ῡ (cm^{-1}): 3275, 3230, 3152, 3038, 2197, 1716, 1646, 1593, 1483. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 1.42 (s, 3H, CH_3), 5.05 (ABq, 2H, CH_2), 7.13-7.48 (m, 9H, H_{Ar}), 7.41 (s, 2H, NH_2), 12.37(s, 1H, NH) ppm. Anal. Calcd for $C_{22}H_{17}N_5O_2$: C, 68.92; H, 4.47; N, 18.27%. Found: C, 68.63; H, 4.58; N, 18.52%.

3. Results and discussion

The schematic preparation of SNPs is shown in scheme 1. Firstly, the silica gel was activated using a mixture of HCl: H_2O (1:1). The mixture of activated silica gel, anhydrous cobalt salts, $Co(NO_3)_2$ or $CoCl_2$ in ether as a solvent was stirred to give SiO_2@Co SNPs. Theses nanoparticles were characterized by the FT-IR, XRD, FE-SEM &EDX, and ICP-OES analyses.



Scheme 1. Preparation of SiO_2@Co salts $CoCl_2$ and $Co(NO_3)_2$)

3. 1. Characterization of the SiO_2@Co (Cl^-, NO_3^-)

3.1.1. FT-IR spectra

The FT-IR spectra of the silica gel (a), SiO_2@$CoCl_2$ (b), and SiO_2@$Co(NO_3)_2$ are presented in Fig. 1. The adsorption bands at 3000-3500 cm^{-1} and 1635 cm^{-1} are corresponded to Si-OH stretching and twisting vibration of OH groups, respectively (Fig. 1a-c). In addition, the adsorption bonds of O-Si-O stretching and Si-O rocking are observed at 1097 and 467 cm^{-1}, respectively. Moreover, the adsorption bonds of Si-O bending can be seen at 968 and 800 cm^{-1} (Fig. 1a-c). The Co-O stretching vibration is observed at 620 cm^{-1} (Fig. 1b-c) [35], which shows the presence of cobalt metal on the silica structure.

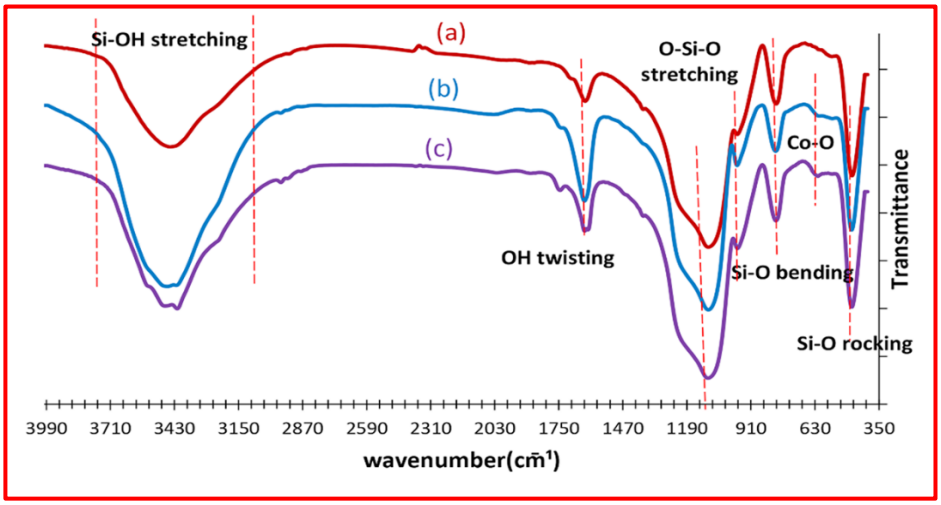


Fig. 1 The FT-IR of the silica gel (a), SiO_2@$CoCl_2$ (b) and SiO_2@$Co(NO_3)_2$ (c)

3.1.2. XRD patterns

XRD patterns of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) SNPs are indicated in Fig. 2. XRD patterns of both nanoparticles show the broad diffraction bands at 2θ= 23.73° for SiO_2@$Co(NO_3)_2$ and 2θ =22.11° for SiO_2@$CoCl_2$, which is the characteristic of silica and confirm the amorphous structure of these nanoparticles [36, 37]. The XRD patterns of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) SNPs are in agreement with the standard values given in JCPDS card no. 16-0380 [38]. Also, XRD patterns of SiO_2@$Co(NO_3)_2$ (A) show weak peaks at 2θ= 12.12°, 39.43°, 47.41°, 56.05°, and 59.80°, which is the characteristic of cobalt hydroxyl nitrate and indicates the presence of $Co(NO_3)_2$ and $Co(OH)_2$ in SiO_2@$Co(NO_3)_2$ [39, 40]. The XRD patterns of SiO_2@$CoCl_2$ (B) show weak peaks at 2θ = 18.11° and 38.11°, which confirm the existence of $CoCl_2$ in the structure of SiO_2@$CoCl_2$ [41].

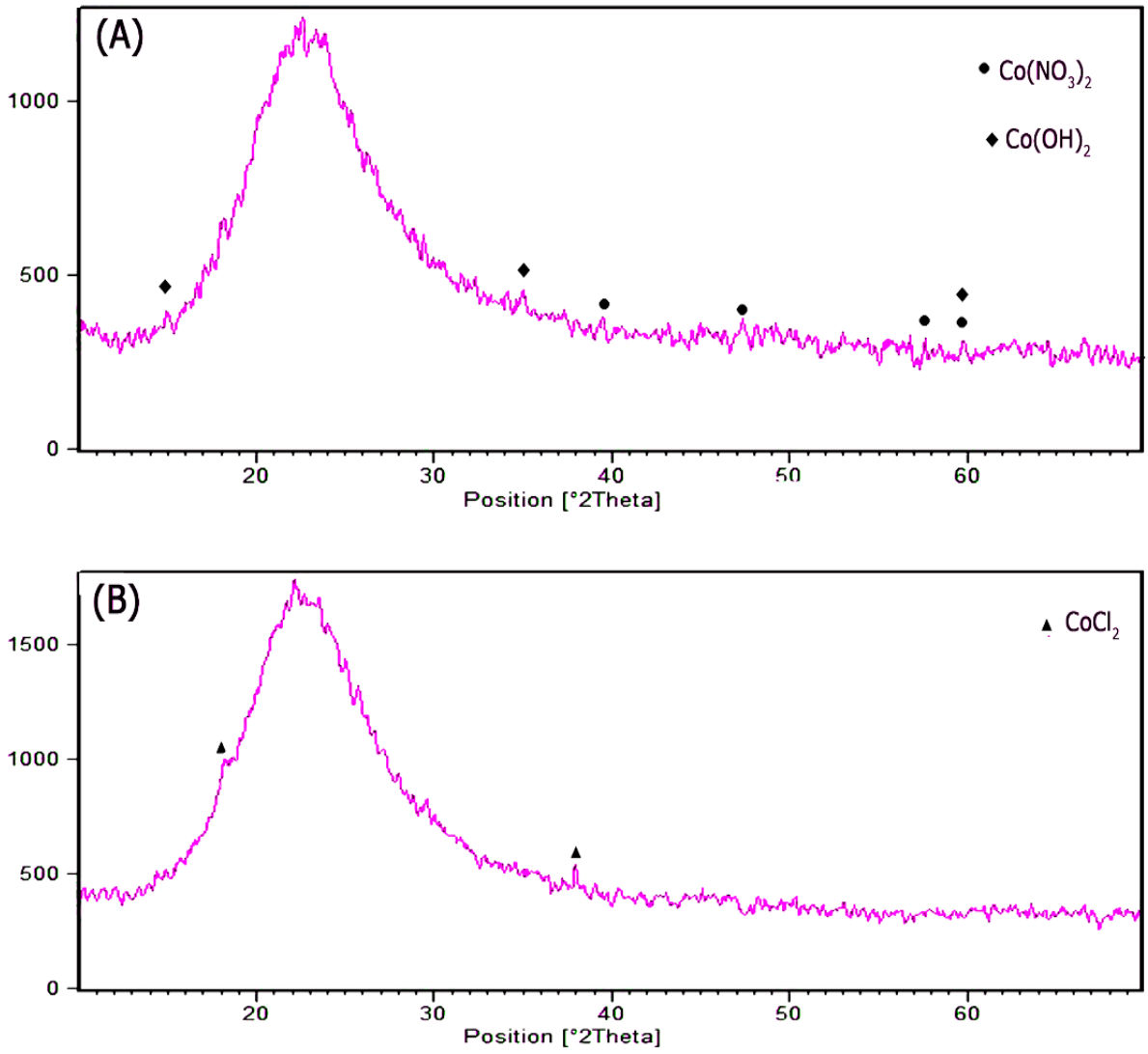


Fig .2 XRD patterns of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B)

3.1.3. FE-SEM, Histogram and EDX analyses

The FE-SEM images and Histogram chart of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) are shown in Fig. 3. The size and morphology of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) were estimated by the FE-SEM images with magnification of 500 nm. SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) are both spherical and the average diameter of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) were estimated to be about 45 and 36 nm, respectively. The histogram charts of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) indicate that the most size of these nonoparticles are in the range of 40-50 and 30-35 nm, respectively. The size distribution of SiO_2@$Co(NO_3)_2$ is

between 20-90 nm while the size distribution of SiO_2@$CoCl_2$ is between 20-65 nm (histogram charts). The energy-dispersive X-ray spectroscopy (EDX) of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) confirm the presence of the elements of Si, O, Co, N and Si, O, Ca, and Cl, respectively (Fig. 4). Also the results showed that the weight percentage (W%) of cobalt in SiO_2@$CoCl_2$ NPs (3.98) is more than that in SiO_2@$Co(NO_3)_2$ NPs (0.91). In addition, the exact amount of cobalt in both SNPs was studied by ICP-OES. The results obtained by ICP-OES indicate that the amount of cobalt in SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B) are 0.44 mmol/g and 2.00 mmol/g, respectively. The weight percentage (W%) obtained from the EDX analysis shows that the relative amount of Co ion in SiO_2 @$CoCl_2$ to Co ion in SiO_2@$Co(NO_3)_2$ is 4.37 [(W% (SiO_2@$CoCl_2$)/W%(SiO_2@$Co(NO_3)_2$)] which is consistent with the result obtained from ICP-OES analysis (4.54). As a result, the amount of Co coated on silica gel for SiO_2@$CoCl_2$ NPs is more than that for SiO_2@$Co(NO_3)_2$ NPs.

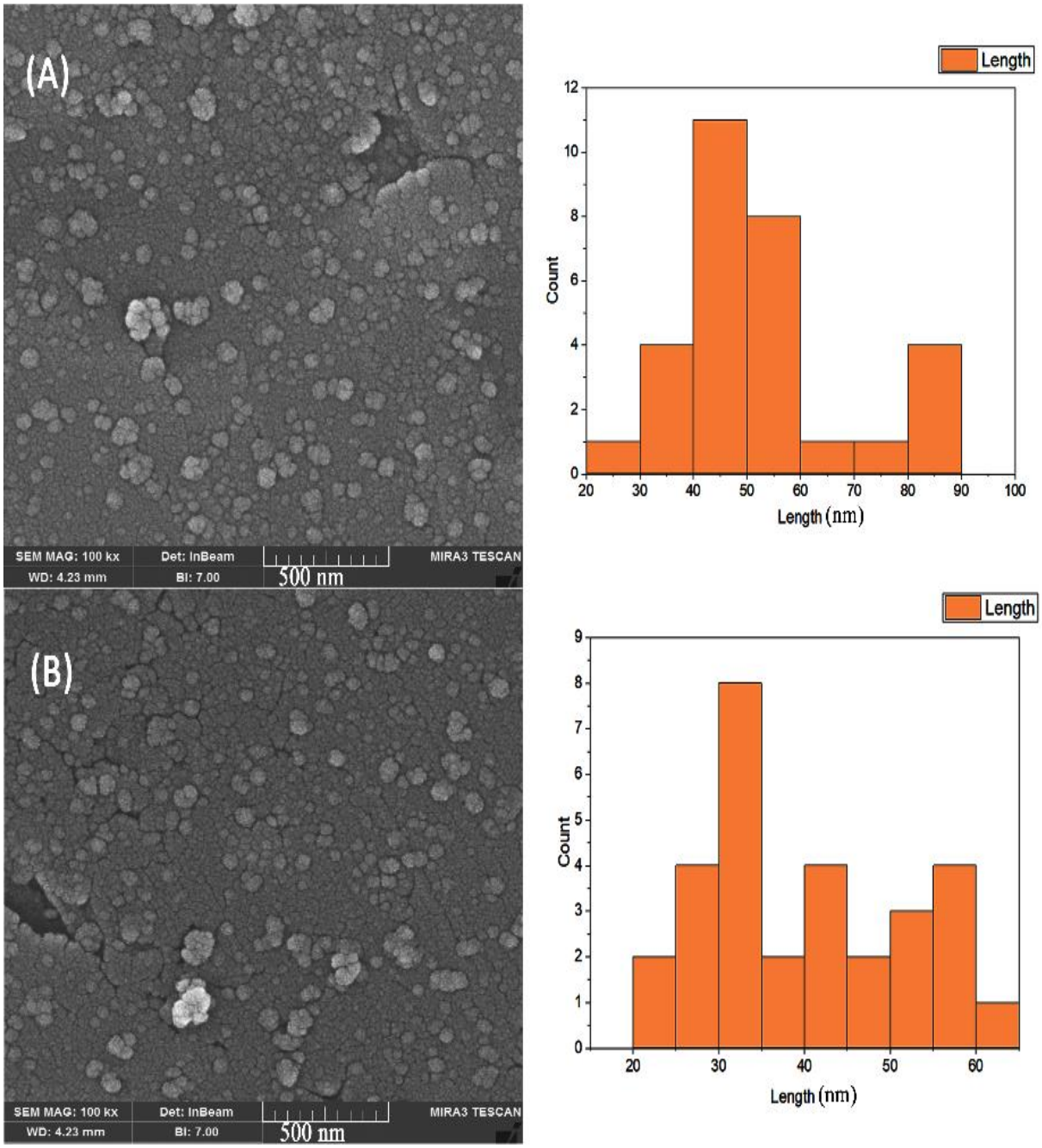
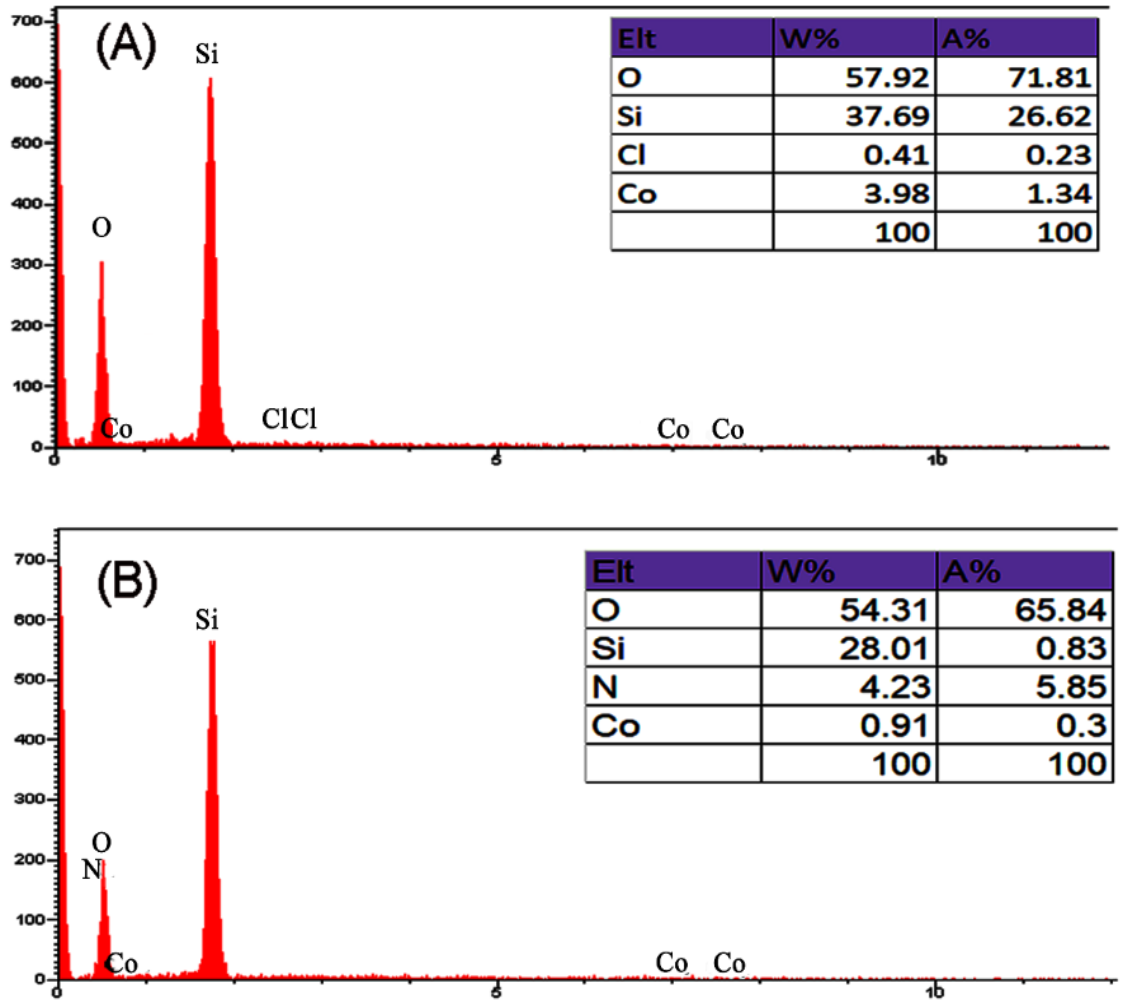


Fig. 3 The FE-SEM of the SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B)



Elt	W%	A%
O	57.92	71.81
Si	37.69	26.62
Cl	0.41	0.23
Co	3.98	1.34
	100	100

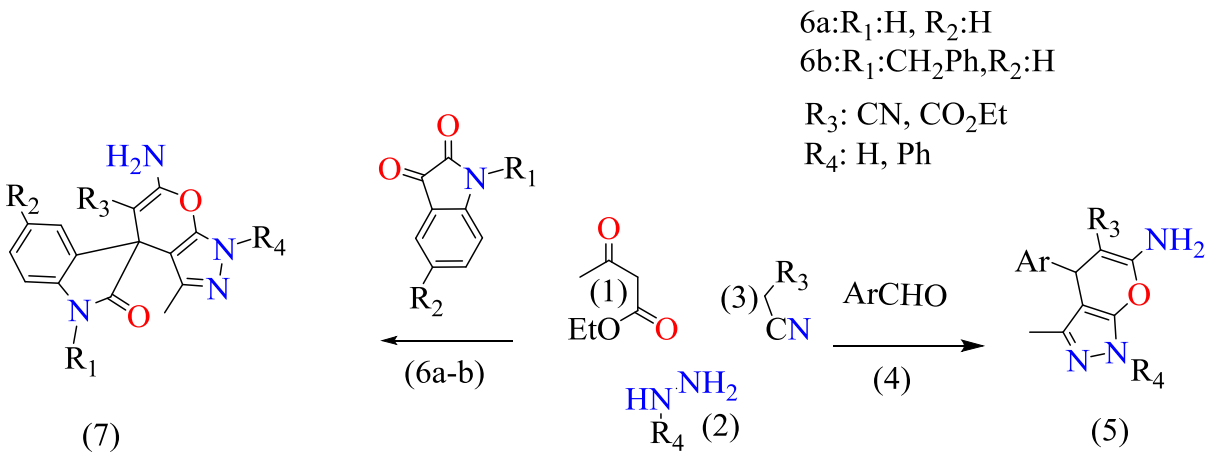
Elt	W%	A%
O	54.31	65.84
Si	28.01	0.83
N	4.23	5.85
Co	0.91	0.3
	100	100

Fig. 4 The EDX analysis of SiO_2@$Co(NO_3)_2$ (A) and SiO_2@$CoCl_2$ (B)

3.2. Study of the catalytic activity of Co salts complexed on the silica gel for the synthesis of pyranopyrazole and spiropyranopyrazole derivatives

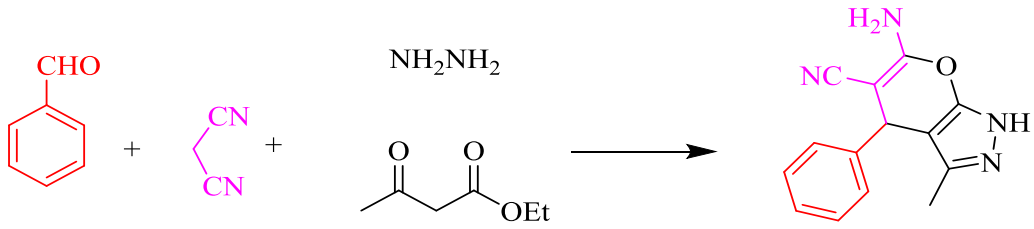
After the characterization of SiO_2@$Co(NO_3)_2$ and SiO_2@$CoCl_2$, the catalytic activity of these SNPs for the synthesis of pyranopyrazole and spiropyranopyrazole derivatives was studied. The reaction of benzaldehyde, malononitrile, hydrazine hydrate, and ethyl acetoacetate was selected as a model. The model reaction was carried out in the presence of 1 mg of SNPs (SiO_2@$Co(NO_3)_2$ and SiO_2@$CoCl_2$) as a catalyst under mild reaction conditions for 5 h (room temperature and ethanol as a solvent). The results are presented in Table 1 (entries 1-2). To achieve the best results in terms of reaction time and the yield of the product, the efficiency of different reaction media and catalyst amounts in the model reaction was examined (Table 1). The best results were obtained at 70 °C by applying 20 mg of SiO_2@$CoCl_2$ and using ethanol as a solvent (Table1. entry 11). After optimization of reaction conditions, various pyranopyrazole and spiropyranopyrazole derivatives were synthesized in good to high yield by using different aromatic aldehydes or isatin derivatives, hydrazine derivatives, and ethylcyanoacetate or malononitrile (Table 2, Scheme 2). Aldehydes with electron releasing and electron withdrawing groups did not follow a specific pattern in this reaction. The results of the present work are comparable with those reported in literature (Table 3). As the results show, SiO_2@$CoCl_2$ is an efficient and appropriate green catalyst for this reaction in terms of short reaction time, high yield, and simple conditions. Furthermore, SiO_2@$CoCl_2$ nanoparticle is a more efficient catalyst than SiO_2@$Co(NO_3)_2$ for the synthesis of pyranopyrazoles, which shows that $CoCl_2$ is better stabilized on the silica gel surface compared to $Co(NO_3)_2$

according to the results obtained from EDX analysis and ICP-OES). As the Co^{2+} cation is similar for both catalysts, anions Cl^- and NO_3^- may affect the catalytic activity. Catalytic activity of Co-based metal salts is dependent on Co^{2+} due to its electrophilic nature, which is strongly directed to the oxygen of carbonyl group [42]. This may also be the reason behind high coating of $CoCl_2$ on the surface of silica gel.



Scheme 2. The synthetic pathway of pyranopyrazoles

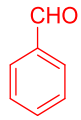
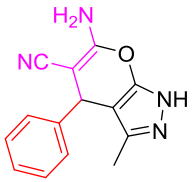
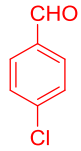
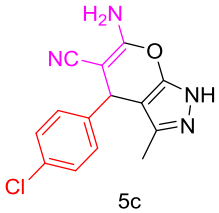
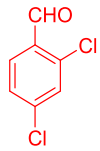
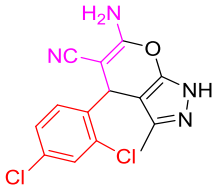
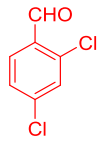
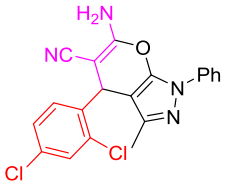
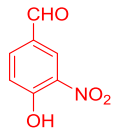
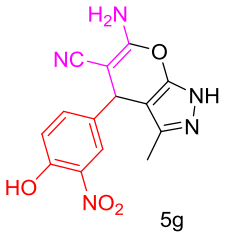
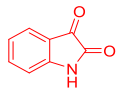
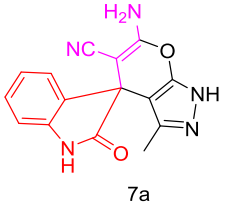
Table 1 The optimization conditions for the synthesis of pyranopyrazoles in model reaction

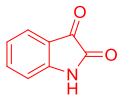
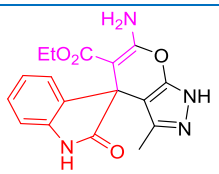
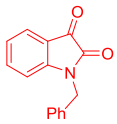
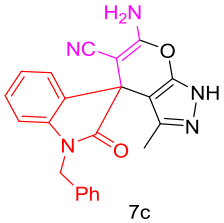
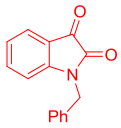
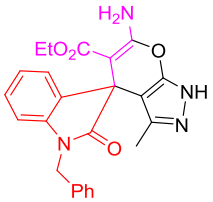


Entry	Conditions/ Solvent	Catalyst (mg)	Time	Yield (%)[a]
1	r.t, EtOH	SiO_2@$CoCl_2$ (10)	5h	78
2	r.t, EtOH	SiO_2@$Co(NO_3)_2$ (10)	5h	67
3	r.t, H_2O	SiO_2@$CoCl_2$ (10)	5h	45
4	r.t, EtOH:H_2O (1:1)	SiO_2@$CoCl_2$ (10)	5h	55
5	r.t, solvent free	SiO_2@$CoCl_2$ (10)	5h	53
6	r.t, EtOH	SiO_2@$CoCl_2$ (5)	5.5h	65
7	r.t, EtOH	SiO_2@$CoCl_2$ (15)	3.5h	82
8	r.t, EtOH	SiO_2@$CoCl_2$ (20)	1h	82
9	r.t, EtOH	SiO_2@$CoCl_2$ (20)	1h	82
10	50℃, EtOH	SiO_2@$CoCl_2$ (20)	1h	87
11	70℃, EtOH	SiO_2@$CoCl_2$ (20)	45 min	90
12	70℃, EtOH	SiO_2 (20)	45 min	<30

[a] isolated yield. Benzaldehyde (1 mmol), hydrazine hydrate (1.5 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol), and SiO_2@$CoCl_2$ NPs as catalyst

Table 2 Synthesis of pyranopyrazoles derivatives in the presence of SiO_2@$CoCl_2$ NPs in optimal conditions

Entry	ArCHO	NH_2NH-R_4	R_3 CN	Product	Time (min)	Yield[a] (%)	mp(℃)	Ref.
1		NH_2NH_2		 5a	45	90	241-243	[43]
2		NH_2NH_2		 5c	50	90	232-234	[44]
3		NH_2NH_2		 5e	45	87	230-232	[45]
4		NH_2NHPh		 5f	80	72	230-232	[46]
5		NH_2NH_2		 5g	55	89	223-225	[4]
6		NH_2NH_2		 7a	45	87	289-290	[45]

7		NH_2NH_2		 7b	100	80	280-283 [47]
8		NH_2NH_2		 7c	40	84	263-264 [45]
9		NH_2NH_2		 7d	100	76	128-129 [4]

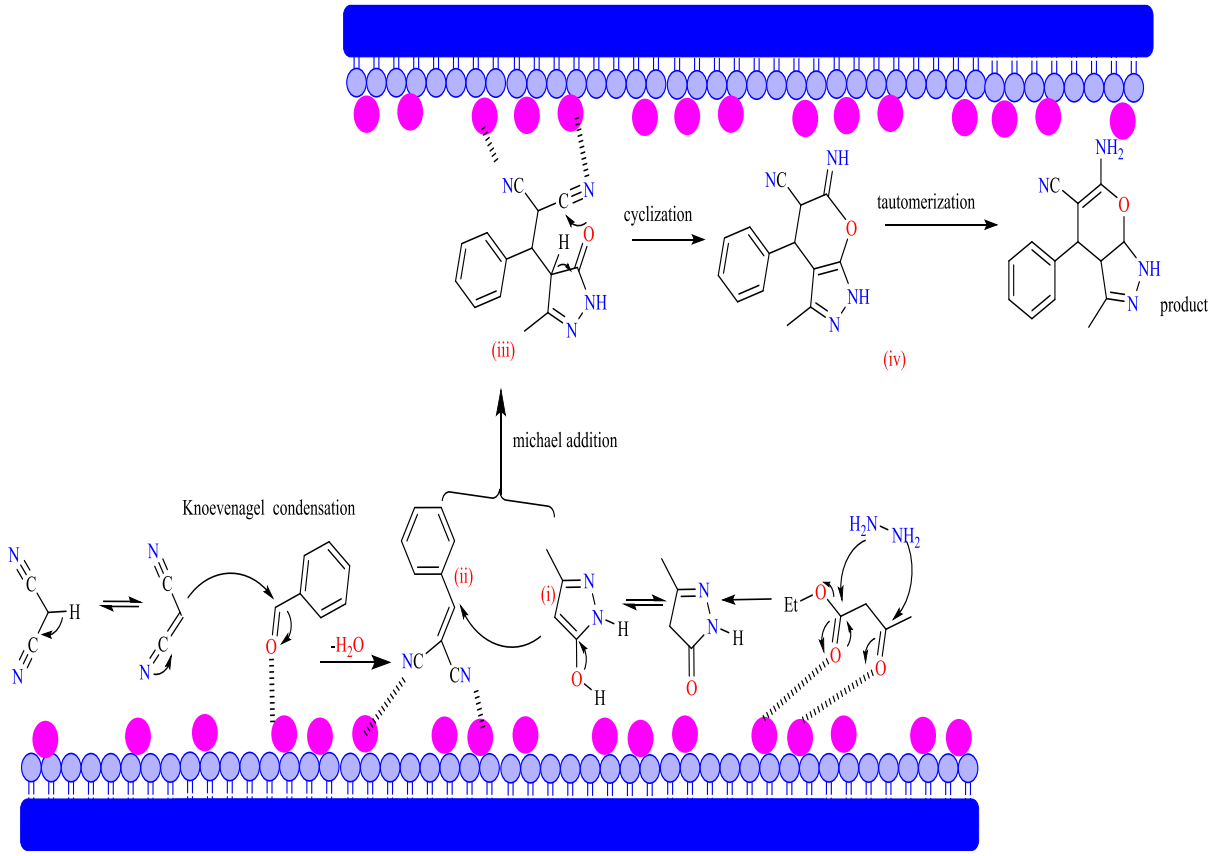
[a] isolated yield.Reaction conditions: aryl aldehydes (1 mmol), hydrazine hydrate (1.5 mmol), ethyl acetoacetate(1 mmol), malononitrile (1 mmol), and SiO_2@$CoCl_2$ NPs in presence of 5 mL EtOH at 70°C.

Table 3 compare of the catalytic activity of SiO_2@$CoCl_2$ NPs with reoprted works for model reaction

Entry	Catalyst	Conditions[a]	Time	Yield (%)	Reference
1	WS-SiO_2 NPs	H_2O, 80℃	30 min	94	[48]
2	Cu-Cytosine@MCM-41	H_2O, 80℃	60min	95	[49]
3	Ni-ytosine@MCM-41	H_2O, 80℃	45min	94	[49]
4	NAPT	EtOH, reflux	25 min	85	[50]
5	$CoCuFe_2O_4$	Solvent Free	45 min	90	[51]
6	SiO_2@$CoCl_2$	EtOH, 70℃	40 min	95	This work

[a]The model reaction: benzaldehyde, hydrazine hydrate, malononitrile, ethyl acetoacetate

A plausible mechanism was proposed for the synthesis of 6-amino-3-methyl-4-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(5a)** as a model of pyranopyrazoles in the presence of SiO_2@$CoCl_2$ (Scheme 3). Initially, the carbonyl group of ethyl acetate is activated with cobalt metal ions and a cross-reaction of hydrazine hydrate and ethyl acetate is performed to give intermediate (i). Simultaneously with the formation of intermediate (i), a Knoevenagel condensation reaction between activated benzaldehyde and malononitrile produce intermadiate (ii). Consequently, a Michael addition between the intermadite (ii) and enolizable compound (i) leads to formation of intermadiate (iii), which is followed by intramolecular nucleophilic cyclization (iv) and tautomerization to afford the product [33, 48, 52]. Also, a similar mechanism for synthesis of **7a**, as an example of spiropyranopyrazoles, in the presence of SiO_2@$CoCl_2$ is acceptable.



Scheme 3. The palusible mechanism for synthesis of 6-amino-3-methyl-4-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (5a) in the presence of SiO_2@$CoCl_2$

3.2. Reusability and recovery of SiO_2@$CoCl_2$ NPs

Based on green chemistry principles, recovery and reusing of catalysts have great importance to chemists [53]. So, the model reaction was performed for studying the recovery and reusability of catalyst. After the completion of reaction, SiO_2@$CoCl_2$ nanoparticles were isolated by filtration. The catalyst was washed several times with ethanol and dried at 80 °C in an oven for 4 h, which was then reused in a subsequent reaction. Fig. 5A shows this catalyst could be reused six times without significant change in activity. The comparison of FT-IR spectra (Fig 5B), FE-SEM analysis (Fig. 5C), EDX analysis (Fig. 5D), and also a comparison of W% cobalt metal obtained from EDX analysis (Fig. 5E) of the fresh and the reused catalyst show no significant change in the structure of SNPs after 6 runs. The obtained results of ICO-OES for fresh and reused catalyst indicates that the amount of 2.00 mmol/g and 1.89 mmol/g of cobalt is leached on silica gel, respectively. As data show, the amount of cobalt on silica gel has decreased after six times. The obtained results confirm that the SiO_2@$CoCl_2$ NPs can be used as a suitable catalyst with the recyclability and reuse in the synthesis of pyranopyrazoles during six runs.

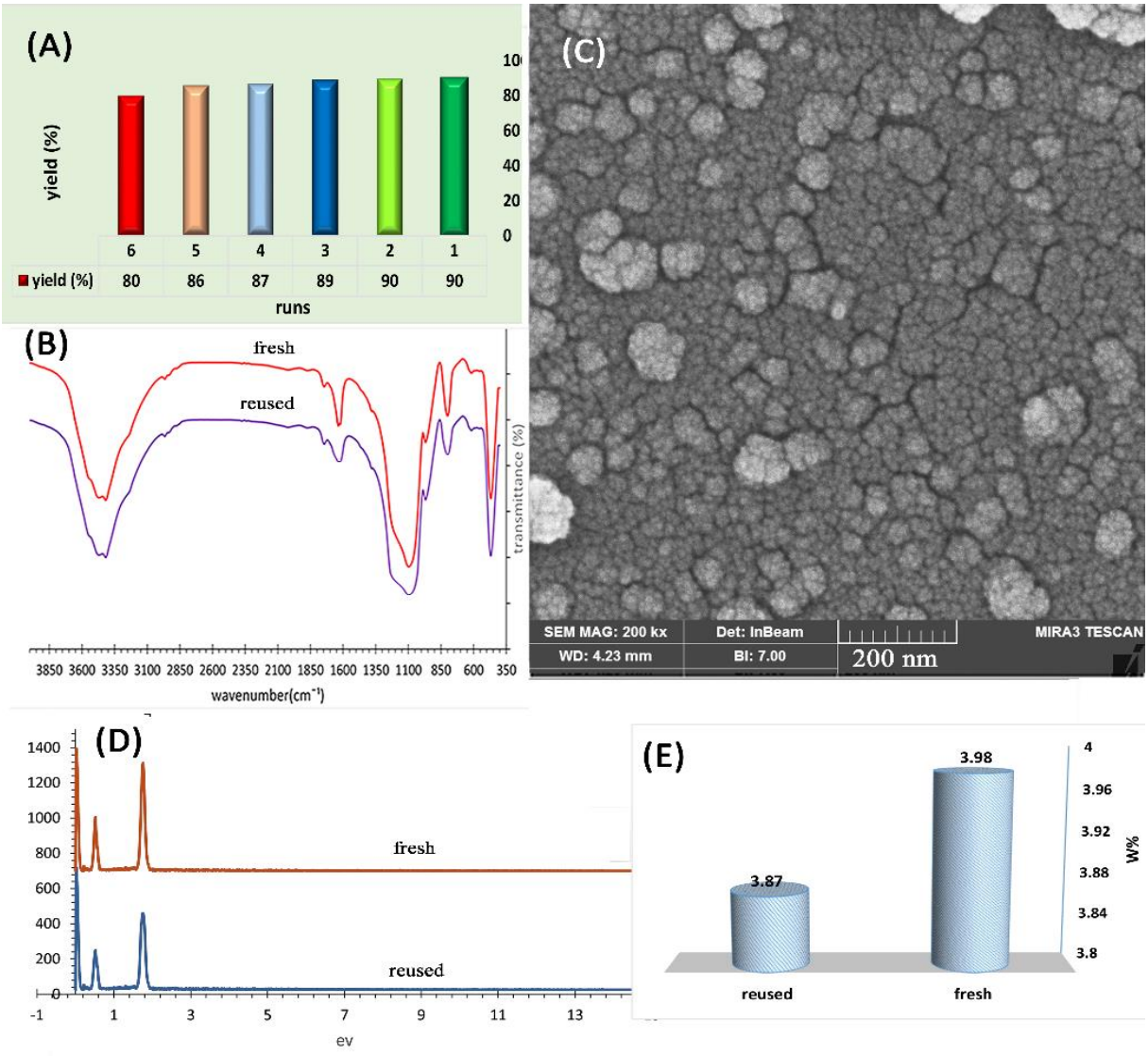


Fig. 5 Reusability and recovery of SiO_2@$CoCl_2$ NPs during 6 runs (A), FT-IR spectra (B) fresh and reused and FE-SEM analysis of reused catalyst (C), EDX analysis (D), and ICO-OES analysis (E) for fresh and reused catalyst

4. Conclusions

Co salts coated on the active silica gel using an inexpensive and simple method were prepared. Characterization of these SNPs was studied with several techniques including-IR, XRD, FE-SEM@EDX, and ICO-OES analyses. These nanoparticles were successfully used as a catalyst for the preparation of pyranopyrazole and spiro pyranopyrazole derivatives via multi-component reaction under mild conditions. The reusability of catalyst, suitable reaction times, high product yields, and easy workup are some advantages of this green procedure. It is noteworthy that SiO_2@$CoCl_2$ NPs is a more efficient catalyst than SiO_2@$Co(NO_3)_2$ for synthesis of pyranopyrazole and spiro pyranopyrazole derivatives due to more loading of $CoCl_2$ on the surface of silica gel support.

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Conflicts of Interest

The authors declare a financial support from research council of Arak University.

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