#### **ORIGINAL PAPER**



# Effect of preparation method on physicochemical properties of a novel Co–Fe nano catalyst

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#### Abstract

The main approach of this study was to investigate the effect of the type of synthesis method on the improvement of catalyst performance in Fischer–Tropsch reaction. For this purpose, a series of the novel catalysts were synthesized using iron and cobalt nitrate salts, tetraethoxysilane and novolac phenolic resin by different method. These catalysts were abbreviated as M1– Co–Fe–novolac/SiO<sub>2</sub>, M2–Co–Fe–novolac/SiO<sub>2</sub>, and M3–Co–Fe–novolac/SiO<sub>2</sub> and characterized using different techniques. The results of the Brunauer–Emmett–Teller and Fourier transform infrared techniques showed that M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst has a higher surface area than the other two ones. This catalyst was analyzed by using X-ray diffraction (XRD), scanning electron microscopy, energy-dispersive X-ray, and temperature-programed reduction (TPR) techniques. The XRD results confirmed the appearance of suitable active phases, such as metal phase, carbide, and low oxidation state of metals. Based on TPR results, the lower reduction temperature, compared with similar samples, confirmed the high activity of the M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst. Catalytic activity and selectivity for Fischer–Tropsch reaction were investigated in the standard conditions by using catalytic tests. The high conversion percentage of CO indicated high activity of the catalyst. On the other hand, the olefin to paraffin ratio (O/P), which was a criterion for catalytic efficiency in industrial, was also acceptable.

Keywords Fischer-Tropsch synthesis · Nano catalyst · Cobalt/iron catalyst · Novolac phenolic resin

## Introduction

It is essential to have a clean process that can provide a reliable alternative to global hydrocarbons fuels with the least environmental tensions [1]. Fischer–Tropsch (FT) synthesis as a capable process can provide a wide range of hydrocarbons including a variety of linear and branched alpha and alcohol compounds [2, 3]. On the other hand, the gasoline and diesel fuel produced by this process do not need to increase the octane number again, and it is free of any sulfur and nitrogen contamination [4, 5]. As a result, the synthesis of FT was considered by many researchers as a suitable source for a wide range of organic compounds [5, 6].

Transition metals such as Co, Fe, and Ru were usually used as catalyst in the Fischer–Tropsch reaction [7–9]. Among all metals that used in industrial catalysts, only Fe and Co have been able to gain the necessary economic and operational acceptance that each of them has its own unique and valuable features. For example, iron has a special place because it is cheaper than cobalt, and cobalt is considered because of its stability and high activity [10]. For this reason, iron and cobalt are used either as individual single-core [11–13] or dual-core systems [14–17].

The active phase is usually selected in such a way as to provide maximum selectivity for the desired products and to minimize the production of undesirable products in the process [6]. For this reason, one of the advantages of using bimetallic catalysts is to increase catalytic activity and selectivity of valuable products [18].

Since the conversion reactions occur on the catalyst surface, the high surface area is very important. If the catalysts are prepared by simple impregnation, the reduction of specific surface is inevitable [19]. To overcome this problem, the use of organic polymers has become widespread. These polymeric compounds provide a more suitable substrate for active phase distribution [16]. For example, Liang et al. reported that the presence of resorcinol

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formaldehyde resin gel during the synthesis of the Co/ $SiO_2$  catalyst is an effective factor in increasing the effective surface area of the catalyst [20]. It is also reported that among different polymers, phenolic resol resins have been used in Co–Fe catalysts and increased the activity and selectivity of Fischer–Tropsch reactions [18]. The polymer resin is decomposed and removed during calcination, and eventually, a porous catalyst with the high surface area is created [16].

The physical properties, chemical composition, and structure of the catalyst have essential role in the Fischer–Tropsch synthesis [21, 22]. For example, active phases of Co with an average pore diameter of 3.5-10 nm have led to an increase in methane production and a decrease in a tendency toward liquid products [21–27]. Since these properties depend on preparation method, we synthesized a novel Co-Fe-novolac/SiO<sub>2</sub> nanocatalyst using different methods and investigated the effect of preparation method on the catalytic activity and selectivity of FT reactions. In other studies, Li et al. [10] also investigated the effect of the chemical composition of the catalyst on its performance in Fischer-Tropsch reactions. By using iron-nickel bimetallic catalysts, they were able to effectively increase  $C_5^+$  production while reducing methane production. According to their results, the use of bimetallic catalysts increases the conversion rate of CO by improving the metal distribution at the catalyst base, and investigated of the Mossbauer spectrum of the catalyst, shows the production of a mixture of iron oxide and carbide on the surface of the catalyst during the reaction. Increasing nickel to iron-containing catalysts, while reducing carbide production, increases metal oxide production at the catalyst surface which continuation of this process causes a sharp shift in the product distribution from heavy hydrocarbons to lighter compounds and eventually methane. Also Shimura et al., by studying different phase species of cobalt alumina catalyst, showed that the porosity and phase structure of the catalyst greatly effect on its activity [1].

The surface area, chemical composition, and structure of the catalyst are dependent on the preparation method. However, the effect of the synthetic method on the efficiency of the FT catalysts has not been sufficiently investigated.

Therefore, in the present work, we synthesized a novel Co-Fe-novolac/SiO<sub>2</sub> nanocatalyst using some different methods and investigated the effect of the preparation method on the catalytic activity and selectivity of FT reactions. The physicochemical properties of the catalysts were characterized by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), Brunauer, Emmet and Teller (BET), temperature-programed reduction (TPR), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) methods.

## Experimental

#### **Catalyst preparation**

The Co–Fe–novolac/SiO<sub>2</sub> catalysts were prepared by three different methods as described below.

Method 1: In the first step two separate solutions A and B were prepared as follow:

Solution A: To a solution of  $Fe(NO_3)_3 \cdot 9H_2O$  (4.1 g, 0.01 mol) and  $Co(NO_3)_2 \cdot 6H_2O$  (8.8 g, 0.03 mol) in 40 mL of ethanol was added tetraethoxysilane (TEOS) (4.2 g, 0.02 mol), and the solution was heated to 70 °C.

Solution B: Solution B was prepared by dissolving novolac phenolic resin (5.0 g) in 40 mL of ethanol. Then, oxalic acid (8.8 g, 0.097 mol) was added to this solution [26].

In the second step, solution B was added dropwise to the solution A and the mixture was aged for 3 h. A creamy white solid was precipitated which was washed twice with absolute alcohol, filtered and dried in the oven at 120 °C for 20 h and calcined at 650 °C in air for 6 h. The obtained catalyst was labeled as M1–Co–Fe–novolac/SiO<sub>2</sub>.

Method 2:  $Fe(NO_3)_3 \cdot 9H_2O$  (4.1 g, 0.01 mol) and  $Co(NO_3)_2$ ·6H<sub>2</sub>O (8.8 g, 0.03 mol) were dissolved in 40 mL of ethanol. Then, ammonia solution (10%) was added to form the hydroxide deposit. Aging for 3 h followed by washing the precipitate twice with absolute alcohol, filtering and drying in the oven at 120 °C for 20 h resulted in a white creamy solid. In another beaker, the novolac phenolic resin solution was prepared by dissolving 5.0 g of resin in 40 mL of ethanol [29]. TEOS (5.2 g, 0.025 mol) and oxalic acid (8.9 g, 0.098 mol) were added to this solution and stirred until the gel was formed. The solid involve metal oxide powder was added to the gel with stirring, and the resulting mixture was heated at 70 °C. Aging for 3 h followed by washing the precipitate twice with absolute alcohol, filtering and drying in the oven at 120 °C for 20 h led to catalyst precursor which was calcined at 650 °C in air for 6 h. The obtained catalyst was labeled as M2-Co-Fe-novolac/SiO<sub>2</sub>.

Method 3:  $Fe(NO_3)_3$ ·9H<sub>2</sub>O (2.05 g, 0.005 mol) and  $Co(NO_3)_2$ ·6H<sub>2</sub>O (4.4 g, 0.015 mol) were dissolved in 20 mL of ethanol. TEOS (2.1 g, 0.01 mol) was added and the solution was heated to 70 °C. Then, the novolac phenolic resin solution (novolac (2.5 g), oxalic acid (8.9 g, 0.098 mol), and ethanol (40 mL)) were added dropwise, and the mixture was aged for 3 h [28]. The mixture was placed in an autoclave with a temperature of 160 °C. The resulting catalyst was calcined at 650 °C in air for 6 h. The obtained catalyst was labeled as M3–Co–Fe–novolac/SiO<sub>2</sub>.

#### **Catalyst characterization**

An ALPHA Bruker FT-IR spectrophotometer (400–4000 cm<sup>-1)</sup> was used for FT-IR spectra. The XRD data were obtained using Equinox 3000 inel, X-ray diffractometer (40 kV, 30 mA) using a Cu K $\alpha$  radiation source ( $\lambda = 1.542^{\circ}$ A) and a nickel filter. A NOVA 2200 Quantachrome instrument was used for recording N<sub>2</sub> adsorption-desorption isotherm at liquid nitrogen temperature (-196 °C) and determination of specific surface area, total pore volume and the mean pore diameter. All samples were degassed in advance at 110 °C in an N<sub>2</sub> flow for 3 h to remove the moisture and other adsorbates. A micromeritic TPD-TPR 290 system was used to recorder the TPR profile of catalysts using a mixture gas of  $(5/95: H_2)$ Ar; v/v) with 50 ml/min flow rate and heating to 820 °C at a heating rate of 4 °C min. The SEM images of catalysts and precursors were prepared using AIS2300C microscope containing an IXRF model 550i accessory for energy-dispersive X-ray (EDX) analysis.

#### **Catalyst performance**

Catalytic performance was performed in a stainless steel-fixed bed reactor loaded with 1.0 g of the catalyst. Gases flow was controlled by a mass flow controller (MFC) and the reaction pressure was measure by back pressure regulator (BPR). Initially, the catalyst was reduced using a H<sub>2</sub> gas flow (30 ml/min) at 450 °C under 1 bar pressure for 16 h. Then the temperature, pressure, mole ratio of H<sub>2</sub>/CO and GHSV were adjusted according to the standard conditions [18]. The gasified products were analyzed on-line by Varian gas chromatograph (star 3600CX) containing a thermal conductivity detector (TCD) and a chromosorb column. The liquified products were analyzed off-line by Varian CP 3800 containing a flame ionization detector (FID) and a petrol TM DH100 fused silica capillary column. The CO conversion and selectivity toward each product were computed after reaching the steady state using the normalization equation:

$$CO \text{ conversion } (\%) = \frac{\text{mol } CO_{\text{in}} - \text{mol } CO_{\text{out}}}{\text{mol } CO_{\text{in}}} \times 100$$
$$S_i(\%) = \frac{n_i M_i}{\text{mol } CO_{\text{in}} - \text{mol } CO_{\text{out}}} \times 100$$

where  $n_i$  is the number of carbon atoms, and  $M_i$  is the mole of the product.

# **Results and discussion**

### **Catalyst characterization**

The changes of the samples during calcination were investigated by FT-IR spectroscopy (Fig. 1). For all synthesized precursors, a broad band was observed above 3000 cm<sup>-1</sup> and was assigned to the water of crystallization of nitrate salts.



Fig.1 FT-IR spectra of Co–Fe–novolac/SiO $_2$  catalysts  ${\bf a}$  precursor and  ${\bf b}$  before the test

There was also a sharp band above  $1641 \text{ cm}^{-1}$  which was assigned to vibrations of the aromatic functional of novolac [18, 30]. These bands were almost disappeared in the FT-IR spectra of the samples, which confirm the approximate decomposition of novolac during the calcination at 650 °C. This result confirms the data obtained from BET method. Two vibration bands were observed in 570 cm<sup>-1</sup> and 670 cm<sup>-1</sup> for the calcined catalysts, which is due to vibrations of Co–O bonds in Co<sub>3</sub>O<sub>4</sub> [31].

Table 1 shows the textural parameters of the catalysts. For all three catalysts, the surface area was much greater after the calcination. This is mainly due to decomposition and release of novolac during the calcination, which has made this catalyst more porous with more surface area [18], Liang et al. reported similar behavior in the Co-resorcinol/SiO<sub>2</sub> catalyst [20]. The highest surface area belongs to M2–Co–Fe–novolac/SiO<sub>2</sub> which was prepared via the method 2. Thus, M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst was selected for more investigation.

The XRD pattern of M2–Co–Fe–novolac/SiO<sub>2</sub> before the test shows slightly amorphous silicate phases (wide peak  $2\theta = 15-30^{\circ}$ ) (Fig. 2). The pattern before the test shows high oxidation states iron and cobalt oxides including

Table 1 Textural properties of the precursor and Co–Fe–novolac/  ${\rm SiO}_2$  Catalyst before the test for three methods

Sample		Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (Å)
Method 1	Precursor	151.384	0.16	12.9
	Before test	318.446	0.41	12.9
Method 2	Precursor	164.831	0.38	12.9
	Before test	343.823	0.41	12.9
Method 3	Precursor	144.816	0.52	12.9
	Before test	296.738	0.82	12.9

Fig. 2 XRD patterns of precursor and M2-Co-Fe-novolac/ SiO<sub>2</sub> catalyst (before and after the test). Black filled circle Co<sub>3</sub>O<sub>4</sub> (Cubic); black circle Fe<sub>2</sub>O<sub>3</sub> (rhombohedral); black filled triangle CoFe<sub>2</sub>O<sub>4</sub> (cubic); black triangle Co<sub>2</sub>SiO<sub>4</sub> (orthorhombic); black filled star Fe<sub>2</sub>SiO<sub>4</sub> (orthorhombic); black filled four pointed star Fe<sub>3</sub>C (orthorhombic); Co<sub>3</sub>C (orthorhombic); black square Fe<sub>3</sub>O<sub>4</sub> (cubic); black filled oval CoO (cubic); black filled diamond Fe (Cubic)

 $Co_3O_4$  (cubic, JCPDS No. 00-042-1467),  $Fe_2O_3$  (rhombohedral, JCPDS No. 00-089-0599)  $CoFe_2O_4$  (cubic, JCPDS No. 00-022-1086). Besides, the metal silicates including  $Co_2SiO_4$  (orthorhombic, JCPDS No. 00-070-2115) and  $Fe_2SiO_4$  (orthorhombic, JCPDS No. 00-076-0512) were formed. However, the phases after the test were mainly found in carbide, metallic, and low oxidation states forms of cobalt and iron, including Fe,  $Co_3C$ ,  $Fe_3O_4$ , CoO, and  $Fe_2SiO_4$  [32].

The EDX technique was used to determine the purity of the catalyst at the precursor level and before the test for M2–Co–Fe–novolac/SiO<sub>2</sub>, which showed their purity (Fig. 3). The signals below 2v are the result of the remaining novolac [30]. This confirms the results of FT-IR, which represented the approximate decomposition of novolac, as well as confirms the X-ray diffraction pattern, which indicates the presence of carbide phases after catalyst testing.

SEM analysis of M2–Co–Fe–novolac/SiO<sub>2</sub> samples is shown in Fig. 4. The precursor shows an irregular dense mass with different sizes which indicates that it has not yet fully completed the preparation conditions. While the catalyst after calcination and before the test shows the progressive growing the crystals on the surface. The catalyst after the test shows an irregular porous surface as more porous as the precursor. This may be due to the release of reactive substances or products of the FT synthesis to active phases or phase changes during the FT reaction [20].

To determine the surface reactivity of the M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst, the TPR technique was used (Fig. 5). Reduction peak temperature indicated the ease of reduction and degree of interaction between different species present in the catalyst sample [33]. Three-peaks in the catalyst spectrum were observed. The first peak at 250 °C is probably due to the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> and/or Co<sub>3</sub>O<sub>4</sub> to CoO [34]. The second peak at 400 °C can be due to the reduction of Fe<sub>3</sub>O<sub>4</sub> to FeO and/or CoO to Co. The last





Fig. 3 The EDX spectrum of the M2–Co–Fe–novolac/SiO $_2$  catalyst in a precursor,  ${\bf b}$  catalyst before the test

peak at 520 °C can be due to reduction of FeO to Fe [35]. Compared to similar Co–Fe catalysts, the M2–Co–Fe–novolac/SiO<sub>2</sub> reduction temperature is lower, which is in agreement with its high catalytic activity [18, 30]. Lower reduction temperatures increase the number of active phases such as carbide and metal phases, which are responsible for converting CO. The final two-peak area is greater than the first peak, indicating a complete reduction of the initial oxide state that in line with the XRD results, a similar situation has been reported in other examples of Co–Fe catalysts [18, 20]. According to the results of FT-IR, XRD, and TPR, during the reduction before testing, the phases of iron oxide and cobalt (Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>) decreased to lower oxidation state (Fe<sub>3</sub>O<sub>4</sub>, CoO).

## **Catalyst testing**

A catalyst activity test was performed to determine the activity and selectivity of the M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst.



Fig. 4 SEM images of M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst in **a** precursor, **b** catalyst before the test and **c** catalyst after the test

Four important factors namely the total pressure (7, 4, and 10 bar), feed mole ratio (2, 2.5  $H_2/CO$ ), GHSV (3, 6 mol/min), and temperature (350 °C, 375 °C) were selected [18, 30]. On the other hand, the conversion of CO was chosen as a response for catalyst activity, while products selectivity was chosen as a measure of catalyst selectivity. The results are summarized in (Table 2).





Table 2 Catalytic performance of the M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst under different operational conditions during FT reaction

Std	H <sub>2</sub> /CO	T (°C)	P (bar)	GHSV <sup>a</sup> (min <sup>-1</sup> )	CO Con.	CO <sub>2</sub> (%)	CH <sub>4</sub> (%)	C <sub>2-4</sub> (P) (%)	C <sub>2-4</sub> (O) (%)	O/P ratio	C <sub>5+</sub> (%)	ROH (%)
1	2	350	7	3	83.74	5.1	6.7	12.7	27.2	2.13	44.1	4.2
2	2.5	375	4	6	77.32	5.2	7.7	12.6	29.1	2.31	40.3	5.0
3	2.5	375	10	6	68.93	6.0	8.3	10.9	24.9	2.29	43.6	6.3

<sup>a</sup>GHSV Gas hourly space velocity

As can be seen, with increasing the GHSV, the CO conversion was decreased, probably because of the less contact time of the feed with the active catalytic phases [36, 37]. Also, with increasing the pressure, the CO conversion was decreased, which is probably related to decreasing in the bulk diffusivity. As the temperature rises, the conversion of CO was decreased, probably because of the influence of heavy products such as waxes onto pores and creation of coke on the catalyst level [18]. Finally, it was observed that by increasing the H<sub>2</sub>/CO molar ratio, the conversion of CO was decreased, which is most likely related to greater effect of the water–gas shift reaction [30].

FTS synthesis yields a wide series of olefin and paraffin products, the former is more valuable and uses in many of industries. The potential application of the catalyst in industry was determined by the aid of O/P ratio. The higher ratio represents better industrial application [38, 39]. The O/P ratio was increased with increasing the GHSV. The O/P ratio depended on the catalyst type, under similar reaction conditions, the O/P ratio of M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst was lower than of Fe–Mn–novolac/SiO<sub>2</sub> catalyst [30], but compared to the same sample [18], the M2–Co–Fe–novolac/SiO<sub>2</sub> catalyst has an acceptable O/P ratio, which confirms the efficiency of this catalyst in the industry (Table 3).

# Conclusions

The Co–Fe–novolac/SiO<sub>2</sub> catalysts were prepared by three different methods. In order to raise the effective surface area of the catalyst, the novolac resin was used. The

Table 3 Comparison of O/P molar ratios for M2–Co–Fe–novolac/ SiO<sub>2</sub>, Co–Fe–resol/SiO<sub>2</sub> catalysts and Fe–Mn-resol/SiO<sub>2</sub>

Entry	Catalyst	O/P ratio	References
1	O/P for Co-Fe-novolac/SiO <sub>2</sub>	2.13	This work
2	O/P for Co-Fe-resol/SiO <sub>2</sub>	1.59	[18]
3	O/P for Fe-Mn-resol/SiO <sub>2</sub>	2.58	[30]

decomposition of the novolac resin during calcination and its removal resulted in an increase in the surface area and pore volume. Based on the results of the BET and FT-IR characterization tests, the M2–Co–Fe–novolac/SiO<sub>2</sub> as the optimal catalyst had a higher effective surface area than two other ones.

Also, based on the results of XRD, TPR, SEM, and EDX, the catalyst had suitable active phases such as metallic phases, carbides, and low oxidation of metals. The lower reduction temperature of the M2–Co–Fe–novolac/ $SiO_2$  catalyst, compared to similar samples, confirmed the greater activity of this catalyst.

Also, the catalytic test indicated the effective CO conversion and an acceptable O/P ratio for the M2–Co–Fe–novolac/SiO<sub>2</sub> sample which confirmed the efficiency of the catalyst for industrial purposes.

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