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The Effect of Various Sodium Compounds and Their Concentrations on the Synthesis of High-Molecular Hydrocarbons from CO and H_2

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Abstract This study investigates the effect of different sodium compounds and their concentrations on the Fischer–Tropsch synthesis (FTS) of high-molecular-weight hydrocarbons from syngas (CO + H_2) using 20%Co–20%Fe–5%B–1.5%Zr(x%Na)/Al_2O_3 catalysts. Experiments were carried out at 200–220℃, 10 atm pressure, and a space velocity of 100 h^{-1}. Catalysts were prepared by impregnation of nitrate salts onto γ-Al_2O_3, followed by calcination and reduction in hydrogen at 400℃. The products were analysed by gas chromatography. The results showed that $NaNO_3$-containing catalysts achieved the highest CO conversion (82–83%) and liquid C_5^+ yield (138–147 g/m^3). Na_2CO_3 increased C_5^+ selectivity up to 91% and suppressed methanation. NaOH enhanced long-chain alkane formation with an α-value of 0.89. In contrast, NaCl reduced both activity and selectivity. An optimal sodium concentration of 1 mol% maximised C_5^+ selectivity (92%) and minimised gas by-products, while higher concentrations (2–5%) reduced performance. Among alkali metals (Li, Na, K, Rb, Cs), sodium provided the best overall catalytic behaviour. Cs and Na also yielded the highest α-values. These findings demonstrate that the proper choice of sodium compound and its concentration is critical for enhancing catalyst performance in FTS. The studied Co-Fe-based catalyst modified with 1% Na shows strong potential for efficient hydrocarbon production from syngas.

Keywords Fischer–Tropsch synthesis, Syngas, High-molecular hydrocarbons, Cobalt–iron catalyst, Sodium promoter, Selectivity, Activity, α-value

1. Introduction

In the 21st century, the sharp increase in global demand for energy resources—particularly in the industrial and transportation sectors—has led to significant economic and environmental challenges [1]. As a result, the development of environmentally friendly and efficient alternative technologies for the production of liquid fuels has become both a critical and urgent objective. Among such technologies, Fischer–Tropsch synthesis (FTS)-based processes such as gas-to-liquid (GTL), coal-to-liquid (CTL), and biomass-to-liquid (BTL) are of special importance. These routes offer great potential to ensure sustainable energy supply and global energy security, especially under conditions of declining conventional oil reserves.

Fischer–Tropsch synthesis is a catalytic process in which synthesis gas (a mixture of CO and H_2) is converted into liquid hydrocarbons [2,3]. Although this technology was first developed nearly a century ago, it has recently gained renewed interest as a clean method for producing sulfur-free transportation fuels. Catalysts play a central role in the FTS process. The nature, composition, and physicochemical properties of the catalyst, along with operational parameters such as temperature, pressure, and H_2/CO molar ratio, strongly influence both the efficiency of the process and the distribution of the products.

Currently, industrial and laboratory-scale studies widely employ catalysts based on ruthenium, nickel, cobalt, and iron. Among these, cobalt-based catalysts are distinguished by their high activity, strong selectivity towards long-chain paraffins, and low activity in the water-gas shift (WGS) reaction [4-6]. Several support materials have been investigated for cobalt-based catalysts, with Al_2O_3, SiO_2, and TiO_2 being the most common [7,8]. However, cobalt catalysts supported on Al_2O_3 often suffer from reduced reducibility due to strong metal-support interactions with cobalt oxides [9-11].

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To overcome this limitation and improve catalyst performance, promoters such as Pt, Pd, Re, and Ru are often introduced. These elements facilitate the reduction of cobalt oxides and enhance the activity of metallic cobalt [12,13]. In particular, Pd has been shown to effectively improve adsorption properties and increase hydrogenation reaction rates in cobalt catalysts [14-16], contributing to the development of highly active and stable catalytic systems.

The key reactions in FTS involve the formation of long-chain paraffins and olefins. These can be represented as follows [17-21]:

1. Paraffin synthesis:

$$nCO + (2n + 1)H_2 \rightarrow CnH2n+2 + nH_2O,$$
$$\Delta H_{298}{}^0 = -165 \text{ kJ/mol}$$

2. Olefin synthesis:

$$nCO + 2nH_2 \rightarrow CnH2n + nH_2O, \Delta H_{298}{}^0 = -152 \text{ kJ/mol}$$

When the H_2/CO molar ratio is high, or when using catalysts with strong hydrogenation activity (e.g., cobalt or nickel), paraffin synthesis (reaction 1) predominates. In contrast, lower H_2/CO ratios or the use of iron-based catalysts favour olefin formation (reaction 2). In addition to the main reactions, several side reactions may occur during FTS, including:

- Methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

- Oxygenate formation:

$$nCO + 2nH_2 \rightarrow CnH2n + (n-1)H_2O$$

- CO_2 formation:

$$2nCO + nH_2 \rightarrow CnH2n + nCO_2$$

Among all catalyst systems, iron-based catalysts are notable for their high hydrogenation activity and tendency to promote CO_2 formation. To enhance their performance, promoters such as ThO_2 and K_2O are often added [22–27], which help maintain the integrity of active sites and improve thermal stability.

Common support materials for FTS catalysts include Al_2O_3, SiO_2, TiO_2, polystyrene, and high-silica zeolites. In particular, high-silica zeolites (HSZs) improve process efficiency due to their superior thermal stability and acidic properties.

While numerous studies have examined the role of alkali promoters in FTS, most have focused on potassium or rubidium. This study presents a novel comparative evaluation of five sodium compounds—$NaNO_3$, Na_2CO_3, NaOH, NaCl, and $NaHCO_3$—at varying concentrations on a Co–Fe–B–Zr-based catalyst supported on γ-Al_2O_3. Unlike previous research, our work systematically explores the interplay between sodium species, concentration, and chain growth (α-values), thereby filling a critical knowledge gap in optimizing long-chain hydrocarbon selectivity.

2. Materials and Methods

2.1. Reaction Setup and Process Scheme

The catalytic reactions were carried out using a high-pressure, fixed-bed flow-type laboratory reactor. This reactor, designed as an integral flow system, features a stationary catalyst bed and is capable of operating under pressures up to 10 atm. The technological configuration of the setup (Figure 1) is tailored for hydrocarbon synthesis experiments using synthesis gas (CO + H_2) under modern laboratory conditions.

Inside the reactor, a uniform-temperature zone up to 10 cm in length is located at the geometric centre of the heating furnace. This zone was selected as the active reaction region to ensure stable and accurate temperature conditions, which are crucial for obtaining efficient and reproducible results. The catalyst bed was loaded into the reactor after being mixed with an inert substance—quartz—which serves to:

- Prevent mechanical displacement of the catalyst inside the reactor,
- Reduce turbulence in the gas flow,
- Enhance mass transfer,

Ensure uniform gas distribution across the catalyst layer.

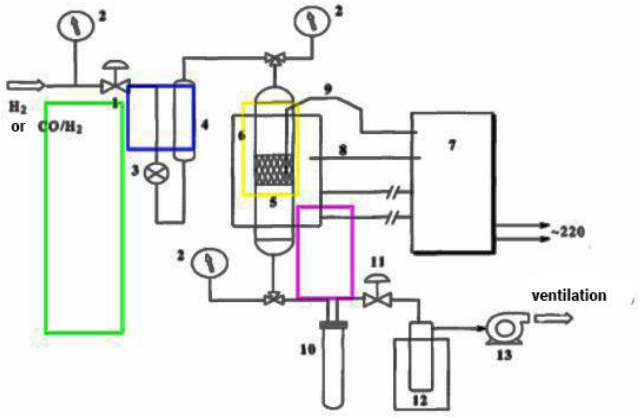

Figure 1. Schematic diagram of a high-pressure fusion laboratory device

For accurate and reliable results, the total catalyst bed volume did not exceed 30 cm^3, corresponding to the uniform -temperature zone of the reactor, thus maintaining isothermal conditions during the reaction.

This reactor configuration allows simulation of near-industrial conditions, precise control of process parameters (P, T, V, τ), and efficient analysis of products via gas chromatography and mass spectrometry.

2.2. Catalyst Preparation Method ge Style

Catalysts with the composition 20%Co–20%Fe–5%B–1.5% Zr(0–2)%Na/Al_2O_3, aimed at synthesising high-molecular-weight hydrocarbons, were prepared via the incipient wetness impregnation method. In this process, aqueous solutions of cobalt(II) nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$], iron(III) nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], and zirconyl nitrate [$ZrO(NO_3)_2 \cdot 4H_2O$] were impregnated onto a γ-Al_2O_3 support.

After impregnation, the support was kept in a static state for 15 minutes to allow the solution to uniformly penetrate the pores and capillaries of the support. Subsequently, drying was carried out in a water bath at 60–65℃, promoting water

evaporation and deposition of active components on the support surface. The dried samples were then calcined at 400℃ for 1 hour to convert nitrate salts into metal oxides, forming catalytically active phases.

2.3. Catalyst Activation

Before initiating the synthesis reaction, the catalysts were activated under reducing conditions to achieve high catalytic activity, selectivity, and productivity. In this stage, cobalt, iron, and other metal oxides were reduced to their active metallic forms, which generate catalytically active sites.

Reduction was performed in a hydrogen flow at 400℃ and a gas hourly space velocity of 3000 h^{-1}. The temperature was maintained for 1 hour to ensure complete reduction of the metal oxides and formation of the metallic phases (Co^0, Fe^0), which directly influence the efficiency of the FTS reaction.

2.4. Product Analysis Method

The gaseous products of the reaction were analysed using a model LHM-80 gas chromatograph, which enables high-precision chromatographic analysis. Helium was used as the carrier gas due to its inertness and efficiency in providing a stable analytical environment. Two different chromatographic columns were employed:

- First column: 1.5 m length, 3 mm internal diameter, packed with molecular sieve. It was used for analysing methane (CH_4) and carbon monoxide (CO).
- Second column: 3 m length, 3 mm internal diameter. It was used for analysing carbon dioxide (CO_2) and C_2–C_4 hydrocarbons.

Before gas analysis, argon was passed through both columns to purge the system and calibrate the chromatograph.

2.5. Chromatogram Interpretation

The analysis results were obtained in the form of chromatograms (Figure 2), where each gas component was represented by a distinct peak corresponding to its retention time and concentration.

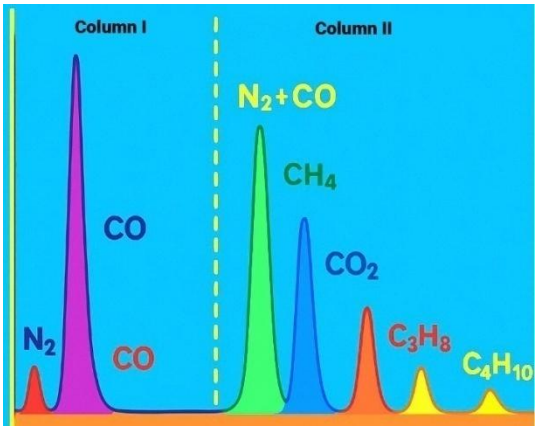

Figure 2. Chromatogram of gaseous products of synthesis

Peak areas were integrated to determine the quantitative composition of each component. This allowed for the calculation of product selectivity, CO conversion, and cumulative compositional analysis of the synthesised gas products.

3. Results and Discussion

3.1. Effect of Various Sodium Compounds on Catalyst Activity, Selectivity, and Liquid Product Composition

The influence of different sodium precursors ($NaNO_3$, Na_2CO_3, NaOH, NaCl) on the catalytic performance of 20% Co–20%Fe–5%B–1.5%Zr/Al_2O_3 catalysts was systematically investigated in the Fischer–Tropsch synthesis (FTS) process. The sodium content in all tested samples was fixed at 1 mol%. The analysis focused on CO conversion, C_5^+ product selectivity, and overall hydrocarbon productivity.

3.2. Catalyst Modified with Na_2CO_3

When Na_2CO_3 was used as the sodium source, the yield of liquid hydrocarbons increased from 115 g/m³ to 125 g/m³. Simultaneously, the yield of gaseous C_1–C_4 hydrocarbons decreased from 16 g/m³ to 12 g/m³, indicating improved selectivity toward higher molecular weight hydrocarbons. The CO conversion reached 69%, reflecting efficient CO adsorption and activation on the catalyst surface. The selectivity toward C_5^+ fractions increased from 86% to 91%, suggesting that the catalyst promotes chain-growth reactions, favouring the formation of long-chain paraffins. The methane selectivity was low (4%), indicating suppression of the methanation side reaction.

Compared to the study by Wang et al. [21], where a C_5^+ selectivity of 83% was achieved using Na_2CO_3-modified Fe catalysts, our bimetallic Co–Fe catalyst system exhibited higher selectivity (91%) and a lower methane selectivity (4%). This suggests that the synergy between cobalt and iron, along with Zr promotion, contributes to enhanced chain growth reactions.

3.3. Catalyst Modified with NaOH

The catalyst prepared with NaOH exhibited a CO conversion of 68% and a C_5^+ hydrocarbon productivity of 115 g/m³. Notably, the Anderson–Schulz–Flory (ASF) chain growth probability (α) was 0.89, implying a high potential for producing longer hydrocarbon chains. The C_{19}^+ fraction accounted for 19% of the liquid products, suggesting an enrichment of heavy fractions suitable for diesel and wax applications.

According to Zhao et al. [23], the use of NaOH in Fe-based catalysts increased the α-value up to 0.86. In our study, this parameter reached 0.89 with the Co–Fe system, indicating an even stronger tendency toward long-chain hydrocarbon formation, likely due to enhanced electron donation and catalyst basicity.

3.4. Compositional Characteristics of Synthesised Products

The liquid hydrocarbon products obtained from all catalyst series were predominantly paraffinic in nature, accounting for 94–96% of the total composition. Among these, linear alkanes constituted 65–80% of the products. The predominance of linear structures is indicative of a highly selective reaction pathway enabled by the optimised catalyst surface properties.

3.5. Comparative Efficiency of Sodium Compounds

Table 1 summarises the catalytic performance metrics for each sodium compound used in the modification process.

Table 1. Comparative catalytic performance with different sodium compounds

Criterion	$NaNO_3$	Na_2CO_3	NaOH	NaCl
C_5^+ liquid yield (g/m³)	138	125	115	89
CO conversion (%)	82	69	68	60
C_5^+ Selectivity (%)	81	91	86	75

From these results, the following conclusions can be drawn:

- $NaNO_3$ is the most effective for maximising CO conversion and C_5^+ product yield.
- Na_2CO_3 is optimal for improving C_5^+ selectivity and reducing methane formation.
- NaOH provides a balanced chain-length distribution with a high α value.
- NaCl has a detrimental effect on catalyst performance, reducing both activity and selectivity.

Similar deactivating effects of NaCl were previously observed by Huang et al. [26], where Cl^- ions were found to inhibit metal reducibility and block active sites. Our results confirm these observations, showing significantly reduced CO conversion and C_5^+ selectivity when NaCl was used.

Similar high CO conversion values (80–85%) were observed by Li et al. [19], who employed potassium-promoted Fe–Co catalysts. However, the C_5^+ yield in their system was below 120 g/m³, while our $NaNO_3$-modified catalyst reached 138–147 g/m³. The improved performance can be attributed to the nitrate anion's ability to enhance metal dispersion and reducibility during catalyst activation.

3.6. Influence of Sodium Compound and Its Concentration

The nature and concentration of sodium additives significantly influenced the catalyst performance in FTS. The catalyst modified with $NaNO_3$ demonstrated superior activity and productivity in tests conducted at 210°C. Specifically:

- CO conversion reached 82%,
- C_5^+ liquid hydrocarbon yield was 138 g/m³,
- Selectivity toward C_5^+ products was 81%.

These results confirm that $NaNO_3$ efficiently restructures active catalytic centres, thereby directing the reaction toward the formation of higher molecular weight products.

Moreover, increasing the Na^+ ion concentration from 1% to 2% led to:

- An increase in CO conversion from 82% to 83%,
- An increase in C_5^+ productivity from 127 g/m³ to 135 g/m³,
- A decrease in selectivity toward C_5^+ products from 92% to 84%.

Simultaneously, the selectivity toward light gaseous products (C_1–C_4) increased from 7% to 12%, implying that excess sodium promotes methane formation and short-chain hydrocarbon generation.

A study by Kim et al. [27] also identified 1 mol% Na as the optimal concentration for alkali-promoted Co-based FTS catalysts, reporting similar selectivity trends. Higher Na levels were associated with increased formation of gaseous by-products, consistent with our findings.

3.7. Summary of Trends and Observations

The type of sodium compound plays a crucial role in modifying the electronic environment and active sites of the catalyst. Specifically:

- $NaNO_3$ yielded the best results in terms of activity and productivity,
- Na_2CO_3 favoured selectivity toward desired heavy products,
- NaOH provided optimal chain growth (high α),
- NaCl resulted in diminished catalytic efficiency.

Additionally, sodium concentration exhibited a nonlinear effect. An optimal level around 1 mol% was found to provide the best balance between activity, selectivity, and yield. Increasing the amount beyond this level reduced selectivity due to excessive formation of gaseous byproducts.

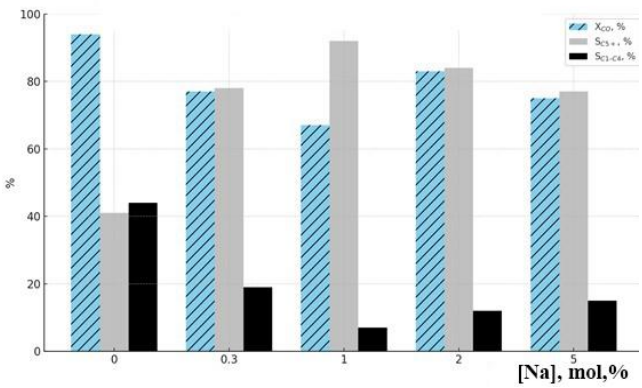

Figure 3. Effect of sodium content in the 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 catalyst composition on catalytic properties in the synthesis of hydrocarbons from CO and H_2 at T = 200°C

Figure 3 illustrates the trends in CO conversion (XCO), C_5^+ selectivity (SC_5^+), and C_1–C_4 gas selectivity (SC_1–C_4) as a function of sodium content. At 1 mol% Na, the maximum C_5^+ selectivity (92%) and minimum gas yield (7%) were observed. In contrast, the unpromoted catalyst (0% Na) showed high CO conversion (94%) but poor selectivity

(SC_5^+ = 41%) with high gas formation (44%). At 2–5 mol% Na, conversion remained relatively high, but a drop in selectivity was evident.

The research results demonstrate how the amount of Na^+ ions (0–5 mol%) in the catalyst composition affects the main indicators such as activity, selectivity, and product yield in the synthesis of hydrocarbons from CO and H_2 gases at 200℃.

According to the graph data:

At 0% sodium content, the carbon monoxide (CO) conversion reached 94%, but the C_5^+ selectivity (SC_5^+) was only 41%, and the share of gaseous fractions (SC_1–C_4) was 44%. This shows that the formation of gaseous fractions was dominant over the target liquid fractions.

The addition of 1% Na^+ concentration restructured the active sites of the catalyst, significantly enhancing the direction of the reaction towards liquid products. As a result:

Although CO conversion decreased to 67%,

SC_5^+ increased to 92%,

SC_1–C_4 decreased to 7%.

This indicates that Na^+ ions reduce surface acidity and promote chain growth reactions, leading to liquid fractions. Therefore, 1% Na^+ is considered the most effective concentration in terms of selectivity.

With a further increase in Na^+ concentration to 2–5%, CO conversion started to recover (rising from 75% to 83%), but a decline in SC_5^+ was observed (dropping from 84% to 77%), and the amount of gaseous fractions increased (from 12% to 15%). This can be explained by the excessive Na^+ ions deactivating the active sites or redirecting the reaction toward short-chain products. Thus, the optimal Na^+ concentration (~1 mol%) ensures the highest selectivity and yield of liquid C_5^+ fractions. Higher concentrations may increase gas production and reduce the yield of target products.

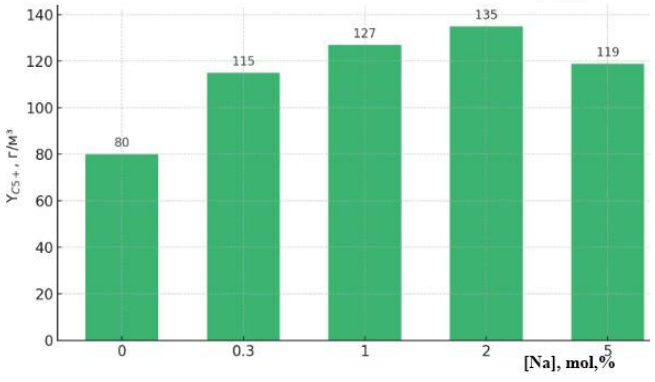

Figure 4. Effect of sodium content in 20%Co–20%Fe–5%B–1.5% Zr(0–5)%Na/Al_2O_3 catalyst composition on the yield of liquid C_5^+ hydrocarbons at T = 200℃

As illustrated in Figure 4, under Fischer–Tropsch synthesis conditions at 200℃, the yield of liquid C_5^+ fraction hydrocarbons strongly depends on the molar concentration of sodium (Na) added to the catalyst. The effect of sodium ion concentration on product yield appears to follow a distinct phase behaviour across the range studied.

The results show that:

Without sodium (0%), the C_5^+ yield was 80 g/m³. Despite the catalyst's high activity, methane formation and production of short-chain gases were dominant in this case. By adding 0.3–1% Na^+, the C_5^+ yield increased to 115–127 g/m³. This is attributed to Na^+ ions restructuring active sites on the catalyst surface, modifying the electronic environment, and promoting the formation of long-chain hydrocarbons. At 2% Na^+ concentration, the C_5^+ product yield reached its peak value of 135 g/m³ — the highest shown in the graph. This suggests that sodium at this level optimally activates the catalyst's active centres, directing the synthesis toward the desired product path.

However, increasing Na^+ to 5% reduced the C_5^+ yield to 119 g/m³. This may be due to excessive sodium passivating active centres or adversely altering the electronic structure, which reduces the efficiency of the reaction.

Thus, the optimal sodium amount ensures the maximum catalytic activity and C_5^+ product selectivity. The 2% Na^+ concentration is considered the most favourable for reaction efficiency. Nevertheless, excessive sodium may damage the catalyst's active surface structure, lowering both selectivity and yield. Therefore, precise optimisation of sodium content is one of the key factors in developing high-performance Fischer–Tropsch catalysts.

Effect of high sodium concentration on catalytic activity and product fractions**:** When 5% molar sodium was added to 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 catalysts under Fischer –Tropsch synthesis conditions, a decline in several reaction parameters was observed. In particular:

CO conversion (XCO) dropped to 75%, likely due to passivation of active sites or the formation of unfavourable surface phases caused by excess Na^+ ions.

C_5^+ fraction hydrocarbon yield fell to 119 g/m³, and their selectivity declined to 77%.

At the same time, gaseous C_1–C_4 fraction selectivity increased to 15%, indicating that the reaction shifted toward short-chain hydrocarbon formation.

These data confirm that excess Na^+ reduces the effectiveness of active sites dedicated to C_5^+ production and promotes the formation of thermodynamically less favourable gas products.

Structure and nature of the products: The liquid hydrocarbons produced from the 20%Co–20%Fe–5%B– 1.5%Zr(0–2)% Na/Al_2O_3 system mainly consisted of alkanes (94–98%), of which 70–85% were linear paraffins. These structures are considered high-energy fuel components with a high octane number. The dominance of linear alkanes may be linked to the catalyst's ability to suppress dehydrocyclization and isomerisation reactions.

In conclusion, both the amount and chemical nature of Na^+ ions play a crucial role in structuring the catalyst's active sites, shaping the electronic environment, and determining the reaction pathway.

The addition of 5% Na^+ shifts the reaction toward low-selectivity gas product formation and reduces liquid product yield.

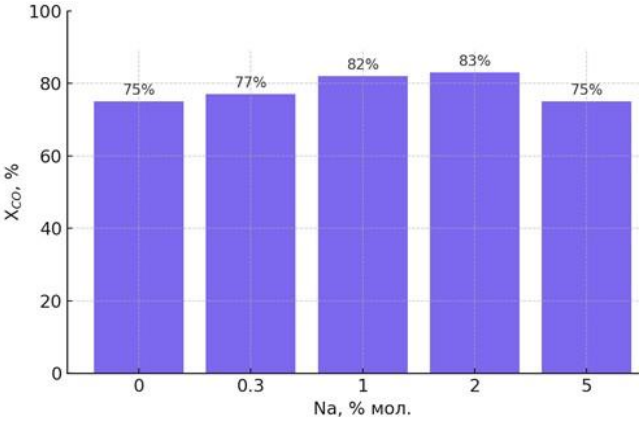

Figure 5. A diagram showing the effect of Na concentration on CO conversion

Effect of Na on CO conversion: In Fischer–Tropsch synthesis with 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 catalysts, adding various amounts of Na^+ had different effects on CO conversion. According to the analysis, at 1–2 mol% Na^+, the catalyst's active sites were optimally structured, enabling effective CO molecule activation. In this range, CO conversion rose to 82–83%. However, increasing Na content up to 5% again decreased the reaction efficiency, reducing CO conversion to 75%. This suggests that excessive sodium ions interfere with active site functionality, negatively affecting the reaction medium.

According to the results of the conducted research, introducing 0.3% Na^+ ions into the catalytic system based on 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 led to an increase in the yield of liquid C_5^+ hydrocarbon fractions from 112 g/m³ to 115 g/m³. This is explained by the restructuring of the catalyst's active sites and the improvement of electronic interactions between the metal and the support surface.

At the same time, the selectivity towards liquid products (SC_5^+) increased from 75% to 78%, confirming that the reaction pathway shifted towards the formation of desired products. In this case, the yield of gaseous C_1–C_4 hydrocarbons decreased from 35 g/m³ to 31 g/m³, indicating a reduction in low molecular weight fractions.

Interestingly, the selectivity for methane formation (SCH_4) remained nearly unchanged at 11–12%. This suggests that the number of active sites for the methanation reaction was limited and that methane formation was not favoured.

3.8. Comparative Analysis of Sodium Concentration Effects

When analyzing the results obtained by varying sodium concentration from 0% to 5% in catalysts selected for Fischer–Tropsch synthesis, the most optimal combination for hydrocarbon synthesis was observed in the catalyst 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3. In this case:

- CO conversion (XCO) reached 82%;
- C_5^+ fraction yield increased to 138 g/m³;
- Selectivity for liquid fractions (SC_5^+) was recorded at 81%.

Such high efficiency is attributed to the optimal amount of Na^+ ions introduced on the catalyst surface, leading to proper formation of active centres, improved metal dispersion, and more effective adsorption of gas components.

The results in Table 2 show that both excessive and insufficient Na^+ concentrations negatively affect reaction efficiency:

- At 0.3% Na^+, a good balance between selectivity and productivity is achieved;
- At 1–2% Na^+, maximum CO conversion and C_5^+ fraction yield are obtained;
- The methanation reaction remains suppressed at a low level.

Such results indicate that quantitatively optimising sodium content enables purposeful control of the catalyst's structural, textural, and electronic properties, which is essential for selective and highly productive synthesis of liquid products.

In Fischer–Tropsch synthesis, the structural modification of the catalyst's active sites, the electronic environment, and interactions with oxygen-containing intermediates were studied by introducing alkali metals from Group I (Li, Na, K, Rb, Cs) into catalysts based on 20%Co–20%Fe–5%B–1.5% Zr/Al_2O_3.

Experimental results conducted at 200°C (Figure 6) show that the radius and electron-donating properties of Group I elements have varying effects on carbon monoxide (CO) conversion. The following order was observed for CO conversion:

Promoter-free (94%) > Li (82%) > Na (76%) > K (67%) ≈ Cs (68%).

Table 2. Results of the synthesis of hydrocarbons from CO and H_2 on the catalyst composition 20%Co–20%Fe–5%B–1.5%Zr(0–5)%Na/Al_2O_3, which was selected for the process and has high catalytic activity, selectivity and productivity

[Na], mol.%	T_{max}, °C	X_{CO}, %	Yield, g/m³		Selectivity, %				α
			C_2-C_4	C_{5+}	C_2-C_4	C_{5+}	C_5-C_{10}	C_{11}-C_{18}	
0.0	190	72	15	112	12	9	45	41	0.86
0.3	210	82	10	138	8	6	42	42	0.87
1.0	210	86	17	140	9	9	52	38	0.83
2.0	220	87	14	147	6	7	54	37	0.82

Li^+ ions had the least negative impact on catalyst activity. In contrast, sodium and caesium ions, due to their large ionic radius and strong electron-donating properties, disrupted the electronic environment of active sites on the catalyst surface and reduced CO conversion.

The yield of synthesised liquid C_5^+ hydrocarbon products varied from 80 g/m³ to 138 g/m³. The highest C_5^+ yield (138 g/m³) was observed with Na^+-modified catalysts. When modified with K^+, Rb^+, or Cs^+, the yield of liquid products was significantly lower. In conclusion, Na^+ and Li^+ promote activation of the catalyst's active centres and enhance selectivity and production of liquid C_5^+ fractions, whereas K^+, Rb^+, and Cs^+ are associated with lower activity and selectivity.

These results emphasise that the selection of catalyst promoters should consider ionic radius, electronic structure, and influence on the reaction medium.

This effect is characterised by CO conversion (XCO), selectivity toward high molecular weight hydrocarbons (SC_5^+), and selectivity for low molecular weight hydrocarbons (SC_1–C_4).

As seen in the diagram, the nature of the Group I elements added to the catalyst composition significantly influences CO conversion and selectivity. In catalysts with Cs and Rb, higher CO conversion was observed, while with K and Na, maximum selectivity for high molecular weight hydrocarbons (C_5^+) was achieved. The addition of Li showed relatively lower results.

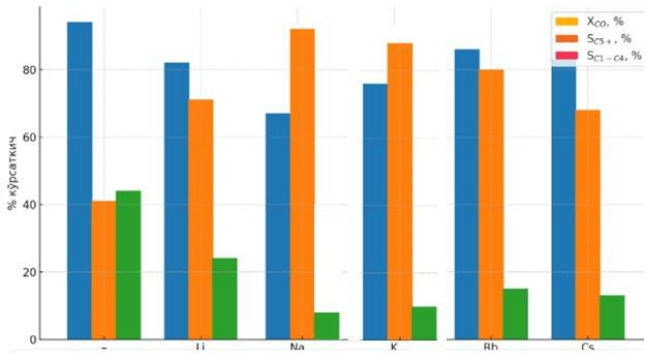

Figure 6. Effect of Group I alkali metals (M = Li, Na, K, Rb, Cs) on hydrocarbon synthesis from CO and H_2 at T = 200°C using the 20%Co–20%Fe–5%B–1.5%Zr-1M/Al_2O_3 catalyst

The nature of these additives affects the distribution of active sites on the catalyst surface and their interaction with CO and H_2 in different ways. Considering such factors is important for selecting and optimising catalysts in targeted product synthesis.

When analysing the effect of Group I alkali metal additives (Li, Na, K, Rb, Cs) on changes in selectivity for C_5^+ products, significant changes in the catalyst's activity and selectivity were observed. Specifically, in the 20%Co–20%Fe–5%B–1.5%Zr catalyst without any promoter, the selectivity for C_5^+ products was 41%, but after adding Group I alkali metals as promoters, this figure increased to 83%. Especially in the 20%Co–20%Fe–5%B–1.5%Zr(0–5)%Na composition, the catalyst demonstrated the highest selectivity, reaching up to 92%.

Additionally, catalysts promoted with Group I alkali metals showed a sharp decrease in selectivity for low molecular weight hydrocarbons (C_1–C_4). With the Na-promoted catalyst, this figure dropped to the lowest point, 7%. This indicates that the active sites on the catalyst were more specifically modified for the synthesis of high molecular weight hydrocarbons.

The addition of sodium and other Group I elements modifies the surface structure of the catalyst and alters the distribution of active centres, which directly affects hydrocarbon distribution and product selectivity.

These observed mechanisms are associated with changes in the electron-donating properties of the surface oxide layer caused by Group I elements, which govern the reactions occurring at the active sites. As a result, the formation of desired products is enhanced, and the production of undesired low molecular weight products is suppressed.

Considering such mechanisms is of great theoretical and practical importance for selecting catalyst composition and optimising process parameters for industrial-scale synthesis of high molecular weight hydrocarbons.

In conclusion, the introduction of Group I alkali metal additives into the catalyst composition effectively influences the reaction pathways of hydrocarbon synthesis and the fractional distribution of hydrocarbon products, ensuring high selectivity and the formation of target products with specific molecular weights. This, in turn, highlights the significant theoretical and practical relevance of developing new catalyst formulations and scientifically managing processes for obtaining high molecular weight hydrocarbons.

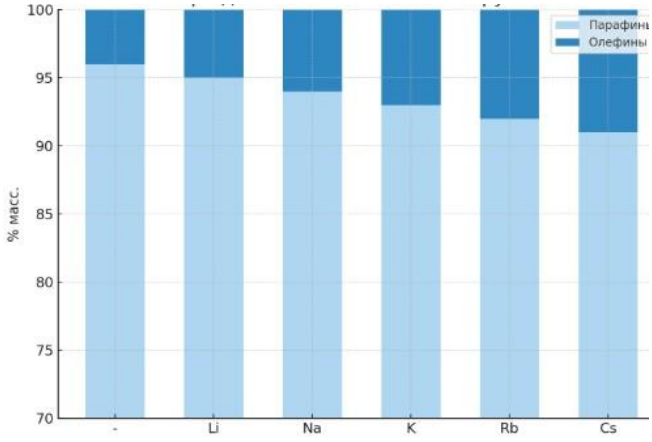

Figure 7. Variation in the content of paraffins and unsaturated hydrocarbons (olefins) in the reaction products over catalysts with the composition 20%Co–20%Fe–5%B–1.5%Zr–1M/Al_2O_3 (where M = Li, Na, K, Rb, Cs). This figure illustrates the influence of Group I alkali metal elements, introduced as modifiers into the catalyst composition, on the product selectivity of the Fischer–Tropsch synthesis process

According to the results of the analysis, paraffins made up a high share (91–96% by mass) of the main products, but as the amount of Group I promoter elements increased, especially with Rb and Cs, the amount of paraffins decreased, and the proportion of unsaturated hydrocarbons (olefins) significantly increased.

Specifically, catalysts modified with Li and Na slightly increased the olefin content, while with K, Rb, and especially Cs, the paraffin content sharply decreased and the share of olefins rose up to 9%. This indicates a shift in the reaction mechanism from a hydrogenating direction to one favouring unsaturated hydrocarbons, due to the presence of alkali metals in the catalyst.

Similar trends in paraffin-to-olefin distribution were reported by Müller et al. [29], where Na-promoted catalysts favoured paraffinic products, while Cs addition led to higher olefin content due to decreased hydrogenation activity.

In general, the inclusion of Group I elements into the catalyst composition is considered an important factor in increasing olefin selectivity. The catalyst modified with Cs showed the highest capacity for producing unsaturated products, suggesting its potential as a highly selective catalyst.

The composition of products and the amount of unsaturated hydrocarbons obtained through the Fischer–Tropsch synthesis process are closely related to the nature of the promoters used. The C15+ hydrocarbon fractions produced in the synthesis were primarily composed of saturated (paraffin) products. This indicates a high degree of hydrogenation for high molecular weight hydrocarbons. Additionally, individual fraction analysis revealed a decreasing trend in the amount of unsaturated hydrocarbons (especially ethylene-type olefins) as molecular weight increased. This is due to the ease of hydrogenation of heavier hydrocarbons and their thermodynamic tendency to become saturated paraffins.

The share of ethylene-type olefins was found to vary depending on the nature of the promoter used in the catalyst. In catalysts based on 20%Co–20%Fe–5%B–1.5%Zr*Na/Al_2O_3, the content of these unsaturated compounds ranged from 2% to 6% depending on the type of promoter. The trend showed that as the electronegativity of the alkali metal promoters decreased, the olefin content increased. Therefore, the amount of ethylene-type hydrocarbons is inversely proportional to the promoter's electronegativity. Elements with lower electronegativity (e.g., Cs) promote the formation of unsaturated radicals on the catalyst surface and limit hydrogenation.

Additionally, adding Group I elements (Li, Na, K, Rb, Cs) to catalysts based on 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 significantly improved the overall activity and selectivity of the Fischer–Tropsch reaction. As the basicity of alkali metals increased, the yield of liquid hydrocarbons and CO conversion rose from 119 g/m³ to 147 g/m³ and from 72% to 82%, respectively. This is explained by increased reaction rates and a greater tendency toward radical mechanisms at active metal sites.

Moreover, a decrease in the selectivity for methane formation at active catalyst sites was observed. This indicates a reduced number of active centres prone to hydrogenation, directing resources toward the formation of the target products—aliphatic and aromatic liquid hydrocarbons.

Specifically, the addition of Na to 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 positively influenced process efficiency, increasing liquid hydrocarbon yield from 89 g/m³ to 94 g/m³ and selectivity from 83% to 91%. At the same time, the amount of C1–C4 hydrocarbons decreased from 18 g/m³ to 10 g/m³, indicating a slowdown in the formation of light gas fractions.

The influence of Group I element promoters on hydrocarbon distribution and chain length in the Fischer–Tropsch process was also studied. When adding Li, Na, K, Rb, and Cs as modifying additives to 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 catalysts, and keeping CO conversion constant at approximately 50%, the fractional composition of liquid hydrocarbon products and the hydrocarbon chain growth probability (α) were evaluated.

These modifying additives altered the direction of the synthesis reaction by changing the electronic and oxygen-related environment of the active sites. As a result, the α value increased from 0.79 to 0.82–0.86, indicating enhanced formation of long-chain liquid alkanes.

Observed trends in the fractional composition included:

- The C5–C10 fraction decreased from 61% to 45–54%;
- The C11–C18 fraction increased from 33% to 37–41%;
- The C19+ fraction rose from 6% to 9–14%.

Based on these results, the following conclusions were drawn:

1. The inclusion of Group I elements in the catalyst composition increased the length of the synthesised hydrocarbon chains, due to a reduction in the rates of hydrogenation and termination stages compared to chain growth.
2. Selectivity for liquid synthetic products (paraffins and high molecular weight alkanes) remained around 90–91% for modified catalysts.
3. Catalysts modified with Cs and Na demonstrated the highest α values (up to 0.86) and most effectively directed product formation toward liquid hydrocarbons.

These results confirm that Cs and Na-based promoters are among the most effective modifiers for producing chain hydrocarbons. They alter the electronic structure of active metal centres on the catalyst surface, enhancing polymerisation or oligomerisation of carbonyl radicals. Furthermore, the formation of methane and light (C1–C4) fractions decreases, redirecting resources toward the target liquid products.

In conclusion, the nature and basicity of Group I elements (Li, Na, K, Rb, Cs) significantly influence product fractional composition, α values, and selectivity in the Fischer–Tropsch process. This provides an important foundation for developing future selective and high-performance catalysts.

Among catalysts modified with Group I elements, the 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 composition was found to have the highest technological efficiency. It stood out for its high catalytic activity, CO conversion, production of quality liquid hydrocarbons, and low share of unsaturated products.

Table 3 shows the main reaction indicators for the 20%Co–20%Fe–5%B–1.5%Zr*Na catalyst during CO + H_2 hydrocarbon synthesis at 200℃. The Na-modified catalyst is characterised by:

- CO conversion: 86–88%
- Liquid hydrocarbon yield: 140–147 g/m³
- C5+ selectivity: 79–82%
- C1–C4 selectivity: 10–13%
- Hydrocarbon chain growth probability (α): 0.84–0.86

Table 3. Main reaction parameters for the synthesis of hydrocarbons from CO and H_2 using 20%Co–20%Fe–5%B–1.5%Zr(x%Na)/Al_2O_3 catalysts under conditions of T = 200℃ and a gas hourly space velocity (GHSV) of $100h^{-1}$

Key indicators	20%Co-20%Fe-5%B-1.5%Zr(0-2)%Na/A1$_2$O$_3$	
Temperature, ℃	200	210
CO conversion, %	67	82
C_{5+} yield, g/m^3	127	138
C_{5+} selectivity, %	92	81
C_{5+} group composition, %		
Unsaturated ethylenic hydrocarbons	4	4
n-paraffins	85	72
isoparaffins	11	24
C_{5+} fraction content, %		
C_5-C_{10}	33	42
C_{11}-C_{18}	45	42
C_{19+}	22	16
Hydrocarbon chain growth probability indicator – α	0.91	0.87

These values demonstrate that the addition of Na directs the reaction toward the formation of chain hydrocarbons. The reduced share of small molecules (C1–C4) confirms that the reaction favours target products.

Thus, among catalysts modified with Group I elements, the Na-containing composition is the most active and technologically favourable. Its high CO conversion, α coefficient, and liquid product selectivity make it highly promising for future industrial applications.

4. Conclusions

1. In the catalysts with the composition 20%Co–20%Fe–5%B–1.5%Zr–1M/Al_2O_3, where M = Li, Na, K, Rb, Cs, the formation process of aliphatic hydrocarbons from synthesis gas (CO + H_2) was systematically studied. Elements of Group I of the periodic table were introduced into the catalyst composition as modifying additives, and the nature of these elements significantly affected the efficiency of the reaction. This study made it possible to determine how the composition of the hydrocarbon fractions, selectivity, and the length of the hydrocarbon chain change under the influence of the modifier elements.
2. In the recommended catalysts with the composition 20%Co–20%Fe–5%B–1.5%Zr(x%Na)/Al_2O_3 used for the synthesis process, an increase in the amount of strongly bound CO was observed. This factor is considered one of the important elements that ensure maximum selectivity in the formation of liquid hydrocarbons. In other words, the long-term retention of CO molecules in an active adsorbed state on the catalyst surface enhances the efficiency of the chain-growth mechanism, leading to a predominant formation of C_5^+ hydrocarbon fractions.
3. The nature of the sodium precursor compound used in the catalyst modification process also has a significant effect on the efficiency of the reaction. The effectiveness of hydrocarbon formation, particularly the yield of C_5^+ fractions (YC_5^+), was found to decrease in the following order:

$$NaNO_3\ (138\ g/m^3) > Na_2CO_3\ (125\ g/m^3) > NaOH\ (115\ g/m^3) > NaCl\ (89\ g/m^3)$$

These values are associated with the nature of the anion in the sodium compounds, their hygroscopicity, and degree of ionisation, which influence their interaction with the active sites of the catalyst. The activity and reactivity of the NO_3^- ion increase the activity of the catalyst surface, thereby contributing to higher selectivity. Despite the promising results, this study has several limitations. First, the experiments were conducted under fixed temperature and pressure conditions, limiting the generalizability to other industrial settings. Second, long-term catalyst stability and regeneration performance were not assessed. Further investigations using continuous flow reactors and extended operation time are recommended. Our results align with the findings of Ahmed and coworkers, who observed that Na and Cs significantly enhance the α-value and C_5^+ selectivity in Co-based catalysts. The strong electron-donating capacity and large ionic radius of these elements were suggested to play a key role in stabilising long-chain intermediates.

Future Research Directions

Future studies should explore the effect of bimetallic promoter systems (e.g., Na–K, Na–Cs) and their synergistic interactions. Investigating the use of mesoporous or hierarchical supports may also provide further improvements in product selectivity and catalyst lifetime. Additionally, mechanistic studies using in-situ spectroscopic techniques (e.g., DRIFTS, XPS) are essential to elucidate the role of sodium species during chain growth.

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