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Study of Modifier Influence on The Catalytic Conversion of Syngas into High-Molecular-Weight Hydrocarbons

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Abstract: This study investigates the effect of sodium-based modifiers on the catalytic synthesis of high-molecular-weight liquid hydrocarbons from syngas (CO + H_2). Catalysts with the composition 20%Co–20%Fe–5%B–1.5%Zr–(0–2)%Na supported on Al_2O_3 and SiO_2 were synthesised using the incipient wetness impregnation method. Various sodium compounds ($NaNO_3$, NaCl, Na_2CO_3, and NaOH) were applied as modifiers. The catalysts were characterised using chromatographic, X-ray diffraction, and technological analysis methods to determine their phase composition, distribution of active sites, and reaction efficiency.

The study highlights the influence of support material nature and sodium loading on CO conversion, hydrocarbon productivity, and product selectivity. According to the analysis, Na modification significantly enhanced the activation of active centres and chain growth probability in Al_2O_3-based catalysts, while this effect was less pronounced for catalysts supported on SiO_2. Additionally, both the sodium source and the sequence of metal deposition on the carrier surface were found to play a critical role in determining overall catalyst performance and product distribution.

These findings confirm the potential of sodium-modified cobalt–iron–boron–zirconium catalysts in achieving high productivity and selectivity in Fischer–Tropsch-type hydrocarbon synthesis. The results provide practical insights for the design of advanced catalytic systems for efficient syngas conversion.

Keywords: Syngas, high-molecular-weight hydrocarbons, catalyst, selectivity, modifier, sodium, cobalt, zirconium, boron, iron.

Introduction:

Syngas, a mixture primarily composed of carbon monoxide (CO) and hydrogen (H_2), serves as an important intermediate for the industrial production of liquid fuels and various chemicals derived from coal, natural gas, and other hydrocarbons [1–5]. Currently, there are three main technological routes for large-scale syngas production: steam reforming, partial oxidation, and autothermal reforming [6–8]. Each method is selected based on the desired H_2/CO ratio and the targeted application.

One of the key strategies for the effective utilisation of associated petroleum gases (APG)—typically released or flared during oil extraction—is to convert them into liquid fuel products. The Gas-to-Liquid (GTL) technology, particularly the Fischer–Tropsch (FT) synthesis, is widely employed for this purpose. FT synthesis allows the conversion of gas condensates and natural gas into sulfur-free, high-quality motor fuels and chemical feedstocks. This technology not only improves energy efficiency but also reduces environmental impact by minimizing waste generation and greenhouse gas emissions. Fuel utilization is one of the most critical contributors to global warming, with the transportation sector ranking second in global energy consumption after industry.

Another promising area involves the use of plasma-assisted processes to dissociate CO_2 molecules into CO and O_2 ($2CO_2 \rightarrow 2CO + O_2$) [9–14]. This approach enables the recycling of excess atmospheric CO_2 to obtain CO as a key component of syngas. The ability to produce syngas from renewable sources positions it as a foundational pillar of future C1 chemical industry development [15–21].

Over the past decade, significant progress has been made in the synthesis of high-selectivity products from syngas, such as diesel fuels, intermediate chemicals, and various organic compounds [22–28]. In FT synthesis, product distribution and efficiency are strongly influenced by the H_2/CO ratio, reaction conditions, catalyst type, and reactor configuration. Catalysts based on iron (Fe) and cobalt (Co) are commonly employed in FT reactions. However, stabilisers used during catalyst suspension preparation often act as catalytic poisons and reduce activity. Consequently, the use of polymer additives for catalyst stabilization has attracted increasing attention [29–35].

This study focuses on FT synthesis under gas–liquid–catalyst (three-phase) conditions, using ultrafine iron-based catalysts in a hydrocarbon medium. The influence of various polymer additives on catalytic performance was investigated. It was found that polymer modification improved the dispersion stability, preserved the active sites, and enhanced the reaction selectivity. In addition, the kinetic characteristics of the Fischer–Tropsch reaction were analyzed in the presence of polymer-modified nanoscale catalytic dispersions [36–40].

The results reveal new opportunities for optimising product selectivity and yield in FT synthesis, contributing to improved syngas utilisation and the production of high-value motor fuels and speciality organic compounds.

EXPERIMENTAL SECTION

Catalyst Preparation

Catalysts with high catalytic activity, selectivity, and productivity were synthesized using the incipient wetness impregnation method. The formulation included aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $ZrO(NO_3)_2$, which were impregnated onto powdered supports in a single step.

After impregnation, the resulting catalysts were dried in a water bath, pressed into tablets, crushed to 1–3 mm particles, and calcined in an air stream at 400 °C for 1 hour. In all catalyst formulations, the cobalt content was maintained at 10 wt%.

Supports used were Al_2O_3 (in extrudate form) and SiO_2 (in spherical granule form). For some samples, the impregnation sequence was varied to evaluate its effect on catalytic behaviour. In one approach, Co and Na nitrates were co-impregnated. In another, alkali metal salts (KNO_3, KOH, K_2CO_3, KCl, $LiNO_3$, $NaNO_3$, $RbNO_3$, $CsNO_3$) were introduced in concentrations of 0.3–5 wt% (Li, Na, K, Rb, or Cs) in the first step, followed by the addition of 20 wt% cobalt via $Co(NO_3)_2 \cdot 6H_2O$ in the second step.

After each impregnation, the samples were dried in a water bath and calcined in air at 400 °C for 1 hour.

Chromatographic Analysis

The analysis of gaseous reaction products was performed using an LHM-80 gas chromatograph with a thermal conductivity detector (TCD). Helium was used as the carrier gas, and the separation was carried out on an activated carbon column (1 m × 3 mm) using the gas-adsorption chromatography (GAC) method.

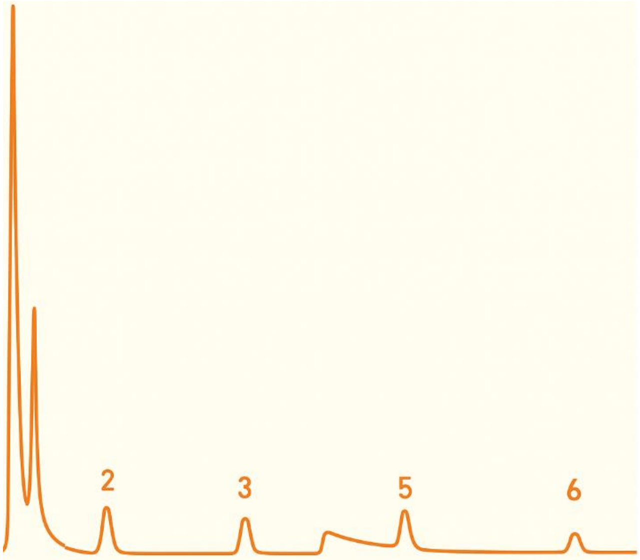

Figure 1. Typical chromatogram of gaseous products obtained from synthesis over the selected high-performance catalyst.
1 – CO, 2 – CH_4, 3 – CO_2, 4 – C_2H_6, 5 – C_3H_8, 6 – C_4H_{10}.

The composition of liquid paraffins was determined using a GC method on a Biokhrom-1 gas chromatograph equipped with a flame ionisation detector (FID). Nitrogen was used as the carrier gas. The separation was conducted on a capillary column (50 m × 0.25 mm) with a stationary phase of OV-101 under a programmed temperature regime ranging from 40 °C to 220 °C.

X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) patterns of the catalysts were recorded using a DRON-4 diffractometer with CuKα radiation (Ni filter). XRD was used to identify the phase composition of the catalysts and supports. Qualitative phase analysis was performed by matching the position and intensity of the diffraction peaks with standard reference patterns.

RESULTS AND DISCUSSION

Catalyst activity and performance under the influence of the nature of the carrier and the Na modifier. In the synthesis of liquid hydrocarbons from syngas (a mixture of CO and H_2), the effectiveness of catalysts is determined not only by the composition of the active components but also by the nature of the support material and the effect of modifiers. In this context, the catalytic properties of the systems 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 and 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/SiO_2 were studied under reaction conditions at Tmax and 200 °C.

For the catalysts prepared in series, the addition of 1% sodium significantly affected the activity of the alumina-based catalyst. In particular, the CO conversion decreased from 94% to 67% (Figure 2), which may be explained by the blocking of active sites or structural transformations.

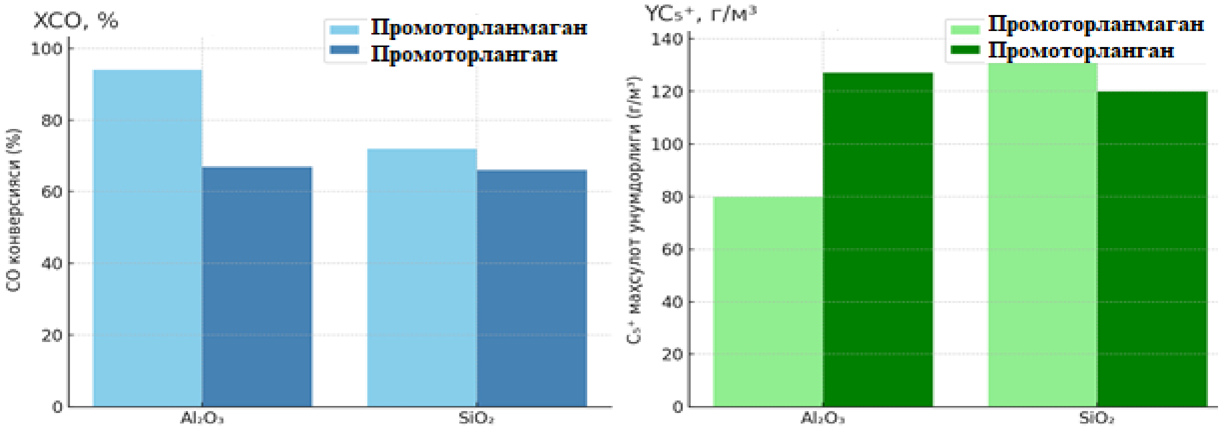

Figure 2. Effect of 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 and 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/SiO_2 catalysts on CO conversion (XCO, %) and C_5^+ product yield (YC_5^+, g/m³) in hydrocarbon synthesis from CO and H_2 at T = 200 °C.

At the same time, the productivity of liquid hydrocarbon products at elevated synthesis temperatures increased significantly — from 80 to 127 g/m^3. This occurred alongside an increase in the α parameter (which reflects the probability of carbon chain growth in the C_5^+ fraction) from 0.68 to 0.91. These results demonstrate how the nature of the support and the modifier influence the catalyst's phase composition, dispersion level, and the properties of active centers. In general, the physical and chemical properties of Al_2O_3 and SiO_2 supports — especially their beta-structure, surface area, porosity, and surface activity — play a significant role in determining reaction efficiency. Notably, in the alumina-based system, the effect of the sodium modifier resulted in high selectivity and productivity toward C_5^+ products, although limited by a lower CO conversion. This confirms that the selection of the support and modifier is one of the key factors in enhancing the activity and efficiency of catalysts for producing long-chain liquid hydrocarbons from syngas.

Effect of Sodium Modifier on the Selectivity of 20%Co–20%Fe–5%B–1.5%Zr/SiO_2 Catalyst. The 20%Co–20%Fe–5%B–1.5%Zr/SiO_2 catalyst stood out in the process of synthesising liquid hydrocarbons from a CO and H_2 mixture, due to its high catalytic activity, high selectivity, and good productivity. When sodium was added in the range of 0–2%, the selectivity indicators — namely, selectivity toward the C_5^+ fraction and toward CH_4 — remained virtually unchanged.

According to the obtained data, the selectivity toward C_5^+ hydrocarbons remained in the range of 87–88%, while CH_4 selectivity remained at about 5%. This stability is likely due to the passivity of active sites on the SiO_2 surface toward sodium, or due to the lack of sufficient acidity and surface polarity. As a result, the sodium modifier had little effect on the catalyst's selectivity profile.

Based on this, it can be concluded that the use of SiO_2 as a support does not benefit from the addition of a sodium modifier in terms of optimising the catalyst's selectivity. This implies that the selection of modifiers must consider the specific nature of the support material, and that comprehensive analysis of the catalyst's structure and surface chemical properties is necessary.

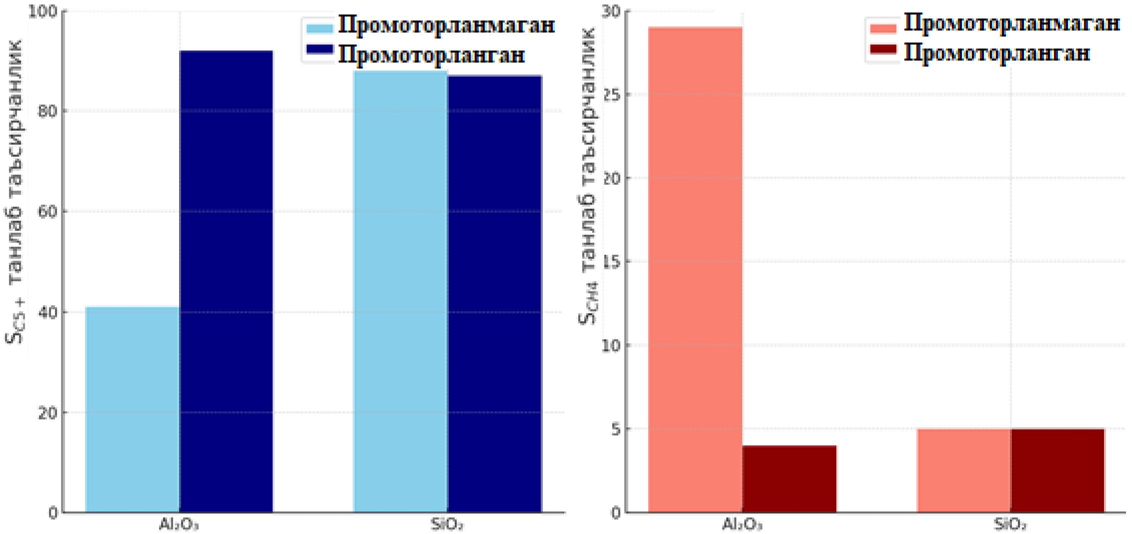

Figure 3. Effect of the support nature in 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3(SiO_2) catalysts on selectivity toward C_5^+ and CH_4 during hydrocarbon synthesis from CO and H_2 at T = 200 °C.

According to the described experimental results, the nature of the support material significantly influences both the selectivity toward C_5^+ fractions and the formation of methane (CH_4) in the synthesis of hydrocarbons from CO and H_2 at 200 °C. As shown in the graph, for the Al_2O_3-based support, the addition of a sodium promoter increased selectivity toward the C_5^+ fraction from 41% to 92%, which is attributed to the redistribution or enhancement of active centres on the catalyst surface. Furthermore, CH_4 selectivity decreased sharply from 29% to 4%, indicating a notable suppression of methanation reactions.

For the SiO_2-based support, the addition of sodium had almost no effect: C_5^+ selectivity decreased slightly from 88% to 87%, while CH_4 selectivity remained stable at around 5%. This behaviour reflects the differences in interaction strength between the support's structural and surface properties and the active metal components.

Overall, these findings confirm that Al_2O_3-based supports offer a better environment for organizing active sites and are more responsive to promoter effects. This is a key factor in developing highly selective and productive catalysts.

A comparative analysis of the catalyst series synthesised at optimal temperatures showed that the introduction of 1% sodium ions into the 20%Co–20%Fe–5%B–1.5%Zr system led to significant modification and redistribution of active centres. This was clearly reflected in the enhanced process efficiency indicators — increased CO conversion, C_5^+ hydrocarbon productivity, and selectivity.

In particular, for the Al_2O_3-based catalyst, the addition of sodium as a promoter increased CO conversion from 72% to 82%. This improvement is explained by the enhanced transformation of active metals (Co and Fe) into highly dispersed active centres and their more effective interaction with the activated gas molecules.

In parallel, the C_5^+ hydrocarbon yield increased from 112 g/m³ to 138 g/m³, indicating that the surface of the modified catalyst favoured reaction pathways leading to carbon chain growth. Selectivity toward target products also increased from 75% to 81%, confirming a higher yield of desired long-chain hydrocarbons.

Furthermore, the presence of sodium resulted in improvements to the textural and electronic properties of the catalyst, including increased surface acidity, redox capability, and adsorption capacity for reactive gases. These changes enhanced overall reaction performance and confirmed the critical role of promoter elements in forming effective active sites. These findings form a strong theoretical and practical basis for designing future highly selective catalysts.

The SiO_2-based 20%Co–20%Fe–5%B–1.5%Zr catalyst was also evaluated as a system with high catalytic activity, selectivity, and productivity. However, the introduction of sodium as a promoter had a more limited effect compared to the Al_2O_3-based system.

Notably, CO conversion remained virtually unchanged at ~86–87%, even with the sodium additive. This suggests that sodium interacts less effectively with Co and Fe active sites on SiO_2 surfaces than on Al_2O_3.

However, the C_5^+ liquid hydrocarbon yield increased modestly from 140 g/m³ to 147 g/m³, and selectivity rose from 79% to 82%. These changes likely result from the sodium ions modifying the environment around active sites, slightly enhancing the pathway toward higher molecular weight liquid products.

Importantly, the yield of gaseous hydrocarbons (C_1–C_4) decreased from 35 g/m³ to 27 g/m³, and their selectivity fell from 18% to 13%. This suggests that the promoter inhibits methane and low-molecular-weight hydrocarbon formation and encourages reactions producing heavier hydrocarbons.

A general trend observed across all tested catalysts was that the presence of Group I alkali metals (sodium) led to an increase in CO_2 yield. For example, in the Al_2O_3-based system, CO_2 production increased from 17 g/m³ to 24 g/m³, and in the SiO_2-based system, from 21 g/m³ to 24 g/m³. This could be due to enhanced oxygen adsorption and oxidation activity on the catalyst surface, stimulated by sodium.

Additionally, the introduction of sodium into the 20%Co–20%Fe–5%B–1.5%Zr system increased the optimal synthesis temperature by 10–20 °C. This indicates a higher thermodynamic energy requirement for catalyst activation, possibly due to sodium ions either passivating surface active sites or enhancing thermal stability.

In summary, the presence of sodium significantly influenced the nature of the active sites, the adsorption of gas molecules, and the reaction mechanism on the catalyst surface — leading to observable changes in overall activity and product selectivity.

Specifically:

- For Al_2O_3-based catalysts, sodium addition substantially improved CO conversion, C_5^+ hydrocarbon productivity, and selectivity. These favourable effects are attributed to the high surface activity of Al_2O_3 and strong interactions between sodium ions and the active centres.
- For SiO_2-based catalysts, the effects were milder — no significant improvement in CO conversion was observed, but a slight increase in C_5^+ selectivity and a reduction in gaseous by-products were recorded.
- In all systems, sodium addition increased CO_2 production, indicating intensified oxidation processes and a more active participation of oxygen on the catalyst surface.

These findings, supported by detailed analysis and tabular data, demonstrate that reaction activity and selectivity in modified catalysts can be significantly enhanced, and that the influence of sodium promoters varies depending on the nature of the support material.

Analysis of the Fractional Composition of Liquid Hydrocarbons and the α Parameter. The results of the study indicate that the introduction of sodium (Na) into catalysts with compositions of 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 and 20%Co–20%Fe–5%B–1.5%Zr/SiO_2 did not significantly affect the fractional composition of the resulting liquid hydrocarbon products. This suggests that sodium modification influenced the reactivity of the active centers rather than fundamentally altering the structural composition of the products. Despite the presence of sodium in the catalyst formulation, the distribution of the main hydrocarbon fractions remained nearly unchanged.

At the optimal synthesis temperature, the chain growth probability (expressed by the α value) was found to be in the range of 0.86–0.87 for Al_2O_3-based catalysts and 0.82–0.832 for SiO_2-based systems. This α parameter, known as the Anderson–Schulz–Flory coefficient, reflects the likelihood of carbon chain elongation in the hydrocarbon synthesis process. Accordingly, Al_2O_3-based catalysts are more likely to yield longer-chain hydrocarbons, contributing to a higher share of heavier fuel fractions such as gasoline and diesel.

In the products synthesized using 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 catalysts, the gasoline fraction (C_5–C_{10}) and the diesel fraction (C_{11}–C_{18}) were generated in nearly equal amounts, accounting for approximately 42–45% and 41–42%, respectively. This balance indicates that these catalysts possess high versatility and the capability to generate a broad range of valuable liquid hydrocarbons. Additionally, the C_{19}^+ fraction (high molecular weight paraffins and waxes) made up 14–16% of the total.

When the synthesis was conducted using SiO_2-based catalysts, a shift in the fractional distribution was observed. The share of the C_5–C_{10} fraction increased to 52–54%, indicating a higher yield of lighter liquid hydrocarbons. Meanwhile, the diesel fraction (C_{11}–C_{18}) constituted 37–38%, and the C_{19}^+ fraction accounted for only 9–10%. This trend may be attributed to the lower efficiency of the active sites on the SiO_2 surface in promoting the formation of long-chain hydrocarbons.

In general, these findings confirm that the incorporation of sodium into Al_2O_3-based catalysts promotes a balanced distribution of gasoline and diesel fractions, thereby enhancing their value as fuels. In contrast, SiO_2-based catalysts are more suited for synthesis processes aimed at producing lighter liquid hydrocarbons, which may be preferable for certain industrial and energy applications. Each of these outcomes presents practical advantages depending on specific operational and end-use requirements.

Influence of Sodium on the Composition of Reaction Products and Catalyst Activity

During the synthesis of liquid hydrocarbons from CO and H_2 gases, the addition of 1% sodium (Na) to the composition of the selected catalyst—characterized by high catalytic activity, selectivity, and productivity—resulted in noticeable changes in the group composition of the reaction products. The introduction of the promoter led to a shift in the distribution between unsaturated hydrocarbons and paraffins, clearly demonstrating the interaction of Na^+ ions with the active sites on the catalyst surface.

Specifically, for Al_2O_3-based catalysts, the concentration of unsaturated hydrocarbons, including ethylene series (such as C_2H_4), decreased from 12% to 3%. This reduction is attributed to the suppression of surface acidity and dehydrogenation reactions by Na^+ ions. Simultaneously, the content of paraffins increased from 67% to 72%, indicating a shift in the reaction environment toward the formation of saturated hydrocarbons.

In contrast, for SiO_2-based catalysts, the trend was less pronounced. The amount of unsaturated hydrocarbons slightly increased up to 2%, while the paraffin content rose from 64% to 68%. This indicates weaker interactions between sodium and the metal-complex active sites on the silica surface, resulting in a less pronounced modification effect.

These analytical results confirm that the most significant promoting effect of 1% Na addition was observed for Al_2O_3-supported catalysts. Sodium ions alter the configuration and electron density of active sites on the alumina surface, steering the reaction pathway toward the formation of paraffinic products.

Additionally, in the synthesis process conducted at 200 °C, the sequence of active metal incorporation into the 20%Co–20%Fe–5%B–1.5%Zr catalyst significantly influenced its physicochemical properties and the formation of active sites. The adsorption sequence of metal ions, their dispersion, and spatial distribution directly affect the selectivity, activity, and productivity of hydrocarbon synthesis.

Therefore, the selection of modifiers and the method of metal impregnation should be based on a detailed understanding of the mutual interactions between components and their behaviour in the reactive environment. This approach is crucial for designing high-performance, selective, and stable catalysts for industrial-scale applications.

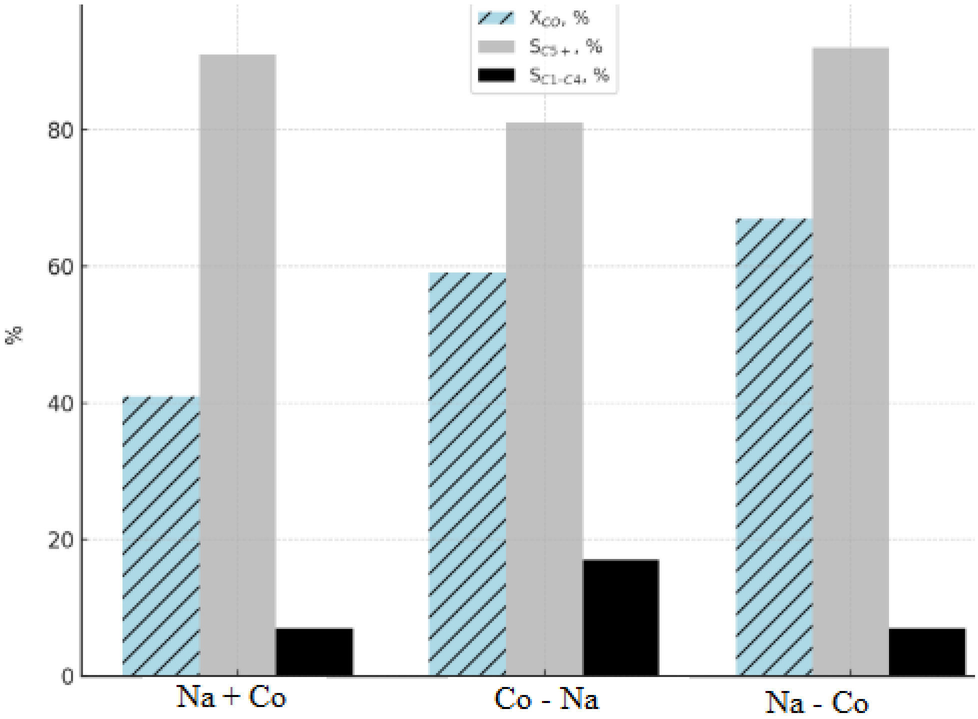

Figure 4. Effect of sodium introduction order on the catalytic properties of 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 catalysts during hydrocarbon synthesis from CO and H_2 at T = 200 °C.

The experimental results show that introducing sodium into the 20%Co–20%Fe–5%B–1.5%Zr/Al_2O_3 catalyst by different methods and in various sequences significantly affects key technological parameters such as activity, selectivity, and productivity in the hydrocarbon synthesis process.

At 200 °C, the method of sodium addition influenced the nature and distribution of active sites and their interactions with CO and H_2 molecules:

- Na + Co method (sodium and cobalt introduced simultaneously):

CO conversion: 41%, C_5^+ selectivity: 91%, C_1–C_4 selectivity: 7%.

This suggests effective formation of high molecular weight hydrocarbons as the main products.

- Co → Na method (cobalt added first, followed by sodium):

CO conversion improved significantly to 59%, C_5^+ selectivity: 81%, but C_1–C_4 selectivity increased to 17%, indicating enhanced formation of undesired methane and light hydrocarbons.

- Na → Co method (sodium added first, then cobalt):

Achieved the highest CO conversion of 67%, C_5^+ selectivity: 92%, and maintained low C_1–C_4 selectivity at 7%.

These results confirm the efficiency of this order for generating valuable products with high selectivity.

In summary, the sequence of sodium introduction directly affects the formation of active sites and their interaction with reactant gases. The Na → Co method enables optimal structuring of active sites and effective activation of cobalt, leading to improved conversion, selectivity, and desired product composition.

Influence of the Cobalt and Sodium Introduction Sequence on Catalytic Properties: Synergistic and Selectivity Effects

According to the results, the catalyst with the composition 20%Co–20%Fe–5%B–1.5%Zr*Na, synthesized using the simultaneous introduction of sodium and cobalt, demonstrated moderate catalytic performance despite its targeted high activity, selectivity, and productivity. Under these conditions, the CO conversion reached 41%, and the yield of liquid hydrocarbons was 77 g/m^3.

Notably, the C_5^+ selectivity remained high at 91%, indicating a strong preference for valuable long-chain products. In contrast, the selectivity toward low-molecular gaseous hydrocarbons (C_1–C_4) was 7%, suggesting their formation was minimal.

In follow-up experiments, the gradual addition of sodium in concentrations ranging from 0 to 5% led to a marked improvement in catalytic performance. The CO conversion increased to 59%, while the yield of C_5^+ hydrocarbons rose to 92 g/m^3, indicating enhanced productivity in hydrocarbon synthesis.

However, excessive sodium content promoted the formation of undesirable light hydrocarbons—the selectivity toward gaseous C_1–C_4 fractions increased up to 17%, which consequently decreased the selectivity for C_5^+ hydrocarbons down to 81%. This indicates a shift in the reaction pathways favouring lower molecular weight compounds.

In general, these findings confirm that controlled sodium addition significantly boosts liquid product yield, while excess sodium may lead to increased formation of gaseous by-products. Therefore, optimising sodium concentration is crucial for balancing catalyst activity and selectivity.

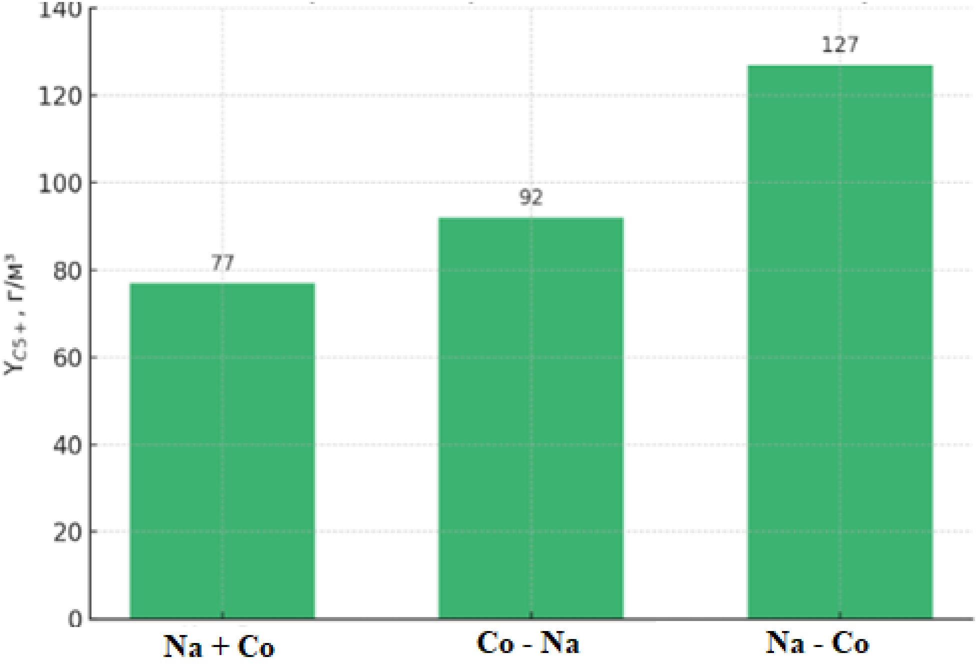

Figure 5. Effect of sodium introduction order on C_5^+ hydrocarbon yield during Fischer–Tropsch synthesis at 200 °C using 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 catalysts.

During Fischer–Tropsch synthesis at 200 °C, the yield of C_5^+ liquid hydrocarbons was found to be highly dependent on the sequence in which sodium was introduced into the catalyst composition. All tested catalysts were prepared to exhibit high catalytic activity, selectivity, and productivity. Among the parameters evaluated, the sodium incorporation method was a key determinant of catalyst performance.

- Na + Co sequence (sodium and cobalt introduced simultaneously):

Yield of C_5^+ hydrocarbons was 77 g/m³, indicating suboptimal distribution of active sites and moderate catalytic efficiency.

- Co → Na sequence (cobalt introduced first, then sodium):

Yield increased to 92 g/m³. This was attributed to the initial formation of cobalt active sites, later enhanced by sodium's promoting effect.

- Na → Co sequence (sodium introduced first, then cobalt):

Achieved the highest yield of 127 g/m³, suggesting that this approach enables better formation and dispersion of active sites, and optimally channels the reaction toward long-chain hydrocarbon products.

Overall, the sequence of sodium incorporation affects not only the chemical composition but also the structure of active sites and the electronic environment on the catalyst surface. Specifically, preliminary sodium introduction allows the surface to be more precisely structured, greatly enhancing the C_5^+ hydrocarbon yield.

These trends underscore the strategic importance of modifier implantation order in catalyst synthesis. It is a critical consideration in the design of high-performance Fischer–Tropsch catalysts.

Furthermore, applying a reverse sequential impregnation method—introducing modifier elements (Na, Zr/B) first, followed by active metals (Co and Fe)—enabled the synthesis of a catalyst with superior performance. This order facilitated the formation of well-dispersed and optimally structured active sites, with improved mutual interactions.

Experimental data confirmed that the CO conversion reached 67%, which is significantly higher than that observed in conventional impregnation methods (e.g., simultaneous or reversed sequences). This improvement is linked to the increased number and enhanced activity of active sites, as well as more efficient adsorption–activation of gas molecules (CO and H_2).

Thus, the reverse sequential deposition technique positively influenced the textural, structural, and electronic properties of the catalyst, leading to improvements in catalytic activity, selectivity, and C_5^+ hydrocarbon yield. It is a promising strategy for the development of advanced catalysts in Fischer–Tropsch synthesis.

Table 1. Catalytic performance indicators for hydrocarbon synthesis from CO and H_2 using 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 catalysts at optimal temperature T = 210 °C.

Introduction Sequence	X_CO (%)	Yield (g/m³)	Selectivity (%)	Composition of C_5^+ hydrocarbons (%)
	CH_4	$C_2–C_4$	C_5^+	$C_2–C_4$
20%Co–20%Fe–5%B–1.5%Zr*Na	72	21	15	99
Na + Co	69	20	14	103
Na → Co	82	16	10	138

These data demonstrate that sodium addition in different amounts (0–2%) has a clear effect on catalyst performance. Specifically:

- CO conversion increased as sodium content rose. The enhanced interaction between active sites and reactant gases resulted in more effective CO adsorption and dissociation.
- The yield of C_5^+ hydrocarbons also improved with sodium addition, attributed to modification of the metal–complex environment, which promotes chain-growth reactions.
- Selectivity shifted in favour of C_5^+ products, suggesting surface conditions that suppress the formation of gaseous by-products.
- However, at excessive Na concentrations, selectivity declined, and the yield of $C_1–C_4$ hydrocarbons increased, likely due to unfavourable changes in active site structure.

In conclusion, optimizing the amount and order of sodium addition provides an effective route to enhance both overall catalyst activity and product selectivity. This serves as a crucial foundation for the rational design of advanced catalysts.

Achieving High Selectivity and Productivity in Hydrocarbon Synthesis via Sequential Introduction of Catalyst Components

The results of this study demonstrate that the sequential introduction of active metals and modifiers during the preparation of the 20%Co–20%Fe–5%B–1.5%Zr*Na catalyst enabled the development of a material with high catalytic activity, selectivity, and productivity suitable for hydrocarbon synthesis.

Under these conditions, CO conversion reached 82%, and the productivity of liquid C_5^+ fraction products increased to 138 g/m³. This indicates that the composition and surface structure of the active sites were optimised for the reaction and that a synergistic effect emerged due to the interaction between the active metals and modifiers.

Selectivity analysis showed that the formation of light gaseous hydrocarbons ($C_1–C_4$) decreased to 14%, indicating a restructuring of the catalyst surface that suppressed the formation of low-molecular products. At the same time, the selectivity toward C_5^+ products increased to 81%, confirming that the reaction pathway was directed toward the formation of target products.

The hydrocarbon chain growth probability (α), a key parameter for evaluating the fractional activity of the catalyst, increased proportionally with liquid hydrocarbon productivity — from 0.84 to 0.87. This value expresses the efficiency of the chain growth reactions. In particular:

- At α = 0.84–0.85, the fractional composition consisted of 47–50% gasoline ($C_5–C_{10}$), 39–40% diesel ($C_{11}–C_{18}$), and 11–13% heavy fraction (C_{19}^+);
- At α = 0.87, gasoline and diesel fractions were produced in nearly equal proportions (42%), while the C_{19}^+ fraction increased to 16%.

An analysis of the group and structural composition of the products showed that the highest proportion of unsaturated ethylene-type hydrocarbons (mainly C_2H_4) — 6% — was observed with the 20%Co–20%Fe–5%B–1.5%Zr*Na catalyst. This indicates that the catalyst also contains active sites capable of partially promoting dehydrogenation reactions.

Additionally, the paraffin content in the products reached 75%, signifying the dominance of long saturated chains and confirming the high energy potential of the fuel, particularly for diesel and aviation fuel applications.

Based on the data in Table 2, the catalytic properties of the 20%Co–20%Fe–5%B–1.5%Zr catalysts under the influence of different sodium promoter compounds — sodium chloride (NaCl) and sodium hydroxide (NaOH) — were evaluated during the hydrocarbon synthesis process. All experiments were conducted under optimal temperature conditions (T_o⍰⍰), and the activity, selectivity, and productivity of the catalysts during synthesis from CO and H_2 were analysed.

The NaCl-modified catalyst showed the lowest catalytic activity in the series, despite optimal temperature:

- Although CO conversion reached 89%, the productivity of liquid C_5^+ fractions remained low, at only 60 g/m³;
- Simultaneously, the productivity of C_1–C_4 gaseous fractions rose to 28 g/m³, indicating reduced selectivity toward desired liquid products;
- Methane selectivity also increased to 11%, pointing to intensified methanation reactions.

NaCl, as an ionic chlorine-containing compound, likely exerts a negative effect on the active sites of the catalyst surface, partially deactivating them and suppressing radical steps in the reaction mechanism, resulting in lower liquid product yield.

Conversely, when sodium hydroxide (NaOH) was used in the preparation of 20%Co–20%Fe–5%B–1.5%Zr*Na catalysts:

- CO conversion increased to 68%;

This improvement is attributed to the stronger basic environment on the catalyst surface, better structural formation of the active sites, and enhanced adsorption–activation of gas components.

In a NaOH-modified environment, the introduced Na^+ ions regulate the interaction between the carrier surface and metal centers. This allows for increased productivity of the liquid fractions while reducing the formation of gaseous fractions (methane and C_2–C_4).

Table 2. Results of hydrocarbon synthesis from CO and H_2 over 20%Co–20%Fe–5%B–1.5%Zr(0–2)%Na/Al_2O_3 catalysts under optimal temperature (T_o⍰⍰) conditions

Sodium Compound	T_o⍰⍰ (°C)	CO Conversion (%)	Productivity (g/m³)	Selectivity (%)	α
			C_2–C_4	C_5^+	C_2–C_4
$NaNO_3$	190	72	15	112	12
NaCl	210	82	10	138	8
Na_2CO_3	210	86	17	140	9
NaOH	220	87	14	147	6

The results in the table indicate how the introduction of various amounts of sodium promoter (0–2%) to 20%Co–20%Fe–5%B–1.5%Zr catalysts, supported on Al_2O_3, affects the main technological parameters of the synthesis process. All tests were conducted under optimal temperature conditions, with key indicators such as CO conversion, gas and liquid product productivity, and selectivity assessed.

The analysis confirms the following:

- Sodium introduction leads to the restructuring of active sites on the catalyst surface. These changes enhance the adsorption and activation of CO and H_2 molecules, improving the efficiency of sequential reaction stages;
- CO conversion increased compared to sodium-free catalysts. Specifically, the addition of a precise concentration of Na^+ ions optimised reaction efficiency and improved conversion rates;
- Liquid hydrocarbon (C_5^+ fraction) productivity increased proportionally with sodium concentration. This reflects the activation of chain growth reactions and the predominance of target high-molecular-weight fractions in the product mixture;
- Simultaneously, the productivity of gaseous fractions (C_1–C_4) and methane selectivity decreased with the optimal amount of sodium, indicating a shift in the reaction toward higher selectivity.

In summary, the data show that introducing an optimal amount of Na^+ ions on an Al_2O_3-supported catalyst surface not only enhances catalytic activity and selectivity but also significantly increases the yield of liquid products. However, excessive sodium may passivate active sites and shift the reaction toward methanation. Therefore, careful control of sodium concentration, combined with structural optimisation, is necessary.

Ultimately, the proper order of component introduction during synthesis plays a decisive role in determining the configuration of active sites, the probability of hydrocarbon chain growth, and the composition and quality of final products. This makes it a key strategic approach for achieving maximum selectivity and high productivity in industrial applications.

CONCLUSION

1. It was determined that the activity of catalysts for the synthesis of liquid hydrocarbons from CO and H_2 is strongly influenced by the nature of the support and the presence of a sodium modifier. The addition of Na to Al_2O_3-based supports significantly increased both the CO conversion and the productivity of C_5^+ liquid fractions.

2. Under the influence of the Na modifier, the structure of active sites on the Al_2O_3 surface improved, the carbon chain growth probability (α parameter) increased, and a balanced distribution of gasoline and diesel fractions was achieved.

3. In SiO_2-based catalysts, the influence of sodium was comparatively weaker. An increase in the proportion of light hydrocarbons in the product composition and a decrease in low-molecular product formation were observed.

4. The type of sodium source had a significant effect on the catalytic properties: while the addition of NaCl reduced catalytic activity, catalysts prepared with NaOH demonstrated high activity and selectivity.

5. The order of metal introduction into the support also influenced catalyst performance: the Na–Co scheme (introduction of sodium before cobalt) yielded the best CO conversion and C_5^+ product productivity.

6. The findings of this study establish the practical basis for developing high-performance and selective catalysts for the Fischer–Tropsch process through the optimal selection of sodium modifiers and support materials.

7. The use of different Na sources (NaCl and NaOH) significantly affects catalyst characteristics. The NaCl additive reduces catalyst activity and promotes gaseous product formation, whereas NaOH enables the formation of a selective and productive system by properly organizing the reactive active sites. Therefore, the choice of sodium source is one of the key factors in catalyst design.

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