

Deliverable report

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Executive Summary

REDIFUEL seeks to demonstrate a process for the production of a new biogenic diesel fuel. The proposed diesel fuel consists of a blend of two main components, both of them of biogenic origin:

(i) a major fraction of high-cetane number (CN) paraffins, i.e. those present in state-of-the-art Gas-to-Liquid (GTL) of Biomass-to-Liquid (BTL) synthetic diesel fuels. This fraction is obtained through a state-of-the-art hydrotreating (hydrocracking/hydroisomerization) process from long-chain normal-paraffin hydrocarbons, with chain lengths in excess of 11 carbon atoms (C_{11+});

(ii) and a second fraction, making up to about 30% of the final fuel blend, of paraffinic alcohols with hydrocarbon chain lengths in the C_6 - C_{11} range.

The Fischer-Tropsch (FT) synthesis,^[1] i.e. the conversion of (bio)syngas (CO+H₂) to synthetic hydrocarbons is a central process of the REDIFUEL production concept. This process step is responsible for the production of those hydrocarbon slates which are precursors for the two aforementioned components in the final biodiesel blend. It is essential for the success of the project to develop a FT process capable to convert (bio)syngas (a mixture of CO and H₂) into synthetic hydrocarbons with high selectivity to:

(i) C_{11+} n-paraffins (alkanes), which can be used as precursors for the high-CN backbone pool of the REDIFUEL blend; and

(ii) alpha-olefins (alkenes) in the C_5-C_{10} range, which can be applied as precursors for C_6-C_{11} alcohols in a subsequent hydroformylation/hydrogenation conversion step. The latter process uses (bio)syngas as co-feed and extends the chain length of the olefin precursors in one carbon atom in the final alcohol derivatives.

 $n \operatorname{CO} + (2n+1) \operatorname{H}_2 \longrightarrow \operatorname{CnH}_{2n+2} + n \operatorname{H}_2 \operatorname{O} \quad (\text{eq. 1, paraffin synthesis})$ $n \operatorname{CO} + 2n \operatorname{H}_2 \longrightarrow \operatorname{CnH}_{2n} + n \operatorname{H}_2 \operatorname{O} \quad (\text{eq. 2, olefin synthesis})$ $\operatorname{CO} + \operatorname{H}_2 \operatorname{O} \longrightarrow \operatorname{CO}_2 + \operatorname{H}_2 \qquad (\text{eq. 3, WGSR})$

Figure 1: Equations for the main chemical reactions involved in a Fischer-Tropsch synthesis process. Equation 3 corresponds to the water-gas-shift reaction (WGSR).

The FT reaction is commercially catalyzed by solid catalysts based on either cobalt (Co) or iron carbide (FeC_x) as active species. The mechanism of the FT synthesis is based on a step-wise polymerization, which renders this reaction intrinsically unselective. Hence, linear hydrocarbon products in a wide range of chain lengths, from methane (C₁) to waxes (C₂₂₊) are inevitably obtained together. The main carbon-containing primary products of the reaction are methane, as well as higher (C₂₊) n-paraffins (n-alkanes) and α -olefins (1-alkenes), see Figure 1. Under optimized reaction conditions, both Co-based and FeC_x-based FT catalysts display similar hydrocarbon productivity values per mass of catalyst, however, the product distributions differ markedly. Cobalt catalysts operate at milder temperatures (around 200°C) and are typically highly selective to long-chain n-paraffins but result in low olefin contents in the products, owing to their high hydrogenation activity which converts essentially all the olefin primary products before they aggress out of the catalyst particles. Iron-based catalysts operate at higher temperatures (250-300°C) and display lower hydrogenation activity, resulting in products with a significant share of α -olefins, particularly in the C₁₀- fraction.



Alongside the FT synthesis, the water-gas-shift reaction (WGSR) occurs concomitantly (Figure 1) converting the CO from (bio)syngas and H_2O (the main by-product of the FT) into hydrogen and CO_2 . Cobalt-based catalysts are essentially inactive for this reaction, leading to overall CO_2 selectivities below 1% (on a molar carbon basis). On the contrary, catalysts based on iron carbide are remarkably active for the WGSR. The (bio)syngas mixture to be applied as feed in the REDIFUEL process displays a H_2/CO molar ratio of about 2 after purification and conditioning primary operations. Hence, any production of CO_2 in the (bio)syngas conversion step (FT reaction) would represent a net decrease in carbon yield and negatively affect the economics and carbon footprint of the overall process.

It ensues from this backdrop that the successful demonstration of the REDIFUEL process requires the development of a Fischer-Tropsch synthesis catalyst whose performance can fulfil the productivity and selectivity requirements of the process concept, i.e. by achieving an unconventional hydrocarbon product distribution in a biogas conversion step, which unites a high selectivity (>60%) to C_{11+} hydrocarbon products with a high selectivity (>25%) to α -olefins in the condensable (C_{5+}) hydrocarbon product fraction.

This report summarizes the major results of tasks targeting the development of a cobalt-based Fischer-Tropsch catalyst reaching the performance goals indicated above and suitable to be operated in a microstructured compact reactor for the conversion of biomass-derived syngas.

Starting point for this study is previous knowledge that cobalt nanoparticles supported on a γ -Al₂O₃ carrier which shows a multimodal porosity, i.e. it features both mesoporosity (pores with diameters in the range of 2-50 nm) and macroporostiy (pores > 50 nm in diameter) lead to enhanced selectivity to C₅₊ α -olefins compared to conventional catalysts supported on strictly mesoporous carriers under otherwise identical reaction conditions.^[2] Building up on these previous findings, first, the role of selected elements as promoters to enhance the selectivity to C₅₊ olefins has been studied under simulated, although industrially relevant FT reaction conditions at the lab scale. Next, aspects related to the granulometry and microscopic particle morphology of the catalyst have been considered. As a result of this research, a scalable recipe for the synthesis of a FT catalyst by incorporation of cobalt and promoter elements on a microparticulate, commercially available Al₂O₃ support material, is described in detail.



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1 Introduction

This report refers to Work Package 2 within the REDIFUEL project (*Development of processes and catalysts for producing biofuels from renewable sources*). Within this package, it refers to the development of a microparticulate Fischer-Tropsch synthesis solid catalyst, based on cobalt as the major active phase, which displays catalytic features compatible with the unconventional hydrocarbon product distribution required as precursor for the REDIFUEL biogenic fuel.

In particular, the foremost goal is to develop a catalyst which, when applied in the form of microparticles (diameter <200 μ m) in a process for the conversion of bio-syngas (H₂/CO≈2) under lab-scale technically-relevant conditions it jointly delivers: (i) mass-specific activity >3.5 mmol CO·g_{cat}·h⁻¹, (ii) selectivity to CO₂ < 2%, (iii) high hydrocarbon chain-growth probability (α >0.8), and (iv) high selectivity to C₅-C₁₀ α -olefins (≥25% in the condensable hydrocarbon products).

The performance of this catalyst has a direct impact on the distribution of synthetic hydrocarbons obtained in the (bio)syngas conversion step, and hence it indirectly influences other activities within the project. Most directly, it has implications for the design of further hydrocarbon conversion steps downstream in the process layout, notably the hydroformylation/hydrogenation of C₅-C₁₀ olefins to the alcohol fraction of the final biofuel (WP2 and WP4). The hydrocarbon product distribution and the abundance of C₅-C₁₀ olefins within the condensable FT products directly dictates which final biofuel compositions are feasible, and it is thus relevant for biofuel formulation activities (WP3). Moreover, the FT product distribution achieved with the herein developed catalyst has a direct influence on pilot testing activities, including the design of FT product rectification operations prior to downstream processing (WP4). Finally, factors such as the FT reaction productivity and the selectivity to less valuable (by)products such as light (C₄-) hydrocarbons and CO₂ has implications for the life cycle assessments of the overall process concept (WP5).

Task 2.1., to which this report pertains, has been successfully implemented since the start of the REDIFUEL project. A suitable catalyst composition has been identified which, in lab-scale tests, reached the performance indicators listed above. In the following, some background information about the catalyst design is summarized. Next, selected results obtained in the context of catalyst development are briefly summarized in section 2. Finally, a detailed recipe for the synthesis and activation of the herein developed FT catalyst is provided.

1.1 BACKGROUND INFORMATION

The FT synthesis is a hydrogenative surface polymerization reaction. The mechanism is schematically depicted in Fig. 2. Straight-chain hydrocarbon molecules develop on the surface of the active phases in the catalyst via the stepwise addition of monocarbonated units which are derived from CO and H₂, and which considered to be CH_x, CO or CH_xO fragments depending on different mechanistic proposals. This step-wise polymerization mechanism renders the reaction intrinsically unselective, and hydrocarbon products in a wide range of chain lengths, from methane (C₁) to heavy waxes (C₅₀₊) are inevitably obtained together as hydrocarbon products. The oxygen in the CO reactant is "rejected" in the form of H₂O, the major carbon-free product of the reaction. If produced, oxygenate compounds make up typically only a very minor fraction of the products under standard operation conditions. Regarding hydrocarbons, the main primary products of the reaction i.e., those desorbing directly from the catalyst surface, are methane, as well as higher (C₂₊) n-paraffins (n-alkanes) and α -olefins (1-alkenes).^[3] Scientific studies using model 2D catalytic surfaces, i.e. in the absence of pore transport restrictions, revealed that α -olefins are the predominant primary hydrocarbon products regardless of the type of catalyst applied.^[4] However, the relative abundance of paraffins and olefins in the final FT product mixture does not resemble these "primary" abundances, as α -olefins can



undergo a number of secondary reactions, primarily hydrogenation, leading to extra n-paraffins as secondary products and, to a lower extent, double-bond shift reactions leading to internal olefin secondary products.^[5] This secondary catalytic processing occurs within the catalyst particles and its extent is a function of the operation conditions, the nature of the catalyst, and the chain-length of the primary hydrocarbon products and thus the molecular weight of the products. Cobalt-based FT catalysts are preferred to convert (bio)syngas feedstocks with H₂/CO molar ratios of around 2, due to their essentially null production of CO₂ as by-product –thus more efficient use of both CO and H₂ reactants–. These catalysts consist of cobalt nanoparticles, possibly promoted by other metals which facilitate their reduction to the catalytically active metallic state, such as platinum (Pt) or ruthenium (Ru), dispersed on the surface of a porous oxide support. Given the significant hydrogenation capacity of these catalysts, most of the α -olefin primary products are hydrogenated before they egress from the catalyst particle where they formed –by pore diffusion– and thus the hydrocarbon products are essentially paraffinic.



Figure 2: Schematic summary of the different reaction pathways at work on the surface of a Fischer-Tropsch catalyst leading to different hydrocarbons and non-hydrocarbon (CO₂ and H₂O) products. For the α -olefin (1-alkene) primary products, the figure shows different secondary reactions they might undergo within the catalyst particles to n-paraffin (alkane) and internal olefin secondary products. The water-gas-shift reaction (WGSR) side-reaction is also indicated. Primary reaction products are depicted in red while secondary reaction products are shown in purple. Adapted from.^[5]

It has been shown in the scientific literature that facilitating the diffusional transport of hydrocarbon products within the particles of cobalt-based catalysts contributes to reducing the average pore residence time of α -olefins in contact with hydrogenation (metal) sites and it thus reduces the extent to which these primary reaction products undergo secondary hydrogenation reactions.^[2, 6] The application of oxide support materials, such as Al₂O₃, with very open porosities is therefore recommended to enhance molecular transport of hydrocarbons within the catalyst particles under FT reaction conditions. In particular, Al₂O₃ support materials jointly presenting:

(i) mesopores (pores with a diameter in the range of 2-50 nm according to IUPAC), which are required to host and stabilize the catalytically active cobalt nanoparticles in a highly dispersed state; along with

(ii) macropores (pores with a diameter >50 nm), along which molecular diffusion rates are significantly higher;

have been shown to result in unusual hydrocarbon product compositions with high olefin contents in the C_5 - C_{10} hydrocarbon chain-length range.^[2]

In addition to enhancing pore transport, the inhibition of hydrogenation sites on the surface of cobalt-based FT catalysts might additionally help increase the olefin share within the condensable hydrocarbon products. Promoter oxides might be added to the catalyst composition to this end. In catalysis, the term "promoter" refers to a chemical element which, added to catalyst composition in amounts significantly lower than those of the active species, modifies the catalytic properties of the latter to a remarkable extent. Essential, however, in identifying suitable promoters to reduce the olefin hydrogenation activity of cobalt-based FT catalysts in the context of REDIFUEL is that no activity for



With this background in mind, the potential of various basic oxides as promoters for cobalt-based catalysts supported on a bimodally porous (meso-macroporous) γ -Al₂O₃ support has been investigated. The following section summarizes the most relevant results collected in the course of such experimental screening at lab-scale.

2 Results

In this part of the study, a base catalyst was synthesized by dispersing cobalt (20 wt%), along with ruthenium as metal reduction promoter (Ru/Co molar ratio of 1/140) on high-surface area γ -Al₂O₃ support materials.

2.1 MICROPARTICULATE, MULTIMODALLY POROUS CATALYST CARRIER

2.1.1 POROSITY CONSIDERATIONS

The porosity of the catalyst support plays a central role for performance, as it has been discussed in section 1.1 (*vide supra*).

The porosity of the AI_2O_3 support materials studied herein was studied by means of mercury intrusion porosimetry, a established method which enables the probing of both mesopores and macropores. Figure 3 shows the corresponding pore size distributions derived from the Hg intrusion isotherms in the intrusion pressure range of 22-50000 psia. In the figure, different colour shades have been applied to delimit the mesopore (2-50 nm) and macropore (>50 nm) ranges according to the IUPAC guidelines.

A first γ -Al₂O₃ support material has been developed in the lab via soft-templating synthesis routes using non-ionic surfactants as porogen agents (see Methods). As shown in the pore size distribution derived by mercury intrusion and included in Figure 3, this material shows two populations of mesopores, one having a mean pore diameter of about 9 nm, and a second one peaking at the boundary between the mesopore and macropore regions (40 nm). In addition, the material displays a second porosity level, i.e. macropores with a broad diameter distribution centred at about 1-2 μ m. This lab-developed meso-macroporous aluminum oxide support materials is hereafter referred to as MMAO.





Figure 3: Pore size distributions derived from Hg intrusion porosimetry for different microparticulate γ-Al2O3 catalyst support materials in the intrusion pressure range of 22-50000 psia.

Next to the lab-developed meso-macroporous alumina support material, two commercially available microparticulate Al_2O_3 supports were investigated. These materials were selected to unite high surface areas, for the dispersion of cobalt active species and promoters, with open porosities to facilitate pore molecular transport processes under operating conditions. The materials are labelled CAO01 and CAO02, respectively, in this report. As shown in Figure 3, CAO01 displays only mesopores, with a most frequent diameter of 20 nm and extending to wider diameters up to 30 nm. While these are relatively wide mesopores, the pore size distribution does not show any evidence for macroporosity in this case. In the case of CAO02, the material shows the narrowest mesopores of all three samples, with a contribution peaking at a pore diameter of ca. 8.5 nm. In this case, however, there is a very significant contribution from macropores with sizes of 1-5 μ m (peaking at ca. 2.5 μ m). Indeed, quantitative analysis of the intrusion isotherm reveals that the macropore volume is the largest for this sample, amounting to 1.08 cm³/g, vs. 0.45 cm³/g for MMAO. This bimodal porosity is a priori very suitable to prepare cobalt-based Fischer-Tropsch catalysts meeting the performance requirements of the REDIFUEL process.

Next to the design of the active species exposed on the catalyst surface, as well as the porosity of the support material, in order to meet the targeted reaction rate, selectivity and stability, the solid catalyst to be developed needs to fulfil a number of technical requirements related to its application in compact, structured reactors. In particular, the flow behaviour and attrition resistance of microparticulate solids depend notably on the morphology of the primary



microparticles. While particles with sharp edges are more prone to suffer from attrition, round particles show more predictable flow properties and lower propensity to the formation of fines upon their handling, loading/offloading and usage in gas-solid flow reactors. The formation of solid fines is deleterious, as they might lead to reactor clogging issues and undesired increases in through-reactor pressure drop. These issues become exacerbated in the case of compact, structured reactors consisting of gas flow channels of reduced dimensions (micrometer or millimeter-sized), such as those applied for the FT process in the context of the REDIFUEL project, for which a reproducible and uniform distribution of the solid upon reactor loading and the prevention of plugging are essential for performance.

Based on the above considerations, attention has been paid to the properties of the AI_2O_3 support material in defining a recipe for a FT catalyst which, next to performance, could also fulfil those technical requirements associated to its application in the microchanelled reactors developed by the INER partner for the REDIFUEL process.

2.1.2 MICROPARTICLE MORPHOLOGY CONSIDERATIONS

First, the particle size and morphology of the MMAO material was examined by means of Scanning Electron Microscopy (SEM). Figure 4 shows representative SEM micrographs of the 200-400 μ m sieve fraction. It is apparent that the lab-scale crashing and sieving approach applied to obtain a given granulometry leads to microparticles which display irregular shapes and sharp edges on their outer surface. In addition, a significant fraction of fines (<20 μ m) is also observed on the surface and within the individual microparticles, suggesting a propensity of the material to undergo attrition during handling.



Figure 4: Scanning electron micrographs, at different magnification levels, of the bimodally porous meso-macroporous γ-Al₂O₃ support material (200-400 μm sieve fraction) synthesized in the lab and used for screening promoter species for FT catalysts.

The above results are clearly suboptimal for a catalyst which is aimed to be applied at process piloting activities in a structured compact reactor. In order to circumvent this issue, a scouting was performed for commercially available porous γ -Al₂O₃ microparticulate catalysts accessible in microparticle morphologies more adequate for the sought application. In particular, the search concentrated on materials shaped by spray-drying and/or spherification routes, which ensure a rounder primary particle morphology. Moreover, having in mind the requirement for a very open porosity, materials displaying wide (>30 nm) mesopores or a combination of mesopores with macropores were targeted. With these specifications in mind, two commercially available porous γ -Al₂O₃ microparticulate solids were selected. These solids are hereafter denoted as CAO01 and CAO02, respectively. After calcination in air at 550°C, these materials consisted of exclusively the γ -Al₂O₃ polymorph. Figures 5 and 6 show representative SEM micrographs of the primary particles for these materials, respectively. In the case of CAO02, the solid is supplied in a wide granulometric range. In this case, the fraction in the particle size range of 80-100 µm was isolated from the commercial batch by means of ultrasound-assisted lab-scale sieves.





Figure 5: Scanning electron micrographs, at different magnification levels, of the commercially available microparticulate γ -Al₂O₃ denoted as CAOO1. The micrographs were recorded for a sieved fraction of the solid in the 80-100 μ m size range.



Figure 6: Scanning electron micrographs, at different magnification levels, of the commercially available microparticulate γ -Al₂O₃ denoted as CAOO2. The micrographs were recorded for a sieved fraction of the solid in the 80-100 μ m size range.

As observed in the micrographs, the primary microparticle morphology is notably more spherical and uniform in both cases than for the lab-synthesized Al₂O₃ material, and the individual particles are essentially edgeless. No fines are observed on the outer surface of the microparticles, which provides an indirect indication for a higher attrition resistance of these materials during their handling compared to the lab-developed support. It is hence concluded that the commercially available microparticulate aluminas are more suitable to fulfil the mechanical and solid flow properties required for their pilot-scale application in the project.

2.2 PROMOTION EFFECTS ON CoRu/γ-Al₂O₃ CATALYSTS

Based on the existing knowledge, summarised in section 1.1., elements which are known to form stable oxides with a remarkable surface Lewis basicity have been selected as promoters. These elements include: a representative alkaline element (sodium, Na), and a representative lanthanide element (Praseodymium, Pr). For these promoters, the loading on the catalyst surface, expressed as atoms of promoter (P) per unit catalyst surface area ($P_{at} nm^{-2}$), was varied systematically in order to assess its influence on the catalytic performance. Preliminary studies with Pr indicated that a promoter surface-specific loading of 1.0 $P_{at} nm^{-2}$ led to optimal promotion effects, striking a balance between catalytic activity and selectivity to olefins in the C₅-C₁₀ range.

Table 1 summarizes the most relevant performance indicators for a series of promoted catalysts when applied for the conversion of a synthetic syngas mixture ($H_2/CO=2$) in a lab-scale reactor setup under otherwise industrially relevant reaction conditions.



Table 1: Summary of catalytic results obtained with the series of promoted $CoRu/Al_2O_3$ FT catalysts. For comparison, the performance parameters for catalysts supported on the corresponding unpromoted $CoRu/Al_2O_3$ catalysts are also included. Reaction conditions: T=200°C, P=20 bar, H₂/CO=2.0. The gas-solid space velocity was adjusted in these tests in order to achieve a constant CO conversion level of 20±3% under pseudo-steady state, ensuring that differences in product selectivity can be ascribed to catalyst composition.

Catalyst	Со	Da	Pb	Reaction rate	S(CH ₄) ^c	S(CO ₂) ^d	S(C 5+) ^e	Olef. C ₅ -C ₁₀ ^f
code	(wt%)	- - -	(M _{at} /nm²)	(mmol CO _{conv} /h·g _{Co})	(C%)	(C%)	(C%)	(C%)
CoRu_CAO01	21.0	-	-	180.8	10.6	0.3	79.0	7.3
CoRu_CAO02	24.5	-	-	148.9	9.5	0.4	79.1	11.1
CoRu_MMAO	20.7	-	-	91.4	8.2	0.6	78.9	14.1
CoRu_1Na_ MMAO	20.6	Na	1.0	32.9	8.0	1.0	76.0	15.0
CoRu_1Pr_ MMAO	22.4	Pr	1.0	36.7	8.4	0.9	70.2	19.4
CoRu_1Pr_CAO02	24.5	Pr	1.0	87.4	10.4	0.4	72.5	16.6
CoRu_0.8Pr/0.2Na_ CAO02	24.5	Pr/Na	0.8(Pr)/0.2(Na)	17.7	7.4	1.7	67.0	19.9

^a Promoter element.

^b Promoter surface content.

^c Selectivity to methane (on a carbon molar basis).

^d Selectivity to carbon dioxide (on a carbon molar basis).

^e Selectivity to hydrocarbons with carbon chains of 5 or more carbon atoms, i.e. liquid at ambient conditions (on a carbon molar basis).

 $^{\rm f}$ Selectivity to C₅-C₁₀ olefins (on a carbon molar basis).

At the CO conversion level of 20% tested, the selectivity to condensable hydrocarbons was close to 80% for all the unpromoted catalysts, with only very minor differences as a function of the nature of the support. Higher differences were observed as to the selectivity to olefins in the C₅-C₁₀ range. Despite its wide average mesopore diameter, the catalyst supported on the strictly mesoporous γ -Al₂O₃ support (CAO01) leads to a product hydrocarbon mixture which is mainly paraffinic. The selectivity to C₅-C₁₀ olefins is ca. 7%. A significant improvement in olefin production within the condensable hydrocarbon products is observed when the Al₂O₃ support material displays a bimodal porosity, i.e. it combines narrower mesopores with notably wider macropores, as for CAO02 and MMAO. In these cases, the CO conversion rate is lower (90-150 mmol CO/ g_{C0} h), likely as a result of a lower metal dispersion, but the overall selectivity to C₅-C₁₀ olefins amounts up to >14%. This noticeable change in product selectivity reflects the enhanced transport rates of the primary reaction products within the porosity of the catalyst, which reduce their residence time in contact with metallic hydrogenation sites and thus the extent of secondary olefin hydrogenation reactions into paraffins.

In addition to the effect of the support porosity, the effect of the oxide promoters on the catalytic activity and selectivity was further assessed by adding them on the surface of the CoRu/Al₂O₃ base FT catalysts. Promotion effects were first investigated on catalysts supported on the lab-developed MMAO support. Promotion of CoRu/MMAO with Na (1.0 Na_{at} nm⁻²) results in a significant decrease in the reaction rate (by a factor of ca. 3), likely as a result of the blockage of metal surface sites. However, this did not result in a significant increase in the selectivity to C₅-C₁₀ olefins (15%). In the case of Pr as promoter, activity decreases to a similar level as with Na. However, the selectivity to the target C₅-C₁₀ olefin fraction increases remarkably (by nearly 40%, to 19.4%). This result points to Pr as a suitable promoter for catalyst design. Next to the decrease in activity, promotion by either Na or Pr leads also to a second undesired drop in the overall selectivity to condensable C₅₊ hydrocarbons, i.e. to a shift of the hydrocarbon product distribution to lighter fractions. Remarkably, the unconventional enhanced C₅-C₁₀ olefin selectivity occurs while retaining the intrinsic inactivity of cobalt-based catalysts for the WGSR, keeping CO₂ selectivities at very low levels ($\leq 1\%$).

Given the considerations mentioned above as it regards to microparticle morphology and catalyst mechanical stability, it stood to reason to translate the beneficial promotional effects discovered with catalysts synthesized on the labdeveloped MMAO support also to catalysts prepared on the commercially available microparticulate supports, which offer better perspectives for a technical operation. In particular, researcher activities concentrated on CAO02, which



displays also a bimodal meso-macroporous architecture and it is thus intrinsically more selective to liquid olefins already in the absence of promoters. Addition of Pr to CoRu/CAO02 had the expected effects, i.e. the overall catalytic activity dropped (to ca. 87 mmol CO/ h g_{co}), the selectivity to C_{5+} hydrocarbons decreased also (to ca. 73%) and the selectivity to C₅-C₁₀ olefins increased significantly to exceed 16%. Also expectedly from the promoter screening performed previously, these effects took place without apparent increments in the WGSR activity, as the selectivity to CO_2 remained <0.5%. However, despite the beneficial effect of Pr as promoter, the selectivity to C_5 - C_{10} olefins with this catalyst did not pair that observed for the CoRu MMAO catalyst. The catalytic tests performed at the lab-scale, and summarized in this report, were at a CO conversion level of 20%. However, higher conversion levels per reactor pass are expected at the benchmarking and piloting FT activities in the REDIFUEL project. A higher syngas conversion implies lower gas space velocities and thus higher gas-solid residence times which are expected to result in a decrease of the selectivity to the target C₅-C₁₀ olefin product fraction with respect to the performance reported in Table 1 at a 20% CO conversion level. Therefore, it was concluded that further increasing the selectivity to this fraction was a priority goal for the herein reported lab-scale catalyst development. As an attempt to increase this parameter, the synergetic joint action of the lanthanide and alkaline promoters was assessed experimentally. As observed in the last entry to Table 1, the joint action of these two promoters on a cobalt catalyst supported on CAO02 led to a further noteworthy increment in the selectivity to C5-C10 olefins, as expected, however, in spite of a lower overall reactivity (reaction rate dropped below 20 mmol CO/ h gco.)

The performance of this dual-promoted catalyst (CoRu_0.8Pr/0.2Na_ CAO02) complied with those performance criteria preset for the FT catalyst in the context of the REDIFUEL process (see Table 2), and it was therefore selected for further benchmarking and upscaling tasks. A detailed and scalable synthesis procedure for this material is provided in section 2.3 of this report.

 Table 2: Assessment of the accomplishment of catalyst performance targets with the selected catalyst formulation.

Goal	Achieved?
Mass-specific activity >3.5 mmol CO·g _{cat} ·h ⁻¹	~
Selectivity to $CO_2 < 2\%$	~
High hydrocarbon chain-growth probability (α >0.8)	~
High selectivity to C ₅ -C ₁₀ α -olefins (≥25% in the condensable hydrocarbon products)	~
Granulometry and microparticle morphology compatible with INER-VTT structured microreactor	~

2.3 RECIPE FOR A FT CATALYST FOR THE REDIFUEL PROCESS

As a result of the catalyst screening and optimization tasks described in the previous sections, a synthesis and activation procedure for a technical FT catalyst was developed. This synthesis and activation protocol is scalable and thus suitable for benchmarking and pilot-scale production and testing by VTT and INER partners in the project. The synthesis route, which is detailed in the following, was shared with INER partner for kg-scale catalyst production.

List of chemicals

Chemical name	CAS number	Purity/concentration
Cobalt(II) nitrate hexahydrate	10026-22-9	99.999%
Ruthenium(III) nitrosyl nitrate solution (in diluted nitric acid)	34513-98-9	Ru ca. 1.5 wt%
Praseodymium(III) nitrate hexahydrate	15878-77-0	99.9%
Sodium Nitrate	7631-99-4	99.00%
Nitric acid (concentrated solution in water)	7697-37-2	ca. 70% in water



List of materials

CAO02 commercial microparticulate Al₂O₃ precursor.

Synthesis and activation procedure

The CAO02 alumina precursor was calcined in a muffle oven under stagnant air atmosphere at 550°C for 5 h (heating rate 2°C min⁻¹) in order to ensure full crystallization into γ -Al₂O₃.

Next the calcined support material was sieved to an 80-100 μm microparticle size using an ultrasound sieve.

The required amount of the support material is dried at 150° C under dynamic vacuum for 12 hours. Next, a 3.4 M aqueous solution $Co(NO_3)_2 \cdot 6H_2O$ (3.4 M) containing also ruthenium (III) nitrosyl nitrate (Ru/Co=0.02, atomic ratio), and further acidified with a nitric acid aqueous solution [0.9 g of 0.25 vol% HNO₃(conc.) in water per 20 g of cobalt nitrate] is impregnated on the dried porous support.

i) In a preferred embodiment, the volume of solution brought in contact with the support is equivalent to 90% of the total mesopore volume of the support, as determined by N_2 physisorption. The solid is then stirred in a rotary evaporator to ensure the distribution of the impregnation solution throughout the entire support by capillary forces.

ii) Alternatively, the volume of the solution is 10 times higher than the total mesopore volume and the water solvent is then removed by slow evaporation under reduced pressure in a rotary evaporator until complete dryness.

After impregnation, the solid is transferred to a tubular reactor and dried at 70° C under N₂ flow (200 cm³ g_{solid}⁻¹ min⁻¹) for 10 hours. In this case, the gas needs to flow through the bed of solid. Then, the nitrate precursors are further decomposed by calcination at 350°C for 4h under the same N₂ flow rate (heating rate of 2°C min⁻¹).

The procedure is repeated multiple times to achieve a final cobalt loading of 20-22 wt% on the alumina support.

The promoter/s are loaded on the calcined Co-Ru/Al₂O₃ catalyst in a subsequent step. The required amount of the calcined CoRu/Al₂O₃ catalyst is impregnated using an aqueous solution of the promoter/s nitrate precursor/s on the dried solid as explained above. The amount of precursors for praseodymium and sodium promoters per unit gram of calcined CoRu/Al₂O₃ catalyst are: 0.116 g of Pr(NO₃)₃·6H₂O and 0.006 g NaNO₃. After impregnation, the solid is dried then transferred to a tubular reactor and decomposed by calcination at 350°C for 4h under N₂ flow (heating rate of 1 °C min⁻¹, 200 cm³ g_{solid}⁻¹ min⁻¹) as explained above.

Prior to catalysis, the catalyst needs to be reduced at atmospheric pressure under H₂ flow (200 mL g_{cat} min⁻¹) at 400°C (1 °C min⁻¹ heating rate, 5 h dwell time). Ideally, this reduction activation is performed in situ, in the FT reactor, prior to the syngas conversion. Should this reduction activation conditions not be fully compatible with the reactor where the catalytic process will proceed, the reduction might be performed ex situ, at a different facility, followed by passivation of the metallic nanoparticles by exposing them to a through-bed gas flow of $1\%O_2/N_2$ (alternatively $1\%O_2$ diluted in other inert gas such as He or Ar) at atmospheric pressure, and a temperature of 20-30°C for 2 hours. Then, the passivated catalyst might be offloaded and handled in the open atmosphere without risk of metal reoxidation, and loaded in the FT reactor. Before catalysis, an in situ treatment in order to reduce the passivation layer around the active metal species needs to be performed. This treatment is performed at atmospheric pressure under H₂ flow (200 mL g_{cat} min⁻¹) at 300°C (1 °C min⁻¹ heating rate, 5 h dwell time).



3 Conclusions

The major conclusions drawn from the results included in this report are the following:

- Oxides of alkaline (Na) and lanthanide (Pr) elements serve as suitable promoters of CoRu/Al₂O₃ Fischer-Tropsch catalysts, favouring an enhancement of the olefin content in the C₅-C₁₀ hydrocarbon product fraction, at the expenses of the overall CO conversion rate, and without any significant enhancement of the water-gas-shift activity at industrially relevant reaction conditions for the conversion of (bio)syngas with a H₂/CO molar ratio of 2.0.
- A commercially available high-surface-area, meso-macroporous, microparticulate γ-Al₂O₃ material has been identified as a suitable catalyst support to disperse cobalt nanoparticles, leading to highly active Fischer-Tropsch catalysts, while compliant with the granulometry and microparticle shape required to be applied in structured compact reactors developed by INER partner and available at the MOBSU of VTT partner.
- The combination of Na and Pr promoters on a cobalt-based Fischer-Tropsch catalyst supported on the abovementioned microparticulate γ -Al₂O₃ material leads to a maximum selectivity to olefins in the C₅-C₁₀ hydrocarbon product fraction, with an overall terminal-to-internal olefin ratio >13 in this fraction, when applied to convert a synthetic syngas mixture with a H₂/CO molar ratio of 2.0 at lab scale and per-pass CO conversion level of 20%.
- A synthesis recipe which is scalable to pilot activities has been defined for a Fischer-Tropsch catalyst which, under simulated industrially relevant operation conditions at the laboratory scale, meets the hydrocarbon product distribution requirements for the biosyngas conversion step in the context of the REDIFUEL process concept. This synthesis recipe has been shared with project partner VTT which is in charge of FT catalyst benchmarking and upscaling activities.

4 Methods

This section describes the experimental setup and as well as the procedural methods employed to synthesize, characterize and test the catalysts described in this report.

4.1 CATALYST SYNTHESIS

Synthesis of macro-mesoporous $\gamma\text{-}Al_2O_3$ support.

High-purity dispersible nano-boehmite (75% Al_2O_3 , Sasol) was used as precursor and a polyethyleneglycolether non-ionic surfactant (Tergitol 15-S-7, Sigma-Aldrich) was employed as porogen to synthesize the bimodally porous γ -Al₂O₃ support. First, a synthesis gel was prepared by dispersing the nano-boehmite precursor in a solution of the surfactant in DI water to achieve a final gel molar composition of Al:EO:H₂O 1:8.1:49, where EO represents the ethylenoxide building units in the polymer (ca. 7 mol EO/mol surfactant). The gel was stirred vigorously at room temperature using a laboratory vertical stirrer (450 rpm) for 5 hours, transferred into a polypropylene autoclavable bottle and treated hydrothermally at 70°C in an oven for 48 h. The resulting gel was transferred into an evaporation dish and let dry at 70°C for 72 hours in an oven with internal air circulation. Finally, the solid was



transferred into a muffle oven, dried at 120°C for 3h, and then heated to 540°C (0.5 °C min⁻¹) for the crystallization of γ -Al₂O₃ and the combustion of the organic porogen. The muffle oven is equipped with convective air-extraction as required to rapidly evacuate volatile organic material and avoid the generation of igniting gas mixtures in the chamber. After calcination, the solid was sieved to the 02-0.4 mm fraction which was further employed for the synthesis of cobalt-based Fischer-Tropsch catalysts.

Synthesis of Co-based catalysts.

Catalysts were prepared by incipient wetness impregnation of the porous γ -Al₂O₃ support previously sieved to 0.2-0.4 mm particle size for catalysts supported on non-commercial supports, or 0.08-0.10 mm for catalysts supported on commercially available microparticulate supports. The support material was first dried under vacuum (423 K) for 4 hours before impregnation under static vacuum with an aqueous solution containing Co(NO₃)₂·6H₂O (3.4 M) and ruthenium (III) nitrosyl nitrate (Ru/Co=0.02, atomic) and further acidified with a 0.25 vol% HNO₃(conc). The volume of solution applied was equivalent to 90% of the total mesopore volume of the support as determined by N₂ physisorption. After impregnation, the solid was dried at 343 K under N₂ flow (200 cm³ gcat⁻¹ min⁻¹) for 10 hours and the nitrate precursors further decomposed by calcination at 623 K for 3 h under N₂ flow (heating rate of 2 K min⁻¹). Several impregnation/calcination cycles were performed when needed to adjust the total metal loading in the catalysts. After each further impregnation step, the total mesopore volume was corrected by the volume of the metal species previously deposited in the pores, assuming a density of 6.1 cm³ g⁻¹ (Co₃O₄).

4.2 MATERIALS CHARACTERIZATION

N₂-physisorption.

Nitrogen physisorption isotherms were recorded using a Micromeritics ASAP instrument after degassing the sample (ca. 100 mg, 0.2-0.4 mm particle size for catalysts supported on non-commercial supports, 0.08-0.10 mm for catalysts supported on commercial supports) at 523 K under vacuum for 10 h. Surface areas were derived using the B.E.T method in the relative pressure (P/P₀) regime of 0.05-0.30. Total mesopore volumes were based on the amount of N₂ adsorbed at a relative pressure P/P₀=0.95. The specific surface area and total mesopore volume were used to determine the amount of the solutions of promoter to be applied when incorporated by incipient wetness impregnation to reach a preset surface-specific promoter content.

Hg-intrusion porosimetry.

Mercury intrusion porosimetry experiments were performed in a Micromeritics AutoPore IV 951 apparatus. 80-150 mg of sample (0.2-0.4 mm particle size for catalysts supported on non-commercial supports, 0.08-0.10 mm for catalysts supported on commercial supports) were dried at 383 K for 72 h before the measurement. The intrusionextrusion isotherms were recorded at room temperature in the pressure range of $6.9 \cdot 10^4$ - $4.1 \cdot 10^4$ Pa with an equilibration rate of 0.1 µL g⁻¹ s⁻¹. For the determination of pore diameter and volume, a geometrical pore model was considered, with a Hg density of 13.55 g cm⁻³ and a contact angle of 141°.

Scanning electron microscopy (SEM).

Scanning electron micrographs were recorded using a S-3500 N (Hitachi) microscope. The samples were added on a pin-stub SEM mount coated with a double-adhesive-face conductive carbon-tab and sputter-coated with a conductive layer of Au before imaging.

4.3 SYNGAS CONVERSION CATALYTIC TESTING

Catalytic experiments were performed in a 316 L stainless-steel fixed-bed reactor (12 mm inner diameter). Gas feeds, i.e. H₂ (99.999%, Air Liquide) and a premixed syngas mixture (CO:H₂:Ar 3:6:1, Ar as internal standard for chromatography, from Air Liquide) were fed using calibrated mass flow controllers (Bronkhorst). The syngas feed



stream was first purified in a high-pressure metal carbonyl trap operated at 30 bar and room temperature and filled with commercial activated carbon pellets (Norit). A mass of 900-1900 mg of the Fischer-Tropsch catalyst (previously sieved to a microparticle size of 0.2-0.4 mm or 0.08-0.10 mm) was blended and diluted with SiC granules (350-560 µm, grit 46) granules and loaded into the reactor to achieve a constant packed-bed volume of 6.5 cm³. A closed capillary sheathing two thermocouples was axially inserted in the bed enabling independent temperature reading and control at the upper and bottom halves of the catalyst bed. Prior to catalysis, the catalyst was reduced at atmospheric pressure under H₂ flow (200 mL min⁻¹) at 673 K (1 K min⁻¹, 5 h). After reduction, the reactor was cooled to 423 K and the gas flow was switched to syngas. After 5 min, the system was pressurized to the reaction pressure of 20 bar, which was further controlled during the reaction experiments using a membrane dome pressure regulator (GO regulator). Next, the reactor temperature was slowly and stepwise increased to the desired reaction temperature (0.5 K min⁻¹ to 473 K) in order to ensure an appropriate heat management at the onset of the exothermic reaction and thereby avoid the creation of hotspots. The gas space velocity was adjusted in order to achieve preset CO conversion levels in all cases, corresponding to total gas flow rates in the range of 50-200 mL min⁻¹ STP.

Downstream of the tubular reactor two consecutive cold traps were set at temperatures of 423 and 373 K, respectively, at the reaction pressure, to collect heavy hydrocarbons and part of the produced water. The rest of all pipelines downstream of the reactor were kept at a temperature of 443 K to prevent condensation. The lighter fraction of hydrocarbons leaving the traps was depressurized in the dome pressure controller and analyzed online by gas chromatography (GC). The online gas chromatograph (Agilent) was equipped with two sampling loops of which one injects towards a capillary column (RTX-1, 60 m) and FID detector for the analysis of the hydrocarbons, and the other injects towards two consecutive packed bed columns (HS-Q 80/120 1 and 3 m respectively) and a TCD detector for the analysis of H₂, CO₂ and C₂-C₃. Along this analysis channel, a molecular sieve column is additionally used to separate Ar, CH₄ and CO, which were detected in a second TCD detector. CO, CH₄ and CO₂ were quantified using relative response factors relative to the Ar internal standard, whereas C₂₊ hydrocarbons were quantified based on their FID signal relative to methane, after calibration with several PIANO analytical standard hydrocarbon mixtures (Sigma-Aldrich). The trapped hydrocarbons were collected, separated from the water fraction and weighed. An aliquot fraction was then diluted in n-heptane (HPLC grade) and analyzed offline by GC. The offline, high-temperature chromatograph (Agilent) was equipped with a capillary column (DB-1, 15 m) and a FID detector. Online and offline chromatographic analysis were added up to obtain the full product distributions. Reported activity and selectivity results correspond to the pseudo-steady state, reached after \geq 10 h on-stream, and characterized by CO conversion variations of < 0.2% h^{-1} .

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Public

7 Risk register

Not relevant risks to be listed here.

Appendix



Figure 7: Sample chromatogram for an online product analysis in a catalytic test with CoRu/MMAO catalyst. Hydrocarbon products in the range of C₁-C₁₆ eluting from a capillary column can be detected in the flame-ionization detector (FID) of the Agilent GC7890B. Permanent gases, light hydrocarbon products (C₂-C₃), as well as water eluting from two consecutive packed columns can be detected using two thermal conductivity detectors (TCDs).





Figure 8: Offline analysis of the waxy hydrocarbon product fraction collected in a trap downstream of the lab-scale fixed-bed reactor over 114 h onstream after the CoRu/MMAO catalytic underwent a 48 h induction period to establish pseudo-steady-state conditions. Products eluting from a capillary column were detected using a FID. As reference, some of the components are labelled with elution time and area%. 1.27% of unassigned area can be attributed to signals below peak assignment limit. The major chromatographic peaks correspond to n-paraffins, with minor peaks corresponding mainly to n-alcohols.

