Supplementary Materials: Detailed Kinetic Modeling of CO_2-Based Fischer–Tropsch Synthesis

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1. Catalyst

1.1. Preparation

Table S1 contains the detailed preparation procedure for the applied catalyst Fe/K@γ-Al_2O_3 (mass ratio Fe/K/Al_2O_3: 15/5.25/100). One should keep in mind the formation of nitrogen oxides during the drying and calcination of $Fe(NO_3)_3$ and should guarantee sufficient venting, especially when preparing large amounts of catalyst. The catalyst is hygroscopic and should be stored in dry air (e.g. in a closed container in the presence of a desiccant).

Table S1. Detailed preparation procedure for Fe/K@γ-Al_2O_3.

Step	Duration / min	Temperature / °C
1 - Preparation of γ-Al_2O_3 support[a]		
(a) Crushing of extrudates and sieving to 100–200 µm		
2 - Incipient wetness impregnation with $Fe(NO_3)_3$[b]		
(a) Drying of support under flowing air	180	120
(b) Impregnation with aqueous $Fe(NO_3)_3 \cdot 9H_2O$ solution: 9 mL solution (1.206 kg L^{-1}) per 10 g support	10	
(c) Drying of impregnated support under flowing air	180	120
(d) Calcination of impregnated support under flowing air	470	30 → 500
	720	500
	470	500 → 30
3 - Incipient wetness impregnation with K_2CO_3[c]		
(a) Drying of support under flowing air	180	120
(b) Impregnation with aqueous K_2CO_3 solution: 9 mL solution (0.103 kg L^{-1}) per 10 g support	10	
(c) Drying of impregnated support under flowing air	180	120
(d) Calcination of impregnated support under flowing air	470	30 → 500
	720	500
	470	500 → 30
4 - Finishing		
(a) Gently crushing agglomerates and sieving to 100–200 µm		

[a] Sasol Alumina Extrudates 1.5/150 TH 100
[b] $Fe(NO_3)_3 \cdot 9H_2O$: Merck Supelco Emsure (>99% purity)
[c] K_2CO_3: Alfa Aesar (>99% purity)

1.2. Characterization

Among other techniques, the catalyst was characterized via N_2-physisorption[1] (performed at KIT-CVT), electron probe microanalysis (Jeol JXA 8530F), and inductively coupled plasma optical emission spectrometry (performed at KIT-IAM). The results are summarized in Table S2 and Figure S1.

The preparation procedure allowed for a good control of the metal loadings which are close to the target values (Fe: 15 wt.-%, K: 5.25 wt.-%). The metal distribution within the catalyst particles appeared to be relatively uniform (based on Figure S1 for an exemplary particle). However, some accumulation of Fe at the particle surface is visible.

Table S2. Key properties of the investigated catalyst determined via N_2-physisorption and inductively coupled plasma optical emission spectrometry.

Catalyst	BET surface area / $m^2\,g^{-1}$	Fe loading / wt.-%	K loading / wt.-%
Fe/K@γ-Al_2O_3	113 [1]	15.1 ± 0.8	5.3 ± 0.3

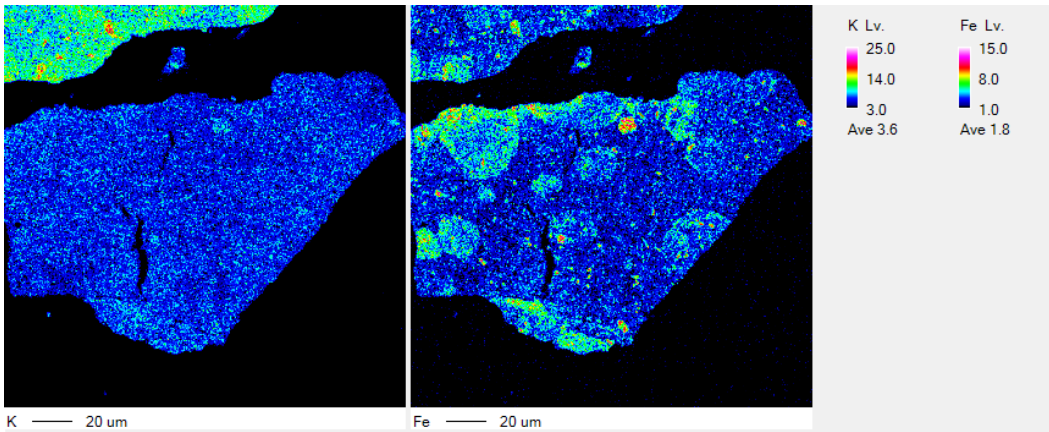


Figure S1. Electron probe microanalysis map of Fe/K@γ-Al_2O_3 with K and Fe distribution for an exemplary particle.

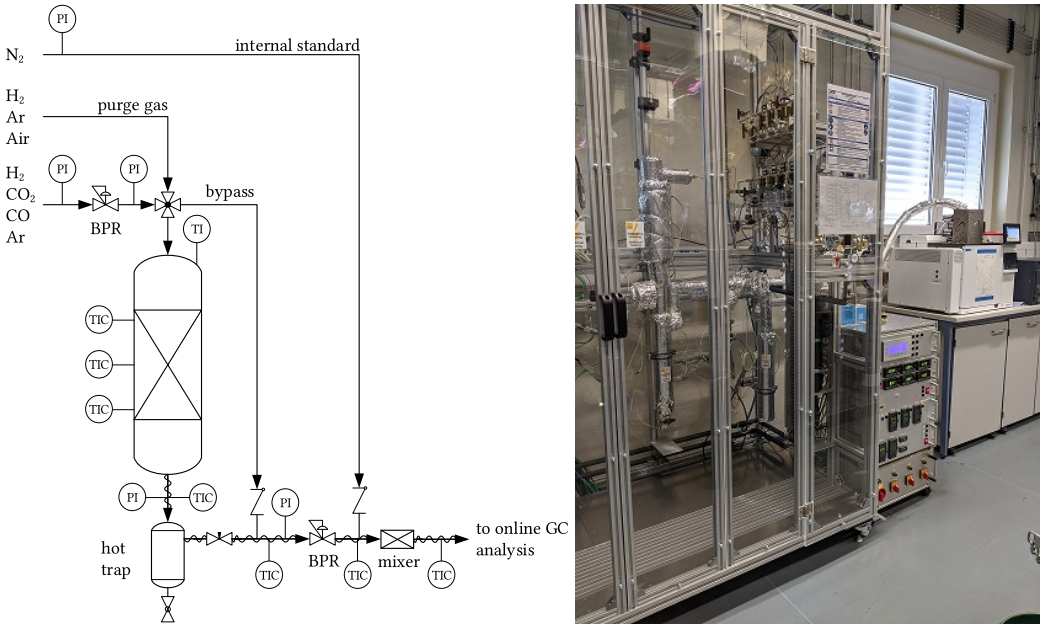
2. Experiments

2.1. Experimental Setup

The experiments were conducted in an automated, continuously operated lab-scale setup that has already been presented in a previous publication of our group [1]. A simplified flow scheme and a photograph of the setup are given in Figure S2. The gases (H_2, CO_2, CO, Ar, N_2) were dosed with mass flow controllers (Brooks SLA5850) with up- and downstream pressures being regulated to ensure calibration conditions at all times. All gases were supplied by Air Liquide (purity: H_2, Ar, N_2 >99.999%; CO_2 >99.995%; CO >99.97%).

The reactor consisted of a 1/2" stainless steel tube (1.4435, ID: 8.5 mm) with 1/2" VCR fittings (Swagelok). The reactor temperature was controlled with 3 separately heated aluminum jackets (100 W), each being 95 mm long with 5 mm distance from each other. The temperature in the catalyst bed was measured with an axially moveable thermocouple (type K) that was led through a centrally positioned 1/8" stainless steel tube (1.4435). For the experiments, the catalyst bed was positioned in the middle zone of the reactor. The fixed bed consisted of 0.5 or 2 g catalyst (100–200 µm) diluted with 5.6 or 2 g silicon carbide particles (200–300 µm). The remaining space was filled with silicon carbide particles (200–300 µm).

The product gas was led through a hot trap (80 °C) to condense the wax fraction. The relatively low temperature in the hot trap was necessary to avoid carry-over problems of long-chain hydrocarbons in the online GC analysis. The remaining gas was superheated, left the setup trough a back pressure regulator (Equilibar LF Research Series), and was mixed with the internal standard (N_2) for the online GC analysis. The system pressures and temperatures were measured at several positions using electronic pressure transmitters (WIKA S-20) and thermocouples (type K). The bypass line allowed for the check of the feed gas composition prior to the experiments. The dosing error was below 2% for all experiments.



(**a**) (**b**)

Figure S2. (a) Simplified flow scheme of the lab-scale setup (reprinted with permission from Brübach et al.[1] Copyright 2022 American Chemical Society); PI: pressure indicator, TI: temperature indicator, TIC: temperature indicator controller, BPR: back pressure regulator; (b) Photograph of the lab-scale setup (date: 18 October 2021).

2.2. Experimental Procedures

For the catalyst activation, we adapted the combined in-situ reduction/carburization method from Landau et al. [2]. The catalyst was first reduced under pure H_2 at 450 °C for 16 h at a flow rate of 100 $mL_N\,min^{-1}\,g_{cat}^{-1}$ and afterwards carburized with diluted syngas (molar ratio H_2/CO/Ar: 1/1/2) at a flow rate of 200 $mL_N\,min^{-1}\,g_{cat}^{-1}$ for 5 h. When the activation was finished, the setup was pressurized with hydrogen and the feed was dosed.

The conditions of the kinetic experiments with key results are given in Table S3. For each condition, the reaction was maintained for at least 24 h to guarantee steady state and produce a sufficient amount of wax for the analysis. Isothermal conditions (±2 K, ±1 K for most experiments) could be assured in the catalyst zone for all experiments. The results for the conversion of CO_2 and the selectivity to CO have already been used in a previous study for a simple macrokinetic model [1].

2.3. Product Analysis

The hydrocarbon product of the reaction consisted of two different phases (gas and wax) which had to be quantified and analyzed separately. Quantification of the gas phase was achieved with an internal standard (N_2). The amount of wax had to be estimated from a carbon balance as the amount of wax was too small to be reliably quantified. Based on reference experiments we concluded that ≈80% of the deficit of the carbon balance had belonged to the wax phase. For experiments with a GHSV ≥ 12,000 $mL_N\,h^{-1}\,g^{-1}$ we did not obtain a wax sample and only considered the gas analysis up to C_8.

The gas phase was analyzed online with a customized GC system (Agilent 8890, customized by Teckso GmbH). It comprised 5 valves, 5 columns, and 3 detectors. Permanent gases (H_2, N_2, CO_2, CO, and CH_4) were separated on micropacked columns (Agilent, HaysepQ & MS5A) and quantified with a TCD. Long-chain hydrocarbons were separated on an HP-5 column (Agilent, 60 m, 250 µm ID, 0.25 µm film) and detected with an FID. C_1-C_6 hydrocarbons were divided from the remaining hydrocarbons on the HP-5, separated on a GS-GasPro column (Agilent, 30 m, 320 µm ID), and detected with a second FID. The quantification of permanent gases was achieved with individual calibrations that were

determined in advance using reference gas mixtures (basi Schöberl). Hydrocarbons were quantified using CH_4 as the reference gas and carbon based relative response factors of 1 for all components. Short-chain oxygenates could not be measured due to the column configuration and were thus not included in the product spectrum.

The wax phase was analyzed via high-temperature GC-FID (Agilent 7890B) on an MXT-1 column (Restek, 30 m, 530 µm ID, 0.25 µm film). The wax samples were dissolved in n-Hexane (Merck Supelco SupraSolv, 5 g L^{-1}) and introduced into the GC via direct injection using a programmable temperature inlet (Da Vinci Laboratory Solutions PTI 1.5). The quantification was performed with a 100% percent method and response factors of 1 for all components.

The product spectrum was extremely complex with several hundred different species (likely more than thousand) comprising n-alkanes, iso-alkanes, cyclo-alkanes, linear alkenes, iso-alkenes, aromatic components, and oxygenates. With the available 1-D GC-FID equipment it was not possible to resolve every species. Thus, up to C_{20} we only allocated 1-alkenes and n-alkanes. All other hydrocarbons for one carbon number were lumped into the group "other". Beyond C_{20} we only determined the carbon number amount.

References

1. Brübach, L.; Hodonj, D.; Pfeifer, P. Kinetic Analysis of CO_2 Hydrogenation to Long-Chain Hydrocarbons on a Supported Iron Catalyst. *Ind. Eng. Chem. Res.* **2022**, *61*, 1644–1654. https://doi.org/10.1021/acs.iecr.1c04018.
2. Landau, M.V.; Meiri, N.; Utsis, N.; Vidruk Nehemya, R.; Herskowitz, M. Conversion of CO_2, CO, and H_2 in CO_2 Hydrogenation to Fungible Liquid Fuels on Fe-Based Catalysts. *Ind. Eng. Chem. Res.* **2017**, *56*, 13334–13355. https://doi.org/10.1021/acs.iecr.7b01817.

Table S3. Conditions and key results of the experiments used in the kinetic study.

#	m_{cat}	m_{SiC}	GHSV	Temperature	Pressure	H_2/CO_2	X_{H_2}	X_{CO_2}	S_{CO}	S_{CH_4}	S_{ethane}	S_{ethene}	$S_{propane}$	$S_{propene}$	$S_{n-butane}$	$S_{1-butene}$	$S_{C_4-other}$	S_{C_5+} [a]	$\frac{S_{C_5+}}{1-S_{CO}}$ [b]
-	g	g	$mL_N\,h^{-1}\,g^{-1}$	°C	bar	-	%	%	%	%	%	%	%	%	%	%	%	%	%
1	0.5	5.6	120,000	300	10	3	6.6	14.4	86.4	2.2	0.2	1.1	0.2	1.2	0.1	0.8	0.1	7.8	57.0
2	0.5	5.6	72,000	300	10	3	8.0	17.2	83.4	2.7	0.2	1.4	0.2	1.6	0.2	1.1	0.1	9.0	54.5
3	0.5	5.6	36,000	300	10	3	10.8	20.6	73.9	3.8	0.4	2.0	0.3	2.6	0.3	1.8	0.2	14.7	56.5
4	0.5	5.6	12,000	300	10	3	18.1	24.5	42.7	6.6	0.8	4.0	0.7	5.5	0.6	3.9	0.5	34.8	60.7
5	2	2	7200	300	10	3	22.9	27.2	26.7	7.3	0.9	5.0	0.8	7.0	0.7	5.1	0.7	45.9	62.5
6	2	2	3600	300	10	3	29.5	31.8	15.1	8.1	1.0	5.5	1.0	8.2	0.9	6.1	0.8	53.3	62.8
7	2	2	1800	300	10	3	36.1	37.4	8.9	8.6	1.1	5.8	1.1	8.9	1.0	6.7	0.9	57.1	62.7
8	2	2	900	300	10	3	40.6	41.1	6.4	8.9	1.2	6.0	1.1	9.6	1.1	7.2	1.1	57.3	61.3
9	0.5	5.6	120,000	320	10	3	8.2	19.1	86.9	2.0	0.2	0.9	0.1	1.1	0.1	0.7	0.1	8.0	60.8
10	0.5	5.6	72,000	320	10	3	9.3	21.2	85.9	2.4	0.2	1.2	0.2	1.4	0.1	1.0	0.1	7.6	53.4
11	0.5	5.6	36,000	320	10	3	12.3	24.2	76.0	3.7	0.3	1.9	0.3	2.5	0.2	1.8	0.2	13.1	54.5
12	0.5	5.6	12,000	320	10	3	20.9	27.8	41.1	7.4	0.8	4.4	0.7	6.1	0.6	4.4	0.6	33.9	57.5
13	2	2	7200	320	10	3	28.9	33.2	19.7	8.2	0.9	5.2	0.8	7.6	0.7	5.7	0.8	50.4	62.8
14	2	2	3600	320	10	3	34.5	36.7	13.4	8.9	1.0	5.7	0.9	8.5	0.8	6.5	0.9	53.5	61.7
15	2	2	1800	320	10	3	39.7	41.0	9.3	9.6	1.1	6.1	1.0	9.3	0.9	7.1	1.0	54.5	60.1
16	0.5	5.6	120,000	280	10	3	3.9	9.0	89.2	2.2	0.2	0.9	0.2	1.0	0.1	0.6	0.1	5.6	51.9
17	0.5	5.6	72,000	280	10	3	5.2	11.5	85.0	2.6	0.2	1.1	0.2	1.3	0.2	0.8	0.1	8.3	55.7
18	0.5	5.6	36,000	280	10	3	7.5	14.7	79.5	3.5	0.4	1.7	0.3	2.1	0.3	1.4	0.2	10.8	52.6
19	0.5	5.6	12,000	280	10	3	12.9	19.5	55.4	5.8	0.7	3.2	0.6	4.3	0.5	2.9	0.4	26.1	58.6
20	2	2	7200	280	10	3	15.2	21.5	42.7	5.8	0.8	3.8	0.7	5.0	0.6	3.5	0.5	36.7	64.0
21	2	2	3600	280	10	3	22.1	25.1	23.0	7.4	1.0	4.9	1.0	6.9	0.8	4.9	0.7	49.3	64.0
22	2	2	1800	280	10	3	28.8	30.6	11.9	8.1	1.2	5.4	1.1	8.0	1.0	5.8	0.8	56.7	64.3
23	2	2	900	280	10	3	35.3	35.6	7.2	8.4	1.2	5.6	1.2	8.7	1.1	6.4	1.0	59.3	63.9
24	2	2	7200	300	10	2	24.4	21.1	35.3	5.6	0.7	4.1	0.6	5.7	0.6	4.2	0.6	42.6	65.9
25	2	2	3600	300	10	2	31.0	23.4	21.9	6.8	0.8	5.0	0.8	7.3	0.7	5.5	0.7	50.4	64.6
26	2	2	1800	300	10	2	37.8	27.6	13.4	7.2	0.9	5.2	0.9	7.9	0.8	6.0	0.8	56.7	65.5
27	2	2	900	300	10	2	43.1	29.6	10.0	7.7	1.0	5.6	1.0	8.8	0.9	6.7	0.9	57.4	63.7
28	2	2	7200	300	10	4	21.8	33.0	21.5	8.5	1.0	5.4	1.0	7.7	0.8	5.6	0.8	47.8	60.9
29	2	2	3600	300	10	4	28.4	39.7	11.5	9.3	1.2	5.9	1.1	8.7	1.0	6.5	0.9	53.9	60.9
30	2	2	1800	300	10	4	34.2	46.0	7.1	9.8	1.3	6.1	1.2	9.4	1.1	7.0	1.0	56.0	60.3
31	2	2	900	300	10	4	38.7	51.2	5.1	10.2	1.4	6.2	1.3	10.0	1.2	7.4	1.1	56.1	59.1

[a] Based on gas phase analysis only, neglecting oxygenates ($S_{C_5+} = 1 - S_{CO} - S_{C_1-C_4}$)
[b] "CO-free" selectivity