Supplementary Content for:

Methanation of residual syngas after LPG synthesis: identifying main effects on catalytic performance with Plackett-Burman screening design

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S1.Used Chemicals

Table 1: Used chemicals in catalyst preparation and testing.

Substance	CAS	Purity	Supplier
Aluminum(III) nitrate hexahydrate	7784-27-2	ACS reagent ≥98%	Sigma Aldrich
γ-Aluminium oxide (1.0 mm spheres)	1344-28-1	97.8%	Sasol
Desiccant Drierite™ (6 mesh)	7778-18-9 7646-79-9	≥98% $CaSO_4$ <2% $CoCl_2$ (Indicator)	Sigma Aldrich
Iron(III) nitrate nonahydrate	7782-61-8	ACS reagent ≥98%	Sigma Aldrich
Magnesium(II) nitrate hexahydrate	13446-18-9	BioUltra ≥99%(KT)	Sigma Aldrich
Magnesium oxide (325 mesh)	1309-48-4	99%	Sigma
Nickel(II) nitrate nonahydrate	13478-00-7	98.5%	Sigma Aldrich
Potassium carbonate	584-08-7	p.a. ACS reagent anhydrous ≥99.0%	Sigma Aldrich
Potassium hydroxide	1310-58-3	99.99%	Sigma
Quartz (crist., 0.6-1.2 mm)	14808-60-7	99%	Carl Roth
Silicon dioxide (SS61137, 3 mm pellets)	7631-86-9	≥99.5%	Saint-Gobain NorPro
Urea	57-13-6	ACS reagent 99.0%	Sigma Aldrich

S2.Detailed description of characterization methods

N_2-Physisorption All samples where outgassed by use of a FLOVAC Degasser (Quantachrome Instruments) at 120°C and a residual pressure of 35 Pa (264 mTorr) for at least 12 h. Sorption measurements were done by the standard method of the QUDADRASORB SI. The measuring cell containing the catalyst (adsorbent) was kept at constant temperature of liquid nitrogen (77.35 K). The dead space around the adsorbent was determined by helium (4.6) 99.996 Vol% from Westfalen. After evacuation of the sample, known quantities of nitrogen (adsorptive) with a purity of (5.0) 99.999 Vol% from Westfalen was added stepwise. The adsorbed volume for each p/p_0 was determined after 300 s equilibration. Saturation pressure p^0 was measured each 3rd point.

X-ray diffraction Measurements were performed at a Siemens D5000 a 2-circle diffractometer with a linear position sensitive detector. All catalysts were measured as flat powder samples at $K_{\alpha 1}$ radiation $\lambda_{CuK\alpha 1}$ = 1.5406 Å (8,047.78 eV) by use of a copper source ^{29}Cu and a monochromator. Qualitative phase analysis was done by the EVA software from Bruker (PDF database) and the Crystallography Open Database (COD).

Inductively coupled plasma atomic emission spectroscopy Elemental analyses were performed on a ICP Spectroflame D. Approx. 30 mg of catalyst were digested in a mixture of 8 mL 40% HF, 2 mL conc. H_2SO_4 and 40 mL H_2O. The samples were measured slightly acidic.

Temperature programmed reduction Qualitative temperature-programmed reductions were made on a TPDRO 1100 Series ThermoFinnigan (CE INSTRUMENTS). As pre-treatment all samples were pestle, heated to 300°C with ramp of 10°C/min flushing with 20 mL/min N_2 and maintained for at least 100 min. Subsequently, after cooling to 50°C the analysis was made with 20 mL/min 10 Vol% H_2 in Ar and a constant heating rate of 10°C/min. The sample was kept at the target temperature of 800°C for 30 min.

Electron microscopy Measurements in transmission and scanning transmission mode were performed on a high resolution FEG TEM (JEM-2200FS, CS corrected) at 200 kV. Some of the analysis was combined with the micro-analytical energy dispersive spectroscopy (EDS).

Gas chromatography Gas chromatographic analyses are performed on an on-line GC from Bruker GC (Scion-456) equipped with three channels: one TCD for H_2, a second TCD for permanent gases (CO, CO_2, CH_4 and N_2) and a FID for hydrocarbons. 10vol% N_2 were used an internal standard to account for volume contraction during reaction.

S3.Detailed description of reactor setup

The reactor tube is made of quartz glass (ID 8 mm) with a porous glass frit (Por. 0). The gas inlet temperature as well as the catalyst bed temperature is monitored by K-type thermocouples. The tubular furnace from Horst GmbH is controlled by JUMO iTRON 16 PID controller and can be heated up to 600°C. All mass flow controllers from Brooks are calibrated with nitrogen by a ProFlow6000 flowmeter. The 1/8" piping and connectors are made of stainless steel (SS316). A copper spiral and a water trap remove generated water. Subsequently a moisture trap from Supelco filled with Drierite™ removes residual water in the gas phase.

S4. ICP-AES Measurements

Table 2 Ratios of mass concentration from ICP-AES measurements for the first set of catalysts. Values in brackets correspond to ideal metal ratios. The amount of potassium was too little to determine properly.

DoE	Fe/Ni		Fe/Si		Fe/Al		Ni/Si		Ni/Al		Mg/Si		Mg/Al	
1	1.06	(1.00)	0.17	(0.16)			0.16	(0.16)						
2							0.36	(0.36)			0.15	(0.14)		
3							0.18	(0.12)			0.14	(0.14)		
4	0.88	(1.00)			0.06	(0.05)			0.06	(0.05)			0.09	(0.13)
5									0.32	(0.32)				
6	1.08	(1.00)	0.04	(0.05)			0.04	(0.05)						
7	1.01	(1.00)			0.15	(0.16)			0.15	(0.16)			0.11	(0.13)
8									0.09	(0.09)				

S5. DOE Analysis

Table 3 Used formulas for calculating impact and error for each factor (A-G).

Term	Formula	Error
Average response upper level	$\overline{R}_+ = \frac{\sum_i^n R_{i,+}}{n}$	$\sigma_+ = \frac{s_+}{\sqrt{n}}$ with $s_+ = \sqrt{\frac{\sum_i^n (R_{i,+} - \overline{R}_+)^2}{n-1}}$
Average response lower level	$\overline{R}_- = \frac{\sum_i^m R_{i,-}}{m}$	$\sigma_- = \frac{s_-}{\sqrt{m}}$ with $s_- = \sqrt{\frac{\sum_i^m (R_{i,-} - \overline{R}_-)^2}{m-1}}$
Change in response (Impact)	$\Delta\overline{R} = \overline{R}_+ - \overline{R}_-$	$\sigma_\Delta = \sqrt{\sigma_+^2 + \sigma_-^2}$

$R_{i,+}$: Single response for upper level

$R_{i,-}$: Single response for lower level

n, m: Number of responses for corresponding level (n = 4, m = 4).