Microemulsion Flame Pyrolysis for Hopcalite Nanoparticle Synthesis: A new Concept for Catalyst Preparation

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Electronic Supplementary Information (ESI)



Fig. S1: X-ray powder diffraction patterns of samples ME-1, ME-2 and the commercial catalyst Carulite 300. Reference data and hkl were taken from ICDD database (International Centre for Diffraction Data).



Fig. S2: Nitrogen physisorption isotherms of a) sample ME-1, ME-2 and Carulite 300 and b) ME-2 and ME-2 densified. The specific surface area slightly decreases upon suspending ME-2 in deionised water, centrifugation and subsequent drying. In contrast the thus obtained smaller inter-particular voids show a higher nitrogen uptake at high relative pressures.



Fig. S3: Temperature dependent desorption of CO₂ and H₂O for sample ME-1 and ME-2 detected by mass spectrometry. Water mainly desorbs at 90 °C, whereas a peak for CO₂ arises at 210 °C.



Fig. S4: Desorption profiles of CO₂ and CO for samples ME-1 and ME-2 upon flushing the reactor with 3 L h⁻¹ N₂ (0 - 10.0 min) simultaneously heating to 300 °C and 1 L h⁻¹ O₂ (from 10.0 min). An oxidative removal of carbonaceous species from the catalyst ME-2 is observable. Offset ME-1 = 0.25 V.



Fig. S5: CO conversion deactivation profiles for ME-1, ME-2 and Carulite 300 at 25 °C with 100 mg catalyst and 0.67 vol.% CO/ 66.00 vol.% N₂/ 33.33 vol.% O₂ (70 mL min⁻¹). Conventional pressing of the particles with p = 200 MPa led to nearly complete loss of porosity. However, in order to guarantee sufficient gas permeance through the catalyst bed, the as received voluminous hopcalite powders were dispersed in water and densified by centrifugation with subsequent drying, grinding and sieving, having grain sizes of 125-250 µm for the catalytic tests. As a consequence of this post-synthetic preparation steps, the specific surface area of the nanoparticles decreased by 20 % with simultaneous increase of the specific pore volume, in fact of the densification and agglomeration of the primary particles (Fig. S2). The smaller inter-particular voids are responsible for the higher nitrogen uptake observed in the physisorption measurements as the pore size distribution shifts towards a more mesoporous character. At the same time V_{dump} decreases significantly by ca. 90 %.



Fig. S6: Powder pattern and Rietveld plot of sample ME-1.



Fig. 7: Powder pattern and Rietveld plot of sample ME-2.

Sample	c_{metal} (M)	d _{micelle} ^a (nm)(PDI)	$n_{\rm D}^{20}$	ρ (g cm ⁻³)	η (mPa s)	S_{BET}^{b} (m ² g ⁻¹)	$d_{\rm BET}^{\rm c}$ (nm)	Mn/Cu ^d (mol mol ⁻¹)	d_{hop}^{e} (nm)	$d_{\rm haus}{}^{\rm f}$ (nm)
ME-1	0.10	4.7 (0.067)	1.412	0.770	2.08	97	11.3	1.96 ± 0.01	13.2	261
ME-2	0.05	4.7 (0.034)	1.413	0.768	1.10	114	9.6	1.93 ± 0.02	17.6	64
Carulite 300	-	-	-	-	-	310	3.6	2.29 ± 0.14	-	-

Table S1: Properties of the inverse microemulsion precursors, resulting particles and the commercial catalyst Carulite 300.

^a determined by dynamic light scattering

^b calculated from multipoint BET-method

 $^{c}d_{BET} = 6 (S_{BET} \rho_{hopcalite})^{-1}$ assuming mono-disperse spherical primary particles with $\rho_{hopcalite} = 5.485$ g cm⁻³ ^d detected by ICP-OES

^e Scherrer-method with diffraction peaks belonging to the Cu_{1.5}Mn_{1.5}O₄ phase

^f Scherrer-method with diffraction peaks belonging to the Mn₃O₄ phase

Experimental Section

Hopcalite nanoparticles were produced by a flame spray pyrolysis process (FSP) from a 8.57 M (ME-1) and a 4.29 M (ME-2) solution of $Mn(NO_3)_2 \cdot 4H_2O$: $Cu(NO_3)_2 \cdot 3H_2O = 2:1$ dissolved in 5.70 g deinonised water which was dispersed in a mixture of 281.24 g n-heptane and 69.06 g MARLOPHEN NP 5 (SASOL) by ultra-sonication to give overall metal concentrations of 0.05 M and 0.10 M for ME-1 and ME-2, respectively. The microemulsions were fed through a commercial nozzle (NPS10, Tethis) with 2.5 ml min⁻¹ and ignited by a surrounding supporting-flame to prevent the main flame from self-extinguishing, all along. The supporting-flame gas flow consisted of 1.50 slm CH₄ and 3.00 slm O₂ (*slm denotes a flow of gas in liters per minute at standard conditions*). The liquid feed was delivered by a micro annular gear pump (mzr-2905, HNP Mikrosysteme GmbH) and dispersed by 7.50 slm O₂ with a dispersion gas pressure drop of 2.0 bar adjusted by a displaceable annular gap encircling the liquid feed capillary. All gas flows were controlled by thermal mass flow controllers (Bronkhorst). The synthesized particles were collected on a binder free glass fiber filter (GF/A Whatman) with the help of a rotary vane pump (Vacuubrand RZ 9). All gases had a purity of 5.0 and were purchased from Air Liquide.

X-ray powder diffraction patterns were collected with a PANalytical X`Pert Pro diffractometer in reflection mode using Ge-monochromated Cu K α_1 radiation. Powder patterns were fitted, refined and analysed using the Rietveld method implemented in FullProf.2k (Version 5.40) software to calculate weight fractions and crystallite sizes (microstructural analysis from FullProf). As a peak profile reference LaB₆ was chosen. Reference data for Cu_{1.5}Mn_{1.5}O₄ (PDF: 01-070-0262) and Mn₃O₄ (PDF: 01-089-4837) were taken from ICDD database. Nitrogen physisorption isotherms were recorded with a Quantachrome NOVA 4000 at -196 °C after activating the samples at 150 °C for 12 h in dynamic vacuum. The specific surface area (*S*_{BET}) was determined by applying the multi-point BET method in the range of p/p₀ = 0.05 - 0.20.

Scanning electron micrographs were obtained from a DSM-982 Gemini (Zeiss) operating at 6 kV. Prior to the measurement the samples were prepared on an adhesive carbon pad and sputtered with gold to obtain the necessary electron conductivity.

The inverse microemulsions were characterised by dynamic light scattering using a Zetasizer Nano ZS (Malvern Instruments). The micelle sizes of ME-1 and ME-2 were measured at 20 °C. Kinematic viscosities of the microemulsions were therefor determined with an efflux viscosimeter and converted into dynamic viscosities by using the liquid density determined with a pycnometer. Average micelle diameters (z-average) were calculated from intensity weighed size distributions with the NNLS-algorithm.

Catalytic tests were performed in a fixed bed tubular reactor ($d_{in} = 6 \text{ mm}$) equipped with two IRsensors allowing for the simultaneous determination of CO and CO₂ concentrations in the exhaust gas stream. The temperature was measured inside the catalyst bed. In a typical setup 100 mg of catalyst were exposed to a gas mixture consisting of 0.67 vol.% CO, 66.00 vol.% N₂ and 33.33 vol.% O₂ (70 mL min⁻¹) for at least 30 min for every temperature. Catalyst activation was conducted by heating to 300 °C in N₂ stream of 3 L h⁻¹ and switching to O₂ (1 L h⁻¹) after 10 min, holding the temperature for additional 50 min. CO and CO₂ signals were recorded during the activation procedure.

Temperature dependent desorption of H_2O , CO and CO_2 was monitored using a NETZSCH STA 409 Luxx equipped with mass spectrometry (NETZSCH QMS 403 Aëolos) streaming with synthetic air (100 mL min⁻¹) and heating from ambient temperature to 500 °C with 10 K min⁻¹.