

Enabling process intensification via 3D printing of catalytic structures

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Abstract: Small-scale, intensified chemical reactors (i.e. Process intensification) mediated by structured catalysts substantially diminishes the advantages of large-scale gas to liquid (transport fuels) process plants and can be realized at low capital costs, minimum energy consumption, and zero/small CO₂ footprints. Current structured catalysts approaches are complex and expensive, simple methods are crucial that are capable of depositing a desired geometry of catalysts into engineered channels. Herein, we developed printable composition by incorporating nickel and molybdenum ions into water soluble PVA and starch; subsequent pyrolysis of organic compounds resulted into three dimensional carbon scaffold with micro/macro interconnected pores (dpore-6.3Å; $d_{\text{pore}}\text{-}100\mu\text{m})$ containing up 25 wt.% catalyst loading. 2D (TEM, SEM) and 3D (X-ray CT) microstructural analyses and catalytic tests (conversion of syngas to alcohols) were carried out for 3D printed catalysts and compared with conventional pelleted catalysts. At high feed flow rate (6000 h⁻¹), CO conversion is rapidly reduced to 16 mol.% for pelleted catalysts, whereas 3D printed catalysts converted 35 mol. % of CO, with the same catalyst loading.

Introduction

Process intensification offers innovative solutions for production of renewable fuels and chemicals, and its successful implementation will lead to sustainable chemical industry with maximum productivity realized at the minimal energy consumption, capital investments and CO₂ footprints ^[1]. In modern chemical industry, the use of Velocys's mircochannel reactors is an example of process intensification in which biosyngas is converted to renewable fuels via Fischer –Tropsch synthesis^[2]. However, widespread application of this technology is hampered by complex design of the reactor, high fabrication cost and low volume of catalyst per unit volume of reactor ^[3]. A possible solution for rapid growth of process intensification is

to design structured, mini-channel catalytic reactors ^[4], and

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precisely deposit catalysts into engineered channels, which match diffusion and transport timescales. Raise of additive manufacturing (3D printing) enables formation of a highly reproducible two-dimensional layer, which is then developed into 3D structures by overprinting sequential layers ^[5]. It has been applied to fabricate of sensors, ceramics, metallic scaffolds, microvascular networks, self-healing materials and tissue engineering scaffolds due to its ability to orderly assemble nanostructures and precisely pattern micro-sized objects in complex 3D architectures^[6]. 3D printing can be adopted for the precise engineering of catalytic structures and allows the catalyst to be placed into the desired geometry. By tuning the size and length of the flow channels, the bulk residence time and pressure drop over the reactor can be precisely set. The catalyst material properties and diffusion lengths can be controlled by manipulating layer height (nozzle diameter) and porosity of the catalyst bulk layers^[7]. 3D printed catalysts have been demonstrated in literatures for catalysts used in Ullmann reactions^[8], Al₂O₃ synthesis^[9], catalytic reaction-ware for chemical synthesis^[10] and platinum metal patterning^[11], while reports on gas phase reactions over 3D printed catalysts are scarce. 3D printing for the design of complex catalytic monolith structures is not widespread^[12], mainly because it is difficult to obtain printable catalyst composition that has less non-catalytic components such as plasticizers, binders, and mechanical strength additives and hard to achieve high loadings of nanoparticles without forming large agglomerated particles. Therefore an optimum printable composition or technique must allow incorporation of catalyst nanoparticles (or in-situ nanoparticle formation) and result to a large fraction (>80 wt. %) of catalytic material in the 3D catalytic structure. Influence of 3D printed structures on the catalyst activity; product selectivity, active particle dispersion, and internal micro/nano structure and meso/macro porosity are not yet fully investigated and remain a research challenge. Herein, we report the use of extrusion based 3D printing techniques for the fabrication of structured NiMo-oxide catalysts that were tested in the catalytic synthesis of syngas to higher alcohols. NiMoO₂ was chosen due to its suitability to form corresponding sulfides or carbides by either subjecting to hydrogen sulphide or methane, respectively. The printable catalyst composition was designed by incorporating aqueous solutions of metal precursors into PVA and starch. Subsequent pyrolysis of organic components resulted into porous carbon scaffold, which served as a catalytic support. By modifying synthesis parameters, we fabricated cellular carbon structures with open porosity, in which catalyst particles are uniformly dispersed across the carbon scaffold, as observed 2D structures by TEM, SEM. X-ray CT 3D images revealed microcracks in samples with a large channel size (500 µm), which can be eliminated by re-designing monolith configuration/geometrical

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shape. To our knowledge, this is the first report providing detailed structural analysis of 3D printed catalysts and highlighting advantages and shortfalls of extrusion based 3D printing methods. Furthermore, during syngas reaction the catalytic activity of 3D printed catalysts was not affected with an increase of gas hourly velocity (34 mol.% at 6000 h⁻¹) whereas conventional pelleted catalysts showed significant drop in CO conversion (16 mol. % at 6000 h⁻¹). This study expands catalyst-engineering approaches, as traditional preparation methods and forms of conventional catalysts (pellets) are grossly sub-optimal for modern highly active nano-structured catalysts^[13]. Furthermore, 3D printing enables an effective control over heat/mass transfer properties of structured catalytic reactors^[14].



Figure 2. SEM images of (a) NiMo/PVA internal microstructure at low magnification; (a-inset) fractured area to observe subsurface morphology; (b) catalyst particles taken at high magnification (x11k) of image (a).

Results and Discussion

Catalytic monoliths with cylindrical shape (d=15; h=80 mm) were printed due to its analytical convenience for testing catalytic performances in tubular reactors (Fig S1). Optical images were taken before and after the thermal decomposition of binders. Fig 1 shows optical images of monolith with square and hexagonal channels.



Figure 1. Optical images of 3D printed NiMo catalysts; (a) square patterned channels, (b)-honeycomb patterned channels; (a*) and (b*) are the corresponding images of NiMo catalysts after pyrolysis of organic constitutes.

By measuring the size of the monolith before and after the heattreatment, ~53% volume reduction and ~70% weight loss was recorded in both cases. The monolith maintained its structural integrity despite of the substantial weight loss and volume shrinkage. In square-patterned monolith, channel size were reduced from 500 to 300 μ m after the transformation of binders; however, hexagonal-patterned monolith exhibited a non-uniform shrinkage of the channels; therefore, square-patterned monolith was used for further studies. NiMo monolith obtained by PVA-Starch possesses hierarchal porous structure. Internal microstructure taken at fractured area is given in Fig 2. The microstructure composed of round and honeycombpatterned cage network arised from strong interactions between the PVA hydroxyl groups and starch molecules. Previously, Xu et al^[15] observed similar porous microstructure during the crosslinking of PVA with PEG/cellulose nanofiber. Subsequent pyrolysis of PVA/starch resulted into interconnected porous carbon scaffold resembling solid cellular structure. In this structure, catalyst particles are randomly dispersed in a form of large agglomerates. High magnification images revealed catalyst particles with a porous architecture formed by aggregation of primary catalyst particles with size of ~100 nm (Fig 1b).

To enhance catalyst dispersion in the carbon scaffold, a crosslinking agent (maleic acid) was added to PVA-water mixture prior to addition of catalyst precursors and starch. Corresponding images of the NiMo/PVA-MA are given in Fig 3.



Figure 3. SEM images of (a) NiMo/PVA-MA internal microstructure at low magnification; (a-inset) fractured area to observe subsurface morphology; (b)microstructure taken at a high magnification (x10k) of image (a).

Internal microstructure shows round-patterned cellular structure with cell sizes ranging from 10 to 60 μ m. Compared to previous NiMo/PVA (Fig 2), the cells are densely packed with carbon particles (~3 μ m). These carbon particles are entrapped within the cells and their surface is covered by (~100 nm) catalyst particles (Fig 3b, catalysts-white dots). Catalyst particles are homogenously dispersed on the carbon scaffold indicating that the cross-linking of PVA with maleic acid is critical for dispersing catalyst particles and preventing particles agglomeration. In both cases, catalyst particles are dispersed on the surface and inner walls of the channels. Dispersion of catalyst particles is homogenous throughout the carbon network particularly in

PVA/MA cross-linked NiMo-3D (Fig S2, EDX-spectra). NiMoprecursors were loaded into commercial activated carbon-pellets by incipient-wetness impregnation to highlight the structural differences between conventional and 3D printed monolith catalysts. Fig 4 shows SEM of NiMo/AC pellets taken at crosssections of a cylindrical pellet (d=0.8 mm).



Figure 4. SEM images of NiMo/AC pellets (a) surface morphology of pellets (a-inset)-low magnification of the pellets; (b) SEM back-scattering images taken at a cross-section of the cylindrical pellets (bright spots correspond to catalyst particles).

Back scattering images (Fig 4b) were taken to show catalyst dispersion on the surface and inner walls of the carbon pellets. Spherical catalyst particles with size of 300 nm were found only on the surface and internal pores were mostly vacant. These images highlight that during incipient-wetness impregnation, diffusion of catalyst precursors into internal pores are hindered by the pore geometry, which results to an agglomeration of large particles on the surface. In this microstructure, most of available pores remain unfilled due to the blockage of surface pores by catalyst particles; this consequently reduces catalyst loading and density of catalytic active sites. Table 1 shows surface are measurements and chemical compositions of the 3D printed NiMo monoliths and NiMo/AC pellets. Nitrogen physisorption measurements revealed BET surface area of 120 and 6 m²/g for 3D printed NiMo/PVA and NiMo/PVA-MA 3D monolith, respectively. Low surface area of NiMo/PVA-MA is attributed to its dense microstructure as observed by SEM (Fig 3), indicating the presence of inaccessible pores within the microstructure. Among them, NiMo/AC pellets exhibited the large BET surface area (228 m²/g) due to the remaining un-filled pores on the inner walls of the pellets, which was depicted by SEM (Fig 4.) All samples contain around ~75wt % of carbon, 21.3 wt. % Mo and 4.5 wt.% Ni (3/1 molybdenum/nickel mol ratio), slightly larger carbon content was found for samples maleic acid cross-linked samples (NiMo/PVA-MA 3D monolith).

 Table 1. Summary of Nitrogen physisorption measurements and ICP/CHNS elemental analysis.

| Sample Name | BET Surface area, m²/g | Average pore size, nm | Carbon, wt% | Ni, wt% | Mo, wt% |
|--------------------|------------------------------|-----------------------------|----------------|------------|---------|
| NiMo/PVA | 120 | 3.4 | 72.6 | 4.71 | 21.01 |
| NiMo/PVA/MA | 6 | 5.3 | 77.67 | 3.84 | 17.50 |
| NiMo/AC pellets | 228 | 2.67 | 68.62 | 4.13 | 20.82 |

Although the 3D printed monoliths exhibited uniform distribution of catalyst particles, available BET surface area is relatively small. In attempt to enhance surface area without breaking the 3D monolith structure, the catalysts were impregnated with KOH aqueous solution and excess water was removed by freezedrying. The same previously reported KOH-activation procedure was followed^[16]. Activation of carbon materials with KOH is wellknown procedure; difficulty is associated with separating the slurry mixture (K₂CO₃+Carbon) during the washing/removal of potassium ions. However, the 3D printed monolith retained its geometrical shape after the activation/heat-treatment making the washing step is much more convenient. NiMo/PVA-MA showed poor uptake of KOH aqueous solution associated with its low porosity. After the freeze-drying white powder (dry KOH) was separated from the catalytic 3D monolith and deposited at the bottom of flask. Therefore, only NiMo/PVA was further characterized and Fig 5 shows SEM images of NiMo/PVA after the KOH activation.



Figure 5. SEM images of NiMo/PVA-3D monolith after KOH activation

Internal microstructure of NiMo/PVA-KOH 3D monolith consists of cellular frameworks with open pores. High dispersion of the spherical catalyst particles with diameters ranging between 100-200 nm were observed. The distribution of catalyst particles is homogenous across the porous carbon surface compared to non-activated samples (Fig 2b). Apparent changes in internal structure is caused by reactive and oxidizing nature of KOH which triggered decomposition of amorphous carbon via C-C bond cleavage producing CO/CO₂ volatiles and open pores. Simultaneously, large catalyst agglomerates, observed before activation (Fig 2b), were broken down into spherical particles (d_o~100 nm) and uniformly dispersed across the carbon network Breakage of large agglomerates (~600 nm) into small particles (~100 nm) might be caused by migration/diffusion of catalyst particles from/into surface of 3D monolith during the impregnation with strong alkaline KOH solution.

Pore size distribution (PSD) of 3D printed monolith before and after KOH activation was measured by nitrogen physisorption. KOH activation step increased both BET surface area and total pore volume from 120 m²/g and 0.2 ml/g (NiMo/PVA) to 640 m²/g and 0.36 ml/g (NiMo/PVA/KOH), respectively. For the PSD calculations, two-dimensional non-local density functional theory model for carbon with heterogeneous surfaces (2D-NLDFT-HS) was used (SAIEUS, Micromeritics). NLDFT models have been used in previous reports to define porous structures of various carbon materials^[17]. Corresponding experimental and

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simulated isotherms along with the resulting PSD before and after KOH activation are given in Fig 6. Bimodal pore size distribution with pore widths centering at 6.1 and 15 Å was observed before the activation. The pore volume around D_{pore} = 6.3 Å significantly increased due to the formation of additional micropores induced by KOH activation (Fig 6).



Figure 6. Nitrogen adsorption experimental and simulated isotherms (inset; blue line corresponds to NLDFT fitting curves) and pore size distribution curves of NiMo/PVA (black triangle) and NiMo/PVA/KOH (red cross).



Figure 7. Pore size distribution curves obtained from Hg-porosimetry measurements NiMo/PVA (black circle) and NiMo/PVA/KOH (red triangle).

Hg-porosimetry was measured to evaluate macro-porosity of samples before and after KOH activation. Large mercury uptake was observed from the KOH activated samples. Both samples exhibit large pore size ~90.8 μ m; however, additional pores with size of 6.98 and 10.6 μ m were formed as a result of KOH activation (Fig 7). The development of new pores is due to the reaction of potassium hydroxide with amorphous carbon [23]. Comparison of pore sizes of two samples indicate that large pores (>100 μ m) were formed as a result of decomposition of organic molecules (Starch, PVA) and more large pores were produced along with small pores (~6-10 μ m) as a result of KOH activation. Porosity measurements revealed that KOH activated

sample is a hierarchal porous catalyst with microporousmacroporous architecture as evidenced from broad micropores region from (d_p=6.3 Å) and bi-modal macropore distribution (~10 and 100 µm). Such catalytic architecture enables fast chemical reactions as the micropores provide superior mass transfer properties and the macropores enhance active site accessibility to feed molecules^[1, 18]. Table S1 (Supplementary file) summarizes the changes in surface area, average (micro, macro) pore sizes and total pore volume occurred after the KOH activation and ICP/Carbon elemental analysis.

Further observations were carried out by TEM to illustrate the structure at nano-scale. Fig 8 shows TEM images of NiMo/PVA/KOH 3D monolith prepared by suspending crushed powder in ethanol. Particles with a diameter of ~50 nm are dispersed in carbon network and catalyst particles are coated by thin graphitic carbon layers as evidenced by an interlayer spacing of ~0.35nm. This suggests that precursor metal ions are encapsulated by PVA polymeric chains during the initial mixing, further carbonization led to the formation of the graphitic carbon shell^[19]. Having such microstructure is advantageous as the carbon layer prevents particles agglomeration by separating the small crystallites and retains the surface area of catalysts during a catalytic reaction.



Figure 8. TEM images of NiMo/PVA/KOH catalysts; (inset) taken at high magnifications.

The key important factor in 3D printed catalysts whether the printed structure can hold its original shape, after removing the organic binders. Since none of the samples contains inorganic binders (clay, calcium salts, glass fibers) to enhance mechanical strength of the monolith and all sample were treated by KOH to produce open porosity, which lead to carbon loss from the structure; it was expected that some structural strength might be lost. To visualize overall structure and identify minor cracks, 3D X-ray CT images were constructed with 1600 images acquired as the sample was rotated 180° at each vertical location (Fig.9). Images obtained from vertical cross-section of the 3D printed samples are given in Fig. 9. Sample with a channel diameter of 500 µm (honeycomb) shows arrays of radial cracks, the length of the cracks is relatively short enabling the catalysts to maintain their original monolithic shape. Similar radial cracks were not observed in samples with a channel diameter of 200 µm (square-patterned). However, this sample (Fig 9a) show irregular channel size along the vertical direction, lower part of the cylinder has larger channel size than the upper parts; this could be associated with non-uniform dispersion of KOH

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resulting to large pore opening in some parts. Comparison of Xray CT images of 3D printed catalysts revealed that 3D catalytic structure with a channel diameter of 500 μ m or higher will have less rigid structure, which can be eliminated by varying the geometries/channel sizes.



Figure 9. X-ray CT images of (a) NiMo/PVA/KOH with honeycomb patterns and (b) NiMo/PVA/KOH with square patterns

Catalytic performances of the NiMo/PVA/KOH 3D monolith were tested for CO hydrogenation reaction at 60 bar, 280°C at various gas flow rates. As a control test, NiMo/AC-pellets were also tested under the same conditions but the samples were impregnated with K_2CO_3 prior to the catalytic tests. The addition of potassium salts to the pelleted catalysts was done; because, ICP analysis results of KOH-activated NiMo/PVA/KOH 3D monolith revealed the presence of 1.23 wt.% of potassium. Fig 10 compares the catalytic activity of NiMo/PVA/KOH 3D monolith with that of NiMo/AC pellets (both contain ~1.2 wt.% potassium), highlighting that the structured catalyst are not severely affected by the contact times. For a given gas hourly velocity, catalytic reaction were conducted at least for 40 hours (Fig.10 inset). Average CO conversion vs gas hourly space velocity is given in Fig 10. Both catalysts show similar CO conversion rates at low flow rates; however, NiMo/AC pellets rapidly lose its activity with the increase of gas hourly space velocity and only 16 mol.% of CO is converted at 6000 h⁻¹. In the case of NiMo/PVA/KOH 3D monolith, significant decrease in CO conversion was not observed, indicating its ability to convert feed molecules under high reactant flow rates. A major difference between two samples is their geometrical shape. In the case of 3D printed monolith, we purposely printed the geometric channels to eliminate pressure drop and produced channel frames/walls with porous cellular microstructure to promote fast diffusion of feed/product molecules from catalytic active centers (Fig 5). Thus, this catalyst architecture with interconnected micropores shortens diffusion path lengths and enhances the overall heterogeneous reaction rate ^[18]. In contrast, the pelleted catalysts are randomly packed; its internal

microstructure show irregular pore size and low catalyst dispersion that led to high internal diffusion resistances and the poor intra-particle mass transfer.



Figure 10. CO conversion as a function of gas hourly space velocity for NiMo/PVA/KOH-3D monolith (red triangle) and NiMo/AC pellets (black circle); (*inset*) CO conversion as function of time on stream at various feed flow rates.

Table 2 shows product selectivity for NiMo/PVA/KOH 3D monolith and NiMo/AC pellets. Methane is one of the undesirable products during the CO hydrogenation, which produced in both AC pellets and 3D monolith product streams.

| Catalysts | | NiMo-3D | NiMo/AC pellets |
|--------------------------------------|--------------------|---------|-----------------|
| X _{co} ^b [mol %] | | 35 | 16 |
| | HCs | 9.1 | 24.7 |
| | C ₁ -OH | 31.4 | 18.6 |
| S ^c [mol %] | C ₂ -OH | 34.6 | 7.2 |
| | C ₃ -OH | 6.8 | 1.39 |
| | Other Oxy. | 0.4 | 0 |
| | Alcohol | 73.2 | 27.1 |
| [mol %] C2-OH in tota | al alcohol | 47.2 | 26.5 |

conversion. [c] C-based, selectivity of products CO2 included



Selectivity to methane with 3D monolith catalysts are remarkably smaller (~9 mol%) compared to NiMo/AC pellets (25 mol%). The reduced selectivity of methane formation observed in the NiMo/PVA/KOH 3D monolith can be due to the fast transport of products from the catalytic active centers, as entrapped oxygenates may undergo further hydrogenation reactions caused by the high diffusion resistance of products in the NiMo/AC pellets. The 3D monolith lowers the extent of secondary reactions as extreme operational conditions (short residence time/high flow rate) can be realized with negligible change in CO conversion. Catalytic results obtained at high gas hourly velocity shows the possibility of developing highly compact chemical reactors with mini-channel architecture. Printing catalysts directly onto the mini-channels would provide optimum conditions for process intensification in which tight control over fluid and heat transport can be achieved.

Conclusions

In this study, we demonstrated 3D printing of catalysts using the ubiquitous 3D printing method (solid free forming). From the anaylsis of microstructure and catalytic properties, it is shown that uniformly dispersed catalyst particles (dp-50nm) on the porous carbon scaffold can be obtained. Catalytic tests revealed high CO conversion rates for NiMo-3D monolith due to favorable diffusion paths created by pore channels with various sizes (d_{pore}=6.3 Å; d_{pore}=10-100 \mu m). Pelleted catalysts showed decrease in CO conversion (16 mol.%) at high feed flow rate (6000 h⁻¹), whereas 3D printed catalysts converted 35 mol. % of CO with the same catalyst loading. This catalyst printing approach enables to develop a highly compact, structured catalytic reactors designed for intensive chemical reactions. Various geometric structures can be printed to match channel passages providing optimal mass and heat transfer properties. Furthermore, 3D printing methods are best suited to highly porous carbon supported catalysts; depending on the polymer used as carbon source various microstructural features can be obtained

Experimental Section

Preparation of catalyst composition for 3D printing

To aqueous solution of (10 wt. %) PVA (87-90% hydrolyzed, average mol. wt. 30,000-70,000), 15 mL (40 wt. %) aqueous solution of ammonium molybdate tetrahydrate (Sigma-Aldrich, 83.0% MoO3 basis) and 10 mL (38 wt. %) of nickel (II) nitrate hexahydrate (Sigma-Aldrich) were added. The mixture was heated at 100°C until homogenous concentrate were formed. Following this, a thickener-starch (Starch-Rice, Sigma-Aldrich) was added to produce extrudable paste (PVA/starch = 1/4). To enhance plasticity of the extrudate, 5mL of diethyl ether were added for every gram of the paste. The same procedures were followed in the experiments with maleic acid (MA) addition used as a cross-linking agent for PVA molecules at the ratio of PVA/MA : 2/1. 3D monolith was printed using a Hyrel 3D (Engine SR) printer equipped with EMO-25 extruder (cold flow) with a nozzle diameter of 500 µm. The printed samples were dried at room temperature conditions for 24 hours, prior to subjecting to heat-treatment. Samples were first heated up to 290°C at a

heating rate of 0.5°C/min, then the furnace temperature was increased at rate of 2°C/min to 700°C and then held for 3 hours. The heat-treatment experiments were carried out under nitrogen atmosphere. As a control experiment, activated carbon pellets (Norit, φ =0.8 mm) were impregnated with aqueous solutions of ammonium molybdate tetrahydrate and nickel (II) nitrate hexahydrate followed by drying and heat-treatment at 500°C for 4 hours, under nitrogen atmosphere. Samples were activated by KOH as follows: 3D printed monolith was immersed into KOH aqueous solution (C/KOH=1/3 mass ratio) and then freeze-dried at 198K. The dried 3D monolith was heat-treated at 700°C for 1 hour under nitrogen flow. The activated 3D monolith was washed with water and then freeze-dried.

Catalyst characterisations

The internal morphology of the samples was observed using a highresolution Transmission Electron Microscope (TEM) (200 kV, JEOL). N2 absorption/desorption isotherms of samples at -196°C were obtained using a TriStar II Micrometrics Surface Analyzer. The pore size distributions of monolith catalysts were measured by mercury intrusion porosimetry (MIP, Micromeritics AutoPore IV9520) up to 60,000psi. A CHNS elemental analyser (Thermo Electron Corp. Flash EA-1112 Series) was used to determine the carbon content. X-ray computed tomography (CT) studies were employed to detect and map the pore structure of 3D printed catalyst. A ZEISS Xradia Versa X-ray microscopes (XRM500) was used (voltage = 80 kV, Power: 7W) to image the samples. Data collection was carried out with 1600 images acquired as the sample was rotated 180° at each vertical location. Scanned images of the samples were reconstructed, visualised and normalised using the Avizo (FEI Visualization Sciences Group). The bulk composition of the catalyst was determined by inductively coupled plasma (ICP) analysis with a Varian Vista Pro ICP-OES instrument after digesting the catalyst using a Milestone Ethos 1 microwave digester. Carbon content of samples was determined by an elemental CHNS/O analyser (FlashEA 1112 series, Thermo Electron Corporation). The catalytic tests were performed at 280°C, 60 bar in a high-pressure fixed bed reactor setup. The stainless-steel fixed bed reactor (i.d. 10 mm; length 100 mm) with a thermocouple positioned inside was inserted in a furnace. The catalyst was reduced under hydrogen atmosphere at 400°C for 3 hours before the reaction. In all catalytic tests, premixed syngas with H2/CO ratio of 2/1 and 4% of N2 (internal standard) was used as feed. The mass flow controller (MFC, Bronkhorst High-Tech B.V) regulated the inlet gas flow rate. The weight of catalyst samples loaded in the reactor is maintained as 2.5 g both for pelleted and 3D monolith. The feed flow rate was varied as 50, 100, 150, 200 and 250 ml/min, respectively. Gaseous products leaving the reactor passed through the condenser to obtain the liquid fraction of products. The outlet gas stream composition was analysed by gas chromatography equipped with a thermal conductivity detector (Shimadzu GC-2014). Liquid samples were discharged from the condenser every 12 hours and analysed by GC equipped with a flame ionization detector (Shimadzu GC-8A). Conversion of syngas and selectivity of products were calculated as previously^[20].

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Keywords: structured catalysts • 3D printing • alcohol synthesis• porous carbon • 3D structure visualization

- J. Gascon, J. R. van Ommen, J. A. Moulijn, F. Kapteijn, *Catalysis Science & Technology* 2015, 5, 807-817.
- [2] H. J. Robota, L. A. Richard, S. Deshmukh, S. LeViness, D. Leonarduzzi, D. Roberts, *Catalysis Surveys from Asia* 2014, 18, 177-182.
- [3] a) S. S. Ail, S. Dasappa, *Renewable and* Sustainable Energy Reviews 2016, 58, 267-286; b) B. Todic, V. V. Ordomsky, N. M. Nikacevic, A. Y. Khodakov, D. B. Bukur, *Catalysis Science & Technology* 2015, 5, 1400-1411.
- [4] a) R. M. de Deugd, F. Kapteijn, J. A. Moulijn, *Topics in Catalysis* 2003, 26, 29-39; b) A. C. a. J. A., Moulijn, *Structured Catalysts and Reactors*, CRC Press, Boca Raton,, 2005; c) A. Holmen, H. J. Venvik, R. Myrstad, J. Zhu, D. Chen, *Catalysis Today* 2013, 216, 150-157.
- [5] a) J. R. Raney, J. A. Lewis, *Mrs Bulletin* **2015**, 40, 943-950; b) B. Derby, *Annual Review of Materials Research* **2010**, 40, 395-414.
- [6] a) J. A. Lewis, J. E. Smay, J. Stuecker, J. Cesarano, *Journal of the American Ceramic Society* 2006, 89, 3599-3609; b)
 S. Lee, T. Boeltken, A. K. Mogalicherla, U. Gerhards, P. Pfeifer, R. Dittmeyer, *Applied Catalysis A: General* 2013, 467, 69-75.
- [7] X. Zhou, C.-j. Liu, *Advanced Functional Materials*, 1701134-n/a.
- [8] C. R. Tubío, J. Azuaje, L. Escalante, A. Coelho, F. Guitián, E. Sotelo, A. Gil, *Journal of Catalysis* **2016**, *334*, 110-115.
- [9] K. A. M. Seerden, N. Reis, J. R. G. Evans, P. S. Grant, J. W. Halloran, B. Derby, *Journal of the American Ceramic Society* 2001, 84, 2514-2520.

- [10] P. J. Kitson, M. D. Symes, V. Dragone, L. Cronin, *Chemical Science* **2013**, *4*, 3099-3103.
- [11] P. Shah, Y. Kevrekidis, J. Benziger, *Langmuir* **1999**, *15*, 1584-1587.
- [12] S. Govender, H. Friedrich, *Catalysts* **2017**, 7, 62.
- [13] a) S. Mitchell, N.-L. Michels, K. Kunze, J. Pérez-Ramírez, *Nat Chem* 2012, 4, 825-831; b) S. Mitchell, N.-L. Michels, J. Perez-Ramirez, *Chemical Society Reviews* 2013, 42, 6094-6112.
- [14] a) A. Tonkovich, D. Kuhlmann, A. Rogers, J. McDaniel, S. Fitzgerald, R. Arora, T. Yuschak, *Chemical Engineering Research* and Design 2005, 83, 634-639; b) in Process Intensification for Green Chemistry, John Wiley & Sons, Ltd, 2013, pp. i-xvi.
- [15] Z. Xu, J. Li, H. Zhou, X. Jiang, C. Yang, F. Wang, Y. Pan, N. Li, X. Li, L. Shi, X. Shi, *RSC Advances* **2016**, *6*, 43626-43633.
- [16] D. Lozano-Castelló, M. A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, *Carbon* 2001, *39*, 741-749.
- a) G.-P. Hao, G. Mondin, Z. Zheng, T. Biemelt, S. Klosz, R. Schubel, A. Eychmüller, S. Kaskel, *Angewandte Chemie International Edition* 2015, 54, 1941-1945; b) G.-P. Hao, W.-C. Li, D. Qian, G.-H. Wang, W.-P. Zhang, T. Zhang A.-Q. Wang, F. Schüth, H.-J. Bongard, A.-H. Lu, *Journal of the American Chemical Society* 2011, *133*, 11378-11388; c) J. Jagiello, J. P. Olivier, *Adsorption* 2013, *19* 777-783; d) E. A. Ustinov, D. D. Do, V. B. Fenelonov, *Applied Surface Science* 2007, 253, 5610-5615.
- [18] C. M. A. Parlett, K. Wilson, A. F. Lee, *Chemical Society Reviews* 2013, 42, 3876-3893.
- [19] W. KICIŃSKI, M. BYSTRZEJEWSKI, M. H. RÜMMELI, T. GEMMING, Bulletin of Materials Science 2014, 37, 141-150.
- [20] M. Konarova, F. Tang, J. Chen, G. Wang, V. Rudolph, J. Beltramini, *ChemCatChem* 2014, 6, 2394-2402.



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