3D printing of NiMo-based catalysts for conversion of syngas into higher alcohols

Waqas Aslam,[a] **Jorge Beltramini,**[a] **Victor Rudolph**[b] **, Muxina Konarova**[a]*

[a]*Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Australia*

[b]*School of Chemical Engineering, The University of Queensland, Brisbane, Australia*

**Corresponding author: m.konarova@uq.edu.au*

Abstract: Process intensification offers innovative solutions for production of renewable fuels and chemicals. Herein, we developed printable composition of the catalyst 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 (d_{pore}-6.3Å; d_{pore}-100μm). Microstructural analyses and catalytic tests (conversion of syngas to alcohols) were carried out for 3D printed 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.

Keywords: 3D printing, microstructural analyses, alcohols synthesis.

1. Introduction

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 CO_2 footprints [1]. A possible alternative for rapid growth of process intensification is to design structured, mini-channel catalytic reactors [1], and precisely deposit catalysts into engineered channels, which match diffusion and transport timescales. 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. 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.

2. Experimental

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. Catalytic performances of the NiMo-based 3D monolith were tested for CO hydrogenation reaction at 60 bar, 280°C at various gas flow rates.

3. Results and discussion

As shown in Fig. 1, internal microstructure of NiMo-based 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. NiMo-based 3D monolith is a hierarchal porous catalyst with micro-macro porous architecture as evidenced from broad micropores region from (dp=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, 2]. Fig. 2 compares the catalytic activity of NiMo-based 3D monolith with that of NiMo/AC pellets, highlighting that the structured catalysts are not severely affected by the contact times. Both catalysts show similar CO conversion at low flow rates; however, NiMo/AC pellets rapidly lose its activity with the increase of gas hourly space velocity. Conversely, in the case of NiMo-based 3D monolith, significant decrease in CO conversion was not observed, indicating its ability to convert feed molecules under high reactant flow rates. Further experimental and results details will be given during the presentation.

Figure 1: SEM images of NiMo/PVA-3D monolith after KOH activation

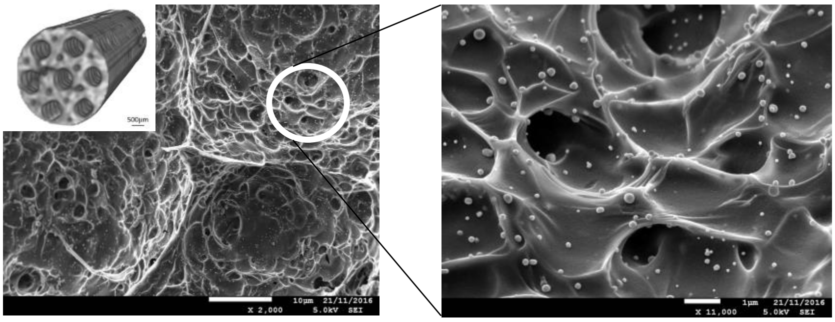
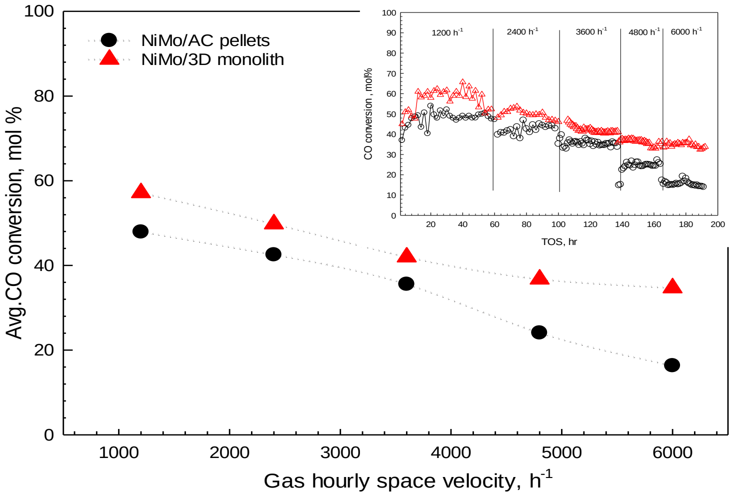


Figure 2: CO conversion as a function of gas hourly space velocity for NiMo/PVA/KOH-3D monolith (red triangle) and NiMo/AC pellets (black circle); (*inset*) CO conversion as function of time on stream at various feed flow rates



4. Conclusions

In this study, we demonstrated 3D printing of catalysts using the ubiquitous 3D printing method. From the anaylsis of microstructure and catalytic properties, it is shown that uniformly dispersed catalyst particles (d_p-50 nm) on the porous carbon scaffold can be obtained. Catalytic tests revealed high CO conversion for NiMo-3D monolith due to favourable diffusion paths created by pore channels with various sizes (d_{pore}=6.3 Å; d_{pore}=10-100µm). 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 heat and mass transfer properties.

References:

1. Gascon, J., et al., *Structuring catalyst and reactor - an inviting avenue to process intensification.* Catalysis Science & Technology, 2015. **5**(2): p. 807-817.
2. Parlett, C.M.A., K. Wilson, and A.F. Lee, *Hierarchical porous materials: catalytic applications.* Chemical Society Reviews, 2013. **42**(9): p. 3876-3893.