Periodic Open Cellular Raney-Copper Catalysts Fabricated via Selective Electron Beam Melting

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Herein, the possibility of generating Raney-Copper catalysts with high geometric complexity is demonstrated. For this, periodic open cellular structures (POCS) composed of a highly brittle Al-Cu alloy containing 29.4 at% copper are fabricated by selective electron beam melting (SEBM) for application in chemical reaction engineering. After selective leaching of aluminum in an NaOH solution, the POCS show a core–shell structure with a nanoporous copper surface layer and a solid core. The fabrication and dealloying processes as well as the microstructure are studied. Moreover, the SEBM-processed Raney-type copper catalysts show a high catalytic activity in methanol synthesis.

1. Introduction

In many processes of the chemical industry, especially in heterogeneously catalyzed gas-phase reactions, a significant reaction enthalpy must be handled. The heat transport to or from the reaction zone is particularly important to avoid cold or hot spots that would lead to productivity, selectivity, or safety problems. Many catalytic reactions are conducted in multitubular reactors, in which the tubes filled with catalyst are surrounded by a heat transfer medium.[1] Further optimization of these reactors is limited due to the specific heat transfer characteristics of the randomly packed catalyst. In particular, heat dissipation from the reaction sites is restricted by the small contact areas between the pellets.[2]

One way to overcome the limited heat transfer capacity of classical fixed bed reactors is to use a catalyst support with solid connections of significant cross-section in the form of an open cellular metal foam[1,2] or simple monolithic structures.[4,5] Significant effort has been put into the understanding of the wall heat transfer coefficient[6-7] optimizing the thermal design of such structures. Because reproducing stochastic foams is only possible to a fairly limited degree,[8-9] current efforts are mainly undertaken to develop metallic periodic open cell structures (POCS) for chemical reactors fabricated via the selective electron beam melting process (SEBM).[10] The powder bed-based additive manufacturing method, SEBM, is a suitable way to fabricate metallic POCS.[11] By controlling the unit cell geometry, different reactor parameters, e.g., pressure drop, can be tailored for gaseous fuel generation.[10] Moreover, suitable models to predict the heat transfer properties of POCS have been developed.[12]

State-of-the-art processes to activate POCS catalytically include multistep procedures, such as coating of the metal cellular structure with a highly porous support layer followed by impregnation of metal salt solutions, calcination, and reduction.[13] A very attractive alternative way to catalytically activate POCS is to use cellular Raney-type alloy structures and to gain the catalytically active interface by leaching the less-noble element from the alloy, e.g., using an aqueous NaOH solution.[14] In the case of Cu-Al alloys, aluminum is selectively removed (2Al + 2NaOH + 6H2O = 2Na[Al(OH)4] + 3H2), whereas copper remains in the form of a nanoporous solid structure. Copper-based Raney-type catalysts have been successfully applied in the water-gas shift reaction or in methanol synthesis.[15-18] However, the use of structured or cellular Raney-type alloys is not very common to date. Only simple geometries such as diffusion-coated wire meshes or plasma spray-coated monolith structures have been achieved so far.[4,5,19]

In our previous work, we demonstrated that Cu-Al Raney-type alloys, which are additively processable, can form catalytically active materials for the methanol synthesis when leached with NaOH solutions after fabrication.[20] Based on our previously achieved knowledge about the processing of copper-based high aluminum alloys,[21] we will demonstrate in this contribution the successful preparation of an additively manufactured, Cu-70Al alloy-based, periodic open cellular structure (POCS) that is catalytically active in methanol synthesis. The POCS have been obtained by additive manufacturing using the SEBM process and
the dealloying has been achieved by leaching with a NaOH to obtain catalytically active POCS (CAPOCS). The catalytic activity of these CAPOCS in the methanol synthesis has been studied.

2. Experimental Section

For all samples, an inert gas atomized prealloyed Cu–70Al powder with a nominal composition of 29.4 at% copper, a balance of aluminum (ECKA Granules GmbH, Fürth, Germany), and a particle size distribution between 45 and 105 μm was used. A new SEBM system named Freemelt ONE (Freemelt AB, Mölndal, Sweden) was used for sample fabrication. Individual struts as well as the CAPOCS were built based on a diamond unit cell (node distance 4 mm) with a cylindrical diameter of 10 mm and a height of 50 mm (Figure 1). Due to the brittle nature of the alloy, an additional support structure ensured structural integrity of the POCS. This led to a cage-like optic, as shown in Figure 1b. The layer thickness was 100 μm. Melting of all samples was conducted by contouring with a line energy of 1.3 J mm⁻¹ and a scan velocity of 0.23 m s⁻¹.

According to the caliper measurements, the individual struts (Figure 1a) and POCS (Figure 1b) showed a strut thickness of 0.9 ± 0.1 mm and 1.3 ± 0.1 mm, respectively. Their surface roughness was measured using a LEXT-OLS4000 (Olympus) laser-scanning microscope and were found to be 35 ± 1 μm (Rₐ).

Computed tomography (CT) measurements were performed using a Fraunhofer CT-alpha with a detector resolution of 1024 × 1024 pixels and a voxel size of 52.9 μm.

To test the leaching ability, the individual struts and POCS were introduced into a stirred aqueous sodium hydroxide solution (4.9 M) at room temperature. The individual struts were leached for 2 h, and the CAPOCS for 45 min. After leaching, the samples were thoroughly rinsed in deionized water, dried under inert conditions, and oxidized in a controlled way to avoid pyrophoric nature of the obtained structure.

To perform proper imaging and energy-dispersive X-ray spectroscopy (EDS) measurements, a leached strut was broken.

![Figure 1.](image_url) a) Photograph of single as-built struts. b) POCS in their as-built state. c) CT-cutaway reconstruction of a SEBM-processed POCS in the as-build state. d) CAPOCS (left) and two individual struts (right) after leaching in an aqueous solution composed of 4.9 M NaOH.
and glued to an electrically conductive sample holder instead of embedding it in a cold setting resin. This was done to avoid contamination during grinding and polishing. The microstructure investigation and phase analysis were conducted with an FEI Quanta 450 scanning electron microscope (SEM) equipped with an EDS detector. Imaging of the nanoporous layer was achieved using a FEI Helios NanoLab 600i SEM. The ligament thickness was evaluated using image processing software.

After the first verification of the processed materials' leaching ability, a more detailed leaching study of the as-built Cu–70Al struts was performed in a cooled double-wall glass reactor with a KPG stirrer at 300 rpm. The leaching was performed in 4.9 M NaOH solution, whereas the temperature was held constant at 20 °C. To analyze the degree of leaching, solid samples were taken after defined durations. The samples were rinsed in deionized water, dried, and passivated for further characterization (see ref. [20] for detailed information). The elemental catalyst composition was determined via inductively coupled plasma optical emission spectrometry (ICP-OES; Plasma 400 from Perkin-Elmer), and the specific surface area was calculated with the Brunauer–Emmett–Teller method from N$_2$ sorption measurements at 77 K. To investigate the catalytic activity in the hydrogenation of CO to methanol, a laboratory plant with a tubular reactor was used.[20] The catalytic tests were performed at 250 °C and 75 bar with a total volume flow of 300 mL min$^{-1}$ and a stoichiometric mixture of CO and H$_2$ (CO:H$_2$ = 1:2).

3. Results and Discussion

According to our differential scanning calorimetry measurement (Skimmer STA 409 CD, Netzsch, Selb, Germany), the applied Cu–70Al powder showed a melting point of 580 °C. During the SEBM preheating process, the top side of the powder bed was heated by the defocused electron beam. However, the temperature of the bottom side of the start plate was measured by a thermal couple and was displayed as the powder bed temperature.

Thus, the temperature of the top powder layer was higher than the displayed process temperature during SEBM due to the relatively low conductivity of the powder bed. Therefore, 450 °C was identified as the suitable preheating temperature at which an appropriate sintering degree of the powder bed was achieved.

To verify the integrity of the as-built CAPOCS, CT measurements were conducted. A CT-cutaway reconstruction of a representative SEBM-fabricated POCS in its as-built state is shown in Figure 1c. One-fourth of the radial volume was removed previously to allow a clear view into the cage-like support system. As expected, the struts are properly molten and fully interconnected. Figure 2a shows a backscattered electron (BSE) image of the cross-section of individual struts. A higher magnification in Figure 2b reveals the microstructure composed of a majority of brighter $\Theta$-phase (Cu$_{13}$Al$_7$) containing 79.8 at% Al and a minority of a darker $\alpha$-Al phase containing 95.8 at% Al with the balance being copper for both phases. This is in good accordance with the previous studies.[20,22–25]

While taking a closer look at a longitudinal strut cross-section (Figure 2c), it becomes apparent that the dendrites grow parallel to the build direction, which is also the length direction of the individual struts (Figure 1a). This textured microstructure of SEBM-processed samples was previously reported in the literature.[26]

The transformation of Cu–70Al into a bulk nanoporous volume and its dealloying ability have been demonstrated by earlier studies.[23,25] Most recently, we successfully applied the same method to an additively manufactured bulk sample while still keeping a stable form that is easy to handle.[20] After leaching of individual struts and POCS in the 4.9 M NaOH solution, a color change of the SEBM-processed samples from metallic silver (Figure 1a) to a copper tone (Figure 3d) was observed. After the controlled oxidation, a dull black (Cu$_2$O) was observed (Figure 1d).

The leached struts and CAPOCS showed high mechanical stability and could be handled without any special care. BSE imaging of a leached individual strut shows that apart from a dealloyed outer layer with a thickness between 170 and

![Figure 2. a) BSE image of a strut cross-section with its magnified view b) revealing a binary $\Theta$-(I) and $\alpha$-Al phase (II) system. c) BSE image of the longitudinal cross-section of a strut demonstrating the orientation of the microstructural dendrites. The build direction is indicated by the dashed arrow.](image-url)
280 μm, there is still a solid unaffected core indicated by a dashed line in Figure 3a. According to our EDS measurements, the unaffected core (II in Figure 3a) exhibits ≈68.5 at% aluminum, which is in good accordance with the initial Al content in the Cu–70Al alloy, whereas the dealloyed rim only has ≈3.4 at% aluminum left (I in Figure 3a). Moreover, SEM images with higher resolution were recorded for a leached individual strut (Figure 3c–f). It can be seen in Figure 3c that there are three distinct features present. The first is a pore-like cavity representing the former α-Al phase, which has been leached out by the dealloying procedure, indicating that this phase does not contain enough copper to form nanoporosity in a relevant time span.\textsuperscript{[23]} The second one is the nanoporous copper ligament structure with a ligament thickness of 23 ± 4 nm (Figure 3e). The third feature in Figure 3c shows small cuboids growing on top of the nanoporosity with the EDS measurement indicating

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**Figure 3.** a) BSE image of a leached strut cross-section (I) for 2 h with the unaffected core (II) indicated by a dashed line. b) BSE image of a strut cross-section taken from a CAPOCS that was leached for 45 min with the unaffected core indicated by a dashed line. c) Magnified SE view of the nanoporous volume with copper oxide cubes (III) and e) its copper ligaments. d) The core–shell boundary of the dealloyed individual strut with the unreacted core (IV), the reaction front (V), and the generated nanoporous volume (VI). The elemental composition of spot VI, V, and IV was analyzed by EDS. f) Detailed view of part (d) showing the nanoporosity in the left part and the reaction front on the right side of the dashed line.
70.3 at\% Cu, 24.9 at\% O, and 3.3 at\% Al (II in Figure 3c). They are considered to be \( \text{Cu}_2\text{O} \) due to its cubic crystal structure.\(^{[27]} \) The reaction front of the dealloying process is shown in Figure 3d, and in a more detailed view in Figure 3f. A dashed line indicates the boundary between the reaction front and the nanoporous volume (Figure 3f).

It is noticeable that the reaction front is a layer with a thickness of \( \approx 1 \mu \text{m} \), which separates the nanoporous area from the unreacted core area. This reaction front does not seem to be porous. It could be that the Al content of the reaction front is a gradual transition between the bulk alloy and the porous layer. However, the used EDS-system resolution did not allow for such a distinction. According to the EDS measurements, the unreacted core (IV), the boundary area (V), and the nanoporous structure (VI) in Figure 3c show 65.8, 32.1, and 11.1 at\% Al, respectively.

The discrepancy in the aluminum content between the measurement VI in Figure 3d and I in Figure 3a can be attributed to the fact that diffusional transport leads to the dissolved aluminum hydroxide content to decrease over time. This, however, is not possible near the reaction front as the leaching process is stopped by rinsing and drying the sample. Similar to the leached individual struts (Figure 3a), the struts of CAPOCS show a core–shell structure with a nanoporous skin and an unreacted core (Figure 3b). Compared with the leached individual struts, the CAPOCS struts exhibit a lower skin thickness of 63–85 \( \mu \text{m} \) and a ligament thickness of 17 ± 4 nm, due to the shorter leaching duration. It is apparent that the potentially needed volume of active material can be tailored via the leaching time, while still preserving the geometry of the CAPOCS through the mechanical stability of the remaining strut core.

CAPOCS with core–shell structured struts are thought to be optimal for the application as structure catalysts for chemical production processes. The nanoporous outer layer of the struts shows high effective reaction surface, whereas the unreacted core ensures high mechanical strength and good heat transfer. The latter property helps to avoid hot-spot formation during exothermal reactions, thus preventing detrimental effects on catalyst selectivity and lifetime.

In Figure 4, the results of our leaching study of the individual as-built Cu–70Al struts are shown. The leaching effectiveness factor is calculated according to Equation (1) based on previous study\(^{[28]} \) as described in the following.

**Figure 4.** a) Leaching effectiveness factor over leaching time for as-built Cu–70Al struts in 4.9 M NaOH solution at 20 °C. b) Specific surface area over leaching time for as-built struts in 4.9 M NaOH solution at 20 °C. c) Methanol productivity plotted over time on stream during hydrogenation of CO using leached Raney-Cu struts (leaching conditions: 25 min in 4.9 M NaOH at 20 °C, \( m_{\text{catalyst}} = 4.35 \text{ g} \), 75 bar, \( V_{\text{gas}} = 300 \text{ mL min}^{-1} \) (\( \text{H}_2/\text{CO} = 2/1 \)). d) Arrangement of tested Raney-Cu struts in methanol synthesis reactor and microscope picture of an activated Raney-Cu single strut (leaching depth = 32 ± 7.3 \( \mu \text{m} \)).
and is plotted versus the leaching time in Figure 4a. It shows a linear increase in leaching effectiveness with an increase in leaching time. This represents a controlled leaching reaction where the generated porous volume can be well controlled by the leaching duration. The specific surface area, determined by N\textsubscript{2} sorption measurements, shows a logarithmic growth with leaching time (Figure 4b). The specific surface area of the individual struts leached for 2 h was determined to be 19.9 m\textsuperscript{2} g\textsuperscript{-1}, which is in good agreement with earlier literature reports.\textsuperscript{[20]}

Moreover, 60 individual as-built Cu–70Al struts were leached for 25 min in 4.9 M NaOH at 20 °C. Subsequently, the dealloyed struts were arranged next to each other in a tube reactor (Figure 4d). The microscopic image of a leached strut is shown in Figure 4d. Due to the short leaching time of 25 min, a leaching effectiveness factor of only 5.5% was achieved (Figure 4a). The leached strut exhibited a thin nanoporous skin layer with a thickness of 32 ± 7.3 μm, which is quite thin compared with the remaining core volume. Regardless of the thin skin layer, good methanol productivity was observed (Figure 4c).

After 15 h of reaction, the as-built Raney-type copper struts still showed a methanol productivity of 1.5 g\textsubscript{MeOH} g\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1}. The calculation method to obtain this specific productivity value, which refers the observed methanol formation rate to the mass of nanoporous copper (g\textsubscript{Cu}, np) in the reactor, was described by Heßelmann et al.\textsuperscript{[29]} The decreasing productivity over time-on-stream (Figure 4c) was attributed to sintering effects in the nanoporous Cu layer. The Raney-type copper struts achieved a quiet low methanol productivity based on the total catalyst mass with 0.06 g\textsubscript{MeOH} g\textsubscript{Cat}\textsuperscript{-1} h\textsuperscript{-1} due to the thin active skin layer, whereas the commercial Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst from Alfa Aesar achieved a methanol productivity of 0.86 g\textsubscript{MeOH} g\textsubscript{Cat}\textsuperscript{-1} h\textsuperscript{-1}.\textsuperscript{[20]} Note that commercial methanol catalysts contained next to Cu also ZnO, which was important for activating and stabilizing the most active catalyst sites for methanol formation.\textsuperscript{[28]} We anticipated, therefore, that CAPOCS, when further optimized and doped with zinc oxide, could enable competitive catalytic reactivities compared with the commercial Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} methanol catalyst. A further optimization of the leaching and doping process for developing better CAPOCS-based methanol synthesis catalysts is in the focus of our on-going studies and the corresponding results will be published elsewhere.

4. Conclusion

In this study, a highly brittle aluminum-based Raney copper alloy was successfully processed via selective electron beam melting (SEBM) to obtain POCS. After partial dealloying using an aqueous NaOH solution, the struts of these POCS showed core–shell structures composed of a nanoporous copper skin layer and a dense core alloy area. In this way, the leaching led to CAPOCS. Applying these structures in a CO hydrogenation experiment using a classical tube reactor setup resulted in an average productivity of 2.0 g\textsubscript{MeOH} g\textsubscript{Cu}\textsuperscript{-1} h\textsuperscript{-1} over 15 h time-on-stream. The nanoporous skin layer exhibits a high reaction surface area, whereas the unreacted core ensures sufficient mechanical stability for the reactor application and improved heat transfer. Thus, the proposed novel approach represents a highly promising approach to develop hot-spot free methanol synthesis catalysts and reactors.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft (DFG LO 2030/1-1, WA 1615/15-1, and INST 90/1043-1 FUGG) is gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

additive manufacturing, cellular structures, electron beam, nanoporosity, Raney copper

Received: December 13, 2019
Revised: January 16, 2020
Published online: February 21, 2020

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