

## 3D-printed monolithic reactors for the hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub>: kinetic modelling

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### 1. Introduction

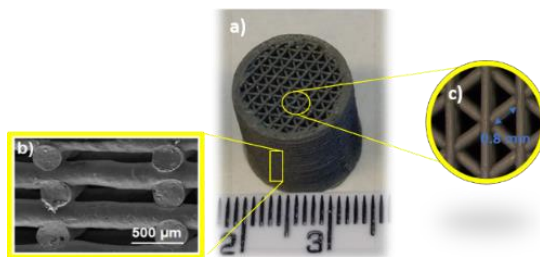
The industrial process to produce dihydroxybenzenes (DHBZ) consists on the hydroxylation of phenol using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant and titanium-zeolite as catalyst (TS-1). The Enichem technology uses a continuously slurry reactor system, employing liquid-phase reactants in aqueous acetone solvent at temperatures ranging from 70 to 100 °C, and a frequent regeneration of the catalyst [1]. Recently, three-dimensional (3D) printed Fe/SiC monoliths, fabricated by robocasting, a direct ink writing technique have been demonstrated to be feasible catalysts for this reaction under organic solvent-free conditions. Phenol selectivity ( $S_{\text{DHBZ}}$ ) and yield ( $Y_{\text{DHBZ}}$ ) to DHBZ of 90 and 25%, respectively, were remained during 260 h on stream at 80 °C over 3D Fe/SiC monoliths with triangular channel geometries [2].

Herein, we offer a better insight into the phenol hydroxylation process over 3D-printed Fe/SiC monolith catalysts by the development and validation of a kinetic model. This model describes the evolution of phenol and H<sub>2</sub>O<sub>2</sub> with the space-time. This study will allow the simulation of the reactor behaviour as well as to prototype an optimized structured catalyst.

### 2. Methods

Cylindrical 3D-printed Fe/SiC structures (D= 13.5 mm, H= 15 mm) with triangular cells ( $\delta_{\text{wall}}= 320 \mu\text{m}$ ,  $\eta= 71 \text{ cell}\cdot\text{cm}^{-2}$ ) and interconnected channels ( $\delta_{\text{channel}}= 868 \mu\text{m}$ ) were robocast by architecting an aqueous colloidal suspension of Fe-doped (0.52 wt.%) SiC powder [2]. The as-printed monoliths were heat-treated at 1200 °C in argon atmosphere into pressureless spark plasma sintering to enhance their robustness (Figure 1).

Hydroxylation experiments were carried out in a quartz up-flow reactor ( $d_i=15 \text{ mm}$ ) loaded with three Fe-doped SiC cylindrical monoliths ( $W_{\text{CAT}}= 3.8 \text{ g}$ ,  $V_{\text{R}}= 3.9 \text{ cm}^3$ ,  $\epsilon_{\text{B}}= 0.65$ ) using isothermal conditions at 80 °C. Phenol was fed together with H<sub>2</sub>O<sub>2</sub> to the reactor at different inlet flow rates (from 0 to 2 mL min<sup>-1</sup>).



**Figure 1.** a) Photograph of the printed honeycomb monoliths, b) SEM image of the internal interconnected channels and c) channel geometry

Thus, the space-time ( $\tau$ ) was ranged from 0 to 254  $\text{g}_{\text{CAT}} \cdot \text{h L}^{-1}$  (equivalent to 0- 17 min of residence time). The concentration of phenol water was ranged between 0.1 and 0.5  $\text{mol L}^{-1}$  keeping the optimum value of phenol: $\text{H}_2\text{O}_2$  molar ratio equal to 1:1 [3].

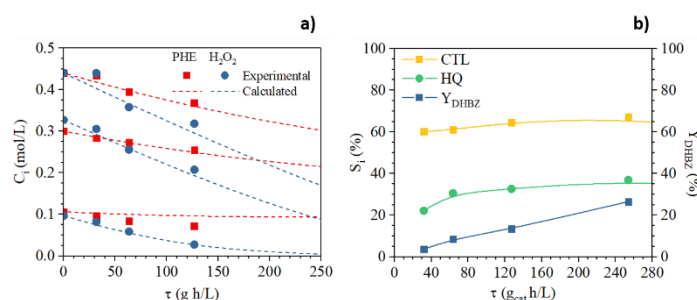
### 3. Results and discussion

The concentration-space time profiles for phenol and  $\text{H}_2\text{O}_2$  are provided in Figure 2a. As can be seen, phenol and  $\text{H}_2\text{O}_2$  concentrations decreased with the space-time. A phenol conversion of 25% with a  $\text{H}_2\text{O}_2$  consumption of the 70% was obtained at  $\tau = 254 \text{ g}_{\text{CAT}} \cdot \text{h L}^{-1}$ . The selectivity and yield to DHBZ showed a constant value after  $\tau = 120 \text{ g}_{\text{CAT}} \cdot \text{h L}^{-1}$ , with values of 94% and 24%, respectively (Figure 2b). The ratio catechol:hydroquinone was 2:1.

External mass-transfer resistance was not expected at the low inlet flowrates employed and the low Reynolds numbers involved ( $\text{Re} < 1$ ). Fluid dynamic behaviour was experimentally considered by using reactors loaded with different number of monoliths (*viz.*  $\text{W}_{\text{CAT}} = 3.8$  and  $2.4 \text{ g}_{\text{CAT}}$ ). The same phenol and  $\text{H}_2\text{O}_2$  conversion profiles *vs.* WHSV were obtained with the three reactors at the corresponding space times  $\leq 254 \text{ g}_{\text{CAT}} \cdot \text{h L}^{-1}$ . Therefore, the plug-flow could be assumed.

Different kinetic models were considered (*viz.* potential with different orders and hyperbolic) in order to reproduce the experimental data of Figure 2a (at 80 °C and different initial phenol and  $\text{H}_2\text{O}_2$  concentrations). The integrate expressions of the rate equations proposed were solved by using OriginPro 2017. The rate equations that minimized the sum of squared residuals were the following:

$$(-r_{\text{H}_2\text{O}_2}) \left( \frac{\text{mol}}{\text{g}_{\text{cat}} \text{ h}} \right) = \frac{(1.7 \cdot 10^{-2} \pm 3.8 \cdot 10^{-3}) C_{\text{H}_2\text{O}_2}}{1 + (11.8 \pm 3.8) C_{\text{H}_2\text{O}_2}} \quad [1] \quad (-r_{\text{PHEN}}) \left( \frac{\text{mol}}{\text{g}_{\text{cat}} \text{ h}} \right) = \frac{(2.3 \cdot 10^{-2} \pm 1.5 \cdot 10^{-3}) C_{\text{PHEN}} C_{\text{H}_2\text{O}_2}}{1 + (11.8 \pm 3.8) C_{\text{H}_2\text{O}_2}} \quad [2]$$



**Figure. 2.** a) Phenol and  $\text{H}_2\text{O}_2$  concentration profiles with space time for experimental and calculated values by Eqs. 1 and 2 and b) Experimental selectivity and yield to DHBZ with space time.

The proposed model, based on the LHHW equations [1, 2], shows that the decomposition of  $\text{H}_2\text{O}_2$  into the active radical species ( $\text{HO}^\bullet$ ) takes place over the Fe active sites. Also, the limiting step of this process is the reaction of the adsorbed radicals with phenol, to yield catechol and hydroquinone.

### 4. Conclusions

The application of monolithic reactors for the production of dihydroxybenzenes has been demonstrated by the modelling of phenol hydroxylation and  $\text{H}_2\text{O}_2$  consumption, assuming plug-flow in each channel. This kinetic model, valid at molar phenol: $\text{H}_2\text{O}_2$  ratios of 1:1 and 80 °C reaction temperature, indicates that macroscopically two independent reactions take place, the  $\text{H}_2\text{O}_2$  decomposition into  $\text{HO}^\bullet$  species and the reaction of these adsorbed radical species with the dissolved phenol.

### References

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