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High conductivity catalyst structures for applications in exothermic reactions

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ABSTRACT

Highly exothermic catalytic reactions are problematic from a thermal management perspective and often dictate the type of reactor, heat exchanger, level of conversion/recycle and contacting scheme that are employed. To investigate the opportunity for enhanced heat transfer structures, $15 \text{ wt\% Co/Al}_2O_3$ catalyst particles ($149-177 \mu$ m dia.) were examined in both a packed bed configuration and after being entrapped within a 7.4 vol.% network of sintered Cu fibers (12μ m dia.). Fischer–Tropsch synthesis (FTS) at 225–255 °C, 20 bar, H₂/CO of 2.0, was utilized as the probe reaction due to its exothermicity and temperature dependent selectivity. Both the hot spot and runaway state were prevented by utilizing metal microfibrous entrapped catalyst (MFEC) compared to the packed bed. In a 41 mm ID reactor, the maximum temperature deviation from the centerline to the reactor wall was only $6.4 \circ C$ for the copper MFEC. In contrast, the packed bed diluted to the same catalyst density and operated at an equivalent condition had a centerline temperature deviation of 460 °C indicating ignition. The more isothermal temperature profile through the catalyst bed of the copper MFEC led to a higher selectivity of heavy products than that of the packed bed. Also, it enabled a larger reactor diameter to be used with more precise and robust temperature control.

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1. Introduction

Typical packed beds with catalyst granules (e.g., 1–3 mm dia.) have poor thermal conductivities and high mass transfer limitations, which make them problematic for highly exothermic reactions. Metal microfibrous entrapped catalysts (MFEC, Fig. 1) developed in our laboratory provide an alternative approach for reactions confronting mass and/or heat transfer limitations [1,2]. It has been shown that in a stagnant gas the radial effective thermal conductivity of copper MFEC was 56 times that of an alumina packed bed, and the inside wall heat transfer coefficient was 10 times higher. The small catalyst particles (e.g., 10–100 μ m dia.) entrapped in MFEC enhance both the internal and external mass transfer rates thereby increasing both the effectiveness factor and the volumetric reactivity.

Fischer–Tropsch synthesis (FTS) was used as a probe reaction in this study because it is a highly exothermic reaction $(\Delta H = -165 \text{ kJ/mol of CO})$ [3] with an adiabatic temperature rise of approximately 1600 °C depending on the product slate [4]. The

main products of FTS are paraffinic hydrocarbons, based on the following equation:

$$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O$$
 $\Delta H = -165 \text{ kJ/mol}_{CO} (1)$

The distribution of the paraffins is most simply described and modeled by the Anderson–Schulz–Flory (ASF) product distribution [5].

$$x_n = (1 - \alpha) \cdot \alpha^{n-1} \tag{2}$$

The chain growth probability factor (α) for ruthenium, cobalt and iron based catalysts at typical operating conditions is 0.85–0.95, 0.70–0.80, and 0.50–0.70, respectively [6].

Efficient heat removal and the resulting intrabed temperature profiles are critical to the FTS process due to product selectivity and catalyst deactivation. The α value strongly depends on the temperature of the active sites and can be significantly reduced at higher temperatures [7,8]. Song et al. [9] proposed an empirical equation to estimate the dependence of the α value on temperature, as follows:

$$\alpha = \left(0.2332 \frac{x_{\rm CO}}{x_{\rm CO} + x_{\rm H_2}} + 0.6330\right) \cdot [1 - 0.0039(T - 533)]$$
(3)

Furthermore, most of the reactants are consumed in the high temperature zone [31]. Should unwanted thermal runaway or the

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