Percolation in thermally conductive catalysts as a key factor for performance in Fischer-Tropsch synthesis

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Abstract: The Fischer–Tropsch synthesis (FTS), which is important for energy and alternative fuels, is a strongly exothermic and temperature sensitive process. Therefore, the use of a catalyst with low thermal conductivity may lead to rapid deactivation. It means that efficient heat removal by thermally conductive additives is of crucial importance. Efficient mass transfer is also important for the viscous product removal. This work shows that a percolating heat-conductive network (characterized by newly introduced interconnectivity function) in combination with extended pore system provides an unmatched performance of composite catalysts in FTS. The electron microscopy and X-ray tomography support the conclusions.

Keywords: Thermal conductivity, X-ray tomography, Fischer-Tropsch synthesis.

1. Introduction

Fischer–Tropsch synthesis (FTS) is the main stage of energy conversion and production of alternative fuels from non-conventional fossils[1]. The fuels produced by FTS are sulfur and nitrogen-free. Cobalt as an active metal have been widely used to prevent formation of oxygenates and aromatics. In presence of cobalt catalyst syngas (a mixture of CO and H_2) can be converted into liquid hydrocarbons, mostly linear paraffins. The combination of FTS conventional catalyst with zeolites in a composite material leads to formation of bifunctional catalyst producing high-quality synthetic oil by eliminating the hydroprocessing stage[2]. As FTS is strongly exothermic, introduction of a heat conductive component (e.g. metal flakes) can be used to provide effective heat removal network[2–4]. Mass transfer is also essential for FTS: the reactants exist in the gas phase, catalyst pores are filled with liquid products, which reduces diffusion rate[3, 5]. However, the quantitative relationship between these parameters has never been revealed.

The aim of the work was to find out and introduce a quantitative measure for the relation of catalytic properties with quality and quantity of contacts among the flakes of a heat conductive component — we name it interconnectivity ʒ. The interconnectivity can be calculated as a product of thermal conductivity by catalyst pore volume (1).

$$ʒ=\lambda\cdot V \qquad (1)$$

2. Experimental

FTS was carried out in fixed-bed reactor. All supports were pellets of a porous nanostructured composite material composed of 30 % of HBeta zeolite, 50 % of Al metal flakes as a heat conductive additive and 20 % of binder. The pellets were made by extrusion with different velocities 0.6 to 3.0 mm/s. The variation of extrusion velocity gave samples with different properties – see Table 1. Catalysts were prepared by impregnation of the supports with $Co(NO_3)_2\cdot 6H_2O$ (20% wt. of Co) and were activated in H_2 at 400°C for 1 h. Activated catalysts were tested in a syngas stream

Table 1. Composite catalysts under investigation

Sample	λ (W/(m·K))	ρ (g/cm^3)	V_{pore} (cm^3/g)
Kat-1	4,294	1,014	0,577
Kat-2	4,422	1,020	0,590
Kat-3	5,157	1,069	0,520
Kat-4	5,244	1,071	0,520

($H_2/CO = 2$, pressure 2 MPa, GHSV = 1000 h^{-1}) at the temperature rising stepwise up to 223°C.

Scanning electron microscopy and X-ray tomography were used to reveal pore structure and metal flake distribution through the sample. Both methods showed that the catalyst pellet represents an interconnecting network of transport pores and percolating aluminum flakes.

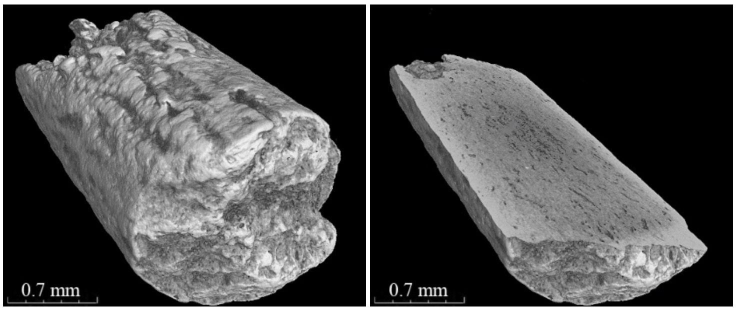

Figure 1. X-ray tomography reveals a network of transport pores (electron microscopy supplements it by the data on a network of percolating aluminum flakes). See whole pellet on the left and a section on the right.

3. Results and discussion

All the catalysts were active in FTS. CO conversion was no less than 80 % with catalyst productivity up to 111 $gC_{5+}/(kg{\cdot}h)$ at 1000 h^{-1} (Fig 2). The decrease in methane selectivity and CO conversion at higher interconnectivity signifies the weaker local overheating in catalysts pellets.

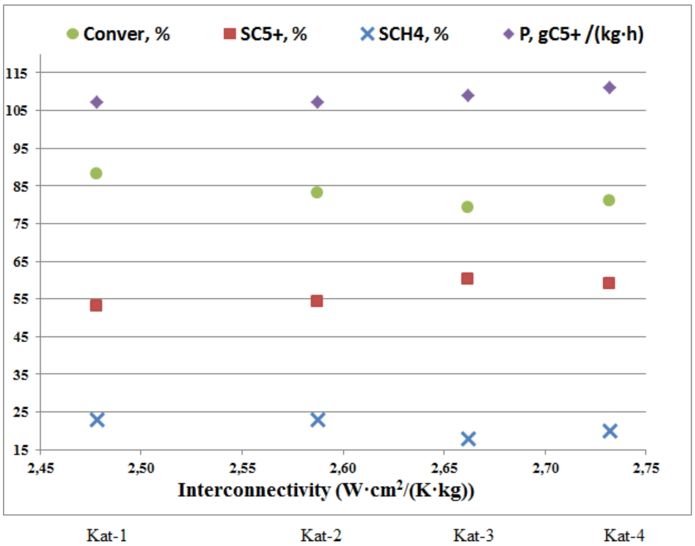

Figure 2. The dependence of main process parameters on the interconnectivity

Furthermore, interconnectivity growth leads to increase in olefins and isoparaffins content and decrease in n-paraffins content in the liquid product. The content of C_5–C_{10} fraction is enhanced and C_{19+} drops with interconnectivity rises from 2.48 to 2.73.

4. Conclusions

It was shown that a percolating heat-conductive network (characterized by newly introduced interconnectivity function) in combination with extended porous system provides an unmatched performance of composite catalysts in FTS. The structural evidence is revealed by both electron microscopy and X-ray tomography.

References

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