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Experimental evaluation of catalyst layers with bimodal pore structure for Fischer–Tropsch synthesis

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ABSTRACT

As catalyst pores are typically filled with liquid, long-chained hydrocarbons during low-temperature Fischer–Tropsch synthesis internal mass transport limitations can impede conversion rate and C₅₊ selectivity. Utilization of transport pores may improve reactant diffusion and thereby reduce these negative effects. In this work preparation, characterization and experimental testing of CoRe/γ-Al₂O₃ catalyst layers, with and without transport pores, of different thickness is presented. All prepared layers with thicknesses in the range from 50 to 600 μm exhibit similar cobalt crystallite sizes of 8.7 nm irrespective of the presence of transport pores. Experimental results showed an increase in methane selectivity from 10 to 40% and a drop of C₅₊ selectivity from 80 to 42% with increasing diffusion length. These negative effects could be retarded by use of transport pores. The highest CO conversion was achieved for layers of about 140 μm thickness exhibiting 50–70% higher values than obtained with the thinnest layers (50–60 μm). This trend holds also for layers with transport pores but use of additional pores did not result in a significant improvement of conversion and space time yield. Nonetheless, on a catalyst mass basis transport pores lead to a benefit in productivity of 25–50%.

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1. Introduction

Fischer–Tropsch (FT) synthesis is a viable process for the conversion of syngas to hydrocarbons that can be used for production of e.g. diesel fuels. To ensure an efficient process a high selectivity toward long chained hydrocarbons is inevitable. Thus the low temperature process on cobalt-based catalysts is typically used for this purpose [1]. Since under reaction conditions some products remain in the liquid phase, the catalyst pores are generally assumed to be filled with liquid that strongly affects the diffusion of the reactants. Especially in fixed bed reactors, where larger particles are usually employed to maintain a low pressure drop [2], diffusion limitations may restrict the productivity and negatively affect the selectivity. Post et al. [3] have shown that severe diffusion limitations limit the rate of carbon monoxide conversion in a fixed bed reactor with catalyst on different supports. Washcoated monoliths utilizing a CoRe/Al₂O₃ catalyst have been evaluated by different groups [4–7], which showed a negative influence of too high

diffusion lengths on activity and product selectivity but also some effects of external mass transport [8,9]. A critical thickness of about 50 μm was found to be the upper limit from which on negative effects of pore diffusion can appear. The group of Iglesia [10–12] has investigated various FT catalysts in fixed bed reactors and could show that diffusion effects do not only negatively affect activity and selectivity, but may also have a positive influence on selectivities due to increased readsorption and subsequent secondary growing of α-olefinic products. However, these positive effects are only marginal, especially for higher diffusion lengths, and thus different approaches have been suggested to overcome these diffusion limitations. The use of egg-shell catalysts, where only a thin outer layer of a larger catalyst particle is active, reduces diffusion limitations [11,13,14]. But as the core of the particles is not catalytically active, a significant fraction of the reactor is filled with inert material which lowers the reactor productivity. Hence the structure of the catalyst can be seen as part of the problem [15,16] and an alternative approach aims at modifying the pore structure of the catalyst. Typically small pores are required to confine the available space for cobalt and cobalt oxide crystallites during catalyst preparation and to obtain a high metallic surface area of the catalyst [17,18]. As the optimum cobalt crystallite size is about 5–6 nm [19,20] catalyst support materials exhibit pore diameters with

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similar size. In this pore size range the diffusion of the reactants in liquid filled pores can be seriously hindered. Although theoretical predictions for ideal structures and empirical equations mostly predict a tortuosity between one and three [21] some experimental results show much higher values of up to 40 [22]. A possible reason for this observation is a restricted diffusion within narrow pores, where the size of the solute is in the same order of magnitude as the pore diameter [23–26]. This phenomenon is similar to the well-known Knudsen diffusion in the gas phase and the dependence of the diffusivity on the pore size is motivation for the use of catalysts with bimodal pore structure. Such catalysts take advantage of narrow mesopores or micropores to obtain a high activity and exhibit a certain volume fraction of macropores to improve mass transport. For simple first order kinetics and one- to two-dimensional problems simulation and optimization results of the group of Coppens [27–30] have clearly shown, that an ideal volume fraction of transport pores has to be found in order to enhance mass transport on the one hand and to preserve the amount of active phase on the other hand. For high Thiele moduli this optimized volume fraction remains constant at a value of 0.5 as long as the transport pores are sufficiently small. For this case a homogenous distribution of transport pores was shown to be almost as beneficial as an optimized spatial distribution of pores. An experimental study from the group of Tsubaki [31,32] of impregnated macroporous, microporous and bimodal catalyst supports has revealed that bimodal catalyst combine an increased activity with high selectivity toward long chained products. Further evaluation of this experimental data with a process model supports the authors assumption of improved mass transport as a result of utilizing transport pores [33]. Despite these promising results, it remains unclear if a real enhancement of the mass transport could be achieved. In this study, only one catalyst sieve fraction with diameters below 149 μm was used, hence the effective diffusion length was not clearly defined. Furthermore the used catalysts were differently prepared and thus effects of the support structure and material on intrinsic activity and selectivity cannot be ruled out. As the pore size is an important parameter during impregnation, drying and calcination [34] preparation of bimodal catalysts can increase reducibility but also cobalt oxide crystallite size [35]. For macroporous structured catalysts, Phan et al. [36] were able to show effects of the bimodal catalyst support itself on intrinsic selectivity and activity without even considering mass transport. Evaluation of catalysts prepared from conventional supports with different pore size and comparison to a bimodal catalyst revealed a positive effect of increasing support pore size on product selectivity. However, a rather ambiguous effect on productivity regarding pore size and use of transport pores was found [37]. Recent work from Wang et al. [38] compares different bimodal catalysts with variable mesopore size but constant micropore size finding the highest conversion at the biggest mesopore size but the highest C_{5+} selectivity for median mesopores. Despite the importance of diffusion length on diffusional limitations, no experimental work has already reported the effects of variation of transport pore fraction and diffusion length.

In previous work based on simulation [39,40] utilizing empirical equations [41,42] we have shown that insertion of transport pores gives rise to enhanced reactor productivity provided that both, diffusion length and transport pore fraction are optimized. Moreover, the resulting optimum strongly depends on the effective diffusion within transport pores and catalyst pores. Thus, evaluation of mass transport effects of transport pores requires a comparable, well defined catalyst with variable diffusion length and transport pore fraction. In this work we present a method for preparation of catalyst layers with adjustable thickness, with and without transport pores, which were prepared from the same catalyst base powder to investigate diffusion limitations during FT reaction.

2. Experimental

2.1. Catalyst preparation

The catalyst powder used in this study contains 20% Cobalt and 1% Rhenium in the reduced state and was prepared by impregnation of a $\gamma\text{-Al}_2\text{O}_3$ support (Puralox UF5/230, 5 μm , Sasol) as described elsewhere [8]. For preparation of the catalyst layers a suspension of the base powder was sprayed on stainless steel plates (25 mm \times 50 mm \times 0.5 mm) using an airbrush (Evolution SOLO, Harder & Steenbeck) with a nozzle of 0.4 mm in diameter operated at 2 bar gauge pressure of nitrogen. The suspension consisted of a mixture of 10 g of catalyst, 7.0 g of colloidal binder (pseudo-boehmite, 20 wt%, 50 nm, pH 7, Alfa Aesar) and 4.0 g polyethylene glycol (20,000 g/mol, Fluka) in 29 g of deionized water and 7.0 g of 2-propanol. The mixture was vigorously stirred and ultrasonically dispersed before spraying the suspension on the metal plates heated to 90 °C. To adjust the layer thickness the number of spraying runs was used as rough estimate and checked by measuring the gain in mass. The still wet layers were then either compacted with a pressure of 1.5 t/cm² for 1 min in a laboratory press (Labo-press P200S, Vogt) or the layers were directly heat treated. Both types of layers, denoted as compacted or uncompact, were then heated in air with a rate of 2 K/min to a temperature of 400 °C, which was kept for 4 h. After cooling to below 50 °C the layers were removed from the oven and used for characterization. The average thickness of each layer sample was measured using a thickness dial gauge (Käfer) at 6 points, allowing to keep the layers intact. Layers with a thickness ranging from 60 to 600 μm were prepared. Each layer thickness was prepared at least two times ensuring that sufficient sample mass was available for analysis and Fischer–Tropsch reaction experiments.

2.2. Fischer–Tropsch experiments

Catalyst testing was conducted similar to previous work [2,43,44]. The catalysts layers were placed in an aluminum inlet with a channel height of 1.5 mm and a width of 25 mm. The catalyst layers were located on one side of the inlet leaving a void channel thickness of about 0.5–1.0 mm depending on the layer thickness. To ensure a good contact to the heated wall of the reactor, an inert carbon felt (GFD2.5 EA, SGL Carbon) was placed above the catalyst layer. The carbon felt is highly porous even after compaction and did not lead to a measurable pressure drop in the channel during reaction. The catalysts were reduced in the reactor with a mass specific flow of pure hydrogen of $10 L_{\text{STP}}/(h g_{\text{cat}})$ starting at a temperature of 120 °C. Subsequently, the temperature was increased up to 350 °C with a rate of 50 K/h and kept there for 16 h. After reduction and cooling down to 150 °C the reaction was started. The reactor was pressurized to 2.1 MPa with a syngas flow proportional to a GHSV of $5000 \text{ m}^3_{\text{SG}}/(\text{m}^3_{\text{cat}} \text{ h})$ and a H_2/CO ratio of 2.0. Argon was used as internal standard and was dosed together with carbon monoxide directly from the gas cylinder (10% argon in carbon monoxide). During activation the temperature was increased up to 190 °C every 12 h in steps of 10 K. After this procedure the system was given time, typically 24–48 h, to reach steady state at each temperature before the temperature was increased again in steps of 10 K to a maximum of 240 °C. During synthesis water and liquid hydrocarbons were separated in a cold and a hot trap, operating at 0 ° and 120 °C, respectively. Gaseous products were analyzed in a Varian GC-450 equipped with a FID, for hydrocarbon analysis, and a TCD detector channel for the permanent gases. Carbon monoxide conversion, X_{CO} , and methane selectivity, S_{C_1} , were calculated as reported elsewhere [44]. The C_{5+} selectivity, $S_{\text{C}_{5+}}$, was calculated on a carbon basis. In accordance to Eq. (1) and (2) space time yield, STY, and mass specific productivity, MTY, were estimated using the

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