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An investigation of efficient microstructured reactor with monolith Co/anodic γ-Al_2O_3/Al catalyst in Fischer-Tropsch synthesis

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ABSTRACT

A new type of microstructured reactor was applied in Fischer-Tropsch synthesis (FTS). Monolith Co/anodic γ-Al_2O_3 plate type catalyst was adopted in the microstructured reactor which has the advantage that the microchannel was achieved through the gap between the catalyst plates, not machining. The γ- Al_2O_3 support was prepared on aluminum plate following the anodization method. And the cobalt was loaded on the anodic γ-Al_2O_3 support by impregnation. The thickness, morphology, structure, reduction behavior and the catalytic performance of the catalyst were characterized by scanning electron microscope (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD), as well as the H_2 temperature-programmed reduction (H_2-TPR). The performance of the catalyst and the microstructured reactor was experimentally characterized in FTS. The CO conversion (19.42%) with 2.7% of CH_4 selectivity and 95.77% of C_{5+} selectivity was obtained with the newly designed microstructured reactor at 220 °C and 2.0 MPa under a gas hourly space velocity (GHSV) of 5,000 h^{-1}. And the activity of the catalyst can be shown greatly in this microstructured reactor. Furthermore, the new developed microreactor is simpler in structure and easier to manufacture at low cost compared with the microchannel reactors requiring precise machining. And the deactivation catalyst after long period operation can be easily replaced for this kind of microstructured reactor.

Introduction

Chemical microstructured reactors (MSR) are devices containing open paths for fluids with dimensions in the submillimeter range [1]. The MSR can be classified into two types according to the catalyst type in gas phase catalytic reaction: packed-bed reactors and the wall-coated reactors. The packed-bed reactor could refill the catalyst easily [2,3].

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However, the pressure drop may increase significantly when the length of the reactor and the size of the catalyst are not optimized. Compared with the packed-bed reactor, the heat transfer rate is higher and the pressure drop is lower for the wall-coated reactors because the catalyst layer contact with the reactor wall directly. Nevertheless, the development of the wall-coated micro reactors are still in laboratory research phase, mainly because the preparation of uniform and well-adherent catalyst layers in metallic microchannels are still a great challenge [4–7].

Different methods were adopted and tested over the last decades including the anodic oxidation of aluminum alloy, high temperature treatment of aluminum containing steel, sol-gel technology, washcoating, chemical vapor deposition (CVD) process, carbon-based coating in microstructures and so on [8–16]. The wall-coated catalyst prepared on the substrate using above methods has lower pressure-drop. But the deactivated catalyst after long period operation is difficult to be wiped off and replaced in the microchannel. Recently, anodic alumina support has attracted great attention due to its well-ordered, densely packed, and nano scale pores. This pore structure is naturally formed when Al plate is anodized [17,18]. Since British researchers Thompson and Wood [19] published the formation law of anodic alumina in different acid electrolytes in Nature in the 1980s, several researchers had already discussed the structure, property, preparation and formation mechanism in the Nature and Science [20,21]. The texture of anodic Al_2O_3 can be controlled by changing the anodization parameters such as current density, time, temperature, electrolyte nature and so on [19,22]. The high surface area with high mechanical adherence and thermal resistance of Al_2O_3 support are suitable for catalytic processes. Pd or Ni/γ-Al_2O_3/Al structured catalysts have already been developed successfully in different catalytic reactions [23,24].

Fischer–Tropsch synthesis (FTS) is a commercial technology for converting natural gas and coal into liquid fuels. FTS is a strong exothermic reaction ($\Delta H_R = -165$ kJ/mol) and often limited by heat and mass transfer rate. Micro reactors with many parallel microchannels and high specific area could improve heat and mass transfer efficiency [5,12,25]. Therefore, micro reactor is especially suitable for FTS [4].

Many researchers have done much work on FTS microreactors [13,26–31]. From the paper involved in above we can see that those microreactors still exist many problems, such as difficulty in changing the deactivation catalyst in wall-coated microchannel reactors and high pressure drop in catalyst microsphere filling microchannel reactor. Moreover, the microchannel reactor with catalyst microsphere packed might be easily blocked especially in FTS.

In this article, a new microstructured reactor filling with anodic alumina plate-type catalyst was designed and manufactured. The catalytic activity and selectivity of the new plate-type catalyst were obtained in the fixed-bed reactor under different space velocities at 2.0 MPa. The computational fluid dynamics (CFD) model was established by software FLUENT based on the experimental results. Then the optimum number of catalyst plates was obtained. Finally, the FTS catalytic performance of new anodic alumina catalyst plate was obtained in the microstructured reactor.

Experimental

The structure of the microstructured reactor

As Fig. 1 shown, the reactor was mainly composed of three parts: shell, flange and the catalyst plates. The catalyst plates were inserted into the shell along the grooves. In order to make sure that the plates can be inserted easily, the width of the groove was larger than the thickness of the catalyst plates. Thereby, the catalyst plates can be replaced easily. The material of the reactor was stainless steel.

In the shell, the grooves were manufactured by wire EDM (wire electronic discharge machining) method. The distance between the grooves was 0.5 mm. The length of the groove was 120 mm. Due to the small distance, in the reaction shell, the mass and heat transfer can be enhanced to assure the temperature uniform. Moreover, the heat transfer module can be added to the reactor to control the reaction temperature.

The flange and the graphite gasket were applied to prevent the leakage of reactant gas from the reactor at high temperature and high pressure conditions. And it can be changed according to the reaction conditions.

Every catalyst plate was 120 mm length, 100 mm width and 0.6 mm thickness. The anodic γ-Al_2O_3 coating was prepared on the Al plate, and the active component was impregnated in the γ-Al_2O_3 support. The Co/anodic γ-Al_2O_3/Al catalyst plates were inserted along the grooves, as shown in Fig. 1.

In order to assure the temperature uniformity of the reactor, computational fluid dynamics (CFD) simulation was conducted using the commercial software FLUENT 15.0 (ANSYS.Inc) to find out optimum number of catalyst plates according to maximum temperature difference in catalyst plates. The code was based on the definite-volume method for space discretization rule and the integral computation of Navier-Stokes equations. The model was composed of three sections, the reaction channel, the cooling channel and the solid wall. The thickness of solid wall was defined by the pressure vessel standard. The Julabo oil was used as the coolant removing the heat generated by reaction.

Simulation had been conducted under stationary conditions. The thickness of the catalyst layer was assumed to be uniform. Gas hourly space velocity (GHSV) was in the range of 5000–10,000 h^{-1} under standard condition. And the ratio of H_2 to CO was 2.

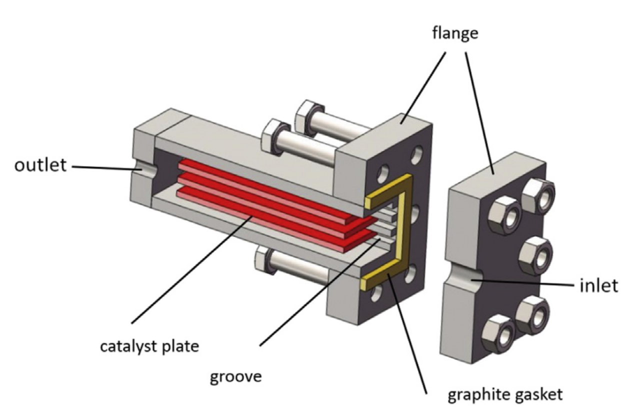

Fig. 1 – Image of microstructuredreactor.