Testing monolithic catalysts in hydrodesulfurization

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Introduction

Hydrotreating is gaining increasing interest due to the stringent fuel legislation on sulphur levels. Catalysts have been in constant development and their performance has been improved over the years, the current launched HDS catalysts being extremely active. Nevertheless, the reactor designs have not changed much. Trickle bed reactors, the most widely used, still present some problems, such as the distribution of gas and liquid or plugging caused by fine solids, which leads to high pressure drop. A proper selection of reactor technology is necessary in order to optimize the efficiency of HDS catalysts. A perfect catalyst deserves a perfect reactor or to put it in another way: in deep desulphiding a very good catalyst does not give satisfactory performance when extensive maldistribution in the reactor takes place. Real breakthroughs might come from the application of non-random packings, so-called structured packings. In particular, monolithic catalysts are attractive. These reactors allow precision that is not possible in random and chaotic systems. The aim of this project is to design and synthesise optimal monolithic reactors and to determine how to perform deep desulfurization in lab scale monolithic reactor.

Experimental

In order to evaluate the performance of monolithic reactors for HDS, it is optimal that highly active catalyst is coated. NiMo/γ-Al$_2$O$_3$ catalysts in powder form were prepared using MoO$_3$ and NiCO$_3$ as metal precursors and were used as reference catalysts. Cordierite monoliths (diameter of 1.5 cm and length of 5 cm) were coated first with two layers of -Al$_2$O$_3$ followed by one layer of α-Al$_2$O$_3$ (by dip-coating method). The γ-Al$_2$O$_3$ layers blocked the macroporosity of the substrate and made rounded channels. The coated monoliths were then impregnated with NiMo solutions (same used to impregnate the powder catalysts). Catalysts screening was performed in gas-phase HDS (thiophene HDS) at atmospheric pressure and 350°C. Some tests were carried out with crushed monoliths with different metal loading, in the same conditions as the powder catalysts. The same trend was found when plotting the reaction rate obtained with the crushed monoliths and the powder catalysts as a function of metal loading.

Catalytic tests were performed in a trickle bed microflow reactor at 225 ºC and 50 bar. Dibenzothiophene was chosen as model compound and hexadecane used as solvent. A stack of 3 monoliths was packed in the reactor and the distribution of the gas and liquid was achieved by placing coarse and fine SiC in the top of the reactor. The reaction was carried out using liquid flowrate of 11 g/h and three different H$_2$ flowrates: 9.4 cm^3/min, 4.7 cm^3/min and 2.3 cm^3/min.

Results and discussion

The conversion obtained with the structured reactor was very low, around 20% (a conversion higher than 90% was expected). This low conversion could be due either to the hydrodynamics (maldistribution occurred) or the active phase (the impregnation technique was not optimal). The later is less likely to explain this difference in conversion because similar conversions were obtained in the thiophene HDS using powder and monolithic crushed catalysts. Another experiment was done with the same monolith but with the channels filled with fine SiC. With SiC in the monolith channels the structured reactor would be similar to a trickle-bed. A conversion of 70% was obtained. This result clearly shows that there was a problem with the hydrodynamics of the system, and that these monoliths cannot be tested in this reaction system. With these low flowrates it is very difficult to guarantee a proper liquid distribution at the top of the reactor. Therefore, we decided to simplify the system and eliminate the effect of distribution of liquid by considering another approach: testing the reaction in a single channel. This was done in the same reaction system and using the same monoliths, by plugging all the channels of the monoliths, except one, using an inorganic cement. These monoliths were also assembled and cemented to the top of the reactor, to assure that the liquid and gas will be fed directly to the single-channel. A cold flow glass system was built to mimic the reactor and check the flow patterns observed with the desired flowrates. Entrance effects were also studied in this system and we concluded that the best way to feed the liquid is by introducing it through a capillary directly into the channel of the monolith, which is placed inside the tube that carries the gas feed. Also in this single channel approach we suffered from inlet and hydro dynamical effect resulting in depending on the gas velocity in bubble flow via Taylor flow in film flow regime. The film flow regime showed the highest conversion due to the longest residence time of the liquid phase. Filling the channel with macro porous SiC the gas flow dependency disappeared.

In both cases multi channel or single channel the inlet effect can be counteracted filling the channels with a macro porous inert material. The hydrodynamic behaviour in this approach will reached a plugged flow regime and reliable measurement can be performed.

Conclusion

A method for testing catalysts in lab-scale reactors in a well-defined system such as monolithic (multi channel) or single channel reactor was achieved by filling in both cases the channel(s) with an inert macro porous material. Inlet gas and liquid flow can be counteracted and the liquid phase will have an optimal contact with the catalytic wall of the channel.. This testing approach can be applied not only to HDS reactions, but also to other catalytic systems.