MASS TRANSFER LIMITATIONS IN A STRUCTURED BED SPIRAL MINI REACTOR

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Summary

Gas – liquid mass transfer limitations in three phase catalytic reactors importantly affect their performance. Process intensification and scale down studies focus on elimination of mass transfer resistances in new reactors. An effective way of proving their elimination and predicting the range of the operating parameters for negligible mass transfer limitations is to evaluate the mass transfer extent and compare it with the reaction rates. The aim of this work is to investigate the mass transfer limitations in a structured bed mini scale multiphase reactor. This type of reactor is called spiral reactor. It consists of a small tube with an internal diameter a little larger than the catalyst extrudate diameter and the catalyst particles form a string bed along the tube length. Hydrogenation of benzene was used as a model reaction for the estimation of mass transfer coefficients under reaction conditions. The reaction kinetics of benzene hydrogenation was studied in a batch stirred reactor. The effects of the gas and liquid superficial velocities on the mass transfer coefficient were studied. Mass transfer limitations have also been investigated with HDS experiments taking into account the effects of the reaction inhibitors hydrogen sulphide and ammonia on reaction kinetics. The mass transfer effects in the spiral reactor become significant as the reaction rate increases, and they are related with the gas to liquid superficial velocities ratio, becoming negligible for rates above 20.

Keywords

Mass transfer, three phase reaction, intensification.

Introduction

Process intensification, making significant reductions in the size of a chemical plant in order to achieve a given production objective (Nigama and Larachi, 2005), becomes more and more attractive in the science community. There are certain advantages in using small scale laboratory units for the study of three phase reaction systems, like the reduction of the units' construction and operation cost, safer and more efficient operation on chemical kinetics investigations, minimization of experimental time as well as improving process capability and control in chemical synthesis (Sie and Krishna, 1998; Kallinikos and Papayannakos, 2007).

The main challenges in collecting meaningful data using mini scale reactors relate with the low gas and liquid superficial velocities needed in downscaling to keep gas and liquid space velocities the same as in bigger reactors.

The spiral reactor (Kallinikos and Papayannakos, 1997) is a structured bed reactor that can be used for any two or three phase reaction system catalyzed by solid particles. It comprises a tube with a diameter a little larger than the diameter of the catalyst particles used, in which the solid particles are successively introduced one by one building a bed with all the particles being in a line. Thus, a 'string bed' of catalyst particles is created. Because the reactor tube is long enough to contain a satisfactory catalyst mass, it can be coiled to form a spiral reactor. Using spiral reactors in scaling down has resulted in much higher liquid and gas superficial velocities than in common small and mini scale reactors due to the small internal reactor diameter. Moreover, both gas and liquid are forced to flow over all the catalyst particles, avoiding by-passing, channeling and poor gas distribution, at any flow rate.

It is common opinion that in fast gas-liquid-solid reactions, the chemical kinetics is often limited by the mass transfer rate of the gaseous species through the liquid to the surface of the catalyst (Losey et al., 2001, Metaxas and Papayannakos, 2007). In the current work the mass transfer limitation on the operation of the spiral reactor is studied using benzene hydrogenation and HDS as model reactions.

Discussion of Results

For the estimation of the mass transfer limitations in the spiral reactor, hydrogenation of benzene in mixture with hexane was attempted as a model reaction over a commercial Ni/Al_2O_3 catalyst in the form of trilobe extrudates. The reaction rates of benzene hydrogenation were estimated with a batch stirred reactor at several industrial reaction conditions. The experiments were conducted at temperatures in the range of 323 to 363 K, at total absolute pressure in the range of 10×10^{-5} to 24×10^{-5} Pa, with benzene content in the range of 1 to 8 % w/w and liquid mixture volume about 50 ml. A 1 m long spiral reactor was built with an SS tube of 2.1 mm internal diameter in which 1.0 $x10^{-3}$ kg catalyst was introduced. Experiments were carried out in a mini – scale laboratory unit.

Mass transfer limitations have also been investigated with HDS experiments taking into account the effects of the presence of hydrogen sulphide and ammonia on reaction kinetics. To this end, reaction experiments with various gas and liquid superficial velocities as well as H_2S and NH_3 partial pressures were carried out.

For the low benzene hydrogenation rates at temperature 323 K, the reaction rate constant obtained with the data from the spiral reactor is similar to the one estimated with the stirred reactor especially for gas to liquid superficial velocity ratios higher than 20. The experiments carried out at 343 K indicate that the performance of the spiral reactor approaches the performance of the stirred reactor for gas to liquid superficial velocity ratios higher than 30. Furthermore, from the experiments performed at 363 K, where the reaction rates are significantly high, the performance of the spiral configuration approaches the performance of the stirred reactor for gas to liquid superficial velocity ratios higher than 80. These results imply that when the reaction rates are not high the influence of the mass transfer limitations is not so important. For high reaction rates, the mass transfer limitations become higher thus the performance of the reactor is affected by the mass transfer limitations.

The overall gas – liquid mass transfer coefficients were estimated using the two film model. From the results it is shown that the values of the mass transfer coefficient are related with the gas to liquid superficial ratıo.

This it is in agreement with the results form the operation of the spiral reactor for gas oil deep desulphurization (Kallinikos and Papayannakos, 2007) where it was concluded that for the same liquid hourly space velocities (LHSV) the performance of the reactor was affected only by the ratio of gas to liquid superficial velocities.

The estimated mass transfer coefficients indicate extended mass transfer effects for low gas to liquid velocity ratios, less than 20. But, for higher u_{GS}/u_{LS} values the estimated mass transfer coefficients appear to reach a plateau.

Similar conclusions have been drawn from the results obtained with the reacting system of gas oil hydrodesulphurization. The performance of the reactor during the HDS process appears to be maximum for gas to liquid ratios higher than 20.

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