ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Dynamic modeling of catalyst regeneration

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Highlights

- Measurement of coke profile in adiabatic pilot reactor.
- Estimation of temperature dependent coke-burn kinetics.
- Characterization of coke reactivity.
- Numerical analysis of runaway behavior.

1. Introduction

The conversion of carbonrich feedstocks such as coal, associated gas, biomass or even waste into automotive fuels has attracted a great deal of focus in recent years in view of fluctuating oil prices and a widespread desire to utilize domestic resources to reduce dependency of imported oil. The carbon containing feed stock is first converted into syngas, subsequently into methanol, and finally the oxygenate compound is converted into synthetic gasoline over a zeolite catalyst. In the process of converting methanol into hydrocarbons, there is a progressive decrease in the catalyst efficiency, which is mainly due to deposition of bulky organic compounds. These compounds are generally classified as *coke*, but may be composed of many different chemical species. Catalyst deactivation by coking is a reversible deactivation where the catalyst can regain its activity when the coke is burned off in a gas stream containing a small amount of oxygen. The reaction between the oxygen in the gas phase and the hydrocarbons in the solid phase, gives rise to a considerable heat production, developing heat waves as the reaction zone progresses downstream through the reactor. The occurrence of heat waves during the regeneration of the coked catalyst is of concern, since a too high temperature may cause damage either to the reactor or the catalyst itself. Therefore, accurate prediction of the hot spots formed during regeneration of the spent catalyst is of great importance.

2. Methods

The methanol-to-gasoline (MTG) pilot is located at the Haldor Topsoe headquarters in Lyngby, Denmark. The pilot is scoped to demonstrate the full methanol-to-gasoline synthesis loop, and is specifically designed to replicate industrial performance, ensuring industrial mass flux in the reactor, void distribution, and adiabatic reactor operation, which is accomplished by using automated heat compensation in a pseudo-adiabatic reactor oven. The spent (coked) catalyst was unloaded in fractions and from these fractions nine small samples were taken, and submitted for total carbon determination. Three of the samples, which were located at the reactor positions; $z = x/L = 0.1$, 0.55 and 0.95, were further analyzed by temperature programmed oxidation (TPO) as well as chemical analysis to reveal the characteristics of the coke. Based on the TPO data, a kinetic coke-burn model was developed by fitting the measured gas evolutions using dynamic mass balances for each gas component coupled with a nonlinear least square methodology, for estimation of both the unknown kinetic parameters as well as to deconvolute the different reactive coke families. The developed coke burn model is further validated by model test in an independent and different reactor system (pilot scale).

3. Results and discussion

Seven reactive coke families was needed to fit the observed diversity in the coke's oxidation reactivity. These seven families can however roughly be divided into a "reactive" and "less-reactive" coke type. The "reactive" coke has a higher H/C ratio of approximately 0.7 whereas the less-reactive has as low as approximately 0.3. The analysis show that the less-reactive type is more evenly distributed along the axial coordinate in the reactor, where the reactive sort is distributed in a "parallel" manner, i.e. the coke is deposited via reactions, that occur parallel to the main reaction, which results in more coke at the entrance region compared to the reactor exit region. By applying the estimated coke profiles for the various reactive coke families together with a detailed reactor model, taking into account both the axial and radial coordinate, as well as time, it was possible to validate the kinetic model by reconstructing the in situ regeneration done in the pilot reactor after reloading the spent catalyst back to the original positions inside the reactor. The model is then used to investigate different regeneration strategies and assess the possibility of thermal runaway and wrong-way behavior. As an example, the numerical analysis shows, that burning only 1wt% of parallel coke with 1vol% oxygen may lead to an unexpectedly high temperature increase of about 550°C, i.e. 400°C higher overheat temperature compared to the expected conventional adiabatic steady-state value.

4. Conclusions

It was found, that the characteristics of the coke deposited on zeolite catalyst in connection methanol-to-gasoline depends on the operating conditions. Analysis show, that the deposited coke has a clear diversity in oxidation reactivity, which means that only part of the coke will react at low temperatures. By performing parameter estimation in a differential equations system, it was possible to develop a kinetic model for the observed diversity in coke-burn rates. After validation the model was used to investigate runaway tendencies in connection with regeneration in adiabatic reactors. It was shown, that the risk of thermal runaway is highest in the initial period of the regeneration, and that this risk can be mitigated by choosing the regeneration a bit less aggressive.

References

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Keywords
Catalyst regeneration, coke, kinetics, mathematical modeling.