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Foreword

The catalytic processing of many industrial feedstocks is frequently accompanied by the deposition of carbonaceous deposits. This deposition process is commonly termed coking and results in a decreased activity of the catalyst, although due to the complexity of the coking effects it is not always possible to relate any decrease of activity directly to the extent of coke deposition. It is important to recognise that the coke deposits originate from the reactions as such and are not generally an impurity. Because of this intrinsic association with the chemical reactions which are occurring, coking cannot be eliminated by purification of the feed or by use of a guard catalyst bed; if reaction occurs, coke deposition must also necessarily result according to the overall chemistry of the process. However, coke formation may be minimised by appropriate choice of reactor and operating conditions, and in certain cases by modification of the catalyst.

As a consequence of the deactivation resulting from coking, catalyst regeneration or in extreme cases catalyst replacement is necessary. This imposes financial penalties and clearly demonstrates the importance of understanding the coking process and as a result enabling better operating strategies to be developed to minimise the effect of coking on deactivation. The present Special Issue contains papers concerned with the following aspects of coking:

(a) General overviews of the problem.
(b) Coking in specific catalytic processes.
(c) Characterisation of coke deposits.
(d) Modelling of coke formation and catalyst deactivation.

The industrial aspects of the effect of coking on catalysts and the different operational strategies available to deal with the problem are discussed in the paper by Rostrup-Nielsen. A further area discussed is the selection of the appropriate system for regeneration of the catalyst and the coupling of the regenerator with the main catalytic reactor. The paper by Trimm extends this industrial aspect for the specific case of steam reforming. Control of coking by modification of the steam carbon ratio and its dependence on the kinetics of the intermediate reactions are emphasised. Minimisation of coke deposition can be effected by addition of trace amounts of sulphur in the feed.

The effect of coke deposition on the methanol to gasoline process using a HZSM5 catalyst has been investigated by Aguayo et al. by both experimental and modelling studies. Fixed and fluidised bed reactor performance under coking conditions has been compared. The paper by Liu and Dadyburjor considers the combined effect of poisoning and coking using the cracking of cumene as a model reaction. An important conclusion resulting from this work is that some characterisation of the number of coke entities can be established per active site. The effect of coking on the deactivation of spinel type nickel catalysts used for acetylene dehydrogenation has been considered by Rodriguez et al. Interesting effects are obtained by modification of the catalyst by ZnO and H_2S pretreatment of the catalyst and addition of this to the feed. Changes in coke morphology occur with H_2 addition while the sensitivity of the catalyst towards deactivation results from promotion action in the catalyst. The industrially important hydrotreating operation in the presence of nitrogen compounds has been studied in the article by Dong et al. It was found that the presence of these compounds facilitates coke formation, yet for the same level of coke the nitrogen coked catalysts gave less deactivation than normal coked catalysts.

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This was due to strong adsorption of nitrogen compounds on non-active catalyst sites.

Characterisation of the coke on catalysts provides useful information on the nature of the coking process. TPO experiments by Querini and Fung have established that coke reaction order changes with catalyst morphology and that gasification of coke deposits with an inert gas yields carbon oxides – a consequence of reaction of coke with support surface hydroxyl groups. The powerful technique of solid state NMR has been used by Snape et al. to investigate cokes produced by FCC catalysts from industrial units and from laboratory studies. The resultant coke composition although mainly aromatic reflects the properties of the feed employed. Filamentous carbon deposits are still an interesting phenomenon and their structure has been studied in the paper by Krishnankutty et al., using TPO of demineralised samples and SEM. Addition of hydrogen changes the structure of the filaments giving rise to different orientation of the graphitic platelets in the filaments.

Modelling studies are reported in the paper by De Groote and Froment and in that of Mann. The former authors consider the modelling of synthesis gas production by partial oxidation of methane with additions of H_2O and CO_2 to the feed. Steam addition was found to give a higher coke content due to dilution of the feed oxygen. In the article by Mann, the important aspects of coke deposition on pore blocking and resultant deactivation are analysed by both 'wedge' shape coke deposition and by stochastic pore network modelling. The results are based on coke deposition occurring for the cracking of cumene over a supported zeolite catalyst.

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The Editors

R. Hughes
University of Salford
Chemical Engineering Unit
Maxwell Building
The Crescent
Salford, Manchester M5 4WT, UK

J. Santamaria, A. Monzon
University of Zaragoza
Zaragoza, Spain