PORE STRUCTURE MODIFICATION BY COKING DURING BENZENE ALKYLLATION WITH ETHANE ON BI-FUNCTIONAL ZEOLITE CATALYSTS

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Abstract

The deactivation behaviour of a new bi-functional Pt/H-ZSM-5 catalyst for benzene alkylation with ethane was studied. The zeolite catalysts at different stages in the deactivation process was analysed using a novel multi-technique approach which involves gas sorption, XRD, SEM and thermogravimetric analysis. In contrast to previous studies, it was observed that there is a direct correlation between the product distribution and the structural evolution of the pore structure as a result of coke deposition, which alters the adsorption kinetics and transport properties in the zeolite catalyst.

Introduction

Ethylbenzene is a key intermediate in styrene synthesis. It is currently produced via acid catalyzed benzene alkylation with ethene, which is a product of highly energy intensive processes (steam reforming of ethane and naphtha). With recent increases in environmental and economical concerns, it strengthened the case for using ethane as an alternative alkylating agent. A bi-functional catalyst has been developed to combine de-hydrogenation of ethane, with alkylation of benzene, in the same catalytic system. The need of capturing a highly reactive intermediate (ethene) before it gets involved in side reactions means that the transport properties and internal distribution of catalytic sites are critical in determining catalyst performance. A particular feature of the system is the loss of activity due to the side reactions leading to the formation of carbonaceous species, loosely called 'coke'. It is a longstanding challenge for catalytic applications in many hydrocarbon processes to increase resistance of the catalyst to deactivation. Therefore, a better understanding of this process will lead to more active, longer lasting catalysts.

This study examined new bi-functional zeolite catalysts for benzene alkylation with ethane, and focused on the effect of coking on the accessibility and mass transport within the zeolite catalyst in relation with changes in surface chemistry and network geometry.

Experimental

The catalyst studied in this work was 1%w/w Pt/H-ZSM-5 material with a silica-to-alumina ratio of 15. The reaction was carried out at 370 °C. After different times on-stream, the reaction was stopped.
Nitrogen and argon adsorption experiments were performed on a Micromeritics ASAP 2020 apparatus at 77 K. Ethane sorption experiments were performed on a Hiden IGA at a range of temperatures between 283 and 303 K.

Thermogravimetric analysis, XRD, and SEM were carried out on the fresh and coked bifunctional 1%w/w Pt/H-ZSM-5 catalysts.

Results and Discussion

Coking during the alkylation reaction leads to a marked decline in the benzene conversion with time on-stream. Nitrogen adsorption isotherms for the fresh catalyst, and also for samples that have been on-stream for 4 h, 24 h and 48 h, are shown in Figure 1. Nitrogen adsorption studies revealed that there is significant loss in total amount adsorbed with time on-stream. The initial adsorption knee, characteristic of micropore filling, occurred at lower relative pressure and amount adsorbed as coking progressed. A shift in the micropore size distribution to smaller pore diameter resulting from coke deposition on the walls of larger micropores was also observed.

![Figure 1: Nitrogen adsorption isotherms for fresh and coked samples](image)

The detailed analysis of the variations in ethane adsorption isotherms and heats of adsorption during time on-stream implied that coking preferably occurred within the micropore network, and not just blocking access to the interior of zeolite crystallites by the formation of a surface layer. The corresponding XRD patterns validate this thesis i.e. pore blockage of the zeolite channels by the carbon deposits.

The mass transfer coefficient of the key reactant, ethane, at a constant amount adsorbed, increased with time on-stream. This suggested that partial blockage of the internal pore structure decreased the diffusion length within the crystallites, which eventually lowered the para-selectivity between diethylbenzene and xylene isomers in the product distribution. The results match the known crystallite size effect but differ from the typical effect of coking, which exhibits para-selectivity enhancement due to steric hindrance.

Conclusion

The results demonstrate the specific deactivation mechanism for this particular alkylation process, thereby enabling the development of an improved catalyst design.