

Cooperative Effects of Zeolite Mesoporosity and Defect Sites on the Coke Formation and Deactivation [1]

Kyungho Lee and Minkee Choi*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

*E-mail: mkchoi@kaist.ac.kr

Understanding coke formation in zeolites is of prime importance for designing solid acid catalysts with enhanced lifetime. In recent years, it has been repeatedly reported that zeolite containing secondary mesoporosity can show increased catalyst lifetime. In these studies, the slower deactivations were generally attributed to the faster diffusion of coke precursors out of the zeolite structure. Although the generation of secondary mesoporosity has been considered as one of the most versatile strategies to retard the zeolite deactivation, in certain cases, even faster deactivation after the mesopore generation has also been reported. This implies that understanding coke formation solely in the view point of diffusion would be a significant oversimplification of a complex coke formation phenomenon.

With this regard, in the present work, the cooperative effects of secondary mesoporosity and defect sites on the amount and location of coke formation and catalytic deactivation of zeolite were investigated in *n*-pentane aromatization using model Ga/ZSM-5 catalysts. Secondary mesoporosity was introduced to a commercial ZSM-5 by alkaline desilication, while the defects sites (i.e., internal silanols) in zeolites were annealed by the ammonium hexafluorosilicate (AHFS) treatment. Aromatization results after supporting Ga showed that both generating mesoporosity and annealing defect sites effectively retarded catalyst deactivation via the suppression of internal coke formation. Internal coke can cause a more severe catalyst deactivation than external coke because the catalytically active acid sites are mainly located in the zeolite micropores, and also internal coke can easily block these micropores even at low coking level. However,

the mesopore generation alone could not efficiently reduce the total amount of coke deposition, but it mainly changed the location of coke. In contrast, the annealing of internal silanols could reduce the overall coke formation. This phenomenon could be explained by the fact that coke precursors are initially generated at the internal defects of zeolite, and then deposited as coke at either the internal or the external surfaces of the zeolite depending on the relative kinetics of the coke precursor diffusion and its polymerization. Consequently, the catalyst with secondary mesoporosity and annealed internal silanols exhibited the slowest catalyst deactivation due to the highly suppression of both internal and external coke formation.

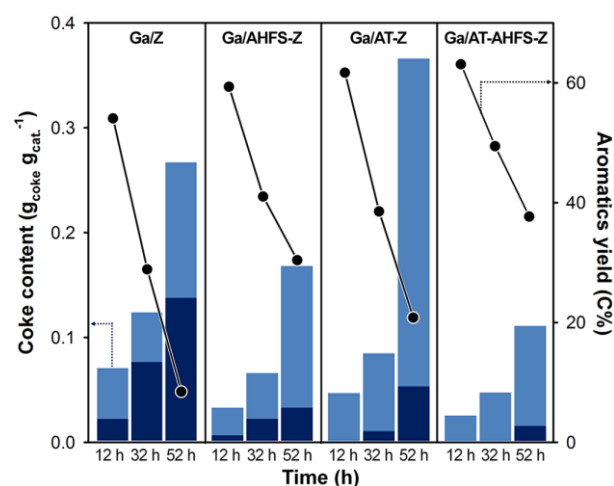


Fig 1. Coke contents after aromatization for the Ga/ZSM-5 catalysts (dark blue bars: internal coke; light blue bars: external coke; scatter plot: aromatics yield).

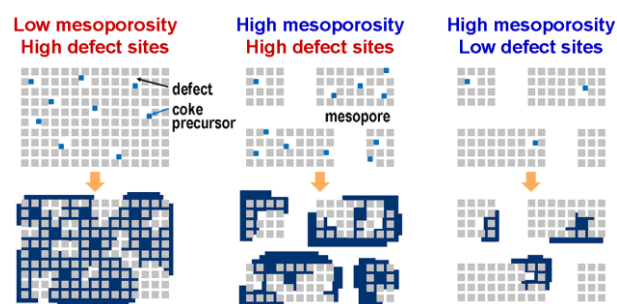


Fig. 2. Schematic illustration of coke deposition behaviors on zeolite catalysts with different pore structure and defect contents.

REFERENCES

[1] Manuscript under revision in *Journal of Catalysis*