# Cooperative Effects of Mesoporosity and Defect Sites of Zeolite on the Resistance to Coke Formation[1]

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**Abstract:** The effects of mesoporosity and defects on the deactivation of zeolite were investigated in *n*-pentane aromatization. Introducing secondary mesoporosity increased catalytic lifetime by enhancing diffusion of coke precursors. However, it could not reduce the total amount of coke. In contrast, annealing of defects could suppress the overall coke formation. This could be explained by the fact that coke precursors are generated at the zeolite internal defects, then deposited as coke at either internal or external surfaces of the zeolite depending on the relative kinetics of coke precursor diffusion and polymerization. Consequently, the catalyst with mesoporosity and annealed defects exhibited the slowest catalyst deactivation.

**Keywords:** Zeolite, Deactivation, Coke

## 1. Introduction

Zeolites are crystalline microporous aluminosilicates widely used as solid acid catalysts in a variety of chemical reactions in the petrochemical and refinery industry. Unfortunately, zeolite catalysts are generally known to deactivate due to coke formation during various acid catalysis, and thus, increasing coke resistance is very important in zeolite catalysis. It has been repeatedly reported that zeolite containing secondary mesoporosity can show significantly increased catalyst lifetime due to the faster diffusion of coke precursors out of the zeolite structure. However, in certain cases, even faster deactivation after the mesopore generation has been reported. This implies that understanding coke formation behavior solely in the view point of coke precursor diffusion would be a significant oversimplification of a complex coke formation phenomenon. In this regard, it is necessary to understand the cooperative interplay between the secondary mesoporosity and other factors such as defect sites on the coke formation and its consequence in the zeolite deactivation.

In the present work, the effects of mesoporosity and defect sites on the deactivation of Ga/ZSM-5 during *n*-pentane aromatization were systematically investigated. The amount and location of coke deposition were analyzed in the course of *n*-pentane aromatization to comprehensively understand the different roles of mesoporosity and defect sites on the catalyst deactivation.

## 2. Experimental

*Catalyst preparation.* Commercial ZSM-5 (Z) was used as the starting material. Desilication by alkaline treatment was carried out to generate secondary mesoporosity in the zeolite (AT-Z). Ammonium hexafluorosilicate (AHFS) treatment was carried out to anneal the defect sites within the zeolite samples (AHFS-Z and AT-AHFS-Z). Ga was supported on the ZSM-5 samples by the incipient wetness impregnation method.

*n-Pentane aromatization.* The reaction was carried out at 823 K, 1 bar (WHSV = 2 $g_{n\text{-C5}}\ g_{cat.}^{-1}\ h^{-1}$). The total amount of coke in the catalyst was analyzed by thermogravimetric analysis. The coke formation inside micropores (internal coke) was calculated from the decrease in the micropore volume determined by $N_2$ adsorption at 77 K, assuming the coke density of 1.22 g $cm^{-3}$.

## 3. Results and discussion

With time-on-stream, all of the catalysts showed gradual deactivation and thus decreasing yields of aromatic products (Figure 1). The deactivation rate decreased in the order of Ga/Z > Ga/AT-Z > Ga/AHFS-Z > Ga/AT-AHFS-Z. The results clearly showed that the presence of secondary mesoporosity and the annealing of defect site are effective for retarding catalyst deactivation.

As shown in Figure 2, the Ga/Z showed the fastest coke formation in the early reaction period (< 32 h).

In contrast, the Ga/AT-Z sample containing secondary mesoporosity showed much slower formation of internal coke while showing faster, and even more, formation of external coke. It has been reported that internal coke deposits can cause a more severe catalyst deactivation than external coke because the catalytically active acid sites are majorly located in the zeolite micropores and internal coke can easily block these micropores even at low coking levels. In this respect, the slower deactivation of Ga/AT-Z than Ga/Z could be attributed to the suppression of internal coke formation, which results from the faster diffusion of coke precursors out of the zeolite micropores. The Ga/AHFS-Z exhibited significantly slower coke formation than the Ga/Z, especially the formation of internal coke. Considering that the Ga/AHFS-Z contains lesser amount of internal silanol groups as AHFS treatment annealed the defect sites that were present in the Z sample, the faster coke formation in Ga/Z compared with Ga/AHFS-Z suggests that the internal silanols can facilitate coke formation. It has been reported that coke formation itself can be regarded as a shape-selective reaction, and thus coke formation is inhibited in the unique 10-membered-ring micropore channels of ZSM-5 due to spatial constraints. The presence of internal defect structures within ZSM-5, however, can allow enough space to accelerate the generation of coke precursors and their subsequent deposition as heavier internal coke.

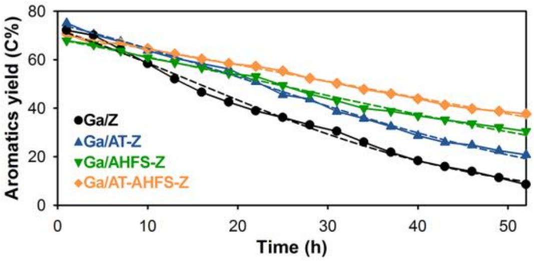

**Figure 1.** Total aromatics yield as a function of time-on-stream for the Ga/ZSM-5 catalysts.

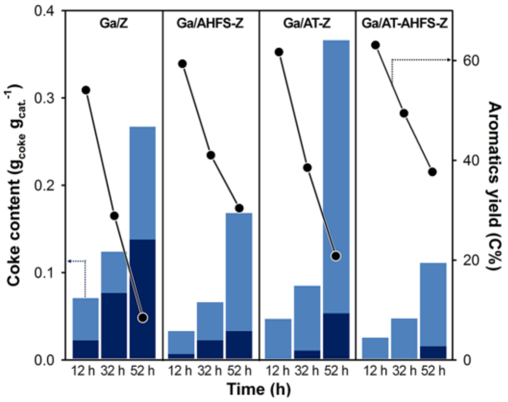

**Figure 2.** Coke contents after 12, 32, and 52 h of *n*-pentane aromatization for the Ga/ZSM-5 catalysts (dark blue bars: internal coke; light blue bars: external coke).

From these results, it appears that mesopore generation alone does not efficiently reduce the total amount of coke formation (it mainly changes the location of the coke deposition), whereas the annealing of internal defect sites can suppress the overall coke formation. This phenomenon can be explained by assuming that coke precursors are mainly generated at the internal defect sites of zeolites and they can be deposited as coke either at the internal or external surface depending on the relative kinetics of coke precursor diffusion and its polymerization (Figure 3). In this respect, the Ga/AT-AHFS-Z sample containing both secondary mesoporosity and annealed defect sites showed the slowest internal and overall coke formation, and exhibited the slowest deactivation.

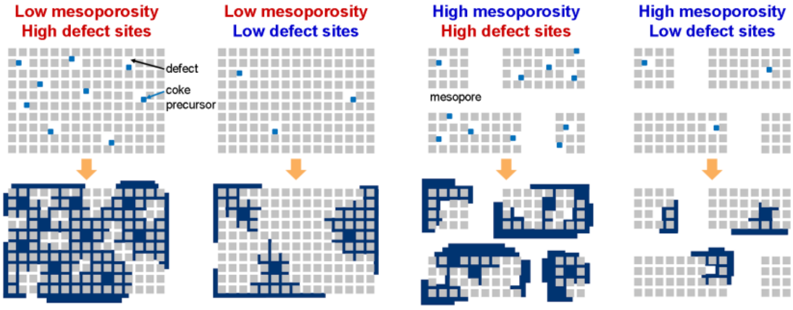

**Figure 3.** Schematic illustration of coke deposition behaviors on zeolite catalysts with different amount of mesoporosity and defect sites.

## 4. Conclusions

In the present work, the effects of mesoporosity and defect sites (*i.e.*, the internal silanols) on coke formation and deactivation of Ga/ZSM-5 during *n*-pentane aromatization were systematically investigated. Analyses of the amount and location of coke deposition during the reaction showed that coke precursors are mainly generated at the internal defect sites of zeolites, and they can be deposited as a coke either at the internal or external surface of zeolite depending on the relative kinetics of coke precursor diffusion and its polymerization. For this reason, the Ga/ZSM-5 having the combination of secondary mesoporosity and annealed defect sites showed the slowest catalyst deactivation among the prepared catalysts.

## References

1. K. Lee, S. Lee, Y. Jun, M. Choi, J. Catal. 347 (2017) 222.