



# Cooperative effects of zeolite mesoporosity and defect sites on the amount and location of coke formation and its consequence in deactivation



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## ARTICLE INFO

### Article history:

Received 25 November 2016

Revised 17 January 2017

Accepted 22 January 2017

Available online 21 February 2017

### Keywords:

Zeolite

Deactivation

Coke

Mesopore

Defect sites

Internal silanol

## ABSTRACT

The cooperative effects of secondary mesoporosity and defects on the coke formation and deactivation of zeolite were investigated in *n*-pentane aromatization using model Ga/ZSM-5 catalysts. 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 treatment with ammonium hexafluorosilicate. Aromatization after supporting Ga showed that the mesopore generation retarded catalyst deactivation via the suppression of internal coke formation while facilitating the external coke formation due to the enhanced diffusion of coke precursors (*e.g.*, alkylaromatics) out of zeolite micropores. Internal coke can cause a more severe deactivation than external coke because the acid sites are mainly located in the zeolite micropores. However, the mesopore generation alone could not efficiently reduce the total amount of coke deposition (it mainly changed the location of coke). In contrast, the annealing of internal silanols could suppress the overall coke formation. This phenomenon could be explained by the fact that coke precursors are initially generated at the zeolite internal defects, and then deposited as coke at either the internal or the external surfaces of the zeolite depending on the relative kinetics of coke precursor diffusion and its polymerization. Consequently, the catalyst with mesoporosity and annealed internal silanols exhibited the slowest catalyst deactivation due to the suppression of both internal and external coke depositions.

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## 1. Introduction

The aromatization of light alkanes has been extensively studied because of its economic and strategic importance to the utilization of natural gas resources as well as light naphtha from petroleum refining. Light alkanes can be efficiently converted to aromatics over acidic zeolites such as ZSM-5 (MFI structure) which are promoted with metal cations such as Ga and Zn [1–3]. It has been reported that these metal cations (Ga and Zn) increase the rate of alkane dehydrogenations [1,3–5], which leads to the favorable formation of alkenes and aromatics over undesired cracking products such as methane and ethane. Among the metal species, Ga is known to have an advantage over Zn because the latter is volatile and unstable under the reductive reaction conditions at high temperature [5]. Brønsted acid sites in ZSM-5 catalyze the oligomerization of short-chain olefins into C<sub>6+</sub> hydrocarbons and their

subsequent cyclization. The commercial aromatization process using Ga-modified ZSM-5 (Ga/ZSM-5) as a catalyst was developed jointly by UOP and British Petroleum (BP) and named “Cyclar” process [6]. Most studies on the reaction date from the 1990s, but interest has recently been renewed by the growing importance of GTL technologies [7–17].

The Ga/ZSM-5 catalysts are known to undergo rapid catalyst deactivation, due to coke formation in the zeolite [18–21]. It has been reported that the main products in the initial stage of propane aromatization are aromatics, but increased amounts of olefins such as ethene and propene are produced with gradual catalyst deactivation [18,19]. This suggests that the active sites for olefin oligomerization and cyclization (*i.e.*, Brønsted acid sites) deactivate prior to the active sites for dehydrogenation (*i.e.*, Ga). Considering the rapid deactivation characteristics of Ga/ZSM-5, the development of a ZSM-5 support having increased coke resistance would be highly desirable to improve catalyst performance during light alkane aromatization.

It has been repeatedly reported that zeolite containing secondary mesoporosity (either inter- or intracrystalline) can show

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