



SAPO-34 and ZSM-5 nanocrystals' size effects on their catalysis of methanol-to-olefin reactions

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ABSTRACT

The catalysis of methanol-to-olefin (MTO) reactions over SAPO-34 and ZSM-5 was strongly shown to depend on the crystallites sizes. Four samples (average size of 50–5000 nm) of each catalyst were characterized for shape, size, acidity and diffusion properties. Materials adsorbed and occluded on them during the reaction were directly monitored *in situ* by IR spectroscopy and analyzed *ex situ* by GC–MS after extraction. Crystallites of 200–500 nm showed the best conversions and lifetimes because of their large external surfaces and short diffusion lengths. SAPO-34 with the smallest crystallites (<150 nm) deactivated rapidly due to pore blocking by heavy coke deposits; similarly sized ZSM-5 exhibited low conversion due to the low number of strong Brønsted acid sites in its micropores. The adverse effects of the nanocrystallinity of zeolite catalysts are discussed in terms of their framework topology, acidity, and diffusivity.

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1. Introduction

The mass production of ethene and propene, two industrially important olefins, relies mainly on the energy-intensive thermal cracking of naphtha [1], leading to interest in developing technologies that can produce lower olefins from nonpetroleum sources. Methanol-to-olefin (MTO) reactions are considered most suitable for this, as methanol can be obtained at large scale from various sources, such as coal, natural gas, and biomass [2,3] and because some MTO process technologies, for example the UOP/Hydro process catalyzed by SAPO-34 (framework type CHA), are now available for licence [4,5].

SAPO-34 is a cage-based, small-pore silicoaluminophosphate (SAPO) molecular sieve. Its framework topology, which is isotropic with common natural zeolite chabazite, consists of large cylindrical 20-hedral (6.7 Å in diameter and 10.0 Å in height) cages accessible through 8-ring (3.8 × 3.8 Å) windows [6]. The MTO reaction's mechanism over SAPO-34 has been reported to be dominated by a hydrocarbon pool mechanism under steady-state conditions [2,7–11]. Hexamethylbenzene (HMB) has been identified as the main reaction intermediate in this small-pore material that acts as a catalytic scaffold for producing ethene and propene.

Hydrocarbon species encapsulated within SAPO-34 cages can react with methanol or dimethyl ether, initiating a sequence of steps which results in primary olefin products and the regeneration of the original organic species to complete the catalytic cycle [6–8].

ZSM-5 (MFI), medium-pore zeolite composed of intersecting straight (5.3 × 5.6 Å) and sinusoidal (5.1 × 5.5 Å) 10-ring channels, was originally developed as a methanol-to-gasoline (MTG) catalyst by Mobil, though it has also been studied as a potential MTO catalyst [2,9]. Its strong acid sites can catalyze further oligomerization followed by cracking to aromatics and paraffins, which can be overcome by post-synthetic treatments such as phosphorous impregnation which imparts high propene selectivity because of olefin methylation-cracking reactions [12,13]. Polymethylbenzenes such as HMB have been reported to form during the MTO in the pores of ZSM-5; methylbenzenes with greater numbers of methyl groups (5–7) that form in ZSM-5 contribute less to the production of lower olefins from methanol than those in SAPO-34 or BEA because of the less available space. The high participation of olefin methylation-cracking in the pores of ZSM-5 causes high propene selectivity in the products. The limited space also suppresses the formation of polyaromatic hydrocarbons (PAHs) in the pores, making deactivation mainly due to coke formation on the external surfaces [13].

In addition to the strength of acid, the acid site density, and the framework topology of the zeolitic materials [2,7–11,14,15], crystallite size also determines microporous solids' MTO performances [14–23]. Under conditions of similar acidity, smaller crystallite molecular sieves generally show lower deactivation rates, though

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