

# Progress on Synthesis and Catalysis of Mesoporous Zeolite Single Crystals

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## Introduction

Zeolites are microporous crystalline materials that are widely used in industry for adsorption, separation and catalysis [1]. A multitude of chemical reactions of industrial interest are catalyzed by zeolites. The zeolite micropores have dimensions close to those of typical reactant and product molecules in many large-scale processes and they are responsible for the characteristic size and shape-selectivity typical of zeolite catalysts [2]. However, for some applications the sole presence of micropores can also result in an unacceptably slow diffusion of reactants and products to and from the active sites located inside the zeolite crystals. Several strategies have been proposed to circumvent this difficulty. During the last years, the introduction of additional intracrystalline mesopores into each individual zeolite crystal has attracted significant attention. Such modification of the zeolite crystals can be introduced either during the hydrothermal synthesis or by suitable post-treatment. The introduction of mesopores during zeolite synthesis by use of an auxiliary carbon mesopore template that can later be removed by combustion has proved to be a simple and versatile approach [3]. It has led to a family of unique catalytic materials that feature both micropores and mesopores in each individual crystal, and exhibits high acidity and hydrothermal stability.

Compared to other currently known methods for introducing mesopores into zeolite crystals, the carbon templating method has several unique features. First of all, it appears to be a general method for introducing mesopores into zeolite crystals, independent of their structure, and it can be done without altering the original Si/Al ratio. Furthermore, this method does not lead to partial destruction of the zeolite crystal. Here, recent developments on an approach based on combination of the fluoride route with a new carbon-templating methodology [4], microwave technique and improved carbon templating procedure [5] are reported. Produced mesoporous single crystal zeolites can be effectively used in the range of catalytic processes including cracking and isomerization of hydrocarbons. Additionally, selected examples of the diffusional reactions with mesoporous zeolite single crystal catalysts are presented.

## Materials and Methods

The mesoporous ZSM-12-type single crystal material with Si/Al=50 was synthesized using a new improved procedure for directly introducing carbon into the reaction mixture. Conventional ZSM-12-type zeolite with Si/Al=50 was prepared by the standard procedure [6] All samples were characterized by XRD, SEM, TEM and adsorption measurements, and tested in the reaction of isomerization and cracking of *n*-hexadecane.

## Results and Discussion

A series of mesoporous and conventional HZSM-12 catalysts with Si/Al=50 were prepared using improved synthesis procedure and tested in the reaction of the cracking and isomerization of the long chain alkane, *n*-hexadecane. In Table 1, the catalyst performances in terms of conversion of *n*-hexadecane are listed.

**Table 1. Catalyst performance in *n*-hexadecane conversion**

Catalyst	Si/Al ratio	Reaction time [h]	Conversion [%]
ZSM-12 meso	50	1.5	9
ZSM-12 conv	50	1.5	4
ZSM-12 meso	50	2.5	16
ZSM-12 conv	50	2.5	8
ZSM-12 meso	50	9	69
ZSM-12 conv	50	9	46
ZSM-12 meso	50	18	69
ZSM-12 conv	50	18	52

In the catalytic conversion of *n*-hexadecane, the mesoporous HZSM-12 is far more active than the conventional HZSM-12 zeolites. Obviously, there is an effect of the presence of mesopores in the catalyst, which can be attributed to a considerably shorter diffusion path within the zeolite crystal than in the case of conventional zeolite catalysts. This is particularly important for reactions that involve reactants as large as *n*-hexadecane. Additional studies of the diffusion of *n*-hexadecane in conventional and mesoporous materials have confirmed the results of the catalytic experiments.

## Significance

The results of this study show the significantly higher conversions of the mesoporous catalysts, which can be explained by the considerably improved mass transport within the zeolite crystal than in the case of the conventional zeolite catalysts.

## References

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