

Mesoporous Zeolites as Hydrocarbon Cracking Catalyst

Thomas J. Pinnavaia* and Hui Wang

Department of Chemistry, Michigan State University, East Lansing, MI 48824(USA)

* pinnavaia@chemistry.msu.edu

Introduction

Zeolites are crystalline aluminosilicates that are widely used in many commercial catalytic processes such as crude oil refining. Due to the change of oil quality and demand for high yields, zeolite catalysts with potentially enhanced mass transportation rates are of current interest. Efforts to increase transport rates include expanding the micropore diameter of the zeolite framework, [1] synthesizing zeolite nanoparticles, [2] and introducing intracrystal mesopores within zeolite crystals [3]. Moreover, studies have shown that aluminosilicate catalysts with uniform small mesopores provided shape-selectivity in large molecule cracking in favor of larger cracked products [4].

Organosilanes have been successfully used in zeolite synthesis to modify crystal size. Nano-sized zeolite can be synthesized using short-chain organosilane, [5] while long-chain organosilane can be used to template uniform mesopores within zeolite crystals [3]. In this report, we use a polymer as the mesoporegen in zeolite synthesis. In order to prevent the polymer from being separated from zeolite phase, the polymer was silylated to be chemically compatible with silica surface of zeolite. In comparison to carbon-templating methods, small and uniform mesopores can be generated through this molecular templating pathway. Upon calcination, intracrystal mesopore can be recovered.

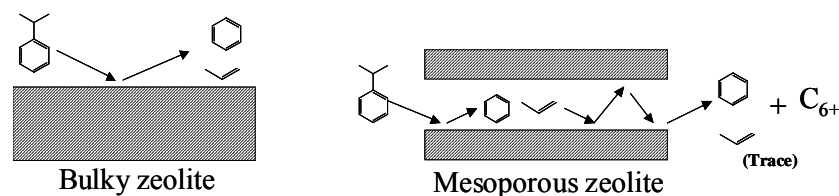
Materials and Methods

Mesoporegen was synthesized by reacting polyethylenimine (PEI) with (3-glycidioxypropyl)-trimethoxysilane (GPTMS) at 80~100°C overnight in ethanol. The molar ratio of N-H in PEI to silane ranges from 1:1 to 5:1. After the removal of solvent, the mesoporegen was dissolved in tetrapropylammonium hydroxide (TPAOH) solution, followed by tetraethylorthosilicate (TEOS) and aluminum tri-sec-butoxide. A typical molar composition of final reaction mixture was 1Al₂O₃: 100 SiO₂: 37 TPAOH: 2000 H₂O: 50 Et: 10 GPTMS. The mixture was put into a Teflon-lined autoclave and heated to 150°C for 3 days. The solid product was recovered by filtration, washing, and drying at 80°C. The product was calcined at 600°C for 4 hours to remove TPAOH and mesoporegen. The final product was denoted as MSU-MFI.

Cumene cracking reactions were performed in a 6 mm i.d. fixed bed quartz reactor with 200 mg catalyst at 200°C. Prior to catalytic testing, the catalysts were ion-exchanged twice with 0.50 M NH₄NO₃ solution followed by calcination at 550°C for 4 hours. The cumene flow rate was 4.1 μmol/min in a 20 cm³/min carrier stream of N₂.

Results and Discussion

In comparison to conventional ZSM-5, MSU-MFI possesses uniform 3 nm intracrystal mesopores, as judged by TEM and N₂ adsorption-desorption isotherms [6]. In addition, the external surface area also is increased substantially. The enhanced mass transport properties of MSU-MFI greatly improves catalytic performance for cumene cracking reaction. Compared to commercial ZSM-5, which has a maximum cumene conversion of 25%, MSU-MFI under equivalent reaction conditions exhibited a maximum cumene conversion of 65%, a 2.6-fold increase. Moreover, the maximum cumene conversion was achieved in a greatly reduced time-on-stream, indicative of enhanced access to reactive sites in the zeolite. Moreover, the product distribution results showed substantial differences. When commercial ZSM-5 was used as catalyst, the molar ratio of benzene to propylene is equal to 1.0, indicative of clean cracking of cumene. However, when MSU-MFI catalyst was used, a benzene/propylene molar ratio of 3 was observed. Scheme 1 shows the possible reaction pathway on different catalysts. On mesoporous zeolite catalyst, reaction products, especially propylene, would likely undergo secondary reaction to form heavier hydrocarbon before escaping from catalyst.



Scheme 1. Cumene cracking on bulk and mesoporous zeolites.

Significance

The presence of small intracrystal mesopores in zeolites is a promising approach to improving mass transfer rates for more efficient catalytic cracking, as well as providing an approach to mediating the distribution of the reaction products.

References

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