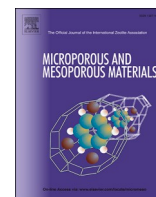




Contents lists available at ScienceDirect

## Microporous and Mesoporous Materials

journal homepage: <http://www.elsevier.com/locate/micromeso>

## Mesopore-selective incorporation of strong Brønsted acid catalytic sites via aluminium grafting on hierarchically porous siliceous MFI zeolite

Wookdong Kim<sup>a</sup>, Jeong-Chul Kim<sup>a</sup>, Seungjun Lee<sup>a,b</sup>, Jaeheon Kim<sup>a,\*</sup>, Ryong Ryoo<sup>a,b,\*\*</sup><sup>a</sup> Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon, 34141, Republic of Korea<sup>b</sup> Department of Chemistry, KAIST, Daejeon, 34141, Republic of Korea

## ARTICLE INFO

## Keywords:

Hierarchical zeolites  
Post-synthetic method  
Aluminum grafting  
External acid sites

## ABSTRACT

Post-synthetic Al grafting onto the surface silanols in mesoporous MFI zeolite has been investigated in an attempt to obtain a model catalytic material that possesses strong Brønsted acid sites at mesopore surfaces of the zeolite, but not inside the microporous framework. To this end, a siliceous MFI zeolite with a mesopore/micropore hierarchy was synthesized using a meso-micro dual structure-directing diammonium surfactant. The hierarchically porous zeolite was treated with anhydrous  $\text{AlCl}_3$  for the formation of Si–O–Al bonding with silanols on the mesopore surfaces. According to solid-state  $^{31}\text{P}$  NMR spectroscopy of the surface-adsorbed phosphine oxides and catalytic activity for decalin cracking, the Al-grafting treatment performed in the conventional manner resulted in the formation of weak Brønsted acid sites, similar to Al grafting on SBA-15 mesoporous silica. To obtain strong Brønsted acid sites, we have developed a method of heating the  $\text{AlCl}_3$ -grafted zeolite in a controlled-humidity chamber before calcination. The resultant zeolite was catalytically active for cracking of hydrocarbons requiring strong acid sites, but not for methanol-to-hydrocarbon conversion. The results support that the moisture treatment caused a local reconstruction of the initially grafted Al–O–Si framework portion to a strong Brønsted acid site. In addition, our model catalytic zeolite material unveiled the catalytic activity of Brønsted acid sites at the mesopore surfaces in hierarchically porous zeolite in *n*-octane cracking. Furthermore, we confirmed that this method was effective for other mesoporous MFI zeolites obtained through a post-synthetic desilication route.

## 1. Introduction

Zeolites are widely used as heterogeneous acid catalysts in the petrochemical industry, due to strong Brønsted acid (BA) Al sites incorporated in the highly microporous crystalline aluminosilicate frameworks [1–5]. Conventional synthetic zeolites are obtained in a fine powdery form, consisting of micro-sized particles. Each axis of a zeolite crystal consists of many hundreds to thousands of micropores. The micro-sized particles have many times higher surface areas in their internal micropores compared to the external surface areas [6]. For this reason, conventional zeolites are often referred to as bulk crystalline zeolites, or simply, bulk zeolites. Normally, BA Al sites exist both in the internal framework and on the external surfaces [4,6]. The zeolite acid sites can catalyze chemical reactions, as long as the acid strength is high enough to cause reactions, and these sites are accessible for the diffusion of reactants and products. Catalytic reactions occurring at the external

surfaces are usually negligible in the case of bulk zeolites. Therefore, zeolite catalysis with bulk zeolites is based on chemical reactions taking place in the internal micropores.

In recent years, zeolites with a mesopore/micropore hierarchy have gained increasing attention in the catalysis field. Such zeolites are often called ‘hierarchically porous zeolites’ or simply ‘hierarchical zeolites’ [7]. Hierarchical zeolites can have intracrystalline mesopores that penetrate the micro-sized zeolite particles, or intercrystalline mesopores built with agglomeration of zeolite nanocrystals, depending on the synthesis gel composition and procedure. The hierarchical zeolites possess a large area of mesopore surface, which is the external surface of microporous materials. As a result, a considerable number of BA Al sites exists on the mesopore surface (i.e., external surface) in the hierarchical zeolites, in contrast to the case of ordinary bulk zeolites [8,9]. The BA Al sites at the mesopore surface are readily accessible and strong enough to catalyze chemical reactions involving bulky molecules that cannot

\* Corresponding author. Center for Nanomaterials and Chemical Reactions, Institute for Basic Science, Daejeon, 34141, Republic of Korea.

\*\* Corresponding author. Department of Chemistry, KAIST, Daejeon, 34141, Republic of Korea.

E-mail addresses: [japuny@kaist.ac.kr](mailto:japuny@kaist.ac.kr) (J. Kim), [roryoo@kaist.ac.kr](mailto:roryoo@kaist.ac.kr) (R. Ryoo).