INVESTIGATION OF THE ACTIVE SITE AND KINETICS ON LEWIS ACIDIC ZEOLITES FOR THE PRODUCTION OF P-XYLENE FROM BIOMASS-DERIVED 2,5-DIMETHYLFURAN AND ETHYLENE

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Abstract

Framework-substituted Lewis acid zeolites (e.g. Sn,Ti,Zr-BEA), have been shown to catalyze the production of *p*-xylene from 2,5-dimethylfuran (DMF) and ethylene. Three-layer ONIOM models of zeolites have been used to calculate adsorption strengths and reaction barriers and parameterize a microkinetic model (MKM) to investigate three potential active sites in these framework-substituted zeolites: a "Closed" system with a metal-atom tetrahedrally substituted for a Si-atom and an "Open" system where the metal-atom is hydrolyzed by water to form active sites at the metal-atom center and at OH groups that are formed. Reaction path analysis with the MKM supports the metal-atom center in the "Open" system as the most active for the dehydration of oxanorbornene to *p*-xylene.

Keywords

Biomass, DMF, Aromatic, Framework-Substituted Zeolites, Lewis Acid, ONIOM, Microkinetic Model

Introduction

Aromatics are high volume chemicals used in the production of plastics and foams, largely produced from the naphtha portion of crude oil (Pellegrino, 2000). A market for biomass-derived aromatics has been established by a variety of industrial consumers (Collias et al., 2014).

The reaction of biomass-derived 2,5-dimethylfuran (DMF) and ethylene to produce *p*-xylene over solid acid catalysts has resulted in yields as high as 90% (Chang et. al, 2014). Studies of the reaction support a two-step mechanism, whereby DMF and ethylene undergo Diels-Alder cycloaddition to form an oxanorbornene intermediate which subsequently dehydrates to form *p*-xylene with the release of water (Nikbin et al., 2013). Ion-exchanged Brønsted acidic zeolites have been shown to effectively lower the dehydration reaction barrier while having negligible effect on the Diels-Alder reaction barrier to facilitate the production of *p*-xylene (Patet et al., 2015a). Investigation of the related ion-exchanged Lewis acidic

zeolites revealed that the dehydration reaction barrier was lowered to a lesser extent than in the Brønsted acidic zeolites and was too high for the production of *p*-xylene (Nikbin et al., 2014).

Recent experimental studies have revealed that framework-substituted Lewis acid zeolites (e.g. Sn,Ti,Zr-BEA) *are* able to catalyze the production of *p*-xylene (Chang et al., 2015). In this work, ONIOM models have been used to investigate the structure and properties of the active sites in these framework-substituted Lewis acid zeolites and how they differ from their ion-exchanged counterparts. Adsorption energies and reaction barriers are calculated and used to parameterize a microkinetic model (MKM) of the system, supporting a metal-atom center which has been hydrolyzed by water as the active site for the catalysis of the dehydration reaction.

Results and Discussion

Three active sites have been investigated for their effects on the Diels-Alder and dehydration reaction barriers. In a "Closed" system, a metal-atom (e.g. Sn, Ti, Zr) replaces a Si-atom in the zeolite framework with the metal-atom center (M) examined as the active site. In an "Open" system, the metal-atom is hydrolyzed by water, so that one of the M-O-Si bonds in the framework becomes a di-bridging $M-(OH)_2-Si$ structure. In this "Open" system, the metal-atom center and the di-bridging OH groups are investigated as potential active sites.

Investigation of the Diels-Alder cycloaddition reaction on all three active sites revealed a negligible effect by the catalysts on the reaction barrier, independent of the chosen active site. Investigation of oxanorbornene dehydration showed differences in the active sites, as seen in *Table 1*. At reaction conditions, adsorption on the "Closed" system is not favored and the reaction barrier remains high. In the "Open" system, adsorption onto the OH group is strongest, but again the dehydration reaction barrier remains high. Adsorption on the metal-atom center in the "Open" system is less favorable than on the OH site, but the dehydration reaction barrier has been lowered by ~7 kcal/mol.

Table 1. Calculated energies in Sn-BEA

Property	System	$\Delta G_{250°C, 37atm}$ (kcal/mol)
Oxanorbornene Adsorption	"Closed" M	3.1
	"Open" M	-3.6
	"Open" OH	-9.3
Dehydration Reaction Barrier	"Closed" M	27.5
	"Open" M	21.0
	"Open" OH	27.9

Analysis of the system using an MKM provides insight into how the calculated energetics affect the system at the reactor-scale. The production of *p*-xylene catalyzed by the Lewis acid zeolites is supported by the MKM and agrees with the experimental results (Chang et al., 2015). Reaction path analysis with the MKM supports the metal atom center in the "Open" system as the most active for oxanorbornene dehydration. Investigation of the Ti-BEA and Zr-BEA systems follow the same trends as Sn-BEA.

Conclusions

Three possible active sites in framework-substituted Lewis acid zeolites have been investigated for their abilities to catalyze the Diels-Alder reaction of DMF and ethylene and subsequent dehydration to form *p*-xylene using ONIOM models of zeolites. An MKM is used to assess the activity of these catalysts, revealing that metal atom centers which have been hydrolyzed by water to form an "Open" catalytic system are the most active for dehydration of oxanorbornene to *p*-xylene.

Methodology

A three-layer ONIOM model of the framework-substituted zeolites has been constructed and implemented in Gaussian 09 and used to calculate relevant adsorption strengths and reaction barriers (Patet et al., 2015b). A microkinetic model parameterized by the ONIOM model calculations was constructed and implemented in Matlab (MATLAB, 2012).

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