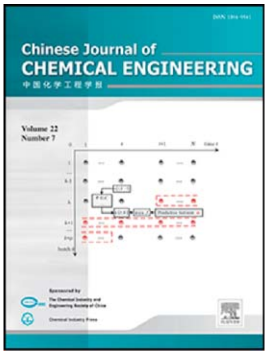

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Catalysis, kinetics and reaction engineering

Benzene Alkylation with Methanol over Phosphate Modified Hierarchical Porous ZSM-5 with Tailored Acidity☆

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ABSTRACT

The acidity and acid distribution of hierarchical porous ZSM-5 was tailored *via* phosphate modification. The catalytic results showed that both benzene conversion and selectivity of toluene and xylene increased with the presence of appropriate amount of phosphorus. Meanwhile, side reactions such as methanol to olefins related with the formation of by-product ethylbenzene formation and isomerization of xylene to meta-xylene were suppressed efficiently. The acid strength and sites amount of Brönsted acid of the catalyst were crucial for improving benzene conversion and yield of xylene, whereas passivation of external surface acid sites played an important role in breaking thermodynamic equilibrium distribution of xylene isomers.

1. Introduction

Xylene is an important chemical material and widely used in producing phthalate plasticizers, polyethylene terephthalate and polybutylene terephthalate. Now instead of the traditional petroleum-based catalytic reformation or naphtha pyrolysis, the alkylation of benzene with methanol over ZSM-5 is a potential way in xylene production [1]. However, the products distribution of benzene alkylation with methanol is complicated, the coke and by-product ethylbenzene from side reaction methanol to olefins are still a great challenge due to the acidity of the catalyst [2]. Moreover, the selectivity of unwanted meta-xylene is limited by the thermodynamic equilibrium distribution of three xylene isomers because of the isomerization on the external acid sites of the zeolite [3-5]. In our previous work, the alkylation of benzene was rationally regulated by decreasing of Brönsted acid sites *via* converted Brönsted acid sites into Lewis acid sites or increasing the Si/Al ratio of hierarchical porous ZSM-5 [2, 6]. However, the effect of the strength of the Brönsted acid sites on the catalytic performance of hierarchical porous ZSM-5 for catalyzing benzene alkylation with methanol is still unexplored. Literatures reported that the strong Brönsted acid sites of the ZSM-5 zeolite could be converted into weaker Brönsted acid sites when ZSM-5 zeolite was treated with phosphoric acid [7-9]. Moreover, the introduction of phosphorus passivated the external surface acid sites and narrowed the pore size, which in turn inhibited the isomerization of xylene [10-12]. Therefore, we conclude that both the acidity and acid sites distribution of hierarchical porous ZSM-5 can be tailored *via* phosphate modification, the catalytic performance was expected to be improved, and the thermodynamic equilibrium distribution of xylene isomers would be broken down at the same time.

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