



High Zn/Al ratios enhance dehydrogenation vs hydrogen transfer reactions of Zn-ZSM-5 catalytic systems in methanol conversion to aromatics



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ABSTRACT

Two series of Zn-ZSM-5 catalysts were prepared by ion exchanging two commercial zeolites with different Si/Al ratios (40 and 15) with increasing Zn loadings. The nature of the Zn sites in the zeolite was studied by spectroscopy using laboratory and synchrotron techniques. All the evidences suggest that catalytic activity is associated with $[\text{Zn}(\text{H}_2\text{O})_n(\text{OH})]^+$ species located in the exchange positions of the materials with little or no contribution of ZnO or metallic Zn. The effect of Zn/Al ratio on their catalytic performance in methanol conversion to aromatics has been investigated. In all cases, higher Zn content causes an increase in the yield of aromatics while keeping the production of alkanes low. For similar Zn contents, high densities of Al sites favour the hydrogen transfer reactions and alkane formation whereas in samples with low Al contents, and thus higher Zn/Al ratio, the dehydrogenation reactions in which molecular hydrogen is released are favoured.

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1. Introduction

Light aromatic hydrocarbons, such as benzene, toluene and xylenes (BTX) are important intermediates in the petrochemical industry. They are commonly used as solvents and for the production of high-value secondary products such as plastics, paints, cosmetics or pharmaceuticals. BTX are traditionally obtained from naphtha via catalytic reforming or steam cracking with a global production in the range of 100 million metric tons per year that

is projected to grow at a rate of 3.5–4% in the next five years [1]. The increase in the global demand of aromatics together with the notion of finite crude oil reserves and the consequential necessity to implement an oil-independent economy makes it crucial to develop alternative processes for the production of BTX from non-petroleum sources. In this context, the possibility to directly convert methanol into aromatics (MTA) over zeolitic catalysts, that was described already 25 years ago [2,3], is attracting a renewed interest from both industrial and academic researchers.

The methanol to aromatics reaction (MTA) falls into the general group of the so-called methanol to hydrocarbons (MTH) transformations, which allow obtaining fuels and chemicals avoiding the use of petroleum. MTH reactions have been widely investigated since their discovery by Mobil in 1976 [4]. The discovery attracted great attention due to the versatility of the process and the availability of methanol from rather abundant and diverse sources, such as coal and natural gas [5,6], biomass or even CO₂ [7,8]. The MTH process involves multiple reaction steps within a quite complex

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