Journal of Catalysis 362 (2018) 146–163

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

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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ARTICLE INFO

Article history:
Received 5 December 2017
Revised 19 March 2018
Accepted 28 March 2018
Available online 22 April 2018

Keywords:
Zn-ZSM-5
Methanol to aromatics
Acidity
Zn sites
Ion exchange

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 $[Zn(H_2O)_n(OH)]^+$ 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.

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 CO_2 [7,8]. The MTH process involves multiple reaction steps within a quite complex

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https://doi.org/10.1016/j.jcat.2018.03.032

mechanism, which has been intensively studied for decades [9–14]. Today, the dual cycle hydrocarbon pool mechanism is generally accepted [11]. According to this mechanism, the process is an autocatalytic reaction in which both alkene and aromatic molecules act as intermediates in two inter-related cycles involving many reactions such as methylation, cracking, hydride transfer, cyclization and dealkylation. Eventually, the reaction between the hydrocarbon intermediates and methanol molecules or the combination of hydrocarbons can lead to the formation of molecules that are too large to be able to diffuse through the zeolite pores and remain trapped within the framework, evolving to form carbonaceous deposits that are the responsible for the deactivation of the catalyst [15–20].

Initially, MTH technology was considered as a powerful alternative to oil-based routes for the production of gasoline compatible with the existing infrastructure. However, further investigations revealed that it is possible to selectively obtain practically any kind of hydrocarbons, including gasoline (MTG) light olefins (MTO), propylene (MTP) or aromatics (MTA), by modifying the catalysts and adjusting the operation conditions [21,22]. Aromatization involves cyclization and hydrogen transfer reactions catalyzed by the Brønsted acid sites of the zeolite [11,22,23]. Olefins act as hydrogen acceptors in the bimolecular hydrogen transfer reaction, forming alkanes as hydrogen rich byproducts. In the case of MTA, the zeolite used as catalyst is partially doped with transition metals, forming a bifunctional system with Brønsted and Lewis acid sites from the zeolite and new metal Lewis sites. The goal of the incorporation of transition metals is to favour the aromatization reactions via additional dehydrogenation functionality. Recently, it has been reported that the hydrogen transfer may also be induced by methanol rather than by olefins, and not just Brønsted but also Lewis sites of the zeolite are proposed to be involved in the hydrogen transfer reactions for the formation of aromatics (and alkanes) [24]. This mechanism involves the presence of oxygenate intermediates such as formaldehyde. When transition metal ions are incorporated in the zeolitic catalyst, a new possibility appears, and the aromatization can take place at the metal Lewis acid sites by dehydrogenation instead of hydrogen transfer, thus forming molecular hydrogen as byproduct and keeping the production of alkanes low. This is interesting, first, because it means that a higher proportion of the carbon atoms from the reactants would be tuned into highly demanded products and, second, because of the intrinsic value of H_2 as byproduct.

Several combinations of zeolites and transition metals have been investigated as MTA catalysts, with ZSM-5 being one of the most interesting topology in terms of stability and selectivity for the process, and Zn the metal that provides the highest yield of BTX products [3,25–28]. A full picture of the interplay between acid sites and metal sites is still missing, but it is known that the location of the metal sites (on the external crystal surface or within the micropores) and the nature of the sites formed have a great influence in the catalytic performance of the final material [28–32]. While only few contributions report the stabilization of unusual Zn^+ species in the zeolitic system [33], metallic Zn, ZnO agglomerates or other Zn^{2+} species are generally proposed as the possible Zn sites formed in the zeolite. According to this proposal, two relatively close Al sites, and hence a quite low Si/Al ratio, would be needed to stabilize the two positive charges of the exchanged cation. However, to compensate the negative charge generated by the presence of an isolated Al^{3+} in the inorganic framework, Zn^{2+} cations can also be incorporated as $\mathbf{Z}[Zn^{2+}(OH)^-]^+$ species [34], where **Z** indicates coordination to framework oxygens (O_{fw}) in the proximity of one framework aluminium (Al_{fw}) site. Again, depending on the elemental composition and the spatial distribution in the zeolite, such hydroxylated species are expected to undergo dehydration reactions at high temperature, and evolve into new Zn^{2+} species [31]. In samples with low Zn content and low Si/Al ratio, monomeric $\mathbf{Z}_2Zn^{2+}$ species are expected. On the other hand, at higher Zn loadings and intermediate Si/Al ratio, two **Z**[Zn(OH)] species (with each Zn cation interacting with one Al site) might be able to form oxygen bridged Zn-O-Zn species.

Not surprisingly, the nature of the Zn sites strongly depends on the distribution of Al sites in the zeolite and hence on the exact preparation method [28,35,36]. Among the different proposed methods to incorporate Zn in the parent zeolite, ion exchange generally provides higher ratio of active cationic species promoting aromatization and dehydrogenation reactions [28]. It is important to note that the incorporation of Zn ions in the exchange positions effectively reduces the amount of Brønsted acid centers, which are also required in order to form the olefins that can undergo cyclization and aromatization reactions. An optimum elemental composition for high aromatization yields should therefore balance the amounts and nature of Zn species with respect to the Brønsted acid centers in the bifunctional material.

In this contribution, we aim to study exactly this balance between acid site distribution and Zn content and its effect on the aromatization activity of HZSM-5 zeolites. For this purpose, samples with increasing Zn loadings have been produced by ion exchange of two parent HZSM-5 zeolites with different Si/Al ratios. In addition to detailed catalytic testing, the samples were characterized by X-ray diffraction (XRD) and N_2-sorption in order to confirm their structural integrity and the accessibility of the micropores. Pyridine adsorption followed by transmission Fourier transform infrared (FTIR) spectroscopy [37] was applied to obtain information on the amount and distribution of acid sites and a combination of in situ and *operando* X-ray absorption spectroscopy (XAS) techniques [38] were used to characterize the nature of the Zn species formed during activation and MTA reaction. We show that, even though high yields of aromatics can be achieved over pure zeolites with a high density of Brønsted acid sites, the presence of Zn at relatively high Si/Al ratio allows to force the aromatics formation mainly via the dehydrogenation pathway.

2. Experimental

2.1. Preparation of the catalysts

Two commercial ZSM-5 samples were used as raw materials: CBV-3024E (Si/Al = 15) and CBV-8014 (Si/Al = 40) obtained from Zeolyst International. Both samples were ion-exchanged, first with a NH_4NO_3 solution (98%) to have them in their ammonium form and, subsequently with excess of $Zn(NO_3)_2{\cdot}6H_2O$ (36.6 g in 1000 ml demineralised-H_2O), one, two or three times, respectively, at 80 °C for one hour in order to produce a set of 8 samples with different acidity and Zn loadings. After each exchange, the samples were filtered and washed with water at 80 °C and dried at 110 °C overnight. In a last step, the materials were calcined at 450 °C for 2 h. Details on the composition of the samples are collected in Table 1.

Parent samples are named as Si/AlX-P, where "X" indicates the Si/Al ratio of each material, and exchanged materials are named as: Si/AlX-YZn, with "Y" denoting the number of Zn-exchanges.

2.2. Catalysts characterization

2.2.1. Laboratory characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded using a Siemens Bruker D5000 instrument with Bragg-Brentano geometry and CuKα radiation (λ = 1.5406). Samples were measured using flat sample holders loaded with 25 mg of powder. The chemical composition of the samples (Si, Al and Zn content)