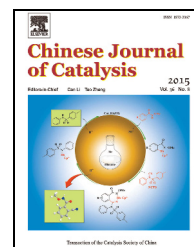


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Article

Methanol to hydrocarbons reaction over HZSM-22 and SAPO-11: Effect of catalyst acid strength on reaction and deactivation mechanism



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ABSTRACT

The conversion of methanol to hydrocarbons has been investigated over HZSM-22 and SAPO-11. Both of these catalysts possess one-dimensional 10-ring channels, but have different acidic strengths. Comparison studies and ¹²C/¹³C isotopic switching experiments were conducted to evaluate the influence of the acidic strength of the catalyst on the conversion of methanol, as well as its deactivation mechanism. Although the conversion of methanol proceeded via an alkene methylation-cracking pathway over both catalysts, the acidity of the catalysts had a significant impact on the conversion and product distribution of these reactions. The stability of the catalysts varied with temperature. The catalysts were deactivated at high temperature by the deposition of graphitic coke on their outer surface. Deactivation also occurred at low temperatures a result that the pores of the catalyst were blocked by polyaromatic compounds. The co-reaction of ¹³C-methanol and ¹²C-1-butene confirmed the importance of the acidity of the catalyst on the distribution of the hydrocarbon products.

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1. Introduction

Light alkenes and liquid hydrocarbon fuels are important petrochemical commodities, and the majority of the compounds belonging to these groups are produced through petrochemical reactions. Dwindling oil supplies and the rapidly

increasing demand for fuels and light alkenes have stimulated significant research efforts towards the development of new processes for the production of these petrochemical products from alternative and abundant resources, such as biomass, coal and natural gas [1,2]. Among these non-petrochemical routes, the methanol-to-hydrocarbon (MTH) route has become a suc-

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successful commercial process [2–4]. Furthermore, a wide range of different zeolites have been investigated as catalysts for the MTH reaction during the past decades [2,3,5], including ZSM-5 and SAPO-34, which are believed to be the most effective catalysts for this process. These catalysts have also been applied to a variety of commercial processes, including methanol-to-olefin (MTO) [4,6], methanol-to-propene (MTP) [7] and methanol-to-gasoline (MTG) [8–10] processes.

Considerable research efforts have also been devoted to developing a deeper understanding of the mechanism of the MTH reaction. The results of previous investigations have shown that the detailed mechanism of the MTH reaction is very complicated and strongly dependent on the topology of the zeolite catalyst. For example, SAPO-34, which consists of large supercages and small 8-ring windows, is currently regarded as the best catalyst for MTO reactions [4,11]. It is noteworthy that the high level of selectivity exhibited by this catalyst for ethene and propene has been attributed to the hydrocarbon pool mechanism [12–14]. Furthermore, polymethylbenzene and polymethylcyclopentadiene, as well as their protonated analogues, have been reported to be important reactive intermediates for the production of alkenes [15–22]. The formation of these bulky intermediates was not only observed over SAPO-34 but was also detected in several other zeolites with wide or intersectional channels, such as H β [23], ZSM-5 [20], SSZ-13 [19] and DNL-6 [24,25]. In a separate study, Svelle et al. [26–28] conducted a series of $^{12}\text{C}/^{13}\text{C}$ -methanol labeling experiments over the medium pore acidic zeolite ZSM-5 to show that the generation of ethene occurred via an separated route, independent of the one responsible for the formation of C_3^+ alkenes. The authors went on to propose a dual-cycle mechanism for this transformation, which consists of an aromatic-based cycle with xylene/triMB as reactive intermediates for the production of ethene and a C_3^+ alkene-based cycle for the formation of propene and higher alkenes. Based on this mechanistic insight, there have been considerable researches about whether the conversion of methanol could run in an independent manner while suppressing the formation of ethene via an alkene cycle by carefully controlling the topology of the catalyst [26]. This assumption was recently validated over the one-dimensional 10-ring zeolite, HZSM-22, which produces hydrocarbons rich in C_5^+ branched alkenes and low in aromatics and ethene [29–32].

In addition to their topological characteristics, the acidic properties of zeolite catalysts can also have a significant impact on their performances for the conversion of methanol. This issue was first reported by Yuen et al. [33] over CHA and AFI catalysts. The results of this study revealed that the acidity of borosilicate sieves was too low to allow for the conversion of methanol to hydrocarbons, and that SAPO-34 displayed lower hydrogen transfer reactivity than SSZ-13. Most recently, Bleken et al. [34] reported the systematic comparison of SAPO-34 and SSZ-13 in the MTO reaction. The results showed that the more acidic SSZ-13 catalyst exhibited higher activity, which leads to a higher methanol conversion than that of the less acidic SAPO-34 catalyst under the same operating conditions. Westgård Erichsen et al. [35] also conducted a comparative study to

determine the effects of the acidic strength of the catalyst on MTO reactions over AFI and SAPO zeolite catalysts. The results showed that the use of a catalyst with a low acidic strength promoted the conversion of methanol via an alkene-mediated mechanism. Taken together, these results show that it is of critical importance to understand the detailed role played by the acidic properties of these catalysts in the formation of alkenes. Furthermore, the performance characteristics of these catalysts could be optimized by tuning their acidic properties, representing an alternative approach to the optimization of these processes, which should therefore be explored in greater detail.

In this study, we have used two one-dimensional 10-ring zeolites, HZSM-22 (TON, 0.46×0.57 nm) and SAPO-11 (AEL, 0.4×0.65 nm), to elucidate the role of their acidic strength on the MTH reaction and their deactivation mechanism.

2. Experimental

2.1. Catalyst preparation

The K-ZSM-22 and SAPO-11 catalysts were supplied by Group DNL0802 of the Dalian Institute of Chemical Physics, Dalian, China. After being calcined at 600 °C for 10 h to remove the organic template, K-ZSM-22 was converted to NH_4 -ZSM-22 by three ion-exchange processes in a NH_4NO_3 solution (1 mol/L) at 80 °C for 6 h. The resulting catalyst was then washed with deionized water, dried over night at 120 °C and calcined at 550 °C for 4 h to give protonated H-ZSM-22. The SAPO-11 sample was calcined at 550 °C for 4 h to give H-SAPO-11.

2.2. Catalyst characterization

The structural properties of two catalysts were characterized using a PANalytical X'Pert PRO X-ray diffraction (XRD) system with $\text{Cu } K\alpha$ radiation ($\lambda = 0.154059$ nm) at 40 kV and 40 mA. The chemical compositions of the catalysts were determined using a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The morphological characteristics of the catalysts were measured by field emission scanning electron microscopy (FE-SEM) on a Hitachi SU8020 system.

The N_2 physisorption isotherms of the samples were measured at -196 °C on a Micromeritics ASAP 2020 system. Fresh samples of the catalysts were degassed under vacuum at 90 °C for 1 h and then at 350 °C for 3 h before being analyzed. The surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) equation, and their micropore volumes were evaluated using the t -plot method.

The spent catalysts were collected and analyzed by thermogravimetric analysis (TGA) on a Q500 SDT thermogravimetric analyzer. In a typical measurement, a small sample (10–14 mg) of spent catalyst was heated in an Al_2O_3 crucible from ambient temperature to 900 °C at a heating rate of 10 °C/min under a stream of air at a constant flow rate of 100 ml/min.

The acidity of the catalysts was determined by the temperature programmed desorption of ammonia (NH_3 -TPD) on a Micromeritics AutoChem 2920 system. The samples were

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