Conversion of methanol to hydrocarbons over conventional and mesoporous H-ZSM-5 and H-Ga-MFI: Major differences in deactivation behavior

Uffe V. Mentzel, Karen T. Højholt, Martin S. Holm, Rasmus Fehrmann, Pablo Beato

Centre for Catalysis and Sustainable Chemistry, Technical University of Denmark, Anker Engelundsvej 1, DK-2800 Kgs. Lyngby, Denmark

A R T I C L E   I N F O

Article history:
Received 15 October 2011
Received in revised form 21 December 2011
Accepted 4 January 2012
Available online 12 January 2012

Keywords:
Zeolite
Gallium
Methanol-to-hydrocarbons (MTH)
Deactivation
Regeneration

A B S T R A C T

Methanol has been converted to hydrocarbons over conventional and mesoporous H-ZSM-5 and H-Ga-MFI. The gallium based zeotypes are analogous to H-ZSM-5, but the Brønsted acidity is introduced by framework incorporation of gallium rather than aluminum, which leads to lower intrinsic acid strength. In the methanol-to-hydrocarbons (MTH) process, H-ZSM-5 is subjected to coke formation leading to catalyst deactivation. Here we show that when the gallium containing zeotypes are employed in the MTH process, only insignificant amounts of coke are present in the deactivated catalysts, indicating distinct differences in deactivation mechanisms of the two different catalysts. This is investigated further through FT-IR measurements as well as catalytic experiments employing regenerated and steamed catalysts. From this it is concluded that the H-Ga-MFI is subjected to irreversible deactivation by steaming (hydrolysis) of the Ga-O bonds in the zeolite structure rather than coke deposition.

1. Introduction

In recent years there has been an increasing political and scientific focus on the depletion of world-wide oil deposits and the environmental impact of the massive usage of fossil resources. Development of alternative technologies is essential in order to meet the demands of the growing world population. The methanol-to-hydrocarbons (MTH) process [1] offers a plausible pathway for production of fuel grade hydrocarbons from alternative sources. Currently methanol is produced on a large scale from natural gas, but it can also be produced from biomass, which could lead to a more environmentally friendly process.

In the MTH process an acidic zeolite catalyst is employed to produce hydrocarbons such as alkanes, alkenes, and aromatics. Product selectivity in the MTH process is highly dependent on the specific characteristics of the employed zeolite, e.g. pore structure, acid strength, acid density, etc., and thus selectivity can be shifted in favor of production of alkenes (the methanol-to-olefins (MTO) process) or heavier compounds such as aromatics (the methanol-to-gasoline (MTG) process). The MTG process was commercialized in the 1980s in New Zealand by Mobil Oil but gasoline production was later shut down due to the situation in the global oil market [1]. The MTO process has been commercialized by UOP, while Lurgi has developed a more specialized MTP (methanol-to-propene) process [2]. The first MTP plant was established in China in 2010 and it has an annual production capacity of 500,000 ton [3].

In a zeolite catalyst acidic sites are created by incorporation of a trivalent metal ion into the microporous framework consisting of tetravalent silicon atoms bridged by oxygen atoms. In H-ZSM-5 this trivalent metal ion is aluminum but other elements such as boron, gallium or iron can also be employed [4,5] leading to zeotype materials. In this work we focus on the H-Ga-MFI zeotype, which is analogous to H-ZSM-5, but with gallium atoms incorporated in the zeolite framework instead of aluminum. Incorporation of gallium in the zeolite framework leads to a lower intrinsic acidity of the individual active sites in the zeolite compared to H-ZSM-5 [6] without compromising the zeolite structure significantly [7].

Several reports exist on conversion of methanol to hydrocarbons over H-Ga-MFI zeotypes [8–11] and typically a higher selectivity towards alkenes is observed compared to H-ZSM-5. The higher selectivity towards alkenes is due to the lower acid strength of the Brønsted sites leading to fewer secondary reactions that convert the alkenes to aromatics [11]. However, in some cases (especially at high gallium loadings), higher selectivity towards aromatics is observed, which is ascribed to dehydrogenation reactions due to the presence of extra-framework gallium species [6,10]. The fact