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Conversion of methanol into light olefins over ZSM-5 zeolite: Strategy to enhance propene selectivity

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ABSTRACT

Four ZSM-5 zeolite materials with varying crystal size, acid site density and morphology were prepared, characterized by BET, XRD, SEM, FT-IR, H/D exchange and n-hexane cracking experiments and tested as catalysts for the Methanol to Olefins (MTO) reaction at 350 °C, WHSV = 1.8 g/gh under atmospheric pressure.

Optimal propene to ethene ratios (>5) were obtained over a material prepared via the fluoride route. Its superior selectivity was tentatively ascribed to its low density of strong acid sites in combination with a long diffusion pathway and few crystal defects.

1. Introduction

The rational design of heterogeneous catalysts to optimize activity and selectivity in a targeted reaction often remains a key challenge in state-of-the-art catalysis research [1–3]. In this context, zeolites occupy a prominent place since they are used in numerous acid-catalyzed reactions [4,5].

Discovered in Mobil laboratories, the transformation of methanol-to-hydrocarbons (MTH) to make high-octane gasoline [6,7], represents a timely and valuable process involving zeolite catalysts. Indeed, the MTH technology has received considerable industrial interest [8–10]. For instance, the Mobil Oil methanol to gasoline (MTG) process [11], the Topsøe integrated gasoline synthesis (TIGAS) process [12], the Lurgi methanol to propene (MTP) process [13] and the Norsk Hydro/UOP's methanol to olefins (MTO) process [14], have either been commercialized or are ready for commercialization [15].

The MTO reaction is considered to be a valuable option for the valorization of stranded gas reserves, and therefore several studies devoted either to the reaction mechanism or to the technology were undertaken [16–23]. In addition, the increasing market worldwide demand toward ethylene and propylene is gradually raising and projected growth rates in coming decades are expected to remain high [24,25]. SAPO-34 silico-aluminophosphate, having the CHA structure, is recognized as a valuable catalyst to generate a high selectivity to light olefins due to its moderate acid strength and small pore opening [22]. However, a high rate of deactivation is usually observed for this kind of material due to the rapid coke deposition [26,27]. ZSM-5 zeolite catalysts are therefore often used despite usually lower olefin yield [28–31].

Several strategies targeted to achieve an increasing selectivity toward light olefins over these MFI catalysts have been tempted: modification of the reaction conditions, raising the steric constraints to increase shape selectivity, change in the reactor configuration [32], or proper tailoring of the Brønsted acidity (density and strength) [29,33]. Moreover, in order to limit/inhibit the consecutive formation of higher alkenes, alkanes and aromatics, the development of new catalyst design at the mesoscopic and macro-scale have also been explored [28–30]. Nevertheless, the preparation of such catalysts remains quite complex and costly.

During the past decade, the exploration of ethane-rich shale gas in the US has made ethane crackers economically favorable over naphta crackers, and led to the construction of ethane crackers as well as retrofitting of naphta crackers [34]. Naphta cracker co-products such as propene are therefore in increasingly short supply, and tuning of MTH selectivity toward propene production

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