



Hierarchical zeolites for methanol and dimethyl ether dehydration into light olefins

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Significance and Relevance

Light olefins have several applications in the chemical industry. To reduce their carbon footprint, they can be produced by dehydration of green methanol or dimethyl ether (DME), that can be synthesized exploiting green H₂ and captured CO₂ through a sustainable and carbon-neutral pathway. Our findings show that a hierarchical structure combined with a milder acidity mitigates the deactivation effects on dehydration catalysts. Thus, a catalyst with strong activity and stability enables more efficient processes, minimizing carbon loss during regeneration and boosting production rates.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport / CO₂ utilization and recycling.

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Light olefins, such as ethylene and propylene, are key components for the petrochemical industry. They are conventionally produced via steam cracking of petroleum hydrocarbons; however, light olefins can be alternatively produced via dehydration of methanol or dimethyl-ether (DME) according to the Methanol-to-Olefins (MTO) or the Dimethyl-ether-to-Olefins (DTO) routes¹. Both methanol and DME can be produced through CO₂ hydrogenation processes starting from green H₂ and captured CO₂.

The dehydration process is generally performed at 300 °C - 450 °C on an acid catalyst (e.g. zeolite); the most investigated materials are SAPO-34 and MFI zeolites. Hierarchical zeolites have recently attracted interest due to lower deactivation rates compared to conventional ones. Their large pores could prevent deactivation, that is commonly related to coke deposition and heavy hydrocarbons formation and may occlude narrow pores. In this work, four different hierarchical zeolites have been synthesized, characterized, and tested to investigate catalytic activity, product distributions and stability over time.

Materials and Methods

On the one hand, two MFI zeolites with a nominal Si/Al ratio of 25 and 50 were synthesized following the procedure reported by Catizzone et al.² The crystallization process was carried out at 170 °C for 4 days. Part of these zeolite samples was treated with NH₄⁺/HF solution at 25 °C for 6 min under stirring³. Then the product was repeatedly washed with distillate water, calcined at 550 °C for 8 hours, ion exchanged and calcined again to reach the H⁺-form. The samples were named ETC-25 and ETC-50.

On the other hand, two hierarchical zeolites with a theoretical Si/Al ratio of 25 and 50 were prepared via hydrothermal synthesis⁴. The solution was crystallized in a Teflon lined stainless-steel autoclave at 170 °C for 5 days. Thereafter, the precipitate was separated by means of a centrifuge and washed with water. The obtained sample was dried overnight at 60 °C and then calcined at 550 °C for 5 h. The two samples were labelled HZ-25 and HZ-50.

Both as-prepared and spent samples were characterized by means of several characterization techniques to investigate the crystalline structure, the textural properties and the acidity. In addition, the samples were tested in a fixed bed reactor to evaluate their catalytic performance. The gas was analyzed by using a gas chromatograph equipped with two columns and two detectors for hydrocarbon quantification. The DME conversion profiles were fitted with an Arrhenius-type 1st-order deactivation rate to find the parameters and correlate them to the variation of the material characteristics.

Results and Discussion

The N₂ physisorption of the as prepared samples showed a specific surface area greater than 340 m²/g for all samples and a bimodal distribution of the pores, meaning that mesopores were formed in hierarchical structures. In addition, the X-ray diffraction proved that all samples have MFI structure. The FT-IR measurements with D₃-acetonitrile as probe molecule showed that the total acidity of ETC-25 and HZ-25 is significantly higher than the acidity of ETC-50 and HZ-50.

Concerning the activity of the samples, Figure 1 presents a comparison of the catalytic performance of a non-hierarchical MFI-25 zeolite and two hierarchical samples (i.e., HZ-25 and ETC-25) tested at 375 °C. The conventional MFI-25 sample is extremely active in DME dehydration, but its performance dramatically dropped during the time on stream⁵. The deactivation was ascribed mainly to coke deposition and heavy hydrocarbons formation. Hierarchical zeolites were indeed less affected by deactivation, and particularly the HZ-25 exhibited a significantly stronger stability. On the contrary, its ethylene production diminished. This phenomenon was ascribed to the different shape and distribution of mesopores that allow larger molecules to diffuse from the particle to the bulk of the gas without trapping them within the inner porosities.

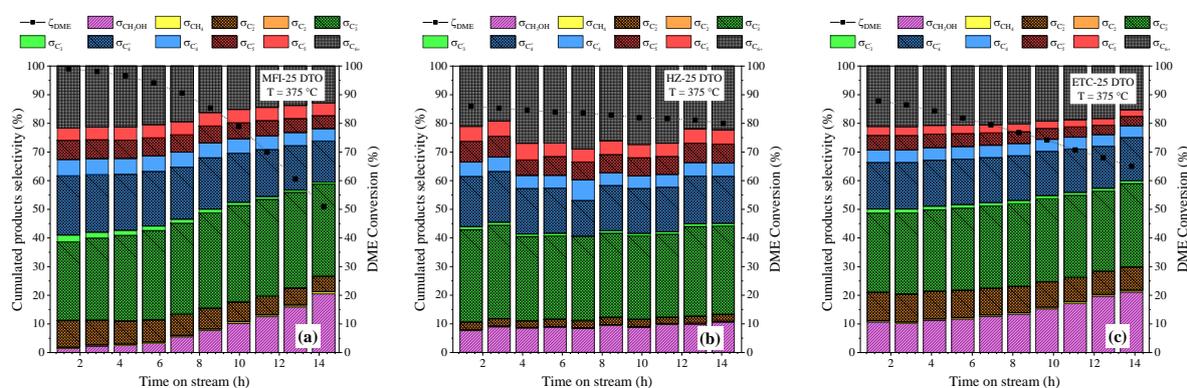


Figure 1. DME conversion and product distribution during DTO tests over time on stream at 400 NL/g/h, 2 bar, 375 °C and 3 vol.% DME/N₂ for (a) MFI-25, (b) HZ-25 and (c) ETC-25.

The acidity reduction (i.e., higher Si/Al ratio) of the MFI-type zeolites improved significantly the stability of the catalysts as summarized in Table 1. This means that the combination of a hierarchical structure and a milder acidity could enhance the total efficiency of the DTO process, reducing carbon losses during the regeneration process.

Table 1. Deactivation parameters of a 1st order deactivation rate for the hierarchical zeolites.

	HZ-25	ETC-25	HZ-50	ETC-50
$k_{d,\infty}$ (h ⁻¹)	$7.1 \cdot 10^1$	$2.6 \cdot 10^5$	$1.5 \cdot 10^{-1}$	1.9
$E_{A,d}$ (kJ mol ⁻¹)	46.3	83.3	17.2	28.5

References

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