Secondary porosity of ill-crystallized or desilicated ZSM-5 zeolites (MFI) and its performance in suppression of coke in the conversion of methanol to olefins and aromatics

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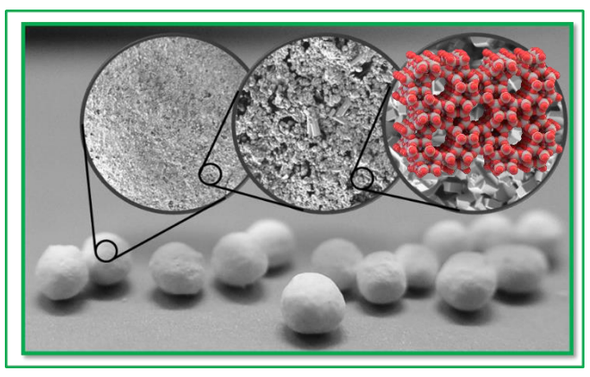
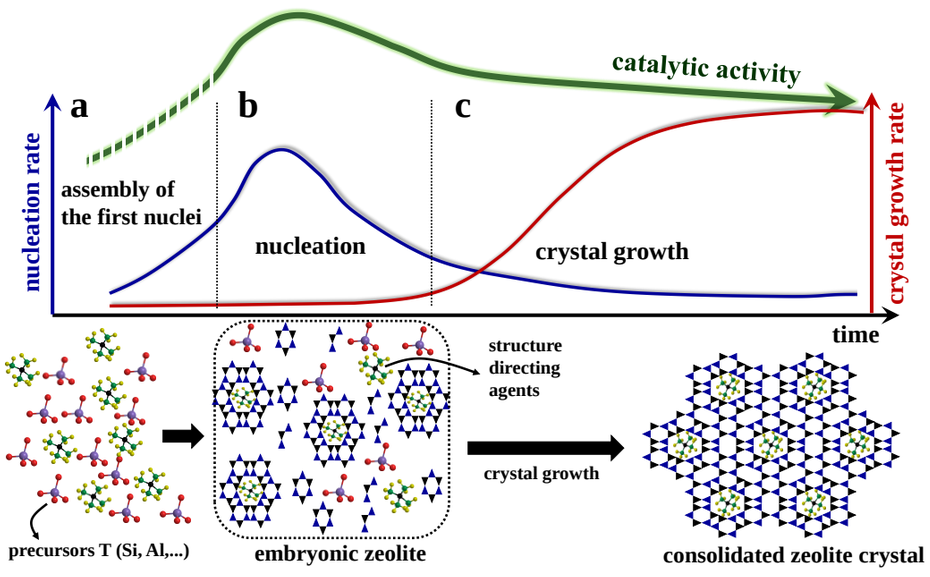
1. Introduction and aims



A few zeolite structures, such as CHA, MOR, and MFI, were studied as catalysts in the MTH reaction. The structural aspects of these catalysts, such as the size of pores and cavities, are essential for catalytic performance, primarily to determine the higher selectivity of olefins and aromatics. Despite the advances in the MTH reaction on zeolites, there is still a deficiency of knowledge on the influence of confinement effects and mesoporosity on the catalyst's performance.

2. Methods

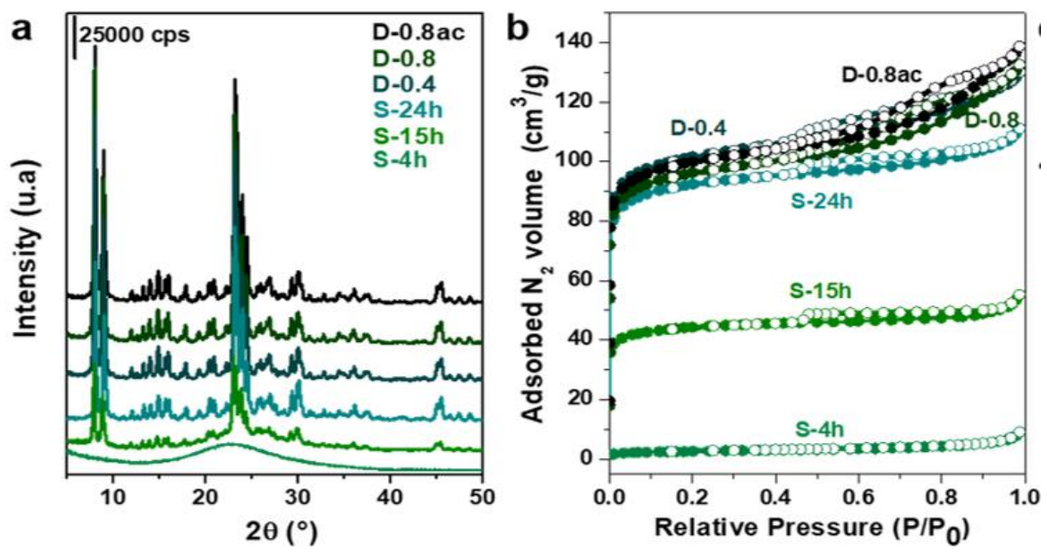
✓ Synthesis of the hierarchical catalysts



✓ Catalytic tests

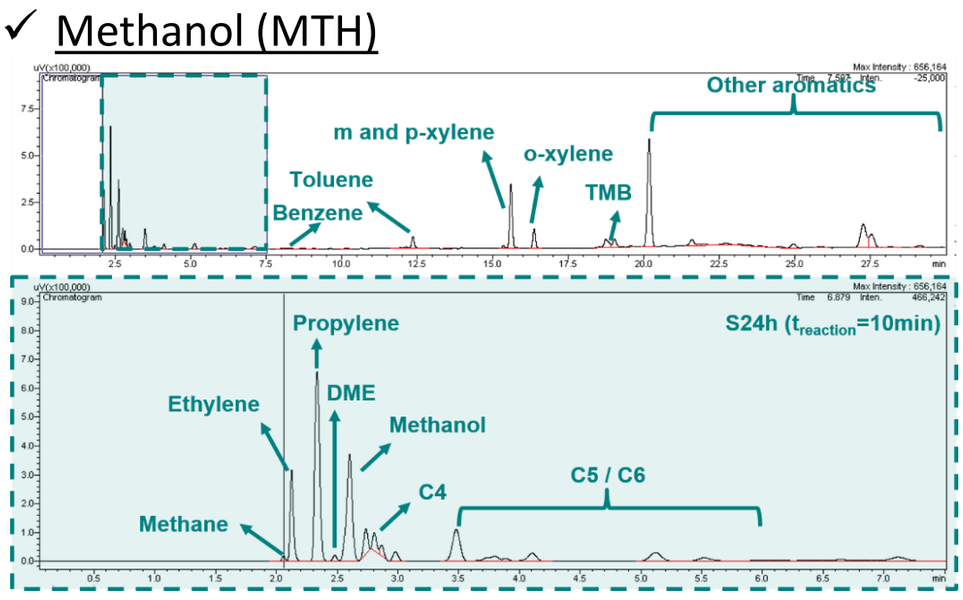
MTH reactions of H-form zeolites were carried out in the vapor phase in an automated Microactivity Reactor, at atmospheric pressure and 400 ◦C, for 28 h. 0.100 g of catalyst was used, and a flow of 0.1 mL/min of liquid methanol was fed through a high-pressure liquid chromatography HPLC pump.

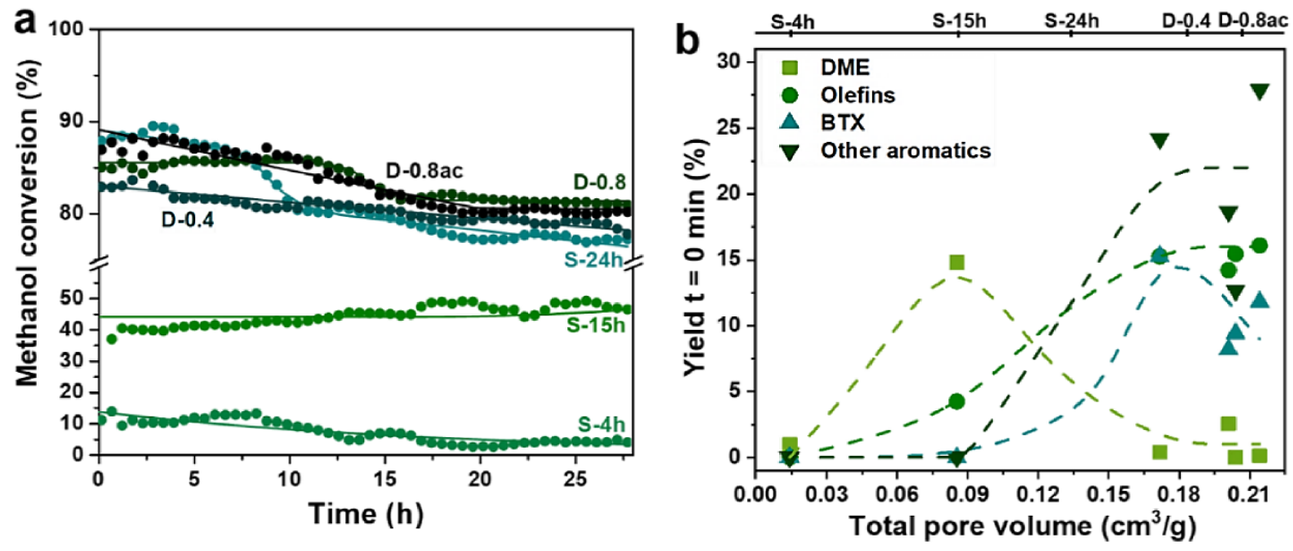
3. Results and discussion



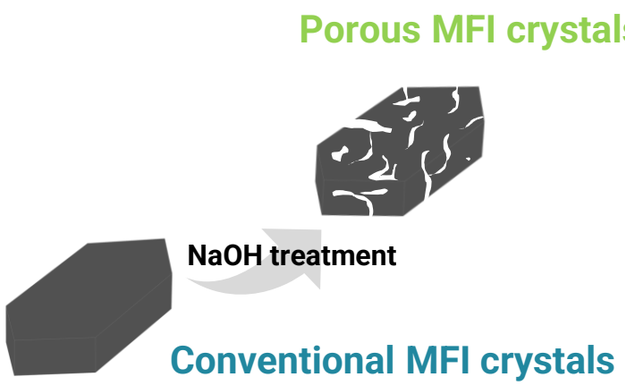
The samples with **different crystallinity degrees and porosity** S-4h, S15h, and S-24h, and hierarchical zeolites (D-0.4, D-0.8, and D-0.8ac), were assessed in the MTH reaction at 400 ◦C. The deactivation after 28 h was more significant for the purely microporous zeolite (12 %) due to the blocking of entering channels with the reaction evolution. The mesoporous catalysts had different selectivities for olefins, alkanes, and aromatics.

✓ Methanol (MTH)

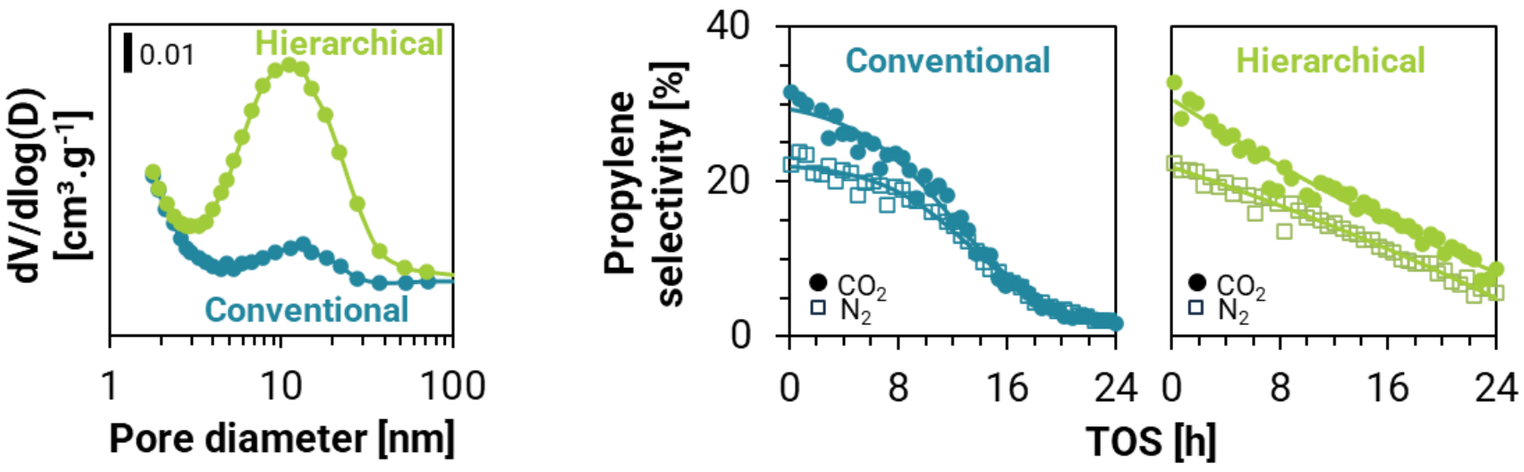




✓ What about ethanol (ETH)?



Catalyst	Crystallinity [%]	Si/Al	V_{micro} [cm³.g^{-1}]	V_{meso} [cm³.g^{-1}]	BAS [µmol of Py.g^{-1}]
Conventional	100	20	0.14	0.04 *	321 *
Hierarchical	100	20	0.14	0.08 *	505 *



4. Conclusions

ZSM-5 catalyst samples, synthesized at different times of hydrothermal treatment, showed an increase in the conversion and selectivity of olefins with increasing micropore volume and degree of crystallinity. In the MTH reaction, the determining factor for higher conversions was the presence of a consolidated microporous structure, that is, the confinement effect is essential for forming reactive intermediate species. The catalytic results of the partially formed samples (S-4h and S-15h) showed that despite the considerable Brønsted acidity and accessibility to the sites, they did not present olefin and aromatics formation.

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