

Zeolite catalysis for (bio)ethanol-to-hydrocarbons processes

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Significance and Relevance

The behavior of protonic and cationic zeolites in the conversion of ethanol to hydrocarbons is described. Evidence is provided for the role of Brønsted acidity typical of zeolites in the ethanol dehydration step as well as in the ethylene oligomerization step(s) producing linear olefins. The role of the cavity in favoring cyclization of the hydrocarbon chain is also taken into account. The behavior of cationic species, such as Ni, Zn and Sn ions, in favoring aromatization is considered. Features of a promising process for producing renewable hydrocarbons from bioethanol are discussed.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion; Fundamental advances in understanding catalysis. Preferred presentation: Oral > Short Oral > Poster.

Introduction and Motivations

In the near future, progressive defossilisation of energy production technologies and of chemical manufacturing is needed ¹ and will certainly occur. However, hydrocarbons will still remain main chemical intermediates, to produce final products such as, e.g., lubricants, detergents and plastic materials ². Hydrocarbon-based biofuels will also be necessary for vehicles that cannot be full-electric or hydrogen-fueled, such as for large long-range shipping and aviation.¹ The zeolite-catalyzed (bio)ethanol to hydrocarbon is a potential new process allowing the renewable production of hydrocarbons. In this paper, mechanistic and compositional aspects for such catalysts are discussed.

Materials and Methods

Commercial H-FER, H-MFI, H-MOR, H-BEA, H-Y and H-USY zeolite samples have been used as the starting protonic zeolite catalysts. P, Fe, Ni, Sn and Zn containing catalysts were prepared by impregnation. Catalysts characterization was done using XRD, FE-SEM, skeletal FT-IR, UV-Vis-NIR techniques, as well as FT-IR spectroscopy of adsorbed CO and pyridine. Used catalysts were characterized by UV-Vis-NIR and DTA-TG techniques experiments. Catalytic experiments were performed at atmospheric pressure in a tubular flow reactor, with GC and GC-MS product analysis.

Results and Discussion

Protonic zeolites were found to be very active in converting ethanol into ethylene using relatively high space velocities.³ The H-MOR sample is the most active, but the H-MFI samples with Si/Al₂ ratios 280 and 50 show higher reaction rates per Al ion, H-FER and faujasites show highest ethylene yield (99.9% at 573 K). At lower temperature and even higher space velocities, diethyl ether is formed with high yield (>70% at 453–473 K with H-BEA and H-MFI (50)). Only using MFI zeolite with relatively high Al content, and with mordenite to a much limited extend, at higher temperature (> 573 K) further conversion of ethylene is observed producing higher hydrocarbons, including aromatics (~29%). Formation of carbonaceous material is also observed over H-MFI, H-MOR and H-BEA. The catalytic activity is certainly primarily due to the strong Brønsted acidic character of the bridging hydroxy groups typical of protonic zeolite.⁴ The different behavior of the protonic zeolite structures appears to be associated to confinement effects: in fact, medium-pore zeolites seem to favor the formation of aromatic hydrocarbons, and carbonaceous material.

Using H-ZSM5 (50) catalyst calcined at 700 K it was found that maximum over-conversion of ethylene to higher hydrocarbons was found at 673 K, while higher hydrocarbons activity was reduced at higher temperatures with increased ethylene production . This is likely due to thermodynamic



limitations on ethylene oligomerization at high temperature.⁵ It was also found that, while the addition of phosphorus and iron decreases the ethylene over-conversion, the addition of 1 wt.% nickel increases the production of aromatics. Instead, the addition of 1 wt.% Zn can also have a positive effect on the production of aromatics, in particular benzene and xylenes.



Figure 1. FT-IR spectra of the hydroxy group in protonic HZSM5 and on 1 Sn wt% -H-ZSM5 catalyst prepared using $SnCl_4 \cdot 5H_2O$ as precursor salt (outgassing at 773 K).

Indeed, to optimize higher hydrocarbons productivity, the addition of cations and optimization of space velocity are both needed. The addition of Sn^{4+} ions increase the conversion of ethanol to C6–C8 aromatic hydrocarbons up to a very interesting 34 % selectivity at 100 % ethanol conversion. In particular, the yield to aromatic-rich gasoline is over 40 % at 773 K and 2700 h^{-1} GHSV.⁶

Characterization data show that the most active Sn-ZSM5 catalyst is still an acid zeolite with limited addition of Lewis acidic Sn ions, part of which are likely introduced in the zeolite pores and part of which produce very small SnO_x nanoparticles on the external surface. In fact, the absorption band of the acidic bridging hydroxy groups is relatively markedly decreased by 1 wt% Sn addition (Fig. 1), likely due to cation exchange. Taking into account the already cited property of ZSM5 zeolite structure in favoring aromatization, the small amount of Brønsted acid sites in this high-silica zeolite, and the limited amount of Sn ions entering the pores, it seems likely that the production of aromatic hydrocarbons is favored by the coexistence of close couples of acids and Sn²⁺ sites (characterized by UV spectroscopy) in the zeolite. Since ethylene is the primary conversion product of ethanol over these catalysts, the aromatization process likely occurs on ethylene oligomeric chains. The role of Sn ions is mainly in favoring the cyclization and dehydrogenation of trimeric and tetrameric ethylene isomers produced by acid-catalyzed ethylene oligomerization.

These data suggest that Sn-doped H-ZSM5 zeolites can be proposed as catalysts for a (bio)ethanol to gasoline process, realized at 650-700 K and relatively low space velocities.

References

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