

Role of zeolite topologies and morphologies in determining life time and selectivity in MTH process

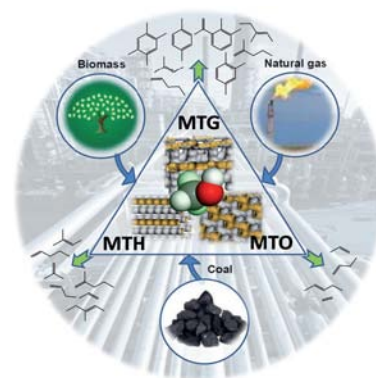
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Concepts

Liquid hydrocarbon fuels play an essential part in the global energy chain, owing to their high energy density and easy transportability. Olefins play a similar role in the production of consumer goods. In a post-oil society, fuel and olefin production will rely on alternative carbon sources, such as biomass, coal, natural gas, and CO₂. The methanol-to-hydrocarbons (MTH) process is a key step in such routes and can be tuned into production of gasoline-rich (methanol to gasoline; MTG) or olefin-rich (methanol to olefins; MTO) product mixtures by proper choice of catalyst and reaction conditions. Synthetic and post-synthetic approaches may also affect the particles morphologies, having a strong effect towards catalysts life time and sometimes also on products selectivities. The contribution will review several commercial MTH projects that have recently been realized, and also will describe some achievements obtained through “*in situ*” characterization of the catalysts.



Motivations Objectives and Results

Shape selectivity is a key to the success of zeolite catalysis. Product selectivity can be explained well in terms of the dimensions of the windows restricting the access to the internal channel system. The effect of the various topologies on product selectivity are significant. All materials of interest show medium-high Bronsted acidity given by the particular distribution of hydroxy groups (recognized to be one of the features responsible of catalysts performances both in terms of activity and lifetime). The need of knowledge about hydroxy group accessibility and acidity has encouraged an extensive use of IR spectroscopy conducted in controlled atmosphere and in combination with *in situ* studies with probe molecules. Many techniques can infer information about the mechanism of heterogeneously catalyzed reactions. With respect to MTH, a primary challenge is to obtain simultaneous information about the gas-phase products and the reaction intermediates which to varying degrees are confined within the pores or cavities of the catalyst. Isotopic labelling is a powerful approach to elucidate reaction mechanisms. The co-reaction of [¹³C]methanol with various unlabeled hydrocarbon species has been widely employed to investigate their reactivity and potential role as intermediates. Transient studies, relying on the abrupt switch from ordinary [¹²C]methanol to [¹³C]methanol have also provided insight on reactive intermediates versus spectator species and information concerning primary and secondary product formation. Thermal quenching of the reaction followed by dissolution of the encapsulating catalyst framework in hydrofluoric acid, liberates the entrapped species making them available to analysis. Spectroscopy has been employed to identify the interaction between acidic sites and methanol and intermediates/products. Solid-state vibrational spectroscopy (FTIR and Raman) and solid-state NMR spectroscopy have proven to be particularly useful, whereas diffuse-reflectance UV/Vis spectroscopy has been employed mostly to investigate species leading to catalyst deactivation.

References

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