DESIGNING METAL-EXCHANGED ZEOLITES FOR NON-OXIDATIVE METHANE UPGRADE TO CHEMICALS

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Abstract

Utilization of methane to produce chemicals has become attractive due to significantly reduced prices for methane gained from recent development in natural gas recovery. However, the lack of suitable catalysts for methane conversion (other than steam reforming) hinders its advances. While intensive research has been conducted on oxidative methane upgrading over decades, the carbon selectivity and the formation of carbon dioxide have been barely improved. In contrast, oxygen-free methane conversion shows superior selectivity towards higher hydrocarbons, but it is much less explored. Here, two related non-oxidative methane upgrade reactions over metal-exchanged zeolites will be addressed. (i) Production of propylene through non-oxidative coupling (NOC) of methane and ethylene over Ag-ZSM-5 could significantly increase feedstock flexibility in ethylene crackers, as increasingly lighter feedstock reduces the formation of propylene by-product. (ii) Methane dehydroaromatization (DHA) over Mo-ZSM-5 can form benzene, one of the most important commodity chemicals in petrochemical industry. Despite numerous studies of the two topics, improvements are still needed to enhance catalytic activity, reduce coking rate, and optimize selectivity. We will discuss how we begin to utilize advanced zeolite synthesis and characterization, in conjunction with density functional theory (DFT) calculations, to judiciously design metal-exchanged zeolites with improved reaction performance for these processes.

Keywords

Methane upgrade, zeolite, metal exchange, rational design, density functional theory.

Introduction

Recent discoveries of large shale and tight gas reservoirs in the U.S. and many other parts of the world have led to an increased interest in natural gas utilization. As of 2011 the proven natural gas reserves total 208.4 trillion m^3 worldwide, of which 7.72 trillion m^3 are located in the U.S. Natural gas is also a significant by-product during oil production and an estimated 150 billion m^3 are being flared annually.[1] The future outlook of shale gas in U.S. energy markets has renewed interest in the production of fuels and chemicals from C_1 chemistry as an alternative to petroleum-based processes.

Non-oxidative upgrade reactions (i.e., NOC and DHA) have better selectivity than oxidative-coupling routes (i.e., OCM), but they require energy input. Amongst the most interesting non-oxidative upgrade technologies are NOC of CH_4 and ethylene to propylene (C_3H_6), and DHA to produce benzene (C_6H_6) and other aromatics. Metal-exchanged zeolites have proven to be active catalysts for these reactions. In our presentation, we will discuss how we are using a combination of synthesis methods and DFT calculations to optimize zeolites for methane upgrading reactions.

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Preliminary Results

We are working on the optimization of non-oxidative methane upgrade catalysts through two rational design approaches: (i) the use of modifiers to tailor MFI habit, which has the potential to increase catalyst lifetime and activity; and (ii) the synthesis of core-shell materials with "passivated" surfaces that reduce non-confined reactions at exterior Lewis and Brønsted acid sites on zeolite catalysts. Recent examples have shown that ultrathin (ca. 2 nm) crystals markedly improve catalyst performance.[2] We have developed a unique method to selectively alter the anisotropic growth rates of zeolite crystals using molecules or macromolecules, termed zeolite growth modifiers (ZGMs), that exhibit specificity for binding to crystal surfaces and altering the bulk habit. As shown in Figure 1, ZGMs employed in the synthesis of zeolite L (LTL type) can alter the nominal cylindrical morphology to either disk-like or high aspect ratio rod-like crystals depending on specific ZGM-crystal interactions.[3]
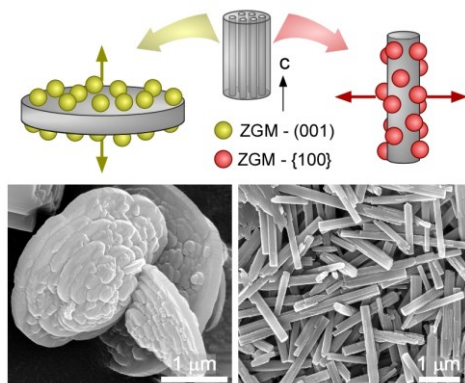

Figure 1. Modification of LTL crystal habit using ZGMs with different specificity.

The selectivity of methane upgrading reactions can be improved using a surface passivation technique wherein a catalytically inactive layer (Si-zeolite) is grown epitaxially on the exterior surface of a catalytically active materials (Si,Al-zeolite). An example of core-shell MFI-type crystals (silicalite-1@ZSM-5) is shown in Figure 2.[4] TEM confirmed the presence of a 10-nm epitaxial layer of silicalite-1 (Fig. 2a and b) grown on ZSM-5 nanocrystals. The thickness of this layer can be tailored based on the judicious selection of synthesis parameters (Fig. 2c).

Conclusions

An economically viable methane-to-higher-value-chemicals upgrade process could revolutionize the chemical industry, which has led to a significant amount of research over the last couple of decades directed at partial oxidation and oxidative coupling of methane using molecular oxygen.[5-7] The main challenge in utilizing methane lies in its thermodynamic stability caused by the strong C-H bonds and the high symmetry of the CH_4 molecule, which does not offer any obvious functional group or polar distribution for activation by another reactant. Thus, high temperatures are required to activate the C-H bond (438.8 kJ/mol). To this end, we present the results of our synergistic studies that employ a combination of synthesis, catalyst testing, and DFT simulations to analyze structure-performance relationships in NOC and DHA reactions towards the goal of achieving superior metal-exchanged zeolite catalysts for methane upgrading.
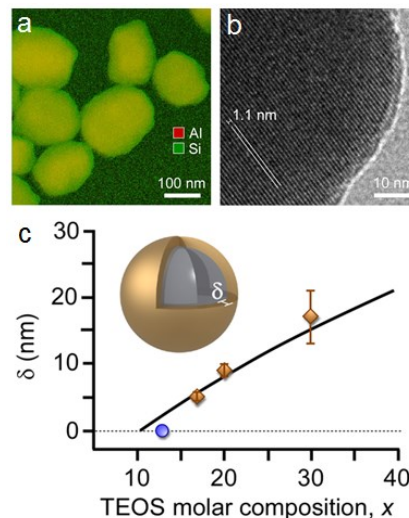

Figure 2.   Silicalite-1@ZSM-5 synthesis.

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