

**Project Title: Identification and Design of Sites for
Methane Conversion to Higher Alkanes under Mild Conditions**

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Synopsis. The proposed research seeks to devise organic-inorganic surface sites capable of converting methane to higher alkanes at mild conditions. The central hypothesis is that organic moieties, created through reaction of suitable precursors with the surface sites on an inorganic solid, can activate methane and start a hydrocarbon chain that will grow by polycondensation. These moieties will circumvent the necessity of generating the start of the chain from methane; and propagation has previously been reported to occur under mild conditions in liquid superacids [1].

Recent Results. During the first project year, three interlinked aims were pursued, which were (i) generation of organic surface moieties on inorganic solids, (ii) acquisition of the spectroscopic signature, and (iii) characterization of the surface species' reactivity. The inorganic solids used were primarily zeolites with various framework types, and various aluminum content including completely dealuminated and thus non-acidic forms. The cationic species were either generated directly through adsorption and protonation, or, if the molecule was too large for the zeolite channels, generated from smaller precursors in several reaction steps inside the pores. The reactants were alcohols such as methanol or butanol, and unsaturated hydrocarbons including linear dienes and trienes, cyclic dienes, and aromatic compounds. Adsorption and reaction were conducted as stoichiometric processes, that is, the surface was charged with a small amount of reactant, generally less than full coverage of the acid sites. After the organic moieties were created, their elementary transformations were investigated as a function of temperature. Surface species and their reactions were monitored by UV-vis spectroscopy and IR spectroscopy, and gas phase products were detected by mass spectrometry and gas chromatography.

Extensive effort was invested in improving spectral interpretation beyond the general classifications that can be found in the literature. A spectral database for neutral and cationic surface hydrocarbon species in zeolites was established, and several correlations between molecular constitution and spectral signature were generated. The comparison with reference solution spectra is essential to corroborate the nature of the species and facilitate band assignments. Somewhat surprisingly, the spectra of unsaturated hydrocarbon species in solution and on the surfaces of solid acids are strikingly similar. This observation pertains to both IR and UV-vis spectra, and to neutral and cationic species. Figure 1 illustrates typical IR spectra of an alkylcyclopentadiene before and after protonation. The formed allylic cation is characterized by an intense band around 1500 cm^{-1} , with the exact position depending on the substitution pattern.

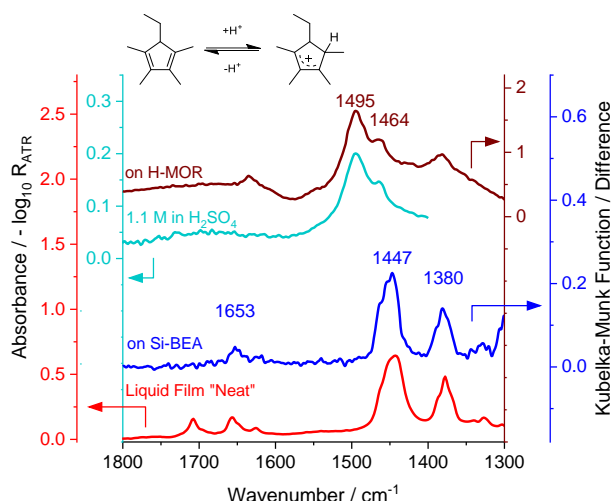


Figure 1: IR spectra of propyltetramethylcyclopentadiene from bottom to top: neutral species as neat liquid and on (nonacidic) dealuminated BEA zeolite, cation in H_2SO_4 and on (acidic) HMOR zeolite.

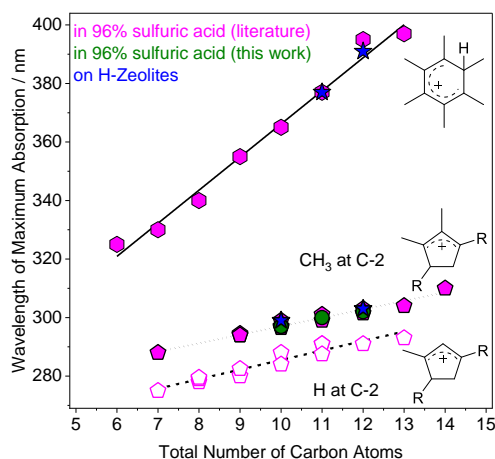


Figure 2: Correlation between wavelength of maximum absorption for substituted benzenium ions and for substituted cyclopentenyl cations of different constitution. Solution data from Refs. [2]-[5] and this work.

Figure 2 demonstrates that the band positions in UV–vis spectra allow determining the number of carbons in the molecule, provided some structural information is available. Excellent linear correlations are obtained for both alkylbenzenium and cyclopentenyl cations. Further, the structure depended on the pore size of the zeolite, for example the 1,2,3-alkyl-substituted allylic species in Figure 2 are favored in large-pore zeolites, whereas smaller pores promote the formation of less substituted species.

The following reaction steps could be observed for linear alcoholic or olefinic reactants with increasing temperature: dehydration (if the starting compound was an alcohol), alkylation, hydride transfer, cyclization to five-membered rings, aromatization and cracking. Evidence for these steps comes from spectra, but also from gaseous product analysis, as illustrated in Figure 3 for *n*-butanol as starting compound. Butenes are formed from adsorbed butoxy species via elimination and react to larger species via alkylation. These oligomeric species rapidly undergo dehydrogenation and cyclization. A band at 293 nm indicates a cyclopentenyl species with about 8 carbon atoms (implying three methyl substituents or fewer larger substituents), indicating dimerization, loss of hydrogen and 1,5-cyclization. Dehydrogenation proceeds via hydride transfer steps and results in the formation of saturated products. Indeed, the increase in concentration of the cyclopentenyl species coincides with the release of butanes, thus closing the hydrogen balance.

While methane has been observed to react in superacids at temperatures below 100 °C, it is reasonable to assume that appreciable methane conversion rates will require higher temperatures and, consequently, organic moieties that are thermally stable. In zeolites, the cyclic species are stable up to temperatures above 400 °C but eventually shrink through cracking reactions.

Summary and Outlook. Experiments demonstrate that independent of the nature and size of the reactant, cyclopentenyl cations are preferred species in zeolite pores. The such generated organic-inorganic sites will be tested for activity in methane conversion. In addition, experiments will be performed towards the generation of radicals on solid acids. For this purpose, redox-active catalysts will be tested.

Impact of the research. Several fundamental insights were developed. For a significant number of linear and cyclic polyenes, UV–vis and IR spectra in nonpolar solvents and on an inert oxide surface are nearly identical. Similarly, spectra of the corresponding cations formed in mineral acids or on solid acids are nearly identical. These findings imply that known increment rules for solution phase spectra are transferable to spectra of surface species. The found correlations imply a vast improvement in the ability to interpret IR and UV–vis spectra of adsorbed polyenes and their corresponding cations. It also follows from these results that for computation of the spectra of such species, the influence of adsorption site and the surrounding zeolite pore may be negligible, and a simple gas phase model may suffice.

Impact of the research on career of PI. The findings were part of a keynote lecture given by the PI at the North American Catalysis Society Meeting in June 2019 in Chicago.

Impact of the research on student: The student gained expertise in the collection and interpretation of UV-vis and IR spectra, developed deep understanding of acid-catalyzed reaction paths on surfaces and learned about computational methods through an informal collaboration. The student communicated the results in an oral presentation at the 26th North American Catalysis Society Meeting.

References. [1] G.A. Olah, G. Klopman, R.H. Schlosberg, *J. Am. Chem. Soc.* **91** (1969) 3261–3268. [2] G.A. Olah, C.U. Pittman, M.C. Symons, *Electronic Spectra. In Carbonium Ions*; Olah, G.A. and Schleyer, P. Eds.; Wiley: New York, 1968; Vol. 1. [3] T.S. Sorensen, *Can. J. Chem.* **42** (1964) 2768–2780; *J. Am. Chem. Soc.* **89** (1967) 3782–3794 and 3794–3803. [4] N.C. Deno, J. Bollinger, N. Friedman, K. Hafer, J.D. Hodge, J.J. Houser, *J. Am. Chem. Soc.* **85** (1963) 2998–3000. [5] M.J. Wulfers, F.C. Jentoft, *ACS Catal.* **4** (2014) 3521.

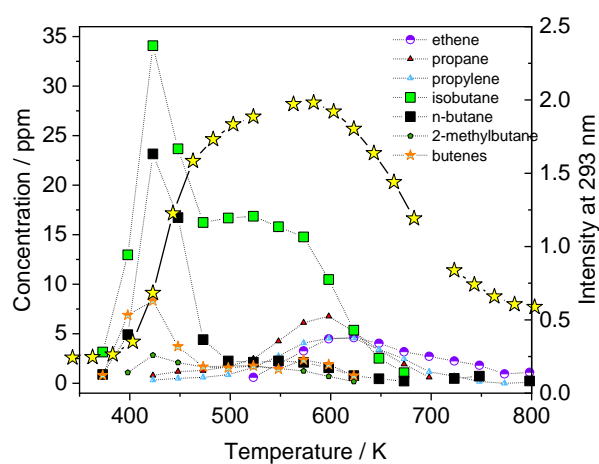


Figure 3: Evolution of gas phase products (as detected by gas chromatography) and surface species during *n*-butanol temperature-programmed reaction on HMOR zeolite. Absorption band at 293 nm indicates the formation of cyclopentenyl species.