INTRODUCTION

Dehydrocondensation of two different alcohols takes place over solid acid catalysts either as a concerted S_N2 reaction [1-6] or as a two-step, less efficient process involving carbenium chemistry [7]. The distinction between the two pathways was determined in this laboratory by ^{18}O retention [2,4], chirality inversion [2,5], and structure of the product isomers [2,3]. Side reactions resulted in symmetrical ethers and olefins *via* dehydration of the C_2+ alcohols, in particular branched alcohols.

Over sulfonic acid Nafion-H resin, it was shown by us that methanol (MeOH) and isobutanol (i-BuOH) react fairly selectively to form methyl isobutyl ether (MIBE) from MeOH/i-BuOH = 1 at 0.1 MPa [2] and 2 at ≈1.35 MPa [6,8] at temperatures between 87 and 117°C by a dominant S_N2 reaction pathway [2]. Oxide catalysts tend to require higher reaction temperatures to achieve appreciable conversions and to catalyze the formations of hydrocarbons, e.g. isobutene, rather than ethers [1].

The objective of this research is to develop scientific background of catalysts and processes for technological advancement in the production of high cetane ethers from alcohols and olefins for use as premium diesel fuels. This involves the goals of synthesizing dual-site and ternary-site strong acid heterogeneous catalysts for activating and coupling alcohols to form ethers. The catalysts need to be selective, operate under mild reaction conditions, and economically produce diesel fuels and additives that have high cetane numbers. This is being achieved by preparing, characterizing, and testing solid acid catalysts, and both experimental and computational methodologies are being employed to delineate the active sites.

In this report, we summarize the first-year study of the catalyst formation, activity, selectivity, kinetics, and nature of active sites in the tungstena-zirconia (WZ) system that had been explored for hydrocarbon isomerizations by Santiesteban et al. [9] at Mobil Technology Co. and has now proven to be active for ether synthesis from alcohols in our work. The specific reaction is that of MeOH + i-BuOH, which gives rise at low temperature ($\leq 127°C$), in order of selectivities and abundances, to methyl-isobutyl ether (MIBE) > isobutene (IB) > isooctene (IO) > dimethylether (DME) >> methyl-tertiarybutyl ether (MTBE).