

New and Improved Catalysts/Processes for Production of Ethylene, Propylene and other Light Olefins via C-1 Chemistry

James A. Guin, Shaobin Wang, Delphine R. Dubois, Jing Liu, Yoon Kook Park, Auburn University

During this year, based on recommendations of the CFFLS Advisory Council and Industrial Advisory Board (IAB) Meeting from August, 2000, and subsequent meetings with CFFLS members, we redirected our project developing novel catalysts for the production of higher ethers as oxygenated fuel additives. The results of our ether work have been summarized in the previous six-month report and are available in literature publications⁽¹⁻⁴⁾. Our redirected project focuses on the development of a non-petroleum source for light olefins, especially ethylene and propylene.

New molecular sieve catalysts are being developed to convert syngas, methanol, and remote natural gas to light olefins by C-1 chemistry.⁽⁵⁾ If desired, these light olefins can be further converted to premium liquid transportation fuels as well as a vast array of products including fuels and fuel additives, e. g. ethanol, dimethyl ether (DME), and valuable chemicals which are currently available only via a petroleum route. Remote natural gas or any other hydrocarbon source such as coal could serve as a raw material for such a process based on C-1 chemistry. In recent years, several paths have been examined to increase selectivity of conversion processes for light olefins. These include ideas such as optimization of the operating conditions using HZSM-5 zeolite, modifications in the HZSM-5, and testing of other natural and synthetic zeolites⁽⁶⁾. Also, various silicoaluminophosphate (SAPO) catalysts have been developed and tested. Recent research sponsored by DOE and NSF has identified methylbenzenes as key intermediates in methanol-to-olefins (MTO) processes, although these compounds do not leave the pores of the SAPO catalyst⁽⁷⁾. The SAPO catalysts exhibit good selectivity; however, they suffer from rapid deactivation by coke formation, possibly due to further condensation reactions of the aforementioned methylbenzene intermediates, which are retained in the pores. It is highly desirable to develop modified SAPO catalysts, or other new catalysts, which will show more stable performance and even better selectivity⁽⁸⁾.

Reaction Conditions. During this year, we have built a quartz tube catalyst-testing unit as shown in figure 1. The unit consists of a nitrogen gas feed stream, which can be saturated with methanol followed by a tubular reactor consisting of a packed bed of catalyst in a temperature-controlled furnace. Typical reaction conditions are: nitrogen flow rate = 60 ml/min; temperature = 400 °C ; pressure = 1 atm, catalyst loading = 0.5 g.

Product Analysis. The reaction products are collected in a gas bulb and analyzed by Gas Chromatograph (GC) using two Varian chromatographs: one equipped with GS-GasPro column and the other equipped with a Plot-Q capillary column. The latter column was found to be necessary for analysis of methanol. The carrier gas used is helium.

Catalyst Preparation. Several catalysts have been prepared and tested for the methanol to hydrocarbons reaction, with special attention given to olefins production. These include HZSM-5 (a commercial catalyst), three supported sulfated zirconia catalysts, and two mesoporous

silicoaluminophosphate (SAPO) catalysts. The sulfated zirconia catalysts are prepared via an impregnation procedure. The MCM (Si-MCM41 and AlSi-MCM41) and SAPO catalysts are prepared from gels, which are subjected to hydrothermal crystallization for an extended time period. An organic templating agent, e. g., tetraethylammonium ion (TEA), is then removed by calcination prior to catalyst testing. Sample preparations are:

Si-MCM41. A solution of 4.1 g of fumed SiO₂, 6.2 g of TEAOH (20 wt.% solution) and 10 g of cetyltrimethylammonium bromide in 40.4 g of H₂O was stirred at a temperature of 70°C for 2 h. The mixture was then aged at room temperature for 24 h. The temperature was increased to 100°C for 48 h under autogenous pressure and then calcined in air at 550°C for 9 h. AlSi-MCM41 is prepared from Si-MCM41, which is mixed with 0.10 M Al(NO₃)₃ for 24 hours, followed by filtration and calcination at 600°C for 2 h.

Supported SZ catalysts. 3 g of Zr(SO₄)₂ was impregnated on 3 g of SiO₂ and calcined at 600°C for 2 h. For SZ/Si-MCM41, 3 g of Zr(SO₄)₂ was impregnated on 3 g of Si-MCM41 and calcined at 600°C for 2 h. For SZ/AlSi-MCM41, 3 g of Zr(SO₄)₂ was impregnated on 3 g of AlSi-MCM41 and calcined at 600°C for 2 h.

SAPO. A mixture (aluminum isopropoxide-15.1 g, H₂O- 26.7 g, 85 wt. % H₃PO₄- 8.6 g and fumed SiO₂ -0.24 g) was stirred at room temperature until homogeneous. 27.2 g TEAOH solution (20 wt.%) as a templating agent was added and stirred until homogeneous (2 h). After that it was synthesized at 200°C for 84 h under autogenous pressure in a Teflon lined vessel and then calcined in air at 550°C for 10 h. A nitrate solution was used to prepare the Ni-SAPO.

Catalyst Testing Results. Reactions were carried out in the quartz tube reactor at 400°C at a nitrogen flow rate of 60 ml/min with 0.5 g of catalyst. Figures 2 and 3 show the results of catalyst testing with a commercial catalyst HZSM-5 used as a reference for this study. The hydrocarbon distribution is centered on C3 with some C5 and C6+ compounds formed. Little deactivation is observed up to 6 hours of reaction time. The olefin distribution is also centered on C3, with some C2 and C4 olefins. Total olefins yield was around 65% with an ethylene yield of about 20%. No DME was formed under these conditions, although some CH₄ is formed. Typical results from the sulfated zirconia catalysts are shown in Figures 4 and 5, where the AlSi-MCM41 support is used. The major product initially (10 min) is ethylene; however after 4 hours of time on-stream the major product becomes DME, indicating that the catalyst deactivates fairly rapidly. Indeed, the breakthrough time of DME formation is sometimes used as a benchmark for catalyst lifetime. This rapid deactivation is probably due to the high acidity of the SZ catalysts. As shown in figures 6 and 7, the laboratory prepared SAPO catalyst provides good yields of ethylene and propylene even after 5 hours on-stream. The total olefins yield was about 90% with the SAPO catalyst and the ethylene yield was about 45%, both of which exceed yields with the commercial HZSM-5. The good ethylene yield with the SAPO catalyst is a due to a combination of molecular sieving pore size effects and mild acidity. Figure 8 shows an extended reaction run using the Ni-SAPO catalyst for 22 hours. The initial conversion of methanol is around 100% and initial yield of ethylene is around 50%; however, after about 5 hours on-stream, the catalyst begins to deactivate and after 22 hours the methanol conversion is reduced to less than 60% with ethylene yield of less than 10%. The balance of the products at this time is DME.

Catalyst Characterization. Several of the prepared catalysts have been analyzed by XRD and SEM. A typical SEM micrograph of a SAPO catalyst made in our laboratory is shown in figure 9. The crystals are 1 to 5 microns in size with cubic morphology typical of SAPO-34. In some micrographs, hexagonal crystals, suggestive of SAPO-5, were also apparent.

An XRD diffraction pattern for one of the synthesized SAPO catalysts is shown in figure 10. The material appears to be well crystallized. Taken together, the SEM and XRD results in figures 9 and 10 suggest the SAPO catalyst is mixture of SAPO-34 and SAPO-5.

Future work. It is planned to prepare additional SAPO based catalysts and to study the effects of preparation conditions on catalytic activity, with emphasis on maximizing olefin yield and catalyst lifetime. Additional metals will be inserted into the framework during synthesis. Further catalyst characterization will be performed by SEM and XRD, as well as other techniques.

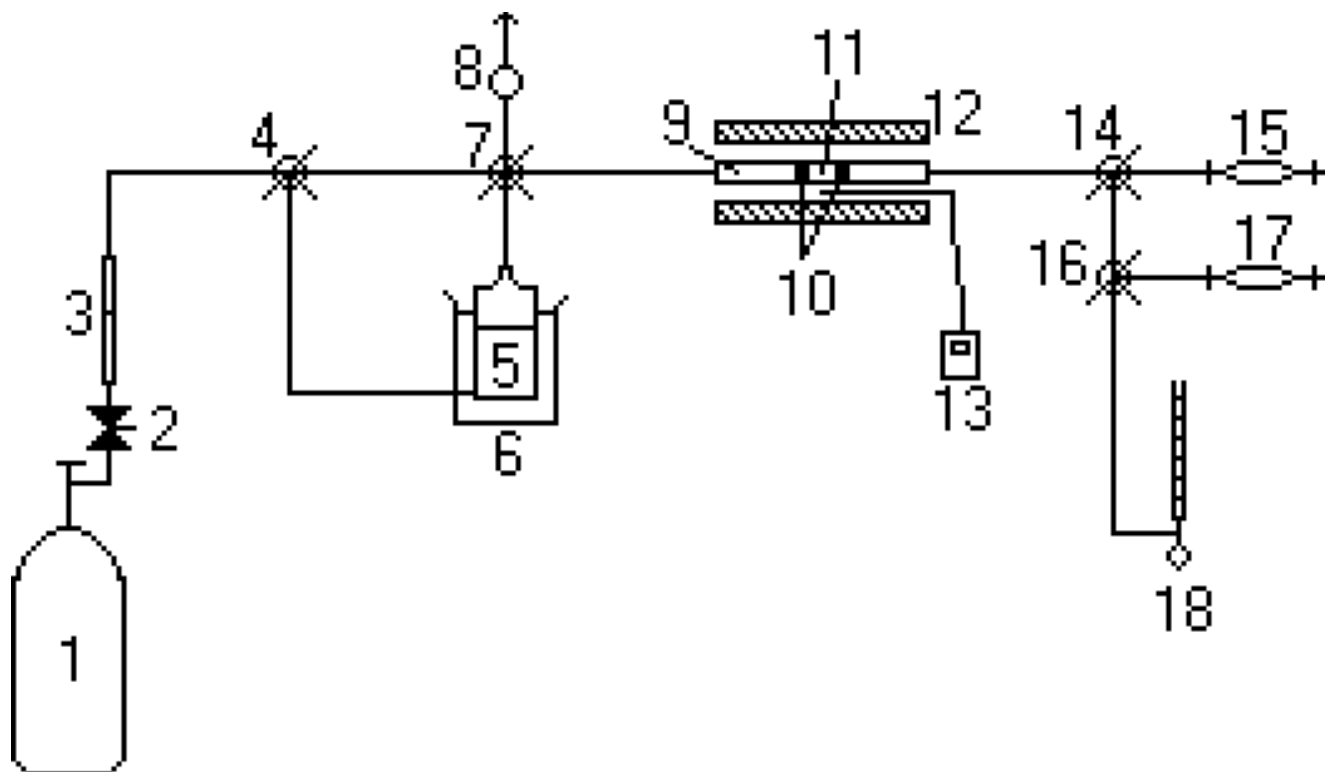


Figure 1. Schematic diagram of quartz flow-type reaction apparatus. (1) Nitrogen gas; (2) needle valve; (3) flow meter; (4) three-way stop-cock; (5) liquid MeOH; (6) water bath; (7) three-way stop-cock; (8) sampling port for inlet methanol; (9) tubular reactor; (10) quartz wool; (11) catalyst; (12) furnace; (13) thermocouple; (14) three-way stop-cock; (15) sampling port for outlet product; (16) three-way stop-cock; (17) sampling port for outlet product; (18) soap-film flow meter.

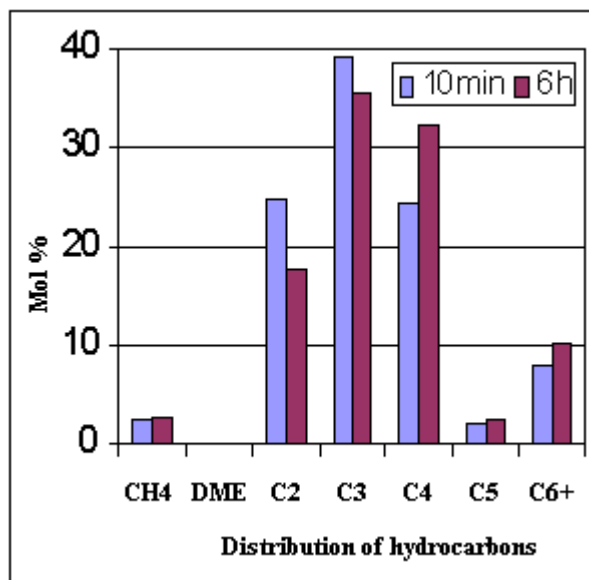


Figure 2. Distribution of hydrocarbons from HZSM-5 catalyst testing.

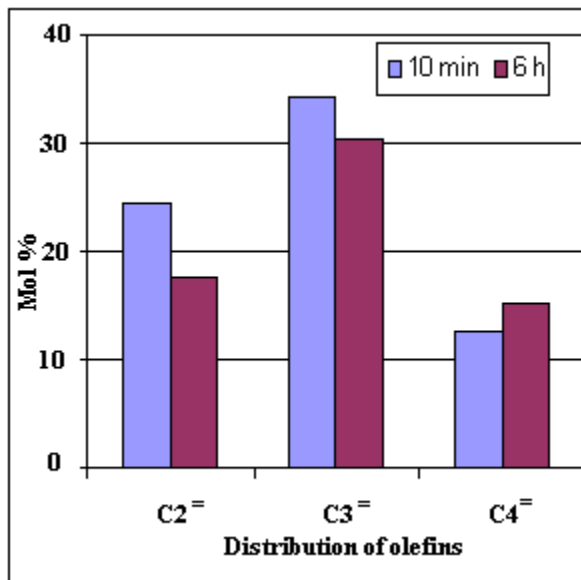


Figure 3. Distribution of olefins from HZSM-5 catalyst testing.

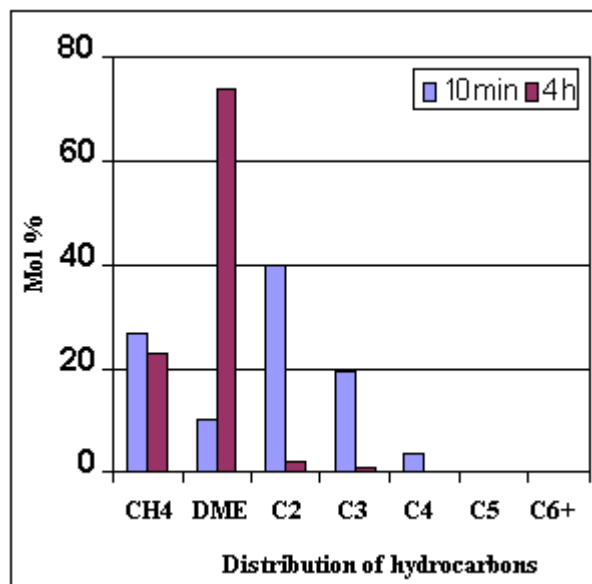


Figure 4. Distribution of hydrocarbons from SZ/AlSi-MCM41 catalyst testing.

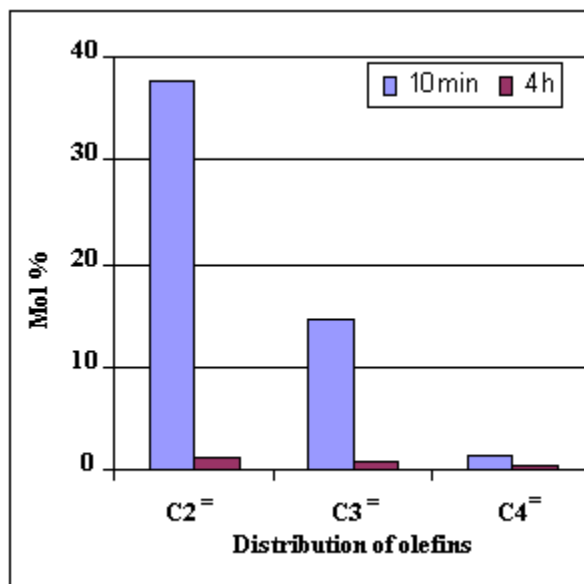


Figure 5. Distribution of olefins from SZ/AlSi-MCM41 catalyst testing.

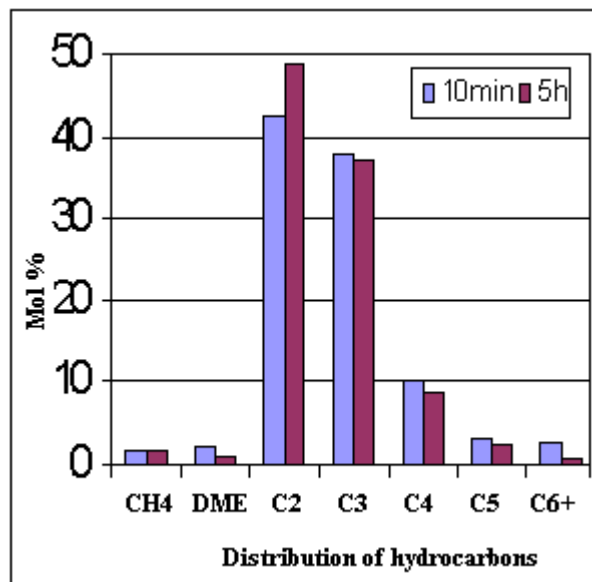


Figure 6. Distribution of hydrocarbons from SAPO catalyst testing.

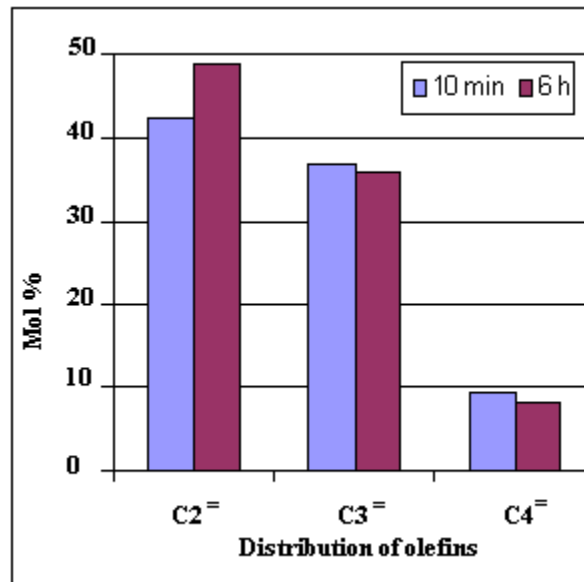


Figure 7. Distribution of olefins from SAPO catalyst testing.

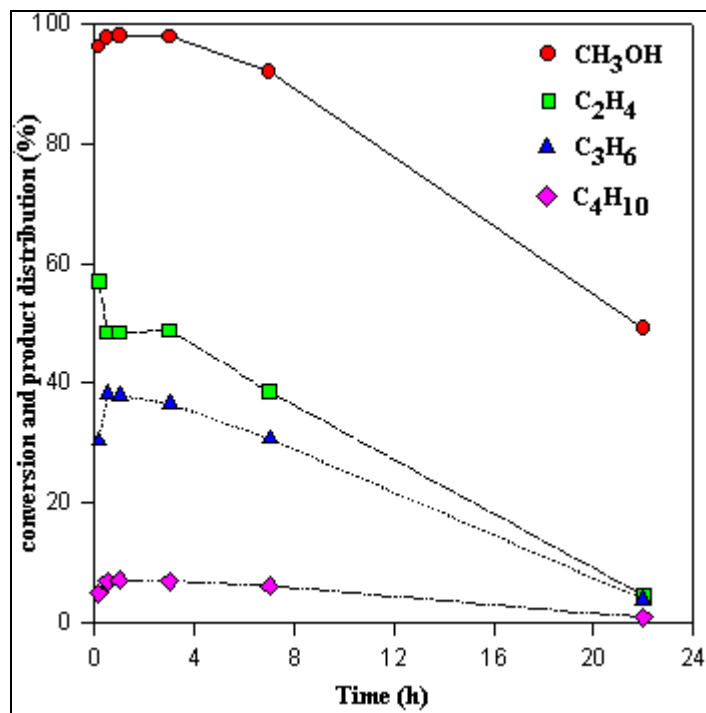


Figure 8. Ni-SAPO catalyst testing for a period of 22 hours.

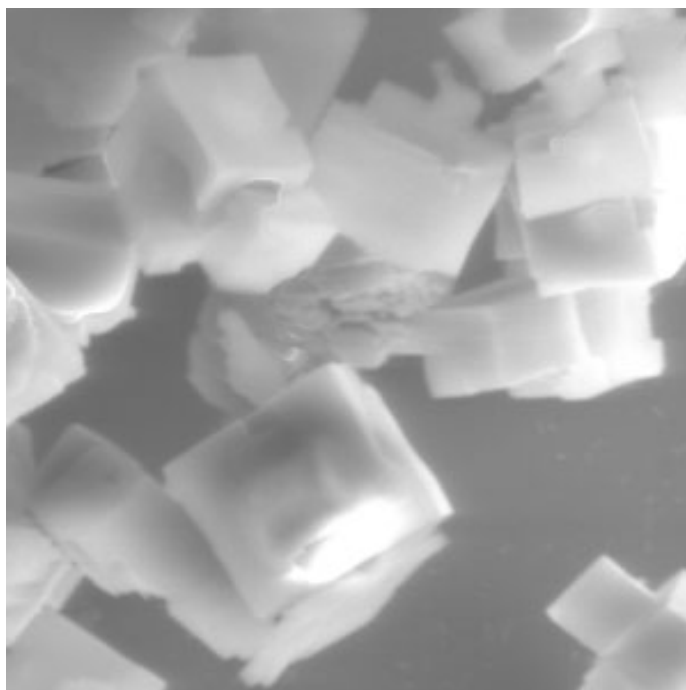


Figure 9. SEM micrograph of SAPO crystals. Magnification 3000X.

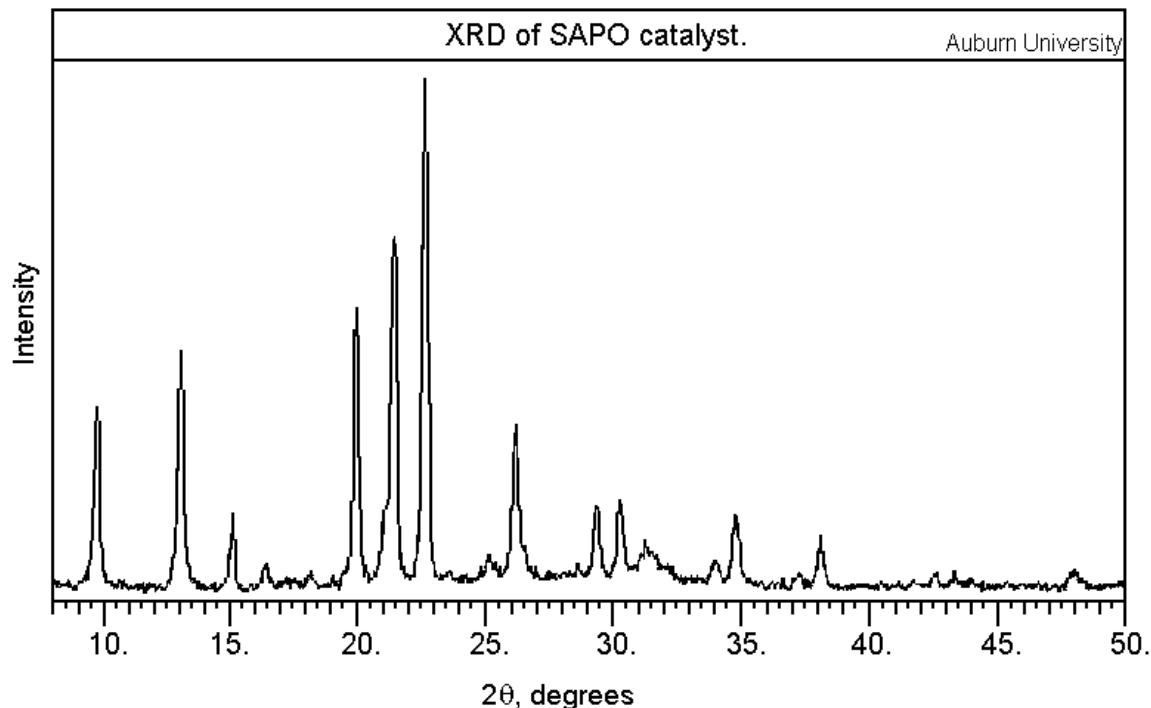


Figure 10. X-ray powder diffraction pattern of SAPO catalyst.

REFERENCES

1. Wang, Shaobin and Guin, J. A., "Silica-Supported Sulfated Zirconia: A New Effective Acid Solid for Etherification" *Chem. Comm.*, **2000**, 24, 2499-2500.
2. Liu, Jing, Wang, Shaobin and Guin, J. A., "Etherification of Dimethylbutenes in Excess Methanol", *Fuel Processing Technology*, **2001**, 69 (3), 205-219.
3. Wang, Shaobin and Guin, J. A., "Si-MCM41 Supported Sulfated Zirconia and Nafion for Ether Production" *Energy & Fuels*, **2001**, 15, 666-670.
4. Wang, Shaobin and Guin, J. A., "Catalytic Activity of Acid-Treated Solids in Synthesis of Ethers from C₆ Olefins and Methanol", manuscript submitted.
5. *Microporous and Mesoporous Materials*, June, **1999**, 29, No. 1-2, 1-218. This entire issue is devoted to methanol conversion to hydrocarbons and olefins. Also see Froment, et al. *Catalysis*, **1992**, 9, 1-64.
6. Gayubo, A. G. et al., *Ind. Eng. Chem. Res.*, **2000**, 39, 292.
7. Song, W. et al. *J. Am. Chem. Soc.*, **2000**, 122, 10726
8. Djieugoue, M. et al., *J. Phys. Chem. B.*, **2000**, 104, 6452.