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The Effect of Supercritical Fluids on Solid Acid Catalyst Alkylation

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The alkylation of isobutane with *trans*-2-butene was explored over six solid acid catalysts in the liquid, near-critical liquid, and supercritical regions through the addition of an inert cosolvent to the reaction feed mixture. The addition of supercritical cosolvents did not result in sustained catalytic alkylation activity. A modest improvement in product yield was obtained with the addition of methane in the modified-liquid region; however, catalyst longevity and product selectivity were decreased compared to cosolvent-free liquid conditions. This paper describes the catalyst screening and selection process, an exploration of catalyst performance with varying concentrations of methane, and an examination of the effects of seven supercritical fluids on catalyst performance. The catalysts included two zeolites, two sulfated metal oxides, and two Nafion catalysts. Three hydrocarbons, two fluorocarbons, carbon dioxide, and sulfur hexafluoride were explored as inert cosolvents added to the reaction mixture.

Introduction

Isoparaffin alkylation is utilized by the petroleum refining industry to couple high-vapor-pressure isoparaffins and olefins (C_3–C_5) to produce a low-vapor-pressure, high-octane gasoline blend stock. The alkylate product is very low in environmentally undesired components such as sulfur, benzene, aromatics, and olefins, and it removes environmentally undesirable high-vapor-pressure paraffins and olefins from the gasoline blending pool. Alkylate is the cleanest gasoline blending stream produced in a refinery; it is a low-sulfur, ultra-clean fuel component; and it is considered to be an essential requirement for producing environmentally sound reformulated gasoline. The U.S. alkylate production stands at over one million barrels per day and constitutes about 13 vol % of the U.S. gasoline pool with demand expected to grow by 25% over the next 5 years.[1,2]

A typical alkylation reaction is shown below. The desired products for isobutane alkylation are the trimethylpentane (TMP) isomers.
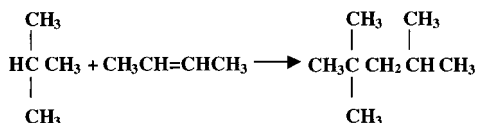
In addition to the TMPs, less branched C_8 products, including dimethylhexanes (DMHs), are formed, as well as heavy alkylation products (C_{9+}) and lighter cracked products (C_5–C_7). The total liquid product (C_{5+}) is referred to as alkylate.

In the current industrial alkylation process, the reaction is catalyzed by concentrated liquid hydrofluoric (HF) or sulfuric (H_2SO_4) acid. The liquid acid processes present serious safety and environmental concerns in both the transport and storage of concentrated liquid acids and the disposal of acid–oil sludges. A solid acid catalyst could replace liquid acids and eliminate many safety and environmental concerns. Technical hurdles to overcome before implementation of the solid catalyst process include rapid deactivation resulting from the buildup of coke, difficult catalyst regeneration, poor product quality, and energy-intensive product recovery. Many of the challenges facing alkylation technology have been discussed by Albright.[3]

Solid catalysts with bound acidic surfaces are known and available, but they unfortunately deactivate quite rapidly under alkylation reaction conditions.[4–6] All solid catalysts tested for alkylation have been shown to have limited useful active catalytic lifetimes because of the deposition and buildup of heavy hydrocarbons, known as coke, on the catalyst surface. Coke deposits cover active catalyst sites and plug the catalyst pore structure, rendering the catalyst useless. Additionally, all catalysts tested for alkylation require high isobutane-to-butene ratios to produce the desired product selectivity. The high feed ratio results in significant energy requirements to separate the products from the excess reactants. Many of the technical challenges surrounding the use of solid catalyst alkylation have been reviewed by Corma and Martinez.[7]

Supercritical fluids (SCFs) have been shown to be effective in controlling catalyst deactivation by extracting coke compounds from porous catalysts, resulting in the extension of catalyst life.[8–10] An SCF is a fluid in which the temperature and pressure are above the critical point of the material. At pressures above the critical point, the fluid density, and hence solvating strength, approaches liquidlike levels. Additionally, SCFs exhibit transport properties, including viscosity and diffusivity, that are more gaslike. This combination of properties makes SCFs extremely efficient for extraction in porous matrixes.[11] Through moderate adjustments in pressure, an SCF's solvating power can be easily adjusted, allowing for the energy-efficient recovery of reaction products.[11] SCFs could potentially aid in simultaneous alkylation reaction and extraction of coke compounds from the porous catalyst, as well as in the separation of the liquid alkylate product. SCF

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properties can be altered with moderate changes in pressure, and the critical point of a reaction mixture can be controlled by the composition of the mixture.

A thorough review of supercritical fluid heterogeneous catalysis was recently provided by Baiker.[12] Baiker points out the advantages of supercritical fluids over gases for enhancing heterogeneous catalyst lifetime because of higher solubilities and enhanced diffusivities of catalyst-blocking agents. However, few studies have compared supercritical fluids to liquid reaction media. Although SCFs provide mass-transfer advantages over liquids, the solubilities of heavy organics are typically lower in SCFs. The lower densities obtained in SCFs compared to liquids reduces reactant concentrations. For the alkylation reaction, where the production of desired products can be limited by the hydride-transfer reaction of surface-adsorbed carbenium ions with the isobutane reactant, the lower reactant concentrations at SCF conditions could potentially lead to poorer product quality or increased catalyst deactivation.

Supercritical fluid conditions have been reported for the alkylation of isobutane.[13-18] These studies fall into two categories: reactions maintained at temperatures above the critical point of the reaction mixture without the addition of SCF cosolvents[13-15] and reactions where the critical temperature of the mixture was reduced by the addition of SCF cosolvents.[16-18] Hussain and Fan et al. explored the reaction at temperatures above the critical point of the excess reactant, isobutane ($T_c = 135$ °C).[13,14] These studies demonstrated extended catalyst activity compared to the reactions in the gas or liquid phase, but the elevated temperatures resulted in undesirable side reactions, including cracking and isomerization, that reduced product value. The reactions were also studied at relatively high excesses of isobutane, which would require energy- and capital-intensive separations. More recently, Gayraud et al. also explored supercritical fluid−solid catalyst alkylation at temperatures above the critical temperature of isobutane.[15] The authors explored a lower excess of isobutane but still reported a reduction in product quality at supercritical temperatures. At these elevated temperatures, it has been suggested that the reaction explored was actually olefin oligomerization and subsequent decomposition.[19]

Clark and Subramaniam studied the alkylation reaction at mild temperatures (50 and 95 °C) and at a low excess of isobutane using carbon dioxide as the supercritical cosolvent,[16] whereas Chellappa et al. explored mild-temperature solid catalyst alkylation using supercritical ethane.[17] By employing an 86-fold molar excess of CO_2 to butene, Clark and Subramaniam demonstrated 2 days of stable catalyst activity at 50 °C. However, at these conditions, both the trimethylpentane selectivity (roughly 5% of the C_{5+} product) and the butene conversion (20%) were rather low compared to industrial yields (>70%) and conversions (100%).[16] Chellappa et al. reported that, at the mild-temperature conditions, the vast majority of products were alkenes, and the predominant reaction was butene dimerization.[17]

Santana and Akgerman also explored the use of carbon dioxide as the supercritical cosolvent[18] under conditions similar to those reported by Clark and Subramaniam.[16] Although Clark and Subramaniam interpreted their results as indicating stable catalyst activity, both studies using CO_2 demonstrated butene conversions dropping from 100% to less than 40% in approximately 2 h time on stream (TOS).[16,18] After about 5 h TOS, both studies showed stable catalyst activity with butene conversions of 20% or less. Thus, the catalysts were already severely deactivated before stable activity was demonstrated. Santana and Akgerman[18] clearly showed that, after the majority of catalyst activity had taken place, the primary reaction products were octenes. Thus, the previous studies exploring the addition of supercritical cosolvents[16-18] focused on the dimerization reaction of butene to octenes.

In this work, we describe the effect of the addition of several inert supercritical fluid cosolvents on solid acid alkylation at moderate temperatures and excesses of isobutane. The reaction of trans-2-butene with isobutane was explored at TOSs when the alkylation reaction was dominant. For the conditions explored, butene conversion and reaction conditions begin to approach industrial requirements, but catalyst lifetimes, product yield, and product quality are still rather poor.

This work examined six different catalysts, selecting one for further study. The effect of methane addition to the reaction mixture was explored, and a comparison of seven different cosolvents is presented for the selected catalyst. Four different reaction conditions were explored, including the liquid phase without the addition of a cosolvent; the supercritical phase; the near-critical liquid; and a liquid phase where cosolvent was added to the reaction mixture, henceforth referred to as "modified liquid". These reaction conditions were obtained by varying the cosolvent concentration in the reaction feed mixture and adjusting the pressure at a fixed reaction temperature. The cosolvent-free liquid condition is presented as a base case. The supercritical region was explored to take advantage of its enhanced extraction and mass-transport properties. The near-critical liquid region was explored because properties approach those of supercritical fluids near the critical point, but lower solvent concentrations and reaction pressures are required. The modified-liquid region was also explored to examine the effect of simple dilution on the liquid-phase reaction. The experimental results demonstrate that the addition of SCF cosolvents does not provide a significant enhancement in solid acid alkylation catalysis over liquid-phase conditions.

Materials and Methods

Catalysts and Chemicals. Six solid acid catalysts were tested. Catalysts were selected that represented several different acid types, total acidities, and porosities. Data and pretreatment methods for each are shown in Table 1. The catalysts included two sulfated metal oxides, sulfated nickel/titania (S/NiTi) and sulfated zirconia (S/ZrO$_2$); two Nafion catalysts;[20] an ultra-stable Y-zeolite catalyst (USY); and a Pt/USY zeolite (Pt/USY) catalyst. The catalysts were pretreated at conditions suggested by the suppliers. All catalysts except the Nafion catalysts were calcined in air before addition to the reactor. The Pt/zeolite catalyst was reduced in flowing hydrogen at 200 °C for 3 h after calcination. All catalysts were dried overnight in the reactor with helium at elevated temperature before use to remove adsorbed water as described below. Instrument-grade isobutane (99.5%) and HP-grade trans-2-butene (99.0%) were obtained from Scott Specialty Gases (Plumsteadville, PA).

Seven different cosolvents were explored that provided differing solvent densities, molecular weights, and

Table 1. Physical Data and Pretreatment Methods for the Catalysts Tested

	catalyst					
	S/NiTi	S/ZrO$_2$	Nafion SAC-13	Nafion SAC-25	USY	Pt/USY
manufacturer	Ashland[a]	MEI[b]	DuPont[c]	DuPont[c]	Zeolyst[d]	Zeolyst[d]
composition	89.8% TiO$_2$	97% ZrO$_2$	87% SiO$_2$	75% SiO$_2$	59.8% SiO$_2$	59.7% SiO$_2$
(wt %)	5.6% S	3% S	13% polymer[e]	25% polymer[e]	39.6% Al$_2$O$_3$	39.5% Al$_2$O$_3$
	4.6% Ni				0.08% Na	0.08% Na
						0.25% Pt
surface area (m^2/g)	87	170	200	200	638	704
pore volume (cm^3/g)	ND[f]	0.2	0.6	0.6	0.48	0.44
average pore diameter (Å)	83	51	98	94	14	14
total acidity (μmol/g)	214	305	130	250	999	1239
pretreatment method						
calcination T (°C)	600	400	—[g]	—	400	400
calcination t (h)	3.0	3.0	—	—	3.0	3.0

[a] Ashland = Marathon Ashland Petroleum LLC, Catlettsburg, KY. [b] MEI = Magnesium Elektron Inc., Flemington, NJ. [c] DuPont = DuPont Fluoroproducts, Wilmington, DE. [d] Zeolyst = Zeolyst International, Valley Forge, PA. [e] Polymer = tetrafluoroethylene/perfluoro(4-methyl-3,6-dioxa-7-octene-1-sulfonic acid) copolymer. [f] ND = no data. [g] None.

dipole moments. Cosolvents added to the reaction mixture included methane (99%, United States Welding, Denver, CO), ethane (CP-grade, 99%, Scott Specialty Gases), propane (CP-grade, 99%, Scott Specialty Gases), carbon dioxide (SFE-grade, 99.9%, Norco, Boise, ID), monofluoromethane (99.9%, Norco), trifluoromethane (99.9%, Norco), and sulfur hexafluoride (99.9%, Norco). Each fluid was added to the reaction mixture (isobutane + *trans*-2-butene) in the molar ratio necessary to attain the desired reaction conditions.

Supercritical Fluid Reactor System. A schematic of the reactor system is shown in Figure 1. Helium (>99.9%) was used to pressure-check the system, to purge the system, and to dry the catalysts in the reactor before use. Two high-pressure syringe pumps (model 260D, ISCO, Lincoln, NE) were employed to supply isobutane for startup and reaction feed mixture for the reaction phase. Isobutane and *trans*-2-butene were premixed in a high-pressure vessel to obtain the desired isoparaffin-to-olefin molar ratio (iP/O). When high concentrations of cosolvents were added to the reaction, the fluids were pumped separately using a syringe pump. Low cosolvent concentrations were premixed with the isobutane/*trans*-2-butene reaction mixture in a pressurized floating-piston accumulator (Temco, Inc., Tulsa, OK) under a back pressure of 49 bar and pumped into the system using an Accuflow Series III HPLC pump (Scientific Systems, Inc., State College, PA). Fluid mixtures flowed past a spring-loaded pressure-relief valve and an Omega PX605 pressure transducer (Stamford, CT). A high-pressure switching valve was used to direct the flow either through or around the reactor. The reactor consisted of a preheated section and a catalytic reaction zone. The temperature of each section was measured by a platinum RTD (Omega PR-17), which was used to control each heated zone independently. The temperatures were controlled by electrical resistance heating using two Omega CN4800 PID controllers. Reactor dimensions were approximately 30 cm × 3.9 mm (l × i.d.). Gas chromatography (GC) samples of the
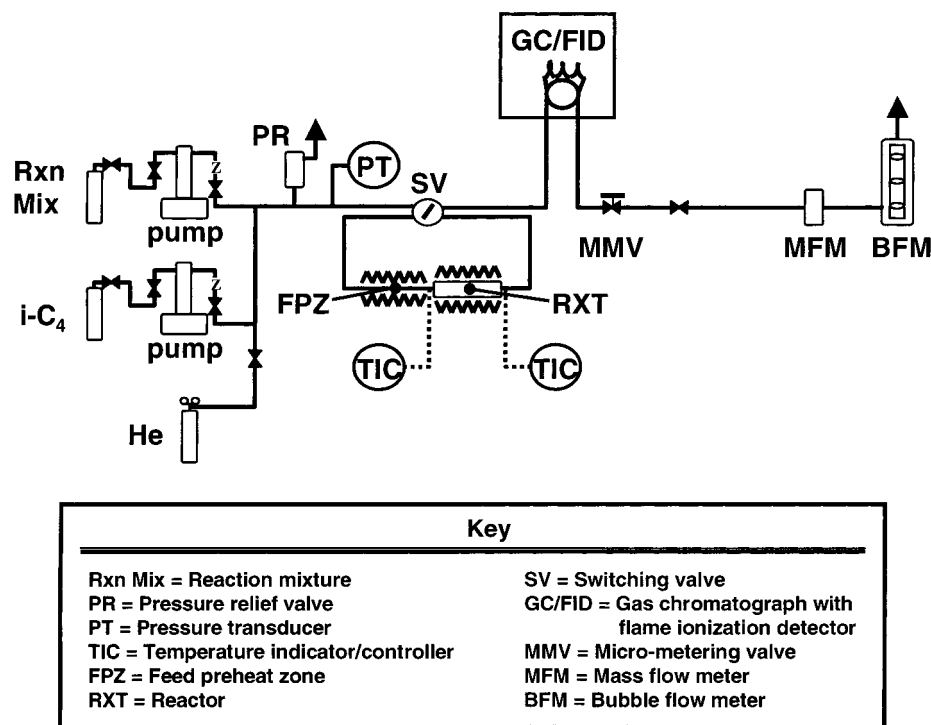

Figure 1. Schematic of the reactor system.

reactor effluent were acquired on-line at reaction pressure using a high-pressure sample valve with a 0.1-μL internal sample loop. After the GC sample valve, the pressure was dropped to atmospheric with a micrometering valve. Gas products exited the reactor system through a mass flow meter, followed by a bubble flow meter.

Testing Method. Experiments were conducted in the plug-flow reactor system using 2 g of catalyst packed into the stainless steel reactor and held in place by plugs of quartz wool at each end of the catalyst bed. Initial experiments were performed with several different catalyst and cosolvent conditions to explore external mass-transfer effects. By varying the feed flow rate and keeping the olefin weight hourly space velocity (OWHSV) constant, it was demonstrated that the reaction was free from external mass-transfer effects. The catalysts were dried overnight in the reactor before use at conditions recommended by the supplier by passing He through the bed at 350 °C (S/NiTi and S/ZrO$_2$), 200 °C (USY and Pt/USY), or 150 °C (Nafion SAC-13 and SAC-25) to remove adsorbed water. Failure to perform the catalyst drying step resulted in significantly reduced catalyst performance. The reaction temperature was set for each catalyst to the desired catalyst-specific value. The run procedure was as follows: The system was initially filled throughout with isobutane at the desired reaction temperature and pressure. At time zero, flow of reaction mixture (isobutane + *trans*-2-butene + cosolvent) was started at the constant flow rate necessary to achieve the desired olefin weight hourly space velocity (OWHSV). The residence time of the plug-flow reaction system was approximately 0.5–1.0 h, depending on total flow rate; thus, products were not initially observed until 0.5–1.0 h into the experiment. The reaction was allowed to proceed until the concentration of trimethylpentanes (TMPs) in the outlet stream decreased to zero, indicating catalyst deactivation.

Experimental Studies. Three sets of studies were performed: a catalyst comparison using all catalysts exploring the effect of methane addition on alkylation, a study of the effect of methane addition on alkylation using the USY catalyst, and a study of seven cosolvents on alkylation using the USY catalyst.

Catalyst Comparisons: Effect of Methane Addition on Alkylation. The initial experimental study focused on catalyst selection. The six solid acid catalysts tested included two sulfated metal oxides, sulfated nickel/titania (S/NiTi) and sulfated zirconia (S/ZrO$_2$); two Nafion catalysts;[20] an ultra-stable Y-zeolite catalyst (USY); and a Pt/USY zeolite (Pt/USY) catalyst. These catalysts represented several different acid types, total acidities, and porosities. Each catalyst was tested both under liquid conditions and with the addition of methane. Liquid experiments were performed in the absence of methane at 42 bar, a pressure sufficient to maintain the reaction mixture in the liquid phase. Experiments conducted with each catalyst using modified reaction mixtures containing methane were performed at 141 bar. The reaction pressure was set at 141 bar when methane was used because this higher pressure was necessary to maintain a single phase. The reaction temperature for each catalyst was chosen separately (see Table 2) on the basis of previously determined optimal performance at liquid conditions (data not shown). Reaction pressures were chosen such that the fluid would be in a single phase at the reaction temperature and feed composition as predicted by the Peng–Robinson equation of state[21] using the Aspen Plus (Aspen Technologies, Inc., Cambridge, MA) process simulation code. Reaction conditions utilized an iP/O molar ratio of 25:1 and an OWHSV of 0.1 g of butene h^{-1} (g of catalyst)$^{-1}$. In these experiments, the methane composition was chosen to adjust the mixture to the desired condition, as predicted by the Peng–Robinson equation of state.[21] These conditions included (1) modified liquid (ML, 2.0–22 mol % CH$_4$), (2) near-critical liquid (NCL, 33–58 mol % CH$_4$), and (3) supercritical (SCF, $\geq$68 mol % CH$_4$).

Effect of Methane Addition on Alkylation Using USY Catalyst. The second experimental study focused on the effect of methane concentration on the performance of the USY zeolite catalyst. The methane composition in the feed was varied from 0 to 73 mol %. Liquid experiments were performed in the absence of methane at 42 bar. Experiments using modified reaction mixtures containing methane were performed at 141 bar. All experiments were run at a temperature of 60 °C, an iP/O molar ratio of 25:1, and an OWHSV of 0.1 g of butene h^{-1} (g of catalyst)$^{-1}$. In these experiments, the methane concentration was adjusted to obtain the desired conditions.

Effect of Other Cosolvents on Alkylation Using USY Catalyst. The third experimental study examined the effect of the remaining fluids (each separately) using the USY catalyst. The SCF cosolvents included three hydrocarbons, two fluorocarbons, carbon dioxide, and sulfur hexafluoride. These cosolvents provided a wide range of densities, molecular weights, and dipole moments. Reaction conditions for the liquid phase and all cosolvent experiments except when methane was employed were chosen to be 60 °C, 111 bar, an iP/O molar ratio of 25:1, and an OWHSV of 0.2 g of butene h^{-1} (g of catalyst)$^{-1}$. The pressure of 111 bar was chosen because it provided a single phase for each individual set of conditions examined for the remaining fluids and was considered to be a reasonable commercial operating pressure. The reaction pressure was set at 141 bar when methane was used because this higher pressure was necessary to maintain a single phase. Cosolvent concentrations were chosen to adjust the modified reaction mixture to the desired conditions, as predicted using the Peng–Robinson equation of state.[21] The concentrations of each cosolvent under ML, NCL, and SCF conditions at 60 °C and 111 bar are shown in Table 3, and the cosolvent concentrations required to provide the reaction

Table 2. Reaction Conditions Used in the Catalyst and Cosolvent Tests for Each Catalyst

catalyst or cosolvent	reaction conditions		
	T (°C)	P (bar) liquid	P (bar) other cond.
methane cosolvent			
S/NiTi	20	42	141
S/ZrO$_2$	5	42	141
Nafion SAC-13	60	42	141
Nafion SAC-25	60	42	141
USY	60	42	141
Pt/USY	60	42	141
USY catalyst			
ethane	60	111	111
propane	60	111	111
carbon dioxide	60	111	111
monofluoromethane	60	111	111
trifluoromethane	60	111	111
sulfur hexafluoride	60	111	111

Table 3. Cosolvent and Reaction Mixture Compositions Employed to Achieve Modified Liquid (ML), Near-Critical Liquid (NCL), and Supercritical (SCF) Conditions

| catalyst or cosolvent | mol % of cosolvent in reaction mixture | | | |
	liquid[a]	ML	NCL	SCF
methane cosolvent[b]				
S/NiTi	0	18	74	80
S/ZrO₂	0	22	78	82
Nafion SAC-13	0	24	ND[c]	ND
Nafion SAC-25	0	16	57	69
USY	0	2.0–22	33–58	≥68
Pt/USY	0	18	58	70
USY catalyst				
ethane	0	19	71	90
propane	0	18	73, 91	−[d]
carbon dioxide	0	20	68	77
monofluoromethane	0	20	78	ND
trifluoromethane	0	20	71	88
sulfur hexafluoride	0	20	75	−

[a] Liquid experiments performed at 42 bar for methane and at 111 bar for all other fluids (see Table 2). [b] Methane as cosolvent with catalysts listed. [c] ND = no data. [d] The reaction mixture would be exceedingly diluted with the cosolvent, or the critical temperature of the cosolvent exceeded the reaction temperature. Thus, experiments at these conditions were not performed.

Table 4. Reaction Mixture Critical Compositions[a] at 0 and 100% Conversion of Butene to Trimethylpentane[b]

| cosolvent | T_c (°C) | 0% conversion[c] | | 100% conversion[d] | |
		cosolvent mol % in feed	P_c (bar)	cosolvent mol % in feed	P_c (bar)
methane[c]	5	79	124	80	133
	20	76	125	76	135
	60	63	112	64	125
ethane	60	84	54	86	56
propane	60	−[e]	−	−	−
carbon dioxide	60	74	73	76	78
monofluoromethane	60	88	61	90	63
trifluoromethane	60	79	56	80	59
sulfur hexafluoride	60	−	−	−	−

[a] Predicted using the Aspen Plus process simulation code with the Peng–Robinson equation of state.[21] [b] Reaction conditions for each cosolvent were chosen such that near-critical compositions were below the 0% conversion composition and supercritical compositions were at or above the 100% conversion composition. This ensured that the reaction took place in the intended phase [c] Assumes no conversion of butene to products. [d] Assumes all butene and required isobutane are quantitatively converted to 2,2,4-trimethylpentane. [e] The reaction mixture would be exceedingly diluted with the cosolvent, or the critical temperature of the cosolvent exceeded the reaction temperature.

critical temperatures are shown in Table 4. A mass balance analysis showed that none of the cosolvents were consumed or formed during the reactions.

Analytical Method. Catalyst characterizations were performed as follows. Elemental compositions were obtained via X-ray fluorescence (XRF) using a Phillips PW 1480 XRF instrument (Natick, MA) after the sample had been fused with lithium tetraborate. Surface areas and pore volumes were determined by nitrogen physisorption using a Quantachrome (Boyton Beach, FL) Autosorb-6 automated physisorption and chemisorption instrument. Catalyst acidity was determined by pyridine titration at 150 °C. The number of acid sites per gram for each catalyst was determined by thermogravimetric analysis (TGA) of pyridine adsorption[22] on a DuPont 951 TGA (Wilmington, DE). In these measurements, the samples were heated at 10 °C/min under a nitrogen purge to the final calcination temperature
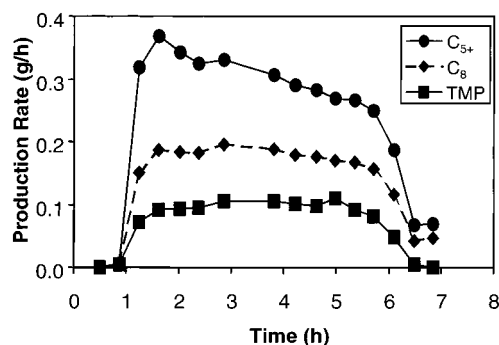
Figure 2. Example data set showing production rates for total alkylate, C₈s, and trimethylpentanes using Pt/USY catalyst at 90 °C, 42 bar, 0.10 OWHSV, and an iP/O ratio of 25.4:1. These curves were numerically integrated, and the areas are normalized for comparison by dividing by the weight of catalyst in the reactor.

(Table 1) and held for 2 h. The samples were then cooled to 150 °C and exposed to pyridine for 1 h by diverting the carrier gas through a pyridine saturator, after which a constant sample weight was observed. The samples were then purged with nitrogen to remove physisorbed pyridine; a purge time of at least 5 h was required to reach constant weight. Total acidity (TA) was determined from the weight gain and expressed as number of micromoles of acidity per gram of sample. Pyridine is a strong base that readily adsorbs to both weak and strong acid sites. Acidity values calculated from pyridine adsorption include both active and catalytically inactive sites.

Gas chromatographic (GC) analyses of the reactor effluent were performed on-line using a Hewlett-Packard 5890 Series II gas chromatograph (Wilmington, DE) equipped with an automated high-pressure sample valve, electronic pressure controller, flame ionization detector (FID), and thermal conductivity detector (TCD). Product separation of on-line 0.1-μL samples was achieved using a 50 m × 0.2 mm (l × i.d.) Supelco Petrocol gas chromatography column (Bellefonte, PA) at a split ratio of 100:1. The oven temperature was held initially at 35 °C for 10 min, ramped to 150 °C at 10 °C/min, and held at 150 °C for 2 min. Helium carrier gas was maintained at a constant linear velocity of 36 cm/s. FID peaks were identified by comparison with a qualitative reference alkylate standard (Supelco, Bellefonte, PA) run under identical conditions. TCD peaks were used to quantify CO₂ and SF₆ when used.

Data Analysis. Yields of products from the reaction were calculated by integrating the production rate versus time data. The production rates (grams per hour) were calculated from the feed input rate (grams per hour) and the product weight fraction (weight percent) and plotted versus time. An example data set for total alkylate (C_{5+}) and for trimethylpentanes (TMP) is shown in Figure 2. The integrals were normalized for comparison by dividing by the total weight of catalyst in the reactor. Thus, data presented as product yield represent a combination of both reaction rate and catalyst longevity.

The alkylation reaction was considered to be complete after TMP product could no longer be detected by GC analysis. This was done because TMPs are the industrially desired products of the alkylation reaction. For example, in Figure 2, TMPs were produced for nearly 7 h of time on stream (TOS), ceasing about 46 min after butene conversion decreased below 100% (not shown in Figure 2). Although reaction products continued to be

observed after that time, these products were not the desired trimethylpentane alkylation products.

Results

The six catalysts selected represented several different acid types, including sulfated mixed metal oxides, supported polymeric acids, and acidic zeolites. Catalyst total acidities ranged from 130 to 1240 μmol/g, and porosities ranged from meso- to microporous. Average catalyst pore diameters ranged from 14 to 98 Å. It was felt that these catalysts would provide a wide range of properties and represent surface reaction to diffusion-controlled phenomena. The seven different SCF cosolvents were chosen to explore differing solvent strengths and transport properties. These cosolvents covered a wide range of densities, molecular weights, and dipole moments. Methane was chosen as the initial cosolvent to explore because it has a low critical temperature and can accommodate the low reaction temperatures explored and because it requires the lowest concentration to reach SCF conditions, potentially simplifying downstream separation.

The reactor feed cosolvent mole percentages required to reach the reaction critical temperatures are shown in Table 4. Two conditions were explored: no conversion of butene to product and complete reaction of butene with a molar equivalent of isobutane to produce a quantitative yield of 2,2,4-trimethylpentane. The two conditions represent the maximum spread of possible conditions at the entrance and exit of the experimental reactor. Cosolvent compositions are reported for the reactor entrance conditions, but they are adjusted in the calculations to account for reactant consumption and product yield. Reaction conditions for each cosolvent were chosen such that near-critical compositions were below the 0% conversion composition and supercritical compositions were at or above the 100% conversion composition (refer to Table 4). This ensured that the reaction took place in the intended phase.

Testing with methane was performed using each of the catalysts. The Pt/USY catalyst performed markedly better than the other catalysts, with the USY catalyst performing as a close second. Because solid-acid-catalyzed alkylation is expected to consume large quantities of catalyst and because platinum is costly, the USY catalyst was chosen for further testing rather than Pt/USY. The data generated from the catalyst testing experiments are copious; thus, only general comparisons of product yields from the various catalysts are first presented below, aimed at showing general differences between the catalysts. Then, detailed results of the effect of methane on alkylation using USY are shown, followed by a comparison of the different cosolvents.

Catalyst Comparisons: Effect of Methane Addition on Alkylation. Comparisons of C_{5+} and trimethylpentane (TMP) yields among the various catalysts tested are presented in Figure 3a and b. As noted above, the Pt/USY catalyst gave the best yields of C_{5+} and TMP of any of the catalysts. The highest yields were obtained under liquid conditions, at about 0.77 and 0.28 g of product per gram of catalyst for C_{5+} and TMP, respectively. The USY catalyst gave the second highest yields but under ML rather than liquid conditions. The Nafion SAC-25 and the S/ZrO$_2$ 600E catalysts both demonstrated modest results. The maximum yields for the Nafion SAC-25 catalyst were obtained under ML conditions, and the maximum yields for the S/ZrO$_2$ 600E
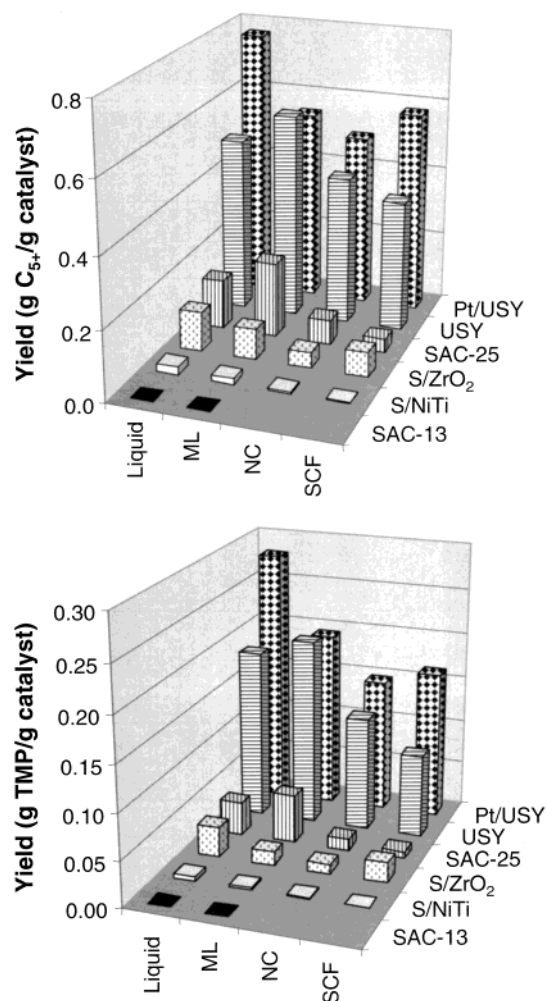

Figure 3. Total product yields for the various catalysts with methane cosolvent under liquid, ML, NCL, and SCF conditions. Reaction conditions: temperature and pressure as listed in Table 2, 0.1 OWHSV, and an iP/O ratio of 25:1. (a) Total alkylate (C_{5+}) yields and (b) total trimethylpentane (TMP) yields.

catalyst were obtained under liquid conditions. Both the S/NiTi and the Nafion SAC-13 catalysts gave poor yields, at less than 0.03 g of product per gram of catalyst.

For the Pt/USY catalyst, as well as for the S/NiTi, S/ZrO$_2$ 600E, and Nafion SAC-13 catalysts, the addition of methane to the reaction mixture decreased product yields compared to those obtained under methane-free liquid conditions. For the USY and Nafion SAC-25 catalysts, however, the addition of small amounts of methane (ML conditions) resulted in slightly increased product yields. For the USY catalyst, the addition of methane increased product yields by 12−16%. The Nafion SAC-25 catalyst yields increased by 45 and 50% for C_{5+} and TMP, respectively, as methane concentrations increased from 0 to 16 mol %. Continued increases in methane concentrations resulted in reduced product yields for both of these catalysts.

Under liquid conditions, once a maximum in the TMP yield was reached for each catalyst, with or without the addition of methane, further increases in the methane concentration decreased the TMP yields. In all cases, operation under SCF conditions was detrimental to TMP yields as compared to operation under methane-free liquid conditions. However, for both the Pt/USY and S/ZrO$_2$ 600E catalysts, product yields increased with
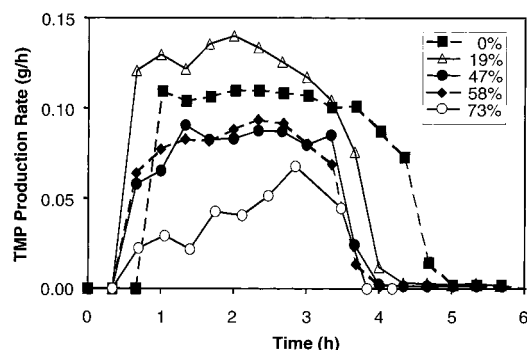
Figure 4. Time courses of trimethylpentane production rate at varying methane concentration using USY catalyst at 60 °C, 0.1 OWHSV, an iP/O ratio of 25:1, and 42 bar for liquid conditions (no CH_4) or 141 bar for ML, NCL, and SCF conditions.
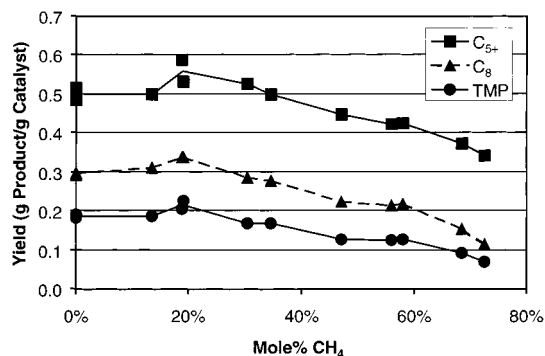

Figure 5. Effect of methane addition on total alkylate and trimethylpentane yields using USY catalyst at 60 °C, 0.1 OWHSV, an iP/O ratio of 25:1, and 42 bar for liquid conditions (no CH_4) or 141 bar for ML, NCL, and SCF conditions.

methane addition from NCL to SCF conditions. For example, the S/ZrO_2 600E TMP yield more than doubled as the reaction changed from NCL to SCF conditions. Despite this improvement, however, the TMP yield was still more than 35% lower under SCF conditions than under methane-free liquid conditions. Because of these results and because solid acid catalysts containing platinum are costly, USY was chosen as the model catalyst for further alkylation experiments. These results do not necessarily suggest that the USY is the best catalyst for alkylation, but within the group examined, it was the most practical for further study.

The results with all catalysts, either with or without added cosolvent, were rather poor. However, because a modest gain in catalyst performance was obtained with cosolvent addition, it was decided to explore the effect of methane concentrations at a higher level of detail.

Effect of Methane Addition on Alkylation Using USY Catalyst. *Yield.* Time courses of trimethylpentane production rates are shown in Figure 4 for various CH_4 concentrations. The experiment in which no methane was added displayed the longest catalyst life, with about 4.0 h elapsing from the onset of TMP production to its cessation. The addition of methane decreased the catalyst lifetime. At the highest supercritical concentration of 73 mol % CH_4, the catalyst deactivated the fastest, with a catalyst lifetime of only about 3.1 h.

The total alkylate, C_8, and trimethylpentane yields from USY catalyst at 60 °C are shown as a function of reactor feed methane mole percentage in Figure 5. The data show slight maxima in the three curves at 19 mol % CH_4. Liquid alkylation (methane-free) conditions
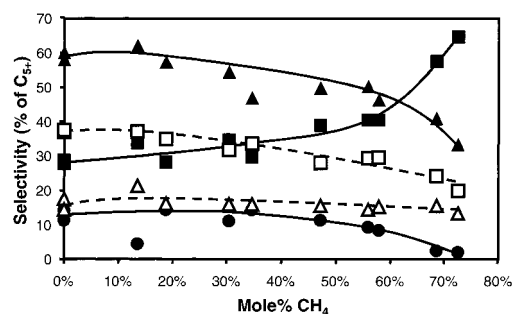

Figure 6. Variation of product selectivity with mole percentage of CH_4 cosolvent for C_5-C_7, total C_8, C_{9+}, TMP, and DMH. Data are presented as percentages of total alkylate yields using USY catalyst at 60 °C, 0.1 OWHSV, an iP/O ratio of 25:1, and 42 bar for liquid conditions (no CH_4) or 141 bar for ML, NCL, and SCF conditions. (■) C_5-C_7, (▲) C_8, (●) C_{9+}, (□) TMP, and (△) DMH. Curves were hand-drawn and are for illustration of trends only. Note that TMP and DMH are included in the total C_8 values.

produced an average of 0.50 g of C_{5+}, 0.29 g of C_8, and 0.19 g of TMP per gram of catalyst. The maximum yields were observed at 19 mol % CH_4 and averaged 0.56 g of C_{5+}, 0.34 g of C_8, and 0.21 g of TMP per gram of catalyst. Further addition of CH_4 above approximately 20 mol % reduced the product yields. At the maximum CH_4 concentration of 73 mol % (SCF conditions), the product yields were as low as 34% of those obtained at the optimum conditions of 19 mol % CH_4.

Product Selectivity. The product selectivities for cracking products (C_5-C_7), C_8 isomers, C_{9+} species, trimethylpentanes, and dimethylhexanes are shown in Figure 6 as weight percentages of total alkylate production. There was a general increase in cracking products with increasing CH_4 addition. Selectivity to cracking products more than doubled over the range of methane addition explored. Selectivity to C_8 decreased from 58 wt % at liquid conditions to 33 wt % at SCF conditions. Selectivity for the desired C_8 and TMP products increased slightly over liquid to about 62 and 37 wt % of total alkylate product, respectively, with the addition of 14 mol % CH_4 but decreased at higher methane concentrations. Increased methane addition also resulted in decreased production of higher-molecular-weight molecules. The C_{9+} selectivity decreased substantially from 14 wt % in the absence of methane to 2 wt % at 73 mol % methane.

The C_8 isomer selectivity as a percentage of total C_8 was explored as a function of methane concentration. In terms of octane rating, TMPs are desired compared to the less branched dimethylhexane (DMH) isomers. There was a slight decrease in the production of trimethylpentanes relative to dimethylhexanes in the range of CH_4 addition studied. TMP selectivity, as a percentage of total C_8 (not shown), was relatively insensitive to methane addition, averaging 61% over the range explored. Over the same range, DMH selectivity increased from 27 to 39%. Thus, over the range explored, the addition of methane to the reaction feed mixture decreased the TMP/DMH ratio from 2.3 to 1.5, thus reducing the overall product quality.

The dramatic reduction in C_{9+} product selectivity under SCF conditions could potentially be due to poor solubility in the supercritical reaction media. Because methane has a low critical density, it was decided to explore a wide range of supercritical cosolvents that could potentially enhance the extraction of heavy coke precursors and extend catalyst longevity.
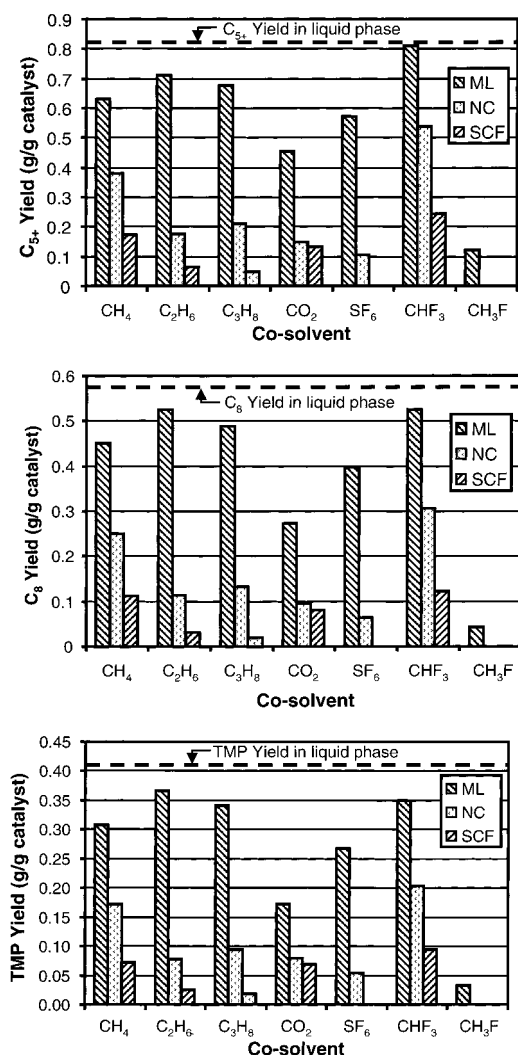
Figure 7. Product yields for the various cosolvents using USY catalyst at 60 °C, 0.2 OWHSV, an iP/O ratio of 25:1, and 111 bar for liquid conditions and all cosolvents except methane or 141 bar for methane. (a) C_{5+}, (b) C_8, and (c) TMP.

Effect of Other Cosolvents on Alkylation Using USY Catalyst. The SCF cosolvents explored included three hydrocarbons, two fluorocarbons, carbon dioxide, and sulfur hexafluoride. The cosolvents provided a wide range of densities, molecular weights, and dipole moments. It was anticipated that the seven fluids could provide a variety of solubilities and transport properties that could enhance the extraction of coke precursors from the microporous USY zeolite catalyst, leading to enhanced catalyst activity maintenance and product yields.

The effects of the various fluids under ML, NCL, and SCF conditions are shown in Figure 7a–c for C_{5+}, C_8, and TMP product yields, respectively. Product yields in the liquid-phase experiments are shown in each figure as dashed lines. The cosolvent concentrations are shown in Table 3, and the reactor feed cosolvent mole percentages required to reach the reaction critical temperatures are shown in Table 4. Reaction conditions were 60°C, an iP/O molar ratio of 25:1, and an OWHSV of 0.2 g of butene h^{-1} (g of catalyst)$^{-1}$. At the higher OWHSV of 0.2 g of butene h^{-1} (g of catalyst)$^{-1}$, the product yields using added cosolvents did not exceed the results obtained under liquid conditions. Regardless of the fluid explored, an increase in cosolvent concentration de-

Table 5. Comparison of Instantaneous Product Yields at Different OWHSVs for USY at 60 °C, 42 bar, methane-free liquid conditions

	OWHSV [g of butene (g of catalyst)$^{-1}$ h^{-1}]			
	0.09		0.21	
iP/O ratio	25.1:1	25.1:1	24.7:1	24.7:1
time (h)	1.7	2.4	1.7	2.4
butene conversion (%)	100	100	100	100
product	yield (g of product/100 g of butene)			
C_{5+}	149	144	159	144
C_5	18	17	16	13
C_6	15	14	13	10
C_7	15	14	15	10
C_8	88	89	109	102
TMP	58	59	79	74
DMH	26	25	30	26
other C_8s	4	5	0	2
TMP/DMH ratio	2.2	2.4	2.6	2.8
C_{9+}	13	11	6.5	10

creased product yield. Thus, for C_{5+}, C_8, and TMP, the yields decreased with reaction conditions as follows: liquid > modified liquid > NCL > SCF.

Under modified-liquid conditions, the best two fluids were trifluoromethane and ethane. The use of trifluoromethane provided the best C_{5+} yields, whereas the C_8 yields in trifluoromethane and ethane were identical. Finally, ethane provided the highest TMP yields. The product yields using methane and propane were slightly lower than those using trifluoromethane and ethane. The yields obtained with carbon dioxide and sulfur hexafluoride were modest compared to those obtained with trifluoromethane, ethane, propane, and methane. The yields obtained using monofluoromethane were poor.

Under NCL conditions, product yields were the highest using trifluoromethane, followed by those using methane. In comparison, modest product yields were obtained with propane (lower concentration), ethane, carbon dioxide, and sulfur hexafluoride. The yields obtained using propane (higher concentration) and monofluoromethane were poor.

Product yields were significantly lower under SCF conditions than under liquid, ML, or NCL conditions. Under SCF conditions, the use of trifluoromethane again provided the highest product yields. Total alkylate (C_{5+}) yields were 0.24, 0.17, 0.13, and 0.07 g per gram of catalyst using trifluoromethane, methane, carbon dioxide, and ethane, respectively. Similar trends were observed for the C_8 and TMP yields.

At the higher OWHSV of 0.2 g of butene h^{-1} (g of catalyst)$^{-1}$, the product yields under liquid reaction conditions increased substantially compared to those obtained at an OWHSV of 0.1 g of butene h^{-1} (g of catalyst)$^{-1}$. The total alkylate yield increased by 64%, while the C_8 and TMP yields more than doubled. Although the catalyst lifetime decreased at the higher OWHSV from 4.0 to 3.1 h, the instantaneous product yields based on the amount of *trans*-2-butene fed to the reactor were significantly higher, as shown in Table 5. The maximum instantaneous yields at the higher OWHSV were between 7 and 36% higher for C_{5+}, C_8, and TMP, while the catalyst longevity decreased only by 22% at the 2-fold higher feed rate. The overall selectivity to cracking products was approximately 20% lower, and the selectivity to C_{9+} compounds decreased by approximately 50% at the higher OWHSV. These

results suggest that the lower reactor residence time at the higher space velocity reduces the production and adsorption of heavier hydrocarbons, reduces cracking, and hence improves the total product yields.

Analogous studies carried out in a continuous stirred tank reactor (CSTR) demonstrated similar behavior (data not shown). The product yields increased as the OWHSV was changed from 0.1 to 0.2 g of butene h^{-1} (g of catalyst)$^{-1}$ under cosolvent-free liquid conditions. The product yields were highest at approximately 20 mol % cosolvent at an OWHSV of 0.1 g of butene h^{-1} (g of catalyst)$^{-1}$ and decreased as the cosolvent concentration was raised further. At the higher OWHSV of 0.2 g of butene h^{-1} (g of catalyst)$^{-1}$, the product yields decreased with increased cosolvent concentration. The CSTR studies employed both methane and ethane, independently, as the reaction cosolvent.

The results from all experiments demonstrated product yields less than expected for complete butene conversion. Ideally, 100% butene conversion would yield 2.04 g of product per gram of butene reacted. The fact that less than 2.04 g of product was formed per gram of butene (Table 5) indicates that butene was consumed for reactions other than alkylation. The other reactions might include butene dimerization and the formation of coke on the catalyst. Identification of these byproducts was beyond the scope of this study; however, this information would be useful for a mechanistic study of the reactions occurring on the catalyst.

Discussion

Of the six catalysts tested, the high-surface-area/high-total-acidity zeolites provided the highest product yields under the set of conditions explored. In general, product yield increased with total acidity in any given phase. The zeolite catalysts had the greatest number of acid sites to catalyze the alkylation reactions and required the greatest molar quantity of coke compounds to deactivate the catalyst. The addition of Pt might also have enhanced the total product yield by promoting the rate-limiting hydride-transfer rate.

Of the top four catalysts, there were two distinct behaviors related to the addition of methane. Both the USY and SAC-25 catalysts demonstrated an increase in product yield with the addition of methane in the liquid phase. However, as the methane concentration was increased further in the near-critical liquid and supercritical regions, the catalyst performance decreased. In contrast, the Pt/USY and S/ZrO$_2$ catalysts both showed a decrease in performance with increases in the methane concentration in the liquid and near-critical liquid regions, but they then demonstrated increases in product yield with a further increase in methane concentration in the supercritical region.

The behaviors of these catalysts with and without the addition of inert cosolvents can be explained using the mechanism of the alkylation reaction.[23] The USY and SAC-25 catalysts benefited from either dilution or reduced reactor residence time afforded by the addition of the cosolvent in the liquid phase. The dilution or reduced reactor residence time resulted in a decrease in the catalyst deactivation rate, which, in turn, improved the product yield per gram of catalyst. Further increases in methane led to a decrease not only in the butene concentration but also, and more importantly for these catalysts, in the isobutane concentration. When the reaction rate is limited by the hydride transfer of

isobutane with the tertiary TMP carbenium ion, the decrease in isobutane concentration leads to increased product cracking and catalyst deactivation. In contrast, the Pt/USY and S/ZrO$_2$ catalysts demonstrated improved performance as the reaction conditions changed from near-critical liquid to supercritical. As the fluid conditions change from liquid to supercritical, mass-transfer properties improve significantly. The results for these two catalysts suggest that the catalysts might be somewhat limited by internal mass transfer and might benefit from the improved mass-transfer properties of supercritical fluids. However, dilution of the reaction mixture by the cosolvent was still detrimental to catalyst performance.

The examination of the effect of the methane concentration in the reactor feed on the performance of the USY catalyst demonstrated a very modest improvement in catalyst performance. Total alkylate, C$_8$, and TMP productions increased somewhat at 19 mol % methane compared to methane-free liquid conditions. However, this increase was accompanied by a somewhat shorter catalyst lifetime and a slightly poorer selectivity to the desired products. Judging from the improved yields at the higher OWHSV, it would appear that the USY catalyst is positively influenced by shorter reactor residence times. Thus, the modest improvements in catalyst performance with the addition of 19 mol % methane at an OWHSV of 0.1 g of butene h^{-1} (g of catalyst)$^{-1}$ were most likely the result of reducing the reactor residence time through the addition of the cosolvent.

The seven cosolvents explored did not improve the catalyst performance for the conditions explored. These results did, however, demonstrate that light hydrocarbon fluids (methane, ethane, and propane) and trifluoromethane were better cosolvents for the isobutane alkylation reaction, whereas the other non-hydrocarbon fluids (CO$_2$, SF$_6$, and CH$_3$F) were poor. These results suggest that any further efforts with supercritical fluids should focus on light hydrocarbon fluids commonly available at petroleum refineries.

In contrast to the work of Clark and Subramaniam and Santana and Akgerman,[16,18] this effort did not demonstrate sustained catalyst activity at supercritical conditions with any of the catalysts or cosolvents examined. At the high levels of butene conversion (100%) and total alkylate yields (>140 wt %) explored in this work, the addition of supercritical fluids decreased catalyst lifetimes and desired product selectivities. We believe that the previous studies showing sustained catalyst activity,[16,18] which were observed at low levels of butene conversion (20%) and TMP product selectivity (5%), were primarily exploring the butene dimerization reaction, not alkylation. Both Chellappa et al.[17] and Santana and Akgerman[18] report that the majority of the reaction product observed under supercritical conditions was made up of alkenes. In this work, we also observed product formation after the cessation of TMP production. In Figure 2 above, for example, butene breakthrough was first observed at 6.1 h TOS, and TMP concentrations were below detectable levels 46 min thereafter. Olefin dimerization and oligomerization reactions are well-known and practiced on an industrial scale but were not explored in this work. Thus, we found that only modest benefits could be obtained by the addition of supercritical fluids and that sustained solid catalyst alkylation activity was not

achieved at industrially relevant conversions and TMP product yields.

Conclusions

This work demonstrated that, for the conditions explored, the zeolite catalysts had the best performance of the six catalysts studied. Exploration of the seven different fluids showed that the light hydrocarbons and trifluoromethane were better cosolvents, whereas the other non-hydrocarbon fluids (CO_2, SF_6, and CH_3F) were poor.

This study was unable to show the improvements in solid acid alkylation catalyst function necessary to replace the liquid acid processes currently used in industry. To develop a solid catalyst process that has the potential to replace the liquid acids, catalysts and/or process conditions must be developed that improve catalyst lifetimes, product yields, and product quality. Improvement needs include catalysts or conditions that suppress coke production or enhance coke removal and improve the hydride-transfer rate-limiting step. These two improvements would result in longer catalyst activity and improved product quality.

Acknowledgment

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