

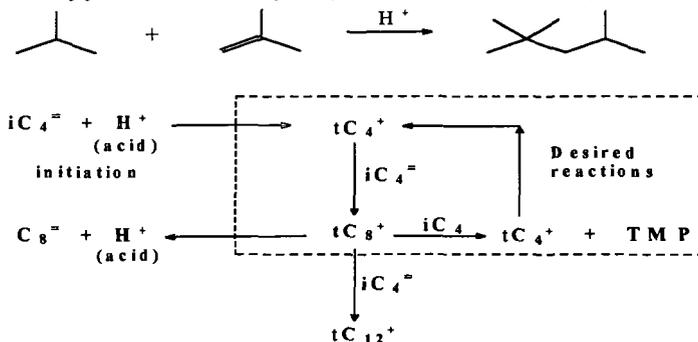
ALKYLATION OF ISOBUTANE AND BUTENES OVER ANION-MODIFIED ZIRCONIUM OXIDE CATALYSTS.

Xin Xiao, Jianmin Chen[†], Shuguang Zhang, John W. Tierney and Irving Wender*
 Department of Chemical and Petroleum Engineering, 1249 Benedum Hall,
 University of Pittsburgh, Pittsburgh, PA 15261

Keywords: alkylation, solid acid catalyst, anion-modified zirconium oxide

Introduction Alkylation of isobutane with butenes is an important industrial process for the production of iso-octane and its isomers, i.e., trimethylpentanes (TMPs). The product, called alkylate, has a high octane number (90-94 RON), low vapor pressure (RVP), no aromatics or olefins. It is a preferred blending stock for reformulated gasoline. The production of alkylate in the US should exhibit steady growth through the year 2000 [1] and will top 900,000 b/d in 1997 [1], about 13 vol% of the US gasoline pool [2]. Two types of commercial processes are now in operation: one based on HF, the other on H₂SO₄. There are considerable environmental concerns about the use of the toxic HF and sulfuric acid presents problems of corrosion and disposal of spent catalysts. Efforts are being made to use HF in a way to reduce its volatility [3]. It is recognized that alkylate production by use of an environmentally benign solid acid catalyst is highly desirable [4-8]. Work on the chemistry and technology of C₄ alkylation before 1993 has been reviewed [9]. A recent symposium was held on the use of solid acid catalysts and processes [10]; none have been commercialized as yet. Major problems for solid catalyst alkylation are short catalyst life time and low selectivity to TMP.

Rao [2] has written a reaction pathway for the isobutane-isobutene alkylation:



Two major undesirable reactions usually occur: competitive side reactions leading to formation of octenes rather than TMPs; and consecutive side reactions leading to higher (C₁₂ and C₁₆) hydrocarbons. To obtain a high selectivity to alkylate, a low olefin concentration must be maintained in the reaction zone; high isobutane to olefin feed ratios and high olefin conversions are necessary. In commercial alkylation processes, the feed isobutane/butenes ratios (external ratio) are typically 5-8 for the H₂SO₄ process and 10-14 for the HF process. Due to high olefin conversion inside the reactor, the internal isobutane/butenes ratios are much higher. However, this ratio is difficult to maintain on a solid catalyst surface because olefin adsorption is much stronger than paraffin adsorption. This may explain a difficulty of the alkylation process over solid catalysts.

Recently, new types of anion-modified metal oxides have drawn increasing attention [11-13]. Metal-promoted ZrO₂/SO₄ and ZrO₂/WO₃ are strong solid acids with activity for hydrocracking and hydroisomerization of hexadecane, polyethylene and Fischer-Tropsch waxes at relatively mild reaction conditions [14-16]. Initial activity has been demonstrated over ZrO₂/SO₄ catalyst for alkylation reaction [7, 17]. In this work we investigated the alkylation chemistry and deactivation behavior over two Pt-promoted anion-modified metal oxide catalysts, Pt/ZrO₂/SO₄ (PtSZ) and Pt/ZrO₂/WO₃ on Al₂O₃ support (PtWZ-Al₂O₃).

Experimental Section

Feed mixture preparation. Isobutane (i-C₄H₁₀, 99.7%; C₃H₈, 0.3%) was obtained from Praxair. A mixture containing isobutene (i-C₄H₈, 8%; i-C₄H₁₀, 91%; C₂H₆, 1%) and a mixture containing cis-2-butene (cis-2-C₄H₈, 20%; i-C₄H₁₀, 80%) were obtained from Air Products. All three are in steel cylinders with dip tubes. Various ratios of isobutane/butene were made by mixing into a

*Correspondence author. [†]Current address: Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China.

500ml steel container kept at dry ice temperature. Before loading of each component, connecting tubes were purged with the feed component to remove air. The steel container with its contents was weighed each time after a component was put in. The final composition of the mixture was calculated and verified by GC.

Catalyst Synthesis. The solid catalysts PtSZ and PtWZ-Al₂O₃ were synthesized following a similar method described elsewhere [15]. ZrCl₄ was dissolved in 1500 ml of distilled water and hydrolyzed at room temperature by slowly adding 28-30% NH₄OH with vigorous agitation until pH = 9 was reached. The mixture was stirred for another 30 min and left to settle overnight. The precipitate [Zr(OH)₄] was filtered and washed with distilled water until no chloride ions were detected. The solid was then dried at 110 °C overnight and ground to below 100 mesh. Sulfation was carried out by treating 10.0 g of the resultant Zr(OH)₄ with 150 ml of 0.5 M H₂SO₄ solution for 30 min with constant stirring. The solid was separated from the liquid by filtration, rinsed with ~150 ml of water and dried at 110 °C overnight. The sample was loaded with 0.5 wt% Pt by incipient wetness impregnation of a H₂PtCl₆ aqueous solution, dried at 110 °C overnight and calcined at 650 °C for 3 hr. Tungsten [WO₃/(ZrO₂ + WO₃) = 8.3 wt%] was loaded on Zr(OH)₄ by incipient wetness impregnation of a (NH₄)₆H₂W₁₂O₄₀ solution. The sample was dried at 110 °C overnight, mixed with γ-Al₂O₃ (ZrO₂:Al₂O₃ = 1:1 by wt), and impregnated with 0.5 wt% Pt (based on total solid) using an H₂PtCl₆ aqueous solution. The sample was dried at 110 °C overnight and calcined at 700 °C for 3 hr.

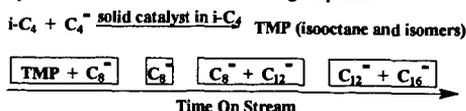
Reactor. A continuous up-flow fixed bed reactor equipped with on-line GC analysis was employed. The isobutane/butene mixture was maintained in liquid phase under He pressure, and fed to the reactor by a piston-type pump. The reactor temperature was controlled by a computer in the range of 30 - 750 °C; pressure was controlled by a back-pressure regulator in the range of ambient to 1000 psig. Various gases, air, He, N₂ and H₂, could be fed into the reactor and the flow rate controlled by a mass flow meter.

Experimental Procedure. Catalysts were formed into pellets and then crushed to 40-60 mesh particles. The catalyst was then mixed with the same weight of 50-70 mesh quartz sand and packed into a 3/8" o.d. stainless steel tubular reactor. Quartz sand was packed before and after the catalyst bed. Before a reaction, the reactor system was purged with He and pressurized. Liquid isobutane was pumped into the reactor and heating started. The feed was switched from an isobutane to isobutane/butene mixture at least 10 min after a stable reaction temperature was reached. Time-on-stream (TOS) was recorded as zero min at the moment of the feed switch. On-line GC analysis (FID detector) was used periodically to analyze product composition. Liquid products condensed by dry ice were kept in a refrigerator (4 °C). After evaporation of isobutane, the remaining liquid products were identified by GC/MS and compared with literature data [18], pure compounds, and boiling points of the species.

Results and Discussion

Alkylation of isobutane and 2-butene. Figure 1 shows liquid product obtained from alkylation of isobutane and 2-butene over a Pt/ZrO₂/SO₄ catalyst at a whsv of 2.0 h⁻¹. The main peak was 2,2,4-TMP, accompanied by 2,3,4- and 2,3,3-TMPs. Dimethylhexanes (DMHs), branched C₈ olefins, C₉ and higher paraffins and olefins as well as C₃-C₇ cracking products were also found. At a lower whsv, 0.25 h⁻¹, under otherwise identical conditions, the catalyst life time was extended and TMP selectivity increased (Table 1). GC analysis revealed that the increase in TMP selectivity at the lower whsv was mainly due to an increase of 2,3,4- and 2,3,3-TMPs (Figure 2). However, fractions higher than C₈ also increased. At prolonged reaction times (1.5 and 5 hr, respectively) TMPs were diminished but selectivities to C₈ olefins and higher hydrocarbons increased in both runs.

Deactivation and regeneration of the catalyst. TMP selectivity was highest at low TOS; C₈ olefins appeared a few minutes later, and gradually replaced TMP as the main peak during alkylation of isobutane and 2-butene over a PtSZ catalyst. At high TOS, C₈, C₁₂ and C₁₆ branched olefins were the main products, as shown in the following sequence:



Conversion of 2-butene remained almost unchanged in the first few hours. The shift in product composition was probably due to adsorption phenomena on the catalyst surface. The catalyst surface was originally covered only by isobutane. When the isobutane/2-butene mixture passed through the catalyst bed, 2-butene first reacted with surface isobutane to yield TMP. The more strongly adsorbed 2-butene then started to replace isobutane from the catalyst surface. After

the concentration of 2-butene reached a certain level, C₈ olefins formed by dimerization of adsorbed 2-butene were the main product. The C₈ olefins reacted further with 2-butene to give C₁₂ and C₁₆ olefins. TMPs as the main product indicated predominant adsorption of isobutane on the catalyst surface, and C₈ olefins as the main product indicated adsorption of 2-butene, and C₁₂ olefins indicated C₈ olefin adsorption. Jong et al. indicated that these side reactions contribute to catalyst deactivation [19]. Low butene concentration is crucial in alkylation to keep good TMP selectivity.

To verify the surface adsorption hypothesis, a series of regeneration experiments on the same catalyst were performed. Since solid alkylation catalysts could be regenerated by air, H₂ stripping [20] and solvent extraction [21], the catalyst deactivation is probably caused by carbonaceous deposits.

Full regeneration was indicated when TMPs appeared as the main product at the beginning of a run. The run was continued until C₁₆ olefins appeared. Without regeneration, only C₈ and higher olefins were observed. As seen in Table 2, the catalyst was successfully regenerated by H₂ accompanied by liquid isobutane flow (400 psig) at 110 °C for 30 min. It can be explained by assuming that the surface was saturated with adsorbed 2-butene and C₈ olefins which were replaced by an excess of isobutane. The catalyst was also successfully regenerated at 71 °C for 2 hr in H₂ and isobutane. However, when the temperature was lowered to 24 °C, the catalyst was only partially regenerated as indicated by both TMP and C₈ olefin peaks at the initial TOS. The catalyst was also regenerated by air at 450 °C and 690 °C. If deactivation of the catalyst were caused by surface lay down of olefins, removal of olefins by desorption would regenerate the catalyst. To test this, He was passed through the reactor which was gradually heated to 450 °C and kept at that temperature for 3 hr, a procedure similar to TPD; the following alkylation reaction showed initial activity to TMPs. Repeated regeneration by He at 450 °C was also successful. The experiments indicated that degradation of the catalyst was caused by strong adsorption of certain species, probably olefins, which covered active sites responsible for alkylation, but the active sites were never destroyed.

Alkylation of isobutane and isobutene. In order to weaken the adsorption of olefins and enhance the adsorption of isobutane on the catalyst surface, the following modifications were made: (1) PtWZ (on a γ -Al₂O₃ support), which has higher hydrogen transfer activity than PtSZ [22,23], was used as catalyst; (2) reaction temperature was increased to 150 °C; and (3) H₂ was used along with the feed. It was found that low H₂ amounts (less than 1 mol% of total feed) was not enough to suppress polymerization reactions while H₂ amounts greater than 100 mol% of isobutene stopped the alkylation reaction by hydrogenation of isobutene. By comparing runs with and without H₂, and other process variables, suitable reaction conditions and product compositions were obtained (Table 3). At 150 °C and 780 psig (supercritical), isobutene conversions reached 100.0% and 2,2,4-TMP selectivity was between 65.1 to 83.2 %. On-line GC analysis of this run at 4.0 hr is shown in Figure 3. The run was stopped after 6.8 hr. No deactivation was observed. TMP selectivity had a tendency to increase with TOS; selectivities were 65.1 % at 1.7 hr and 83.2 % at 6.8 hr. C₈ components other than 2,2,4-TMP were TMP isomers and DMHs. No olefins were observed. All by-products were in trace amounts except C₁₂ branched paraffins, which was about 20 wt%. Total gasoline boiling fractions (C₅-C₁₂) were over to 99 % in all TOS. A run with a lower H₂ to isobutene ratio, i.e., H₂ : isobutene = 1 : 5 (mol), was also made for a longer run time, i.e., 8.3 hr (Table 3). Similar results were observed. The H₂ to isobutene molar ratio was varied from 1:5 to 1:3. Larger amounts of H₂ hydrogenated olefins and decreased the TMP yield dramatically. If the amount of H₂ was lower, TMP selectivity could not be maintained, eventually being replaced by C₈ and higher olefins.

Acknowledgment. The research was supported by the U.S. Department of Energy through the Consortium for Fossil Fuel Liquefaction Science (Grant No. DE-FC22-93PC93053).

REFERENCES

- (1) Gonzalez, R. G., editor, *Fuel Reformulation*, January/February, 1995, 37-41.
- (2) Rao, P.; Vatcha, S. R., *Oil & Gas Journal*, September 9, 1996, 56-61.
- (3) Del Rossi, K. J. US Patent 5,220,096 1993.
- (4) Garwood, W. E.; Leaman, W. K.; Myers, C. G.; Plank, C. J. US Patent 3,251,902 1966.
- (5) Yang, C.; Ossining, N. Y. US Patent 3,851,004 1974.
- (6) Chu, Y. F.; Chester, A. W. *Zeolites*, 1986, 6, 195-200.
- (7) Corma, A.; Juan-Rajadell, M. I.; Lopez-Nieto, J. M.; Martinez, A.; Martinez, C. *Applied Catalysis A: General*, 1994, 111, 175-189.
- (8) Taylor, R. J.; Sherwood, D. E. Jr. *Applied Catalysis A: General*, 1997, 155, 195-215.
- (9) Corma, A.; Martinez, A. *Catalysis Reviews-Science & Engineering*, 1993, 35(4), 483-570.
- (10) *Symposium on New Chemistry with Solid-Acid Catalysts in the Alkylation of Isobutane with Olefins, Division of Petroleum Chemistry*, 212th ACS National Meeting, Orlando, FL, August 25-29, 1996, 668-724.

- (11) Song, X.; Sayari, A. *Catalysis Reviews-Science & Engineering*, 1996, 38, 329-412.
- (12) Arata, K. *Applied Catalysis A: General*, 1996, 146, 3-32.
- (13) Misono, M.; Okuhara, T. *CHEMTECH*, November, 1993, 23-29.
- (14) Wen, M. Y.; Wender, I.; Tierney, J. W. *Energy & Fuels*, 1990, 4, 372.
- (15) Venkatesh, K. R.; Hu, J.; Wang, W.; Holder, G. D.; Tierney, J. W.; Wender, I. *Energy & Fuels*, 1996, 10, 1163-1170.
- (16) Shabtai, J.; Xiao, X.; Zmierzczak, W. *Energy & Fuels*, 1997, 11, 76-87.
- (17) Guo, C.; Yao, S.; Cao, J.; Qian, Z. *Applied Catalysis A: General*, 1994, 107, 229-238.
- (18) Durrett, L. R.; Taylor, L. M.; Wantland, C. F.; Dvoretzky, I. *Analytical Chemistry*, 1963, 35(6), 637-641.
- (19) de Jong, K. P.; Mesters, C. M. A. M.; Peferoen, D. G. R.; van Brugge, P. T. M.; de Groot, C. *Chemical Engineering Science*, 1996, 51(10), 2053-2060.
- (20) Zhang, S. Y.; Gosling, C. D.; Sechrist, P. A.; Funk, G. A. US Patent 5,489,732 1996.
- (21) Cooper, M. D.; Rao, P.; King, D. L.; Lopez, R. R. US Patent 5,326,923 1994.
- (22) Iglesia, E.; Barton, D. G.; Soled, S. L.; Misco, S.; Baumgartner, J. E.; Gates, W. E.; Fuentes, G. A.; Meitzner, G. D. *11th International Congress on Catalysis - 40th Anniversary Studies in Surface Science and Catalysis*, 1996, 101, 533-542.
- (23) Iglesia, E.; Soled, S. L.; Kramer, G. M. *Journal of Catalysis*, 1993, 144, 238-253.

Table 1. Liquid Product Composition after Evaporation of isobutane

TOS range min	whsv, h ⁻¹	C ₅ -C ₇	C ₈			C ₉ +
			TMPs	other paraffins	olefins	
20 - 70	2.00	4.2	24.6	0.7	17.4	53.1
138 - 285	0.25	2.3	32.7	7.0	7.5	50.5

Catalyst: PtSZ, 40-60 mesh, mixed with the same weight of 50-70 mesh quartz sand.
Reaction temperature, 30 °C; liquid pressure, 400 psig (no H₂); i-C₄:2-C₄* = 20.

Table 2. Various Successful Regeneration Conditions for a PtSZ catalyst for Alkylation of Isobutane with 2-Butene^a

110 °C	30 min	H ₂ /i-C ₄ H ₁₀
71 °C	2 hr	H ₂ /i-C ₄ H ₁₀
690 °C	3 hr	air
450 °C	3 hr	air
450 °C	3 hr	He

* The same catalyst was used.

Table 3. Alkylate Compositions from On-line GC Analysis

TOS, hr	Product Composition				
Run No. 1 (a)	C ₅ -C ₇	2,2,4-TMP	other C ₈	C ₉ -C ₁₂	C ₁₃ +
0.9	2.8	73.7	2.6	20.5	0.4
1.7	1.5	65.1	4.5	28.6	0.3
3.1	0.0	74.4	0.9	24.8	0.0
4.0*	0.3	79.4	2.3	18.0	0.0
4.6	0.0	78.3	1.0	20.6	0.1
6.3	0.0	80.3	1.2	18.1	0.4
6.8	0.0	83.2	0.9	15.9	0.0
Run No. 2 (b)	C ₅ -C ₇	2,2,4-TMP	other C ₈	C ₉ -C ₁₂	C ₁₃ +
5.2	4.7	67.4	7.9	20.0	0.0
5.7	3.4	72.2	7.1	17.3	0.0
6.8	3.1	79.4	6.8	10.7	0.0
8.3	5.1	77.2	11.3	6.4	0.0

Conditions: 150 °C; 780 psig; PtWZ-Al₂O₃ catalyst; (a) whsv, 0.5 h⁻¹; H₂:i-C₄:i-C₄* = 0.3:16.3:1(mol), (b) whsv, 1.5 h⁻¹; H₂:i-C₄:i-C₄* = 0.2:16.3:1 (mol). * See Figure 3.

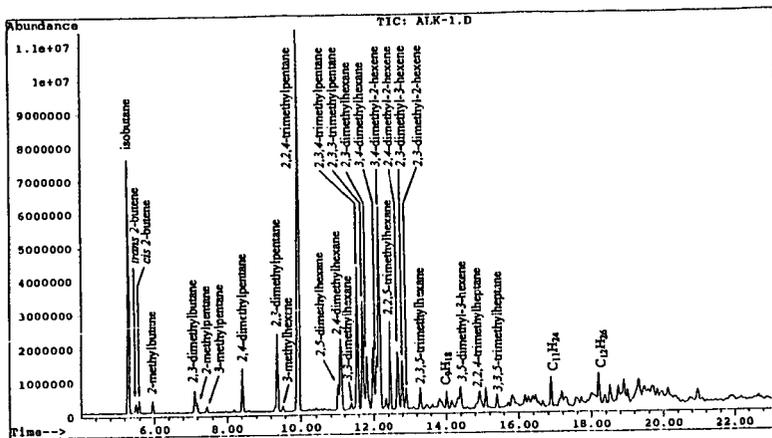


Figure 1. Liquid Products from Alkylation of Isobutane and 2-Butene (fixed bed reactor; isobutane/butene ratio, 20; 30 °C; 400 psig; WHSV, 2.0 h⁻¹; catalyst, PtSZ).

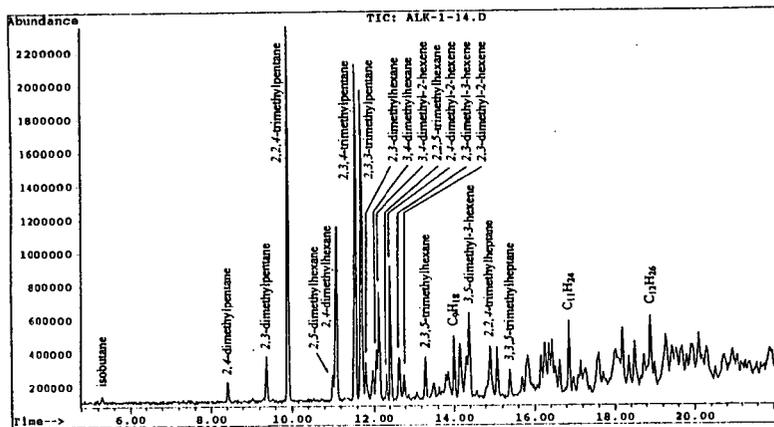


Figure 2. Liquid Products from Alkylation of Isobutane and 2-Butene (fixed bed reactor; isobutane/butene ratio, 20; 30 °C; 400 psig; WHSV, 0.25 h⁻¹; catalyst, PtSZ).

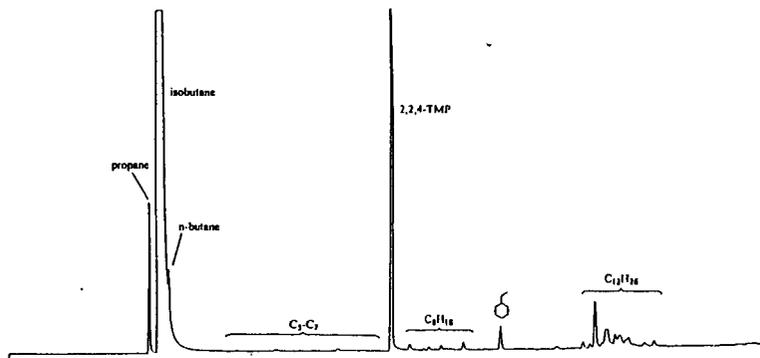


Figure 3. On-line GC Analysis of Alkylate from Isobutane and Isobutene at 242 min TOS (fixed bed reactor; I₂: I-C₁: I-C₂* = 0.3 : 16.3 : 1; 150 °C; 780 psig; WHSV, 0.5 h⁻¹; Pt(WZ-Al₂O₃).