

HYDROCRACKING OF POLYOLEFINS OVER METAL-PROMOTED,  
ANION-MODIFIED ZIRCONIUM OXIDES

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## 1. Introduction

Post-consumer plastic makes up about 13 wt% of the 48 million tons of total packaging wastes generated annually<sup>(1)</sup>. Plastics are non-biodegradable, constitute an increasingly large volume of solid wastes (20 vol.% in 1990), and are not being recycled to a significant extent<sup>(1)</sup>. Pyrolysis, as an alternative for plastic waste recycling, usually results in unsaturated and unstable oils of low yield and value. Significant amounts of char are formed on pyrolyzing plastic wastes.

Liquefaction of plastic wastes could be a useful way of producing desirable liquid transportation fuels. Thermoplastics such as polyethylene (PE), polypropylene (PP) and polystyrene (PS) make up more than 75 wt% of plastic wastes<sup>(1)</sup>. The liquid products obtained from them are likely to have a high volumetric energy content because of their relatively high (H/C) atomic ratio. It is known that strong liquid superacids such as Magic acid ( $\text{HSO}_3\text{F}:\text{SbF}_5$ ) are effective in converting paraffinic wax to t-butyl cations at room temperature; however, the stability of these liquid acids is poor at the high temperatures and reducing environments<sup>(1)</sup> needed for improving the H/C ratio of the products. In this paper, we discuss the results obtained from the hydrocracking of high density polyethylene (HDPE), PP and PS over metal-promoted anion-modified zirconia catalysts, viz.,  $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ ,  $\text{Ni}/\text{ZrO}_2/\text{SO}_4$  and  $\text{Pt}/\text{ZrO}_2/\text{WO}_3$ . Strong solid acids such as these are active in a variety of acid-catalyzed hydrocarbon reactions<sup>((1),(1),(1),(1),(1))</sup>; they are environmentally benign, non-corrosive (unlike strong liquid acids) and are easily separated from product streams. They are also characterized by long-term activity in the presence of hydrogen<sup>(1)</sup> in reactions such as n-butane isomerization and higher alkane cracking<sup>(1)</sup>.

## 2. Experimental

The sulfated zirconium oxides were prepared as described in a previous publication<sup>(11)</sup>. Modification of  $\text{ZrO}_2$  by tungstate ( $\text{WO}_3$ ) was achieved by wet impregnation of ammonium metatungstate onto  $\text{Zr}(\text{OH})_4$ , followed by drying and

calcination at 700°C for three hours. Incorporation of Ni on to anion-modified zirconia was achieved using wet impregnation of  $\text{Ni}(\text{NO}_3)_2$  followed by drying at 110°C overnight and calcination at 600°C or 700°C for three hours. The amounts of Pt and Ni promoted onto the catalysts were 0.5 wt% and 2.0 wt% respectively, based on the final weight of the catalyst. HDPE (density 0.95,  $M_{\text{ave}}=250,000$ ) was obtained from Solvay Polymers; PP (isotactic, density 0.85,  $M_{\text{ave}}=250,000$ ) and PS ( $M_{\text{ave}}=280,000$ ) were obtained from Aldrich Chemicals Inc. A Pt/ $\text{Al}_2\text{O}_3$  catalyst (1 wt% Pt) was purchased from Aldrich and was activated at 450°C in air for one hour before use. All of our polymer reaction studies were conducted in a 27 cc stainless steel microautoclave attached to a 15 cc reactor stem. The catalysts were activated at 450°C in air for one hour before use; to minimize exposure to moisture, they were then charged immediately into a dried (110°C) reactor which was then quickly sealed. After cooling to room temperature, the reactants were added through the reactor stem. The feed to catalyst ratio was 5:1 by weight in all experiments. The reaction pressure (initial) at 325°C and 1200 psig (cold)  $\text{H}_2$  were 1835 psig; initial reaction pressures at 375°C experiments for 1200 psig (cold)  $\text{H}_2$  and 750 psig (cold)  $\text{H}_2$  were 1930 psig and 1210 psig respectively. The reaction products were analyzed using a GC-MS (Hewlett Packard 5970B) and a gas chromatograph (Hewlett Packard 5890 II) with an FID detector.

Simulated distillations of products obtained were conducted using an HP 5890 Series II gas chromatograph (with a TCD detector) controlled by a HP 3396A integrator which is programmed to run the ASTM D2887 distillation method. The entire product mixture is dissolved in carbon disulfide ( $\text{CS}_2$ ) to form a homogeneous mixture;  $\text{CS}_2$  is not detected by the TCD detector of the simulated distillation unit. The result is given as a series of boiling points, one after every 5 wt% of the sample is eluted. Sulfur and tungsten analyses of the catalyst samples were performed by Galbraith Laboratories, Inc.

### 3. Results and Discussion

The physical properties of some of the catalysts used in the study is shown in Table 1. It is evident that the introduction of an anionic group onto  $\text{ZrO}_2$  results in increased surface area and lower particle size. Crystallographic retardation of  $\text{ZrO}_2$  is induced by the anion-derived group, causing the active catalysts to be in the metastable tetragonal form even after calcination at 600-700°C.

Hydrocracking of HDPE at 325°C (1200 psig (cold)  $\text{H}_2$ , 60 min.) over the Pt/ $\text{ZrO}_2/\text{SO}_4$  catalyst gave a 25 wt% conversion, mainly to gases ( $\text{C}_1\text{-C}_6$  alkanes), perhaps due to poor mass transfer during reaction so that liquid products from the initial cracking of HDPE underwent multiple cracking to gases. When HDPE was

reacted at 375°C and 1200 psig (cold) H<sub>2</sub> (for 25 min.) over the same catalyst, more than 99 wt% of HDPE could be converted to liquids (69 wt%) and C<sub>1</sub>-C<sub>5</sub> gases (~ 35 wt%) (Table 2). Total conversion was based on solid recovered which likely consisted of polyethylene molecules of shorter chain length than the starting HDPE. When the same reaction was conducted with a Ni/ZrO<sub>2</sub>/SO<sub>4</sub> catalyst, HDPE conversion exceeded 96 wt% with slightly different liquid and gas yields (Table 2).

The isomerized/normal ratios of products (alkanes) formed over Pt/ZrO<sub>2</sub>/SO<sub>4</sub> and Ni/ZrO<sub>2</sub>/SO<sub>4</sub> catalysts are compared in Figure 1, for the conversion data shown in Table 2. Large amounts of isoparaffins are obtained for each carbon number, close to an order of magnitude higher than their straight-chain counterparts, indicating predominant kinetic control during reaction. The more stable branched carbenium ions could abstract a hydride ion from an oligomeric fragment or react with hydride ions formed from the dissociation of molecular hydrogen over the metal as suggested by Iglesia et al.<sup>(1)</sup> and are thus easily desorbed from the catalytic sites before an equilibrium is reached. Impregnation of Ni on ZrO<sub>2</sub>/SO<sub>4</sub> resulted in a higher iso/normal ratio of C<sub>4</sub>-C<sub>9</sub> alkanes from HDPE than that obtained with Pt. This may be due to the lower hydrogenation activity of Ni (based on n-hexadecane hydrocracking experiments<sup>(1)</sup>) resulting in correspondingly lower concentration of hydride ions on the catalyst surface; the adsorbed carbocations could undergo a higher degree of skeletal transformation before desorption from the active sites by hydride transfer.

The product distribution from polyolefin hydrocracking can be controlled to obtain either high yields of C<sub>5</sub>-C<sub>12</sub> isoalkanes or gases with high selectivity to isobutane and isopentane (useful as precursors to gasoline alkylate or octane-enhancing oxygenates). Reaction time and temperature were found to be the most important parameters controlling this distribution. This is illustrated in Table 3 where increasing the reaction time from 25 min. to 60 min. at 375°C resulted in high yields of C<sub>1</sub>-C<sub>5</sub> alkanes from HDPE at the expense of gasoline-range products. Note that the selectivity to isobutane and isopentane remained above 67 mol%, regardless of the gas yield. Only small amounts of methane and ethane were formed. This indicates that isobutane and isopentane are the terminal products from the multiple cracking of HDPE and once formed, they probably do not further participate in the reaction by remaining in the gas phase.

Hydrocracking of HDPE over a Pt/ZrO<sub>2</sub>/WO<sub>3</sub> catalyst at 375°C and 1200 psig (cold) H<sub>2</sub> for 25 min. also resulted in complete conversion of the polymer with a slightly lower yield of C<sub>1</sub>-C<sub>5</sub> light alkanes compared to that obtained using Pt/ZrO<sub>2</sub>/SO<sub>4</sub> (Table 4). Also, the iso/normal ratio of cracked products were lower in the case of the tungstate-modified catalyst as compared with the sulfated zirconia catalyst. PP and PS could also be hydrocracked over the metal-promoted anion-modified zirconia catalysts at 300-325°C and 750-1200 psig (cold) H<sub>2</sub>.

Despite the high activity of sulfated zirconia catalysts for polyolefin hydrocracking, the loss of sulfur during reaction (from sulfur analysis of recovered catalyst) makes them unlikely candidates for reactions at long on-stream times. However, no appreciable loss of tungsten was observed from the Pt/ZrO<sub>2</sub>/WO<sub>3</sub> catalyst recovered from HDPE hydrocracking reactions indicating that this catalyst was more stable in severe reducing environments. Catalyst characterization revealed no sintering or agglomeration during reaction; XANES analysis indicated that the oxidation state of tungsten (+6) was also not affected during reaction.

#### 4. Conclusions

Metal-promoted, anion-modified zirconia catalysts are effective for the hydrocracking of polyolefins, giving either high yields of gasoline-range isoalkanes or gases rich in isobutane and isopentane. The ratio of isomerized/normal alkanes obtained depend strongly upon the nature of the promoter metal and anion-derived group present on zirconia. While Pt exists in the zerovalent state on the surface of the catalysts, Ni exists as NiO and needs to be reduced *in situ* before providing an active hydrogenation function. The sulfated zirconia catalysts lose sulfur during reaction whereas tungstate-modified catalysts are stable (no loss in W content and its oxidation state) during polyolefin hydrocracking in severe reducing environments.

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Table 1 Physical properties of some anion-modified metal oxides.

Catalyst	S or W conc. (wt%)	Calc. Temp. (°C)	BET Surface Area (m <sup>2</sup> /g)	Avg. Particle Size (Å)	Crystalline Phase
Pt/ZrO <sub>2</sub> /SO <sub>4</sub>	1.63	630	102.5	90 ±5	Tetragonal
Pt/ZrO <sub>2</sub> /WO <sub>3</sub>	7.07	700	62.0	92 ±5	Tetragonal
ZrO <sub>2</sub>	0	500	47	132 ±5	Tetragonal

Table 2 HDPE hydrocracking over metal-promoted sulfated zirconia catalysts.<sup>a</sup>

Product Range	YIELD (wt%) obtained with	
	SZPt0.5	SZNi2.0
Conversion	99 wt%	98 wt%
Gases (C1-C5 alkanes)*	35.0	30.0
Alkanes in:		
Gasoline range (C5-C12)	63.7	65.6
Diesel range (C13-C20)	0.3	2.4
C21 and above	trace	trace

a: Conditions were 375°C, 1200 psig (cold) H<sub>2</sub>, 25 min.; \*The distribution of C5 into gas and liquid products is controlled by VLE and can be determined by data given in Tables 3 and 4 respectively.

Table 3 Effect of reaction time on product distribution from HDPE hydrocracking.

Reaction time --	25 min.	60 min.
<i>Product range</i>	<i>Yield (wt%)</i>	
C <sub>5</sub> -C <sub>20</sub> liquids	64.0	4.0
C <sub>1</sub> -C <sub>5</sub> gases	35.0	95.0
<i>Gas product</i>	<i>Selectivity (mol%)</i>	
methane+ ethane	4.4	6.4
propane	5.0	5.0

<b>isobutane</b>	<b>44.5</b>	<b>44.5</b>
<b>n-butane</b>	<b>6.7</b>	<b>13.1</b>
<b>isopentane</b>	<b>30.8</b>	<b>22.5</b>
<b>n-pentane</b>	<b>8.6</b>	<b>8.5</b>

Table 4 Effect of modification of anion-derived group on product distribution from HDPE hydrocracking.

Catalyst →	SZPt0.5	WZPt0.5
Conversion	99 wt%	98 wt%
Yield of C <sub>1</sub> -C <sub>5</sub> gases	35.0 wt%	25.0 wt%
Yield of C <sub>5</sub> -C <sub>12</sub> alkanes	63.7 wt%	73.0 wt%
ALKANE	Iso/normal ratio	
C4	3.6	2.7
C5	2.9	1.9
C6 <sup>#</sup>	4.4	3.1
C7 <sup>#</sup>	6.7	5.5
C8 <sup>#</sup>	6.7	7.6
C9	20.7	11.6
C10	24.0	12.2
C11	1.0/trace	12.0
C12	0.3/trace	10.8
C13	trace	12.0
C14 and above	trace	0.2/trace

a: Conditions were 375°C, 1200 psig (cold) H<sub>2</sub>, 25 min.; <sup>#</sup>excluding small amounts of cycloalkanes formed.

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