

HYDROCRACKING OF POLYOLEFINS TO LIQUID FUELS OVER STRONG SOLID ACID CATALYSTS

K. R. Venkatesh, J. Hu, J. W. Tierney and I. Wender
Department of Chemical and Petroleum Engineering
University of Pittsburgh, Pittsburgh, PA 15261

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INTRODUCTION

Post-consumer plastic makes up about 13 wt% of the 48 million tons of total packaging wastes generated annually¹. Plastics are non-biodegradable, constitute a increasingly large volume of solid wastes (20 vol. % in 1990)², and are not being recycled to a significant extent³. 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 the bulk of plastic wastes⁴. 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 environments⁴ 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 sulfated zirconia catalysts, viz., $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ and $\text{Ni}/\text{ZrO}_2/\text{SO}_4$. Strong solid acids such as these and other anion-modified metal oxides are active in a variety of acid-catalyzed hydrocarbon reactions^{5,6,7,8,9}; 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 hydrogen¹⁰ in reactions such as n-butane isomerization.

EXPERIMENTAL

The sulfated zirconium oxides were prepared as described in a previous publication¹¹. Incorporation of Ni on to sulfated 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 for three hours. The amounts of Pt and Ni promoted onto ZrO_2/SO_4 were 0.5 wt% and 2.0 wt% respectively, based on the final weight of the catalyst. HDPE (density 0.95, $M_{w,c} = 125,000$), PP (isotactic, density 0.85, $M_{w,c} = 250,000$) and PS ($M_{w,c} = 280,000$) were obtained from Aldrich Chemicals Inc. and were used as received. A $\text{Pt}/\text{Al}_2\text{O}_3$ 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) H_2 were 1835 psig; initial reaction pressures at 375°C experiments for 1200 psig (cold) H_2 and 750 psig (cold) 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 (CS_2) to form a homogeneous mixture; 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 analyses of the catalyst samples were performed by Galbraith Laboratories, Inc.

RESULTS AND DISCUSSION

Hydrocracking of HDPE at 325°C (1200 psig (cold) H_2 , 60 min.) over the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$

catalyst gave a 25 wt% conversion, mainly to gases (C_1 - 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_2 (for 25 min.) over the same catalyst, more than 99 wt% of HDPE could be converted to liquids (69 wt%) and C_1 - C_6 gases (~30 wt%) (Table I). 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/ZrO₂/SO₄ catalyst, HDPE conversion exceeded 96 wt% with slightly different liquid and gas yields (Table I). Table II lists the detailed product distribution of the liquid products formed from the reaction of HDPE over Pt/ZrO₂/SO₄ and Ni/ZrO₂/SO₄ catalysts, for the results shown in Table I. Large amounts of isoparaffins are obtained for each carbon number, close to an order of magnitude higher than their straight-chain counterparts. The high iso-/normal alkane ratios obtained at these temperatures is due to a kinetic rather than a thermodynamic effect. 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.¹² and are thus easily desorbed from the catalytic sites before an equilibrium is reached.

Impregnation of Ni on ZrO₂/SO₄ resulted in a higher iso/normal ratio of C_4 - C_9 alkanes from HDPE than that obtained with Pt. This may be due to the lower hydrogenation activity of Ni (based on n-hexadecane hydrocracking experiments¹³) 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.

Hydrocracking of HDPE over a Pt/ZrO₂/SO₄ catalyst was conducted with a lower hydrogen pressure (750 psig (cold)) with other conditions the same as in Table I. The same total conversion (99 wt%) was obtained in this reaction but with a higher yield of liquid products (79.8 wt%) and a correspondingly lower yield of gases (19.2 wt%). Comparison of the liquid products from HDPE reactions at both values of hydrogen pressure are given below.

Reactions with PP were conducted under the comparatively milder temperature of 325°C in the presence of 1200 psig (cold) H_2 ; at these conditions, PP was converted almost entirely to C_1 - C_6 gases for a reaction time of one hour. When the reaction time was reduced to 20 minutes, PP conversion was ~100 wt% with about 90 wt% yield of liquid products. Product analysis showed (Table III) that 78.6 wt% of C_5 - C_{12} gasoline range compounds were present in the liquid products together with 11.4 wt% products in the diesel range (C_{13} - C_{20}). Similar results were obtained with a Ni/ZrO₂/SO₄ catalyst in the reaction of PP (Table III). It appears that at sufficiently high temperatures, the hydrogenation activity of Ni approaches that of Pt in these reactions. It was found earlier that, in hydrocracking of n-hexadecane at milder conditions (160°C, 350 psig (cold) H_2), Ni/ZrO₂/SO₄ showed little activity whereas high conversions were obtained with a Pt/ZrO₂/SO₄ catalyst¹⁴. A cheaper, non-noble metal such as Ni can be effective in these reactions but requires a higher temperature for activation by hydrogen. As was the case with HDPE, high ratios of iso/normal paraffins was obtained. We found that PS could also be converted to benzene, alkylated aromatics and bicyclics at 300°C with 1200 psig (cold) H_2 .

The reaction of polypropylene at 325°C and 1200 psig (cold) H_2 over a ZrO₂/SO₄ (in the absence of either Pt or Ni) catalyst which has strong acidity but no hydrogenation function, resulted in no appreciable conversion of polypropylene. The white ZrO₂/SO₄ catalyst turned black during reaction indicating deactivation, possibly by coking. This result confirms the finding by others^{5,12} that the presence of a hydrogenation metal on ZrO₂/SO₄ provides stability to the catalyst by resisting coke formation in a variety of hydrocarbon reactions. On the other hand, a one wt% Pt supported on γ -Al₂O₃ catalyst (strong hydrogenation function but weak acidic function) also gave almost no conversion of PP at 325°C and 1200 psig (cold) H_2 . It appears that at the conditions employed for hydrocracking of these polymers, both strong acid and hydrogenation functions are required for high yields of low molecular weight branched alkanes in the gasoline range.

We conducted simulated distillations of the product mixtures from polymer hydrocracking reactions to analyze their boiling point characteristics. The boiling point distribution of the liquid products obtained from the hydrocracking of HDPE (Table 3) at 375°C for 25 minutes over Pt/ZrO₂/SO₄ under two different initial hydrogen pressures are shown in Figure 1. Reactions under 750 psig (cold) H_2 and 1200 psig (cold) H_2 seem to have only a marginal effect on the boiling ranges of the liquid products obtained. More than 90 wt% of the products are in the gasoline (C_5 - C_{12}) range (i.e., between 90°F (32.2°C) and 421°F

(216.1°C)) indicating the possibility of converting HDPE to a high quality liquid fuel. A similar boiling point curve was also obtained from the simulated distillation of the products from PP over Pt/ZrO₂/SO₄; more than 70 wt% of the products obtained boil in the gasoline range. A strong tendency towards isomerization over these metal-promoted sulfated zirconia catalysts was observed for both HDPE and PP hydrocracking; this is reflected by the similar boiling point curves obtained from products of both polymers.

Despite the high activity of the sulfate-modified zirconia catalysts in these reactions, they have questionable long-term stability at these severe reducing conditions. Sulfur analyses of the catalysts after hydrocracking of HDPE revealed that the catalysts lost about 34 wt% of their starting sulfur contents during reactions at 375°C and in the presence of high H₂ pressures. Since the presence of SO₄²⁻ anions on the catalyst surface is responsible for the strong acidity of these catalysts, loss of sulfur during reaction implies loss of activity for longer periods of time.

CONCLUSIONS

Sulfate-modified metal oxides promoted by a hydrogenation metal exhibit high activities for the hydrocracking of HDPE, PP and PS. While HDPE and PP are cracked predominantly to gasoline range branched alkanes (C₅-C₁₂), PS is hydrocracked to benzene, alkylated aromatics and bicyclic compounds. Impregnation with a non-noble metal such as Ni, which showed little activity in alkane hydrocracking at milder conditions (160°C and 350 psig (cold) H₂) resulted in high activity for polymer hydrocracking at 325°C+, indicating that activation of Ni occurs at higher temperatures. The long-term stability of these catalysts for these reactions is in doubt due to their loss of sulfur. Novel catalyst formulations which have higher stability under severe reducing conditions are currently being investigated.

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Table I Product (alkane) distributions obtained from HDPE hydrocracking over Pt/ZrO₂/SO₄ (0.5 wt% Pt) and Ni/ZrO₂/SO₄ (2.0 wt% Ni). Reaction conditions: 375°C, 1200 psig (cold) H₂, 25 min. Conversion is based on recovered solid.

PRODUCT	Yield (wt%) obtained with	
	Pt/ZrO ₂ /SO ₄	Ni/ZrO ₂ /SO ₄
Conversion	99 wt%	98 wt%
Gases (C1-C6)	30.0	28.0
Liquids:		
C4-C12	68.7	67.6
C13-C20	0.3	2.4
C21 and above	trace	trace

Table II Composition of liquid products from HDPE hydrocracking over Pt/ZrO₂/SO₄ and Ni/ZrO₂/SO₄ catalysts at 375°C, 1200 psig (cold) H₂, 25 min.

PRODUCT	YIELD (wt%) of ISO-(NORMAL) ALKANES	
	Pt/ZrO ₂ /SO ₄	Ni/ZrO ₂ /SO ₄
C4	3.6 (1.0)	2.5 (0.1)
C5	13.9 (4.8)	8.5 (0.1)
C6	25.3 (5.7)	13.5 (0.7)
c-C6	3.0	trace
C7	14.8 (2.2)	16.4 (0.8)
c-C7	3.5	1.6
C8	10.6 (0.8)	15.1 (0.5)
c-C8	0.4	0.9
C9	6.2 (0.3)	14.1 (0.4)
c-C9	trace	0.8
C10	2.4 (0.1)	10.4 (0.3)
C11	1.0 (trace)	6.3 (trace)
C12	0.3 (trace)	3.5 (trace)
C13	trace	2.2 (trace)
C14	trace	0.9 (trace)
C15-C20 (iso+normal)	trace	0.3
C21 and above (iso+normal)	trace	trace
TOTAL	85.0 (14.9)	96.2 (3.7)

Table III Results from PP hydrocracking over sulfated zirconia catalysts promoted with 0.5 wt% of Pt and with 2.0 wt% Ni. Reaction conditions were 325°C, 1200 psig (cold) H₂, 20 min. PP conversion was near 100 wt% for both reactions.

PRODUCT	Yield (wt%) obtained with	
	Pt/ZrO ₂ /SO ₄	Ni/ZrO ₂ /SO ₄
Gases (C1-C6)	10.0	14.5
Liquids:		
C4-C12	78.6	76.0
C13-C20	11.4	9.5
C21 and above	trace	trace

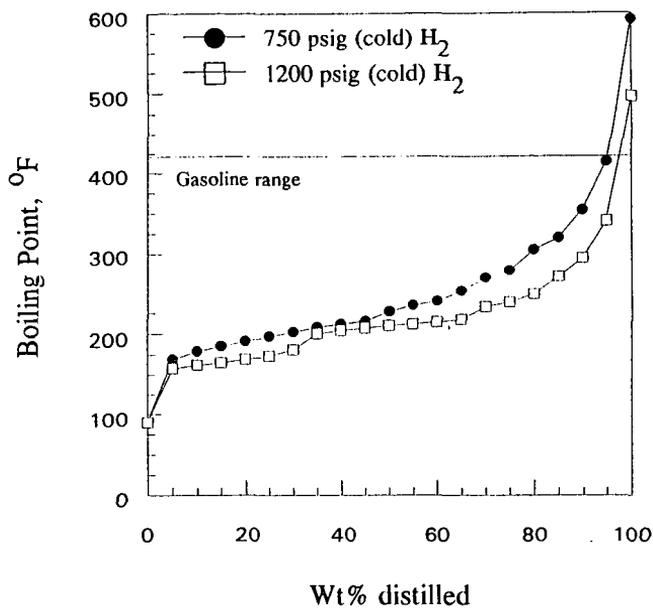


Figure 1 Boiling point curves obtained from the simulated distillation of products from HDPE hydrocracking over a Pt/ZrO₂/SO₄ catalyst at 375°C for 25 minutes under two different initial H₂ pressures.