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CLEAN GASOLINE REFORMING WITH SUPERACID CATALYSTS

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CLEAN GASOLINE REFORMING WITH SUPERACID CATALYSTS

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January - March, 1992

Task 1. Project Work Plan

Task completed.

Task 2. Heteroatom Removal

Task completed.

Task 3. Optimization of Chlorided Pt-Alumina Catalysts

Several experiments were performed during this quarter to establish a method to increase the amount of chlorine that can be added to and retained by the alumina and Pt/alumina catalysts. Previous chloriding studies using alumina prepared in-house (-100 mesh powder) and then impregnated to contain different concentrations of Pt (.4, 1.0, 2.0 and 4.0 wt.%) indicated that the chlorine content of these catalysts were approximately 3 to 4 wt.%. Continued flow of the chloriding agent, CCl_4 , over the catalyst did not increase the chloride level above about 3-4%. For these runs, the chloriding pretreatment was accomplished using a reaction temperature of 300°C and a nitrogen pressure of 250 psig (100 sccm/min.). The CO_2 content of the product gas stream was measured to monitor the extent of reaction and the chloriding procedure was termination when the CO_2 concentration reached a maximum. The maximum CO_2 content obtained in these experiments were always below 1 mole percent which correlated to the low chlorine content of the catalysts.

The initial experiment in the development of a method to produce a catalyst with a high chlorine content was done using a commercially available alumina pellet catalyst ($197 \text{ m}^2/\text{g}$). The experiment was performed in a glass plug flow reactor using a reaction temperature of 300°C , a nitrogen flow rate of $10 \text{ sccm}/\text{min}$. at atmospheric pressure and CCl_4 as the chloriding agent. The experiment was run for approximately 32 hours and the CO_2 content of the product gas stream was continuously monitored. The objectives of this experiment was to determine if the conditions (temperature, flow, etc.) would produce a catalyst with a higher chlorine content and to determine if the AlCl_3 formed would sublime and collect in the cold receiver. The loss of the AlCl_3 would contribute to a low chlorine concentration in the catalyst bed.

The maximum CO_2 concentration was significantly higher (16.3 wt.%) than the experiments done at 250 psig (Figure 1). The maximum CO_2 occurred at 75 minutes which was similar to that obtained in the high pressure experiments. After approximately 8 hours of chloriding, a solid was observed in the bottom of the receiver which follows the reactor. Upon completion of the experiment, the chlorine content of the catalyst pellets and the solids at the bottom of the reactor was determined. The catalyst contained 10.4 wt.% Cl and the solids contained 50.3 wt.% Cl.

The results from this experiment suggested that using nitrogen as the carrier gas for CCl_4 at atmospheric pressure and a low flow rate could produce an alumina catalyst with a high chlorine content (ca. 10 wt.%). The data also confirmed that AlCl_3 is lost using these reactions conditions; however, this requires relatively long reaction times (ca. 8 hrs.). Normal chloriding reaction times are usually on the order of 90

minutes. Therefore, loss of AlCl_3 should be minimal during chloridation and should not lower the chlorine content of the catalyst.

A 0.4 wt.% $\text{Pt}/\text{Al}_2\text{O}_3$ (-100 mesh) was chlorided using the similar conditions as discussed above (300°C, 50 sccm N_2 at atmospheric pressure). Prior to the chloridation, the catalyst was reduced at 450°C in hydrogen (250 psig, 100 sccm/min.) overnight. The CO_2 content was continuously monitored in the product gas stream (Figure 2). The CO_2 data in Figure 2 indicated a maximum CO_2 yield of 3.1 wt.% which is considerably lower than that obtained for the Al_2O_3 pellets. In addition, the maximum occurred at a shorter reaction time (ca. 15 min.). These data suggest that the chlorine content of the powdered catalyst will be lower than that obtained in the Al_2O_3 (pellet) experiment. The chlorine analysis of this catalyst ($3.66 \pm .30$ wt.%) confirmed this observation.

The data from these experiments suggested that: (a) the form of the catalyst (pellet or powder) may influence the maximum chloride retention, (b) surface area may affect the chloride retention, and (c) the addition of Pt may affect the chloride addition. To investigate if the form of the catalyst has an effect on the chloridation of the catalyst, the Al_2O_3 pellets were ground to -100 mesh. Both the pellet and the powder were chlorided using the same reaction conditions as reported above. The results shown in Figure 3 clearly demonstrate that the form of the catalyst has a strong influence on the chloride content of the catalyst. The Al_2O_3 pellets contained over twice the chloride of the pellets which had been ground to -100 mesh (13.7% vs. 5.79% respectively.)

A commercially available high surface area ($340 \text{ m}^2/\text{g}$) alumina powder was obtained to determine the effect of surface area on the chloride content of the catalysts. This catalyst was chlorided using the same procedure as previously discussed. The chloride content of this catalyst (8.71%) is also shown in Figure 3. As can be seen the high surface area Al_2O_3 powder contained a higher amount of chloride (8.71 wt.%) than the powdered Al_2O_3 pellets ($196 \text{ m}^2/\text{g}$); however, the chloride content of the high surface area alumina was significantly lower than that of the pellet form of the lower surface area Al_2O_3 . Several attempts to pelletize the high surface area alumina were made; however, the pellets produced did not have sufficient strength to load in the reactors. The results indicate that both the form of the alumina catalysts and the surface area are important variables in determining the amount of chloride added to the catalyst.

To determine the effect of Pt on the ability of an alumina catalyst to react with CCl_4 to form AlCl_3 , the pelleted alumina was impregnated with 2 wt.% Pt. The concentration of 2 wt.% was chosen on the basis of previous activity tests (at low catalyst chloride contents) which showed this Pt concentration to be the most active in the conversion of methylcyclohexane and n-pentane. Two chloridation experiments were done with this catalyst. In the first experiment, the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst was chlorided without being reduced. In the second experiment, the catalyst was reduced prior to chlorination. The chloride content of the catalysts from these two experiments are compared to the chloride content of the alumina pellets in Figure 4. The addition of Pt to the alumina pellets significantly reduced the amount of chloride added to the catalyst. Reduction of the catalyst prior to chloridation slightly improved the amount of

chloride added; however, the difference between the chloride content of the reduced and non-reduced catalyst (.9 wt.%) is probably within experimental error. The results do indicate an increase in the amount of chloride added to the catalyst when compared to those chlorided at higher pressure and using a powdered Al_2O_3 . The chloride content of this catalyst; however, is sufficiently high enough to be active. Literature and patent references suggest that a 5 to 8 wt.% chloride content is sufficiently high enough to produce an active isomerization catalyst.

The chlorided Pt (2 wt.%) / Al_2O_3 (pellet) catalyst was tested using methylcyclohexane and n-pentane as feedstocks. The amount of CO_2 in the product gas stream for two chloriding runs (Test #9B and Test #11) and the two curves generated for the activity tests (Run #57, Run #58, Run #59) are shown in Figure 5. The two chloridation tests (Test #9B and Test #11) of the 2% Pt / Al_2O_3 (pellets) differ in the length of time used to chloride the catalyst. Test #11 terminated the chloriding pretreatment when the maximum CO_2 yield was verified. Test #9B continued chloridation until the CO_2 concentration passed the maximum yield until the concentration of CO_2 was low (< .5 mole %) and constant. Test #9B produced the catalyst with a higher chloride content (7.22 wt.% Cl) when compared to the chloride content of the catalyst when chloriding was terminated after the maximum CO_2 yield was observed (5.93 wt.%). All subsequent chloriding pretreatment were done using this method.

The CO_2 data obtained for the chloriding pretreatment of the 2% Pt / Al_2O_3 (pellets) prior to activity testing with methylcyclohexane (MCH), n-pentane and hydrotreated Illinois #6 naphtha are also shown in Figure 5. The CO_2 curves are

essentially the same and suggest that the Cl content of the catalysts used in the activity testing should be similar to that of Test #9B (7.22 wt.%) and therefore should be active catalysts.

The process conditions used in the activity testing of the chlorided Pt (2 wt.%) / Al₂O₃ are shown in Table 1.

Table 1
Process Conditions for Activity Testing

	<u>PFR #57</u>	<u>PFR #58</u>
Catalyst	2% Pt/Al ₂ O ₃ /Cl	2% Pt/Al ₂ O ₃ /Cl
Feed	MCH + .25 wt.% CCl ₄	n-C ₅ + .25 wt.% CCl ₄
Temperature	100 - 300°C	100 - 300°C
Pressure	100 psig	100 psig
H ₂ :Feed	3:1	3:1
WHSV	1.0	1.0

The catalyst was reduced using a reaction temperature of 450°C in hydrogen (250 psig; 100 sccm) overnight. Prior to the chloriding pretreatment, the reactor temperature was reduced to 300°C and purged with nitrogen to remove hydrogen. The catalyst was chlorided with CCl₄ at 300°C using a nitrogen flow of 50 sccm at a pressure of 1 atmosphere. The reactor exit gas was checked for hydrogen using gas chromatography prior to the start of the chloriding pretreatment. The chloriding of the catalyst was started when the gas stream showed no detectable hydrogen. During the chloriding, the CO₂ content of the product was continuously analyzed until the yield of CO₂ became constant. The CCl₄ entrainment vessel was valved out and the

reactor temperature was dropped prior to the start of the liquid feed and the gas feed was switched to H_2 .

The conversion of MCH at each reaction temperature is shown in Figure 6. The data indicate that higher reaction temperatures are required to convert the cycloalkane feedstock. Although significant conversions of the MCH were obtained, the major products were the 2-C cyclopentanes (the dimethylcyclopentanes and ethylcyclopentane), and methylcyclopentane. The product distribution is shown in Figure 6a. The data in Figure 6a show that very little ring-opening occurs at the lower temperatures (100-150°C). Only at the higher temperatures (200-300°C) does the yield of isoalkane become significant.

In addition to changing the reaction temperature, total pressure was changed while holding the reaction temperature constant (250°C). The total pressure was varied from 50 psig to 150 psig. The data in Figure 7 indicates that the conversion of MCH shows a slight increase with increasing pressure in the range studied. However, the product distribution indicated that the major products were the 2-carbon cyclopentanes (Figure 7). The data suggests that at higher pressures (300 psig - 900 psig), the amount of isoalkanes in the product may increase. An additional run will be made at these higher pressures to determine whether ring-opening occurs at these pressures.

An additional run was made using n-pentane as the feedstock and the 2% Pt/ Al_2O_3 (pellet) catalysts. The catalyst was chlorided using the same method as the previous run and produced a similar CO_2 curve as shown in Figure 5. Therefore, it was assumed that the chloride content of the catalyst was similar (ca. 7.22%). The

conversion of n-pentane as a function of temperature is shown in Figure 8. Also shown in Figure 8 is the conversion of n-pentane using a powdered Pt (2%)/Al₂O₃ which contained a lower chloride content (4.60%). The catalyst containing the higher chloride content significantly increased the conversion of the n-pentane for all temperatures studied.

The data obtained to date suggest that the higher chloride content (7.22 wt.%) catalyst is more active than the same catalyst with a lower chloride content (4.60 wt.%) as defined by the conversion of n-pentane and methylcyclohexane. However, for the cycloalkane, conversion is primarily to other cycloalkanes with little ring-opening. The normal alkane produces the isoalkane as the primary reaction product. Additional studies of reaction parameters, such as total pressure, will be done to determine what process parameters change are required to open the cycloalkane rings to produce branched alkanes.

Task 4.   Testing of the Optimum Pt/Cl Alumina Catalysts

An activity run using the chlorided Pt (2 wt.+)/Al₂O₃ (pellets) and the hydrotreated Illinois #6 naphtha (+ .25 wt.% CCl₄) is currently in progress. The catalyst was chlorided in an identical manner as discussed above and produced a similar CO₂ curve as shown in Figure 5 (Run #59). A reaction temperature of 200°C, WHSV = 1.0, H₂:naphtha = 3.0, and 100 psig H₂ (100 sccm/min.) were the conditions used to process the naphtha. As an indication of catalyst activity during this run, the ratios of i-C₄/n-C₄ (Figure 9) and i-C₅/n-C₅ (Figure 10) were monitored. The data in these figures indicate the catalyst is initially active in the isomerization of these alkanes. However, the activity is decreased rapidly. The data obtained suggest that loss of

activity will occur at approximately 77 hours on stream. The loss of activity will be investigated by switching to a feedstock of 1-octene to determine the hydrogenation activity of the Pt on the catalysts.

The conversion of methylcyclohexane, a major component of the naphtha was also monitored during the run. The major products obtained from the MCH were the 2-carbon cyclopentanes.

Task 5. Preparation of Zirconia Superacid Catalyst

Three additional Zr based catalysts were prepared as follows:

SR003

This catalyst was prepared from zirconium oxynitrate precursor (Magnesium Elektron). This solution contains 20% by weight ZrO_2 . 245 gm of zirconium oxynitrate solution was taken in a beaker. To it was added 1.5 wt.% Fe and 0.5 wt.% Mn, as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Johnson Matthey, Inc.) and $\text{Mn}(\text{NO}_3)_2$ respectively. This mixture which appeared yellowish red, was stirred thoroughly (Solution A). Solution A measured 400 cc. In another beaker 400 cc of 1N NH_4OH solution was made (Solution B).

200 cc of distilled water were taken in a 2ℓ Morton flask. This was vigorously stirred. Solutions A and B were added concurrently approximately at the same rate into the Morton flask. The addition of these two solutions was very slow. The change in pH was monitored constantly by dipping a pH electrode in the solution of the flask. The stirring was vigorous. Even after all of the solutions A and B were completely discharged into the flask still no precipitation occurred and the observed pH at this point was 1.1. More of the 1N NH_4OH was slowly added to the flask, and at a pH of

5.2, gelling occurred. The precipitate became like a rock. More water was added, and the stirring was continued. This precipitate was washed about 8-10 times with excess of water, and the cake was dried at 120°C for about 20 hours. The dried cakes were hard; hence, they were ground, and dried again at 120°C for about 20 hours.

The dried, fine powders were calcined at 500°C for 4 hours in a muffle furnace. After calcination the powders were kept in the oven at 100°C until sulfation. The XRD pattern obtained from this material is presented in Figure 11, which exhibits only the tetragonal phase.

The calcined powders weighed about 50 gm. This was sulfated using 10 cc of 1N H_2SO_4 per gram of the catalyst. The powders were stirred in the required amount of 1N H_2SO_4 for about 2 hours. Then the sulfuric acid was filtered off, and the sulfated catalyst was dried at 100°C for about 10 hours. The XRD pattern obtained from the sulfated sample similar spectrum as shown in Figure 11.

SR009

This catalyst was made from ZrCl_4 salt. One liter of 0.3M ZrCl_4 was mixed with 400 cc of water. The pH of this solution was 1.55. Then 600 cc of 2N NH_4OH was dumped into the zirconium salt solution. Gelling occurred at a pH of 5.63. These gels were vigorously stirred and poured into a funnel for filtration. The precipitate was washed several times until a negative test for Cl^- ions was obtained. In this method of preparation the addition of base was rapid, and stopped right at the gelling time. The washed precipitate was dried at 120°C for about 50 hours. After drying the granules were ground and dried again. This sample was sulfated using 15 cc of 1N H_2SO_4 per

gram of catalyst. The powders were stirred in the required amount of 1N H_2SO_4 for about 17 hours. Then the sulfuric acid was filtered off, and the sulfated catalyst was dried again at 120°C for about 10 hours. The sulfur analysis obtained from this sample indicated about 4.15 wt.% S.

SR011

This catalyst was made from ZrCl_4 salt precursor. About 1.32ℓ of 0.3M ZrCl_4 solution was made in a 4ℓ beaker. The required amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Mn}(\text{NO}_3)_2$ were added to the zirconium salt solution so as to make the composition of 1.5 wt.% Fe and 0.5 wt.% Mn. While this was stirred vigorously, about 1.5ℓ of 2N NH_4OH was dumped into this solution. The final pH was 10.0. The precipitate was washed several times until a negative test for Cl^- ions was obtained. For the final two washings ethanol was used. This catalyst was dried in the oven at 120°C for about 16 hours. These granules were crushed to powders, and sulfated using 15 cc of 1N H_2SO_4 per gram of catalyst. The dried powders were stirred in the required amount of sulfuric acid overnight. Then the sulfuric acid was filtered off, and the catalyst was dried at 120°C for about 8 hours.

Task 6.   Testing of Zirconia Superacid Catalysts

A series of experiments were performed to determine the effect of the activation temperature on the sulfated zirconia catalysts with respect to the conversion of methylcyclohexane. The catalysts were tested for activity in batch reactors using a temperature of 150°C, 4g catalyst/2g MCH, a residence time of 2 hours and 1 atmosphere of hydrogen. The conversion of methylcyclohexane for an Fe/Mn/ ZrO_2 / SO_4 catalyst activated at 450°C, 550°C and 725°C is shown in Figure 12.

This catalyst, activated using the 725°C temperature and an activation time of 2 hours showed the highest conversion. Similar results for other zirconia catalysts were obtained. The zirconia catalyst showing the highest activity in the batch reactors will be tested in the plug flow reactors using the 725°C activation temperature during the next quarter.

During the activity testing of the sulfated zirconia catalysts the role of Pt and the necessity of having the metal on the catalyst was questioned. The sulfated Zr catalysts which contain Pt and have been reported in the literature are not reduced prior to activity testing. This is presumably done to prevent the loss of SO_4^{2-} as H_2S during the reduction step. The literature suggests that Pt is necessary for hydrogenation of the olefin intermediates to prevent coke formation which causes deactivation of the catalysts.

Two catalysts had been prepared from the same precursor (ZrCl_4). One catalyst was impregnated with .6 wt.% Pt and sulfated (SA #4) and the other catalyst was just sulfated (SR009). The two catalysts were activated at 725°C for 2 hours in air prior to the activity tests. The catalysts were tested in the batch reactors using a reaction temperature of 150°C, a 2 hour residence time, 4g catalyst/2g model compound, and 1 atmosphere of hydrogen. Cetane and methylcyclohexane were used as the feedstocks.

The conversion of cetane and methylcyclohexane is shown in Figure 13. As can be seen in Figure 13, the catalyst without the Pt produced a higher MCH conversion. This initial data suggests that Pt may not be required on the sulfated

catalysts. The catalyst containing no Pt (SR009) will be impregnated with .5 wt.% Pt to further define this question.

Task 7.   Poisoning by N and O Compounds

No scheduled activity.

Task 8.   Reports and Documentation

Quarterly reports will be generated as required.

Figure 1. CO₂ content of the product gas stream under 1 atm. of N₂.

Figure 2. CO₂ content in product gas stream(.4 % Pt/Al₂O₃(powder))

Figure 3. Effect of the form and surface area of Al catalysts on chlorine addition.

Figure 4. The effect of Pt impregnation on chlorine addition.

Figure 5. Reproducibility in the chloriding of a 2 % Pt/AL₂O₃ catalyst.

Figure 6. Conversion of MCH using a 2 % Pt/Al₂O₃/Cl(7.22 %) catalyst.

Figure 6a. MCH product distribution using a Pt(2%)/Al₂O₃/Cl(7.22 %) catalyst.

Figure 7. The effect of total reactor pressure on MCH conversion.

Figure 7a. Product distribution as a function of temperature.

Figure 8. Comparison of n-C5 conversions using catalysts with different Cl contents.

Figure 9. i-C4/n-C4 ratios in Ill. #6 naphtha using a 2 % Pt/Al₂O₃/Cl(7.22 %) catalyst.

Figure 10. i-C5/n-C5 ratios in Ill. #6 naphtha using a 2 %pt/Al₂O₃/Cl(7.22 %) catalyst.

Figure 11. X-ray diffraction patterns from SR003. (A) Pattern before sulfation, and (B) after sulfation.

Figure 12. The effect of activation temperature on methylcyclohexane conversion.

Figure 13. Comparison of activity of a sulfated Zr catalyst with and without Pt.

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