

CHLORIDATION AND ACTIVITY OF Pt/Al₂O₃ CATALYSTS

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INTRODUCTION

Current advanced coal liquefaction processes produce a naphtha that contains a high fraction of naphthenes. This will likely remain true for any improved process at lower temperatures. Conversion of this naphtha to gasoline by today's reforming processes will lead to a gasoline with a very high percentage of aromatics. Environmental considerations require that the aromatic and olefinic content of gasolines be drastically reduced. Petroleum refiners are making an intense effort to produce a gasoline containing more alkanes; for the short term alkylate will be utilized to accomplish this.

The high naphthene content of naphtha from coal liquefaction means that it would not be a suitable transportation fuel for the future. Tomorrow's clean gasoline will be low in heteroatoms and will contain mainly isoparaffins instead of aromatic and naphthenic hydrocarbons. Thus, if coal liquefaction is to advance from an emerging technology to a viable commercial process, a means must be found to reform the naphtha to a clean gasoline that will find acceptance in the market place.

Currently naphtha reforming is conducted at high temperatures and produces a high concentration of aromatics. The objective of this study is to reverse this trend in reforming by operating at low temperatures where thermodynamics favors a high concentration of isoparaffins.

An approach taken was to effect isomerization using an active catalyst (e.g., 1-3). Although a wide range of catalysts were investigated, much effort was centered on a heavily chlorided Pt-alumina catalyst. For example, Pt on a special silica-alumina could only operate at 350°C, and heavily chlorided Pt-alumina catalysts have been used for isomerization of alkanes at higher temperatures (350°C or greater). However, for naphtha reforming to produce alkanes it is desirable to operate at lower temperatures to be able to obtain a high octane product. It is likely that the chlorided Pt-alumina catalyst will have sufficient activity to produce a high fraction of the isoparaffins; however, the question concerning the ability of the catalyst to operate effectively in the presence of a high concentration of naphthenes (such as found in a coal-derived naphtha) requires further study. An objective of this paper was to develop a method to obtain a heavily chlorided Pt-alumina catalyst and to determine the activity and selectivity of these catalysts in reforming coal-derived naphtha and model compounds.

EXPERIMENTAL

Two aluminas, one a commercially available pellet (S.A. = 196 m²/g) and one which was made in-house (S.A. = 149 m²/g), were used in this project. The alumina powder was

made by precipitating $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (.5M in Al) with NH_4OH to a pH of 7.6. The gel was copiously washed with distilled H_2O and dried. The dried alumina was calcined at 500°C in air for 16 hours. Platinum was impregnated on the aluminas with chloroplatinic acid. An acetone solution containing the desired concentration of Pt was added to the alumina carrier and stirred overnight. The acetone was removed by rotoevaporation. The catalyst was dried overnight and stirred in a dessicator. Surface areas were determined by the BET method.

A plug flow reactor system was used for reduction, chloridation and activity testing of the catalysts.

Chloride analysis were done using standard ion chromatography techniques.

Methylcyclohexane and n-pentane were obtained commercially and dried using molecular sieves (3A) prior to use. All gases (N_2 and H_2) were ultra high purity (99.999%) and passed over molecular sieves prior to introduction into the reactor system. The naphtha sample was obtained from the Wilsonville advance liquefaction pilot plant. The naphtha was hydrotreated in the CAER PIPU pilot plant prior to use with the chlorided $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst.

RESULTS AND DISCUSSION

A. Chloride Pretreatment. In the initial set of chloriding experiments, the Pt impregnated alumina powder (S.A. = $149 \text{ m}^2/\text{g}$) catalysts were used. The catalyst was reduced prior to the pretreatment using a temperature of 450°C and 260 psig H_2 (100 sccm/min.) overnight. Chloriding was done at 300°C using nitrogen at 250 psig pressure (100 sccm/min.) and CCl_4 as the chloriding agent. The CCl_4 partial pressure in the gas phase was controlled by the temperature of the vessel containing liquid CCl_4 that was used to saturate the nitrogen stream. Gas samples were taken to monitor the CO_2 content of the product gas by gas chromatography. In addition, gas samples were analyzed in the region of maximum CO_2 production and in the initial stage of chloridation by GC/MS. No COCl_2 or CO were found in the product gas stream in any of the samples using nitrogen as the carrier. The only compounds detected were N_2 , CO_2 , and at the end of the final time period of chloridation, CCl_4 . Thus, CCl_4 reacts with alumina to produce CO_2 as the only carbon containing product; however, it is not known whether the chloride containing species is AlOCl , AlCl_3 , or some more complex alumina compound is formed. However, it appears that chloriding occurs in steps with the first product being an alumina oxy chloride followed by subsequent formation of AlCl_3 . Thus, for discussion purposes the reaction is written in two steps:



The four Pt/Al₂O₃ catalysts were chlorided using this method. A typical CO₂ generation curve obtained using the .4 wt.% Pt/Al₂O₃ catalyst is shown in Figure 1. Because of the dead volume between the CCl₄ saturator and the catalyst bed, the time taken as zero does not coincide with the time that CCl₄ first contacts the catalyst bed. As can be seen in this figure, the CO₂ generated goes through a maximum at .31 mole % in 90 minutes. The low amount of CO₂ generated, which was typical for this set of catalysts suggested that the amount of chloride added would be lower than the 8-13 wt.% required for an active isomerization catalyst (4). Analysis of the catalyst indicated that the chloride content was $3.66 \pm .30$ wt.%. The chloride content of these Pt/Al₂O₃ catalysts did not exceed 4 wt.% and appeared to correlate with the maximum CO₂ content generated during the chloriding pretreatment.

The next set of experiments performed in an attempt to increase the chloride content of the catalyst used the commercially available Al₂O₃ pellets. The method for the chloriding pretreatment was also changed. Nitrogen was used for the CCl₄ entrainment at atmospheric pressure and 100 sccm/min. The reactor temperature remained the same (300°C). The CO₂ concentrations generated during the chloridation of the alumina pellets are shown in Figure 2. As can be seen, the amount of CO₂ produced was significantly greater than the amount shown in Figure 1. The maximum CO₂ generated (23.2 mole %) was also obtained at a shorter reaction time (10 min.). The chloride content of the catalyst was determined to be 13.70 wt.%. These data suggested that the observed increase in chloride added to the alumina pellets may be due to the form of the catalyst (pellets vs. powder).

In the next chloriding experiment, the alumina pellets were ground to -100 mesh (S.A. = 200 m²/g) to determine if the form of the catalyst affects the amount of chloride addition. The powdered alumina was chlorided using the same procedure as that used for the alumina pellets. The CO₂ generated during the chloridation of this sample is shown in Figure 2. As can be seen, the maximum CO₂ content is lower and required a longer reaction time to obtain. This correlates with the lower chloride content (5.79 wt.%) of the powdered catalyst. One possible explanation for the data shown in Figure 2 is that for the alumina pellets, the CCl₄ penetrates the pellet and reacts rapidly (reactions [1] and [2]) with the alumina to produce a chlorided alumina compound and produce CO₂. The penetration of CCl₄ into the pellet and the escape of the CO₂ out of the pellet was not believed to be diffusion limited. It is believed that the diffusion of AlCl₃ from the interior of the catalyst or particle is slow because of diffusion, or a process that resembles diffusional limitations. Thus, it is viewed that AlCl₃ forms uniformly throughout the catalyst particle or pellet but that it is lost from the catalyst bed by desorption from the surface boundary of the catalyst particle or pellet. The geometric surface boundary of the pellet is much smaller than that of the same amount of catalyst when it is present in powder form. Hence, it is believed that the rate of chloridation is similar in both the powder and the pellet. However, desorption to the gas in the void volume and transport from the catalyst bed is much slower for the pellet than for the powder.

With the development of a method of chloride addition which produced an alumina with a sufficiently high chloride content, the next set of experiments used the alumina pellets impregnated with 2 wt.% Pt. This catalyst was reduced as described above and chlorided using the same procedure as in the alumina pellet experiments. In addition this catalyst was also chlorided without prior reduction. The chloride content of the resulting catalysts are shown in Figure 3. The data shown in Figure 3 indicate that the addition of Pt to the alumina pellets decreases the chloride content of the catalysts when compared to that of

the alumina pellets. The reduced catalyst produced a slightly higher chloride content than the catalyst which was not reduced prior to chloridation. Without further data, it is not possible to unambiguously determine the cause for the lower chloride content; however, the data does suggest that the impregnation of the alumina with the Pt has removed a number of sites that react with the CCl_4 .

The data presented above indicate that a 2% $\text{Pt/Al}_2\text{O}_3$ (pellet) can be chlorided to produce a catalyst containing a high chloride content (7.22 wt.%) and that the extent of chloride addition can be monitored by the amount of CO_2 produced during this pretreatment. The reproducibility of this method is illustrated in Figure 4 which shows the CO_2 generation curves for a number of chloride pretreatments. Note that in Test #11, the chloriding pretreatment was terminated just after the CO_2 production reached a maximum. The resulting catalyst had a 5.93 wt.% chloride content. This run suggests that using this method of monitoring the extent of chloridation can accurately produce a series of catalysts with varying chloride contents.

B. Isomerization Activity. The isomerization activity of the 2% $\text{Pt/Al}_2\text{O}_3$ catalysts which have different chloride contents is shown in Figure 5. For all of the reaction temperatures studied, the $\text{Pt/Al}_2\text{O}_3$ (pellet) catalyst containing 7.22 wt.% Cl affected significantly higher conversions of n-pentane. The product distribution obtained for both of these catalysts were similar. The major product of the runs was isopentane (> 99%). In addition, minor amounts (ca. 0.1 - 0.2 wt.%) of isohexanes were also produced. Very little hydrogenolysis was observed for both of the catalysts. The data obtained from these isomerization runs with n-pentane suggest that the higher conversions are obtained with catalysts with high chloride concentrations.

The chlorided 2 wt.% $\text{Pt/Al}_2\text{O}_3$ (pellet) was also tested with methylcyclohexane (MCH) using a number of reactor temperatures. The results indicated that although conversion of MCH were relatively high, the major products were 2-carbon cyclopentanes (~ 95+ wt.%) which indicated that little ring-opening of the MCH was accomplished. In an attempt to change the selectivity of the catalysts for the conversion of MCH, the total hydrogen pressure of the reactor was increased while holding the temperature constant. The effect of pressure on the conversion of MCH is shown in Figure 6. Increasing the reactor pressure from 100 to 730 psig slightly increases the conversion from 60 to 80 wt.%. However, the increase in pressure significantly changes the product distribution (Figure 7). The 2-carbon cyclopentanes, which are the major products of the conversion of MCH at lower pressures, significantly decrease in concentration with increasing pressure. It appears from these data that in order to obtain ring opening at lower temperatures, higher reactor pressures are required.

A hydrotreated naphtha derived from processing an Illinois #6 coal at Wilsonville was obtained as a reforming feedstock using the chlorided 2% $\text{Pt/Al}_2\text{O}_3$ (pellet) catalyst. The catalyst exhibited an initial high activity in producing branched alkanes; however, this activity decreased rapidly with time on stream. It appears that the low concentration of heteroatoms remaining in the hydrotreated naphtha poisons the catalyst rapidly.

SUMMARY

The extent of chloridation of a $\text{Pt/Al}_2\text{O}_3$ catalyst can be monitored by determining the CO_2 concentration in the product gas stream. The pellet form of the catalyst can be pretreated to produce a catalyst with a higher chloride content when compared to the powdered form

of the catalyst. The Pt/Al₂O₃ catalyst containing the higher chloride content has a significantly higher isomerization activity using n-pentane as the feedstock. In order to open the cycloalkane ring to produce branched alkanes, higher reactor pressures are required at low reaction temperatures.

ACKNOWLEDGMENT

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REFERENCES

1. E. F. Schvarzenback, *Proc. Am. Petrol. Inst.*, **37**, Section III, 354 (1957).
2. D. H. Belden and V. Haensel, *Proc. Am. Petrol. Ind.*, **37**, Section III, 354 (1957).
3. T. Y. Yan, T. J. Huang, W. O. Haag, U.S. Patent 4,049,539, September, 1977.
4. A. G. Goble, P. A. Lawrance, *Proc. 3rd Int. Cong. Catalysis*, Amsterdam, Vol. 1, 320, 1964.

Chloridation tests, using 0.4 wt% Pt on alumina powder,
5.00 gram catalyst load, reduced overnight at 450 C, 250 psig H₂,
65.00 gram carbon tetrachloride load in chloriding bomb,
chlorided at 300 C, 250 psig, 100 sccm nitrogen

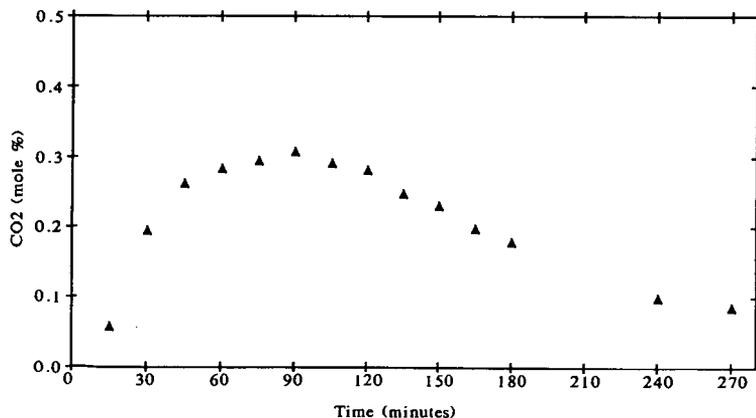


Figure 1. Carbon dioxide content of product gas during chloridation.

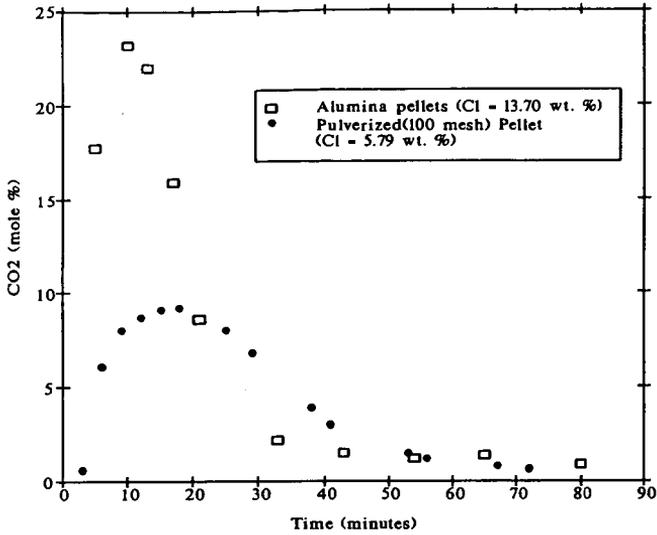


Figure 2. CO₂ production during chloridation of alumina catalysts (5.00 gram load, 65.00 g CCl₄ load in chloriding bomb, chlorided at 300 C, 1 at, N₂ @ 50 sccm).

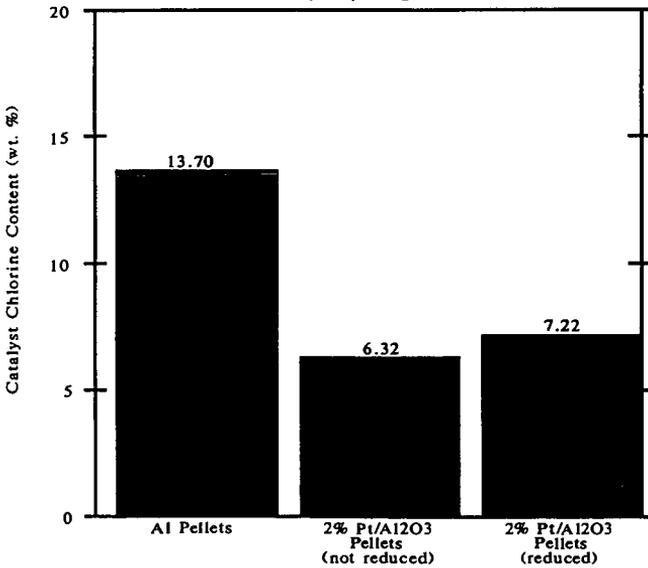


Figure 3. The effect of Pt impregnation and reduction on chloride addition. (same conditions as Figure 2.)

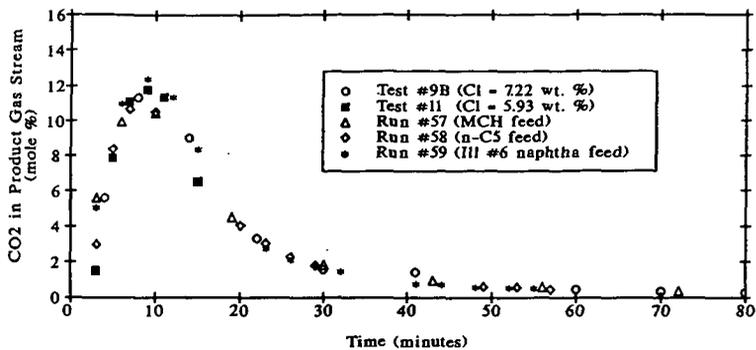


Figure 4. Reproducibility in the chloriding of a 2 % Pt/Al₂O₃ catalyst (pellet) (same conditions as in Figure 2).

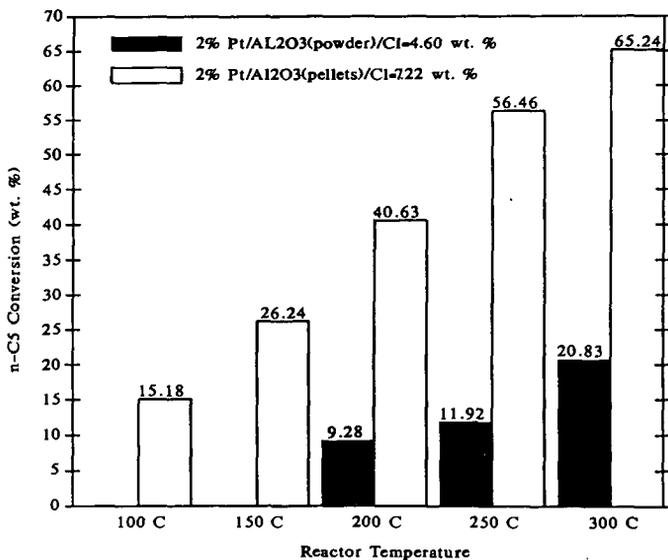


Figure 5. Comparison of n-C₅ conversions using catalysts with different Cl contents (WHSV=1.0, pressure=100psig).

Chlorided 2.0 wt% Pt on alumina pellets
 methyl cyclohexane + 0.25 wt% CCL₄
 hydrogen:methylcyclohexane feed mole ratio = 3:1
 250 C, 100-730 psig, WHSV- 2.0 g/hr per g catalyst

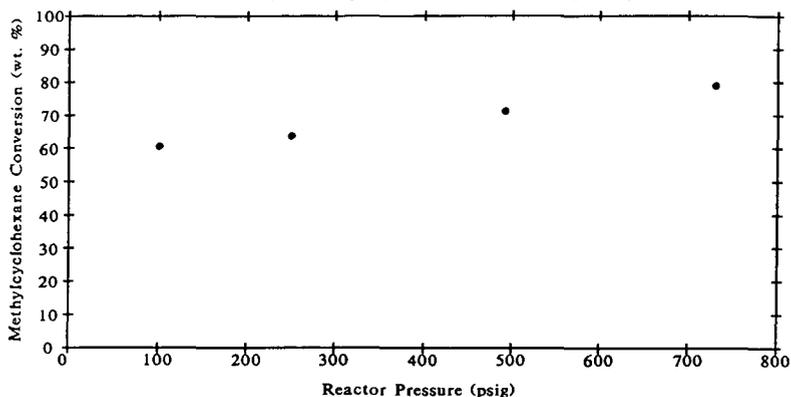


Figure 6. Effect of hydrogen pressure on MCH conversion.

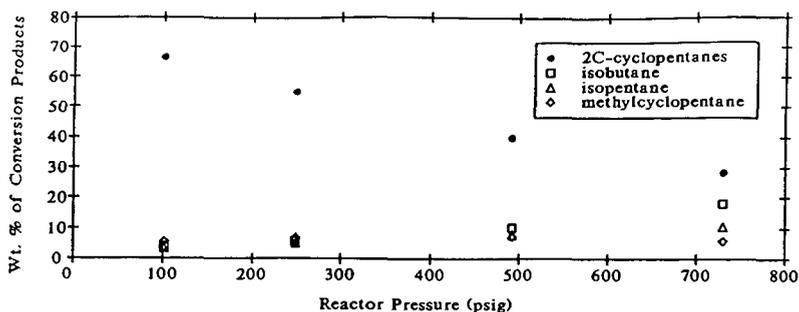


Figure 7 Effect of H₂ pressure on product selectivity (same conditions as Figure 6).