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A Comparison of Hydrocracking and Hydrogenolysis Reactions

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Introduction

Catalytic cracking of petroleum to obtain lower boiling hydrocarbon fractions is today the most important catalytic process. Reforming of the middle and heavy fractions of cracking products is a close second to this process. Hydrocracking is a special form of catalytic cracking. It is performed in the presence of hydrogen and has proved to be very flexible to meet the fluctuating market demands for gasoline. By applying different operating conditions it is possible to convert 75 % of petroleum to gasoline or 60 % to middle distillates (light fuel oil, diesel, jet fuel) in the same reactor. Light gasoline, a major product of hydrocracking, has a high octane number due to its high isoparaffin content.

The hydrocracking is carried out at a hydrogen pressure of about 35-200 Atm and at 300-450 °C on bifunctional catalysts, such as Pt/Zeolite. Low space velocities (LHSV) of about one is used.

New restrictions on the lead-content of gasoline force the refiners to find alternative ways to produce gasolines of high octane numbers. The two strong alternatives are:

1. Hydrocracking,
2. Alkylation.

Since the erection of the first hydrocracking plant in 1959 the world hydrocracking capacity has been increased rapidly (1968: 25 Miot, 1970: 50 Miot) (1). The trend to no-lead gasoline indicates that many new hydrocracking plants will soon be operating all over the world.

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General

A general equation for the heteregeneous catalytic cracking reaction in the presence of hydrogen is

$$C - X + H_2 \rightarrow C - H + H - X \quad (I)$$

where the atom X is C, N, S, O or a halogen. Hydrocracking requires a dual function (bifunctional) catalyst, having

a) Acid centers for cracking and isomerisation, and

b) Metal or metal oxides for hydrogenation/dehydrogenation.

A side reaction of hydrocracking is hydrogenolysis and it is represented also by the equation (I). It requires monofunctional catalysts. These are usually hydrogen activating metals, such as Ni, Co, Ru, Pt, Ir, Rh, etc. Hydrogenolysis has drawn special attention in the search of alternative ways for the production of SNG (Substitute Natural Gas). Indeed Hydromethanisation (2) and the SNG from naphtha – of British Gas Council – are industrial applications of hydrogenolysis. The addition of methanators to the existing Lurgi Pressure Gasifiers seems to be the most promising solution to satisfy the growing demand for SNG (3) The new and yet not commercially operated methanators require a thorough study of hydrogenolysis reactions.

This study intends to explain the differences between these two related reactions and to which extent hydrogenolysis plays a role in commercial hydrocracking processes.

Experimental

The experiments have been carried out in a flow system, made of stainless steel. High hydrogen pressures (up to 50 Atm) and low hydrocarbon space velocities (0,3-0,5 h^{-1}) have been used. Hydrogen was dried and purified in a Deoxo unit. After being saturated with the hydrocarbon the mixture was preheated to reaction temperature before entering the reactor. Reaction temperature was controlled within ± 1 °C. About one or two mililiters of catalyst were used for the conversion.

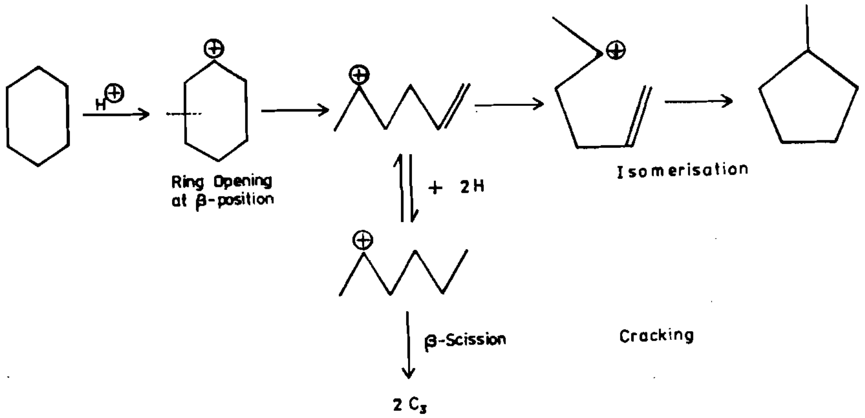
The reaction products were analysed by gas chromatography. Details of temperature programmed GC-analysis were explained elsewhere (4). For the complete analysis of mixtures, two capillary columns (PPG and Squalane) and a packed column (Reoplex/Al_2O_3) were used.

Bifunctional hydrocracking catalyst (catalyst B), 0,5 % Pt/Ca/Y-Zeolite, was a commercial one and obtained from The Union Carbide Int. Co. Monofunctional 5 % Pt/Al_2O_3 catalyst (catalyst M); used in this work, was prepeared as explained below: 0,440 g of $PtO_2.\ xH_2O$ was mixed with 6,688 g Al_2O_3 in water. This slurry was stirred continuously, water being slowly evaporated. More water was added and this procedure was repeated 5-6 times till $PtO_2.\ xH_2O$ was uniformly adsorbed on Al_2O_3. This way of preparation ensures an acid-free catalyst which is of vital importance in hydrogenolysis reactions. A reliable hydrogenolysis catalyst must not have acidic properties, otherwise it may initiate hydrocracking reactions of ionic nature.

Results and Discussions

Hydrocracking and hydrogenolysis of methylcyclopentane (MCP) and cyclohexane (CH) were carried out under the same reaction conditions. The aim was to find out the fraction of hydrogenolytic reactions taking part on bifunctional catalysts. A short comparison of the results is given in Table 1.

The bifunctional catalyst, Pt/Ca/Y-Zeolite (B), as compared to monofunctional Pt/Al_2O_3 (M) was much more active. The combination of hydrogenation/dehydrogenation component (Pt) and the acid component (Zeolite) gives excellent rates of conversions. Hydrocarbon reactions on such bifunctional catalysts can be explained through carbenium-ion mechanism.



The conversions on M are about three magnitudes of order smaller than those of B. This large difference indicates that the hydrogenolytic reactions are not significant during commercial hydrocracking operations

The careful study of the reaction products reveal the fact that these two reactions proceed quite differently from each other.

TABLE I

Comparison Between Monofunctional and Bifunctional Catalysis of Naphthene Conversion

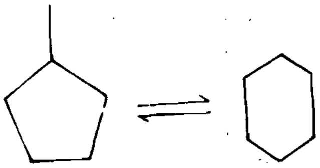
Catalyst M: 5 % Pt/Al_2O_3 Monofunctional
Catalyst B: 0,5 % Pt/Ca/Y-Zeolite Bifunctional
T: 275°, H_2:HC(*): 20 Mol/Mol, P: 40 Atm, LHSV: 0,3 h^{-1}

Feed	Methylcyclopentane		Cyclohexane	
Catalyst	B	M	B	M
Conversion (Wt %)	27,12	0,07	74,03	0,02
Analysis of products (Wt %)				
Ring opening	25,4	30,0	6,2	—
Isomerization	66,3	57,9	92,3	68,4
Paraffins $< C_6$	3,9	12,1	0,6	31,6
Naphthenes $< C_6$	0,2	—	400 ppm	—
Aufbau ($> C_6$) (**)	4,2	—	0,9	—
Products of ring opening				
n-Hexane	38,3	3,7	41,2	100
2 Me Pentane	32,9	60,4	31,8	—
3 Me Pentane	21,8	35,9	21,7	—
2,2 Di Me Butane	4,2	—	3,1	—
2,3 Di Me Butane	2,8	—	2,2	—
Paraffins $< C_6$				
C_1	1,3	30,6	2,2	100
C_2	0,4	—	2,2	—
C_3	6,3	—	4,8	—
C_4	52,0	—	48,7	—
C_5	40,0	69,3	42,1	—

(*) H_2: HC: Ratio of hydrogen to hydrocarbon

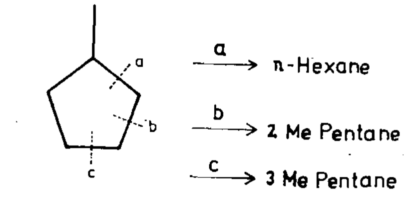
(**) Aufbau products are hydrocarbons which contain more carbon atoms than the feed hydrocarbons.

1. The main reaction in both cases is isomerization, isomerization of CH being faster than that of MCP.

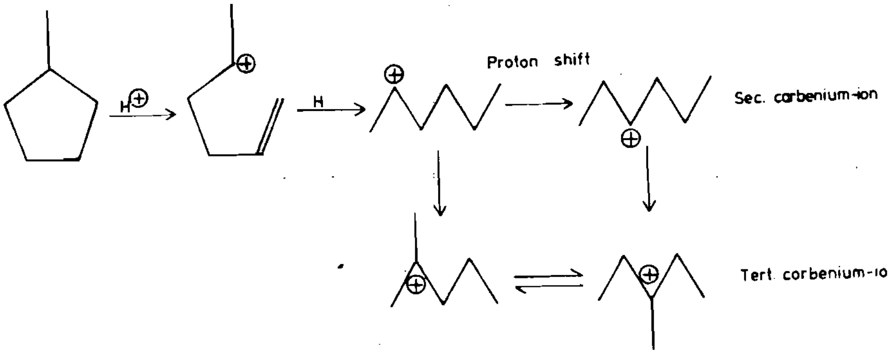


Thermodynamic equilibrium is reached with catalyst B.

2. Ring opening of MCP is faster than that of CH. The hydrogenolytic ring opening of a C_5-ring is favoured over C_6-ring due to its orbital geometry. The low concentrations of n- Hexane among ring opening products indicate that the rupture of secondary-tertiary C-C bonds is very difficult. The ration of b and c type ruptures corresponds to statistical probability; the 2 Me Pentane: 3 Me Pentane ratio for eight different experiments under varying conditions is 2, 1: 1. A probable scheme of ring opening during hydrocracking is illustrated below:



Ring opening



This ionic rearrangement is closely coupled with thermodynamic equilibrium. A set of experiments, performed to show the effect of increasing retention time on the composition of ring opening products, have indeed shown that n-Hexane quantity was increased with the time at the cost of others. At long retention times the amount of n-Hexane exceeded even the thermodynamically predicted concentrations.

3. Cracking on B seems to be a disproportionation reaction. The amount of paraffins smaller than C_6 were almost equal to the Aufbau products larger than C_6. The fact that the Aufbau products were all made of C_7 and C_8-alkylcyclohexanes indicates that two moles of the original hydrocarbon combine to form an intermediate which quickly disproportionates to a paraffin and a naphthene. Cracking on M favours the production of methane, a typical hydrogenolysis reaction. One is encouraged to think that cracking to paraffins smaller than C_6 may proceed without the preliminary ring opening. The only detectable crack-product of cyclohexane hydrogenolysis was methane which was formed by a successive demethanation of an activated (i. e. chemisorbed on an active Platin atom) cyclohexane molecule.

Conclusion

The role of hydrogenolysis reactions taking part on the hydrogenation/dehydrogenation component of a bifunctional hydrocracking catalyst is of no practical importance. The existence of such reactions can at best be suggested by the presence of small amounts of methane and ethane. As is well known a carbenium ion mechanism operating through β-scissions, produces no hydrocarbon smaller than C_3. The reaction velocities of hydrocracking on such powerful catalysts are several magnitudes of order larger than those of hydrogenolysis.

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