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Platinum impregnated zeolite β as a reforming catalyst

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It is shown that Pt impregnated β zeolite has a high reforming capability for naphthenic feeds such as methylcyclopentane and methylcyclohexane, which are transformed in aromatic and cyclic saturated multibranched molecules with higher octane numbers. The temperature plays a major role in these reactions. The cycloolefinic intermediates produced by the dehydrogenation of the feed molecules are alkylated with the carbonium ions produced by the ring opening of other feed molecules. The disproportionation of the alkylated compounds is suggested to be responsible for the enlargement of the feed molecules. This disproportionation, the isomerization of the cycloolefinic intermediates, and some cracking particularly for methylcyclohexane, are proposed to be responsible for the product distribution under the present conditions.

Keywords: Reforming; zeolite β; naphthenes; aromatics

1. Introduction

Zeolite β, synthesized originally by Mobil [1], has 12-ring pores and can be obtained in a wide range of SiO_2/Al_2O_3 ratios [2], fact that can alter dramatically the product distribution. A detailed structural characterization of zeolite β [3,4] shows that if possesses straight and tortuous channels with sizes between those of ZSM-5 and Y zeolite. Because of its pore size it can provide shape selectivity for medium size molecules like those used in reforming. Less work has been carried out with zeolite β than with other zeolites; it was employed for catalytic cracking [5,6], disproportionation and transalkylation reactions among aromatics [7,8], and impregnated with Pt for hydrodewaxing of petroleum oils [9,10]. Zeolite β impregnated with noble metals behaves as a bifunctional catalyst.

Naphthenic molecules like methylcyclopentane and methylcyclohexane constitute a large fraction of the hydrocarbons used in reforming reactions. Therefore,

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a catalyst that could modify these molecules in order to increase their octane number would be of interest. In the present study we examine how the product distribution changes as a function of temperature for the reforming of methylcyclopentane and methylcyclohexane over Pt impregnated β zeolite under low severity conditions. At relatively low temperatures, the isomerization of the feed naphthenes constitutes the dominant reaction, since the thermodynamic equilibrium prevents the production of aromatics. At somewhat higher temperatures, zeolite β stimulates bimolecular alkylation reactions of cycloolefin intermediates produced by the dehydrogenation of the feed molecules, with carbonium ions, formed via ring opening of other feed molecules. The disproportionation reaction of the alkylated intermediate, the isomerization of cycloolefin intermediates produced by the dehydrogenation of feed molecules, additional dehydrogenation, as well as some cracking particularly for methylcyclohexane, are responsible for the wide spectrum of products detected. The yield of aromatics increases with increasing temperature. The enlargement of the C_5 ring to the C_6 ring observed with methylcyclopentane and the dibranching and the formation of aromatics observed with both feed molecules are of importance for the octane number upgrading of naphthenes.

2. Experimental

Zeolite β has been prepared hydrothermally from an aluminosilicate gel using tetraethylammonium hydroxide (TEAOH) as template. The SiO_2/Al_2O_3 ratio of the produced zeolite was found by atomic absorption to be 23. Details regarding the preparation method and characterization of the zeolite supported Pt by XRD, NH_3-TPD, FTIR, BET, H_2-chemisorption, will be published later. The platinum loaded zeolite (0.5 wt% Pt) was prepared by impregnation of its protonated form with H_2PtCl_6 (Aldrich 8 wt% solution in water) [7]. After impregnation, the catalyst was dried overnight at 130°C.

The catalytic runs were performed at 200–400°C under atmospheric total pressure by co-feeding ultra high purity H_2 (99.999%) and the naphthenic molecule. The hydrogen was bubbled at an appropriate flow rate (5 ml/min) through a metalic bubbler containing the organic feed at 24°C. Complete saturation of the gas stream with the feed molecule was achieved. The reactants were methylcyclopentane (Aldrich 98 wt%) and methylcyclohexane (Aldrich 99 wt%), typical representatives of naphthenic feed stocks. The H_2/oil molar ratios were 4.8 and 16.5, respectively. The reactor, a stainless steel tube of 1/8 inch o.d. was located vertically in a temperature controlled furnace. In each experiment 100 ± 2 mg of catalyst were loaded in the reactor. The catalyst was activated in situ by oxidation at 400°C for 2 h with ultra high purity oxygen (99.999%) followed by purging of the bed with He (99.999%) for 15 min at 400°C. The final step of reduction of the catalyst took place with ultra high purity H_2 (99.999%) at 400°C for 2 h. After this treatment, the Pt dispersion was found to be 0.06. The on-line analysis of the products was carried out with high resolution capillary gas chromatography. For this purpose a GC/MS (Hewlett-Packard 5890 series II) has been employed, loaded with a Poraplot capillary column, a high performance capillary column (HP-1) and a molecular sieve packed column (5A). A PC unit was attached to the chromatograph for the manipulation of the data.

3. Results and discussion

The product distribution over β zeolite for both feed molecules indicates that the reaction temperature controls the types of reactions that take place.

3.1. METHYLCYCLOPENTANE

At low temperatures, around 200°C, the total conversion is 18.9% and the methylcyclopentane is transformed exclusively to cyclohexane (fig. 1). It is of interest to note that even at the lower temperature of 150°C, the only product was cyclohexane, regardless the conversion. This is due to the dual functionality of β supported Pt, which enables the fast dehydrogenation over the Pt sites, followed by the isomerization of the cyclopentene olefinic intermediate to cyclohexene over the acidic sites of the zeolite via a carbonium ion mechanism [11], and the further hydrogenation over the metallic sites. Other researchers

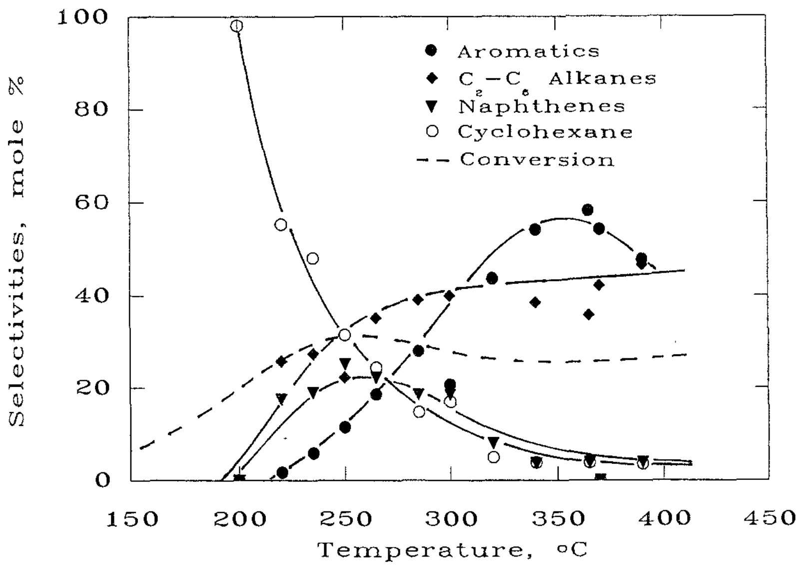

Fig. 1. Mole selectivities from methylcyclopentane over zeolite β as a function of temperature, WHSV = 1.76 h^{-1}, after 1 h on stream.

Table 1
Product distribution from methylcyclopentane (WHSV = 1.76 h^{-1}) and methylcyclohexane (WHSV = 0.68 h^{-1}) over Pt supported zeolite β after 1 h on stream at different temperatures

Product (mol%)	Methylcyclopentane			Methylcyclohexane		
	285°C	340°C	390°C	285°C	335°C	390°C
methane	–	–	–	–	–	–
ethane	0.1	0.2	0.3	0.2	0.4	0.7
propene	–	–	0.9	–	–	0.2
propane	0.9	1.5	2.1	3.3	4.9	6.6
i-butane	3.3	2.0	3.3	11.2	9.8	13.1
n-butane	1.9	1.1	1.1	2.5	3.2	3.6
i-pentane	1.9	1.1	1.5	6.9	5.4	6.8
n-pentane	0.3	0.3	0.6	1.7	1.8	1.7
cyclopentane	0.6	0.5	0.4	1.4	1.1	0.8
2-methylpentane	1.2	1.1	–	2.5	1.4	1.3
3-methylpentane	–	–	–	0.8	0.6	0.4
methylcyclopentane	77.1	81.0	78.0	7.9	3.6	2.8
benzene	2.4	4.2	2.4	2.0	2.5	1.1
cyclohexane	3.3	0.7	0.4	0.4	–	–
1,3-dimethylcyclopentane	1.2	0.3	0.4	14.1	5.6	5.9
1,2-dimethylcyclopentane	–	–	–	1.8	0.5	0.4
methylcyclohexane	2.1	0.4	0.4	18.0	7.9	16.4
toluene	1.4	2.1	3.1	14.1	31.0	22.6
1,4-dimethylcyclohexane	0.8	–	–	1.5	–	–
ethylbenzene	0.4	0.4	0.5	0.5	0.8	0.8
o-xylene	0.3	0.5	0.8	1.4	3.1	2.4
m-xylene	1.1	1.7	2.2	5.9	10.3	7.2
p-xylene	0.3	0.3	0.6	1.4	2.5	2.0
1,2,3-trimethylbenzene	0.2	0.4	0.2	0.3	1.8	1.4
1-ethyl-3-methylbenzene	0.1	–	0.2	0.1	1.0	0.8
1-ethyl-4-methylbenzene	0.1	0.5	0.4	0.1	0.8	0.9

[12] using the same feed molecule over Pt/HZSM-5 found a zero cyclohexane yield at temperatures below 240°C. Experiments carried out by us at 200°C over ZSM-5 with the same Pt loading as the zeolite β have shown negligible conversion and cyclohexane yield.

The product distributions at various temperatures with methylcyclopentane as a feed are listed in table 1. Increasing the temperature, the rates of the reactions which lead to the enlargement of the C_5-cyclic saturated ring to branched C_6 rings (either aromatic or saturated) become larger (table 1). This behavior is of interest because significant yields of higher carbon number products with larger octane numbers are obtained. Table 1 shows that approximately equal molar amounts of C_5 and C_7 and of C_4 and C_8 hydrocarbons are formed. This suggests that a bimolecular alkylation reaction [13] between cyclo C_5-olefinic intermediate molecules formed over Pt sites and C_6 carbonium ions intermediates formed via ring opening over the acidic sites takes place. The disproportionation of the alkylated intermediate thus obtained results in the enlargement and dibranching of the feed molecules. In addition, the isomerization over the acidic sites of C_5 cyclic olefinic intermediates (formed over Pt sites by dehydrogenation) to C_6 cyclic rings also occurs. The selectivities for the lighter alkane molecules produced via hydrocracking are favored by an increase in temperature (fig. 1), but remain moderate even at high temperatures. This is probably a result of the moderate acidity of zeolite β. The selectivity for aromatics has a maximum at 370°C, while the maximum for the generated naphthenes is around 250°C. The formation of aromatics starts at the surprisingly low temperature of 220°C, where even small amounts of tribranched aromatics were detected. The generation of aromatics is a result of the further dehydrogenation on the Pt sites of the C_6 cyclic branched olefinic intermediates, and is favored by higher temperatures.

The very small C_1/C_5 and C_2/C_4 ratios, observed with zeolite β even at high temperatures, indicate that hydrogenolysis [13] occurs to a very small extent. Ring opening takes place at relatively high temperatures and has as a result the production of 2-methylpentane, since the probability of opening of the secondary–secondary C–C bonds is much higher than that of the tertiary–secondary C–C bonds [14]. The existence of a weak maximum (fig. 1) is due to coke formation, since this feed leads to cyclic intermediates that are coke precursors [15]. Higher hydrogen pressures will have as a result the hydrogenation of the unsaturated coke precursors and hence will lead to a significant reduction of the deactivation rates [16].

For the same weight hourly space velocity (WHSV), γ-alumina (Puralox SB a-230 of Condea Chemie GmbH) impregnated with 0.5 wt% Pt exhibits mainly ring opening, with the generation of 2- and 3-methylpentanes up to 350°C. The metal dispersion on alumina was 0.60. The selectivities for benzene and toluene become greater at higher temperatures. However, no dibranched cyclic compounds are generated. This indicates that the alkylation reaction does not occur on Al_2O_3, probably because of its lower acidity.

3.2. METHYLCYCLOHEXANE

The effect of temperature on the product distribution of methylcyclohexane over Pt impregnated β zeolite is presented in fig. 2. At low temperatures, the generation of naphthenes, mainly 1,3-dimethylcyclopentane dominates (table 1). This is because of the fast dehydrogenation of the methylcylohexane over the Pt sites followed by a subsequent B isomerization [12,17] of the produced carbenium ion over the acidic sites. In the B isomerization, which proceeds via protonated cyclopropanes, either a new branch is generated or an existing one disappears [17]. The conversions and the naphthene selectivities of ethylcyclohexane observed earlier [12] at these low temperatures over Pt/HZSM-5 and

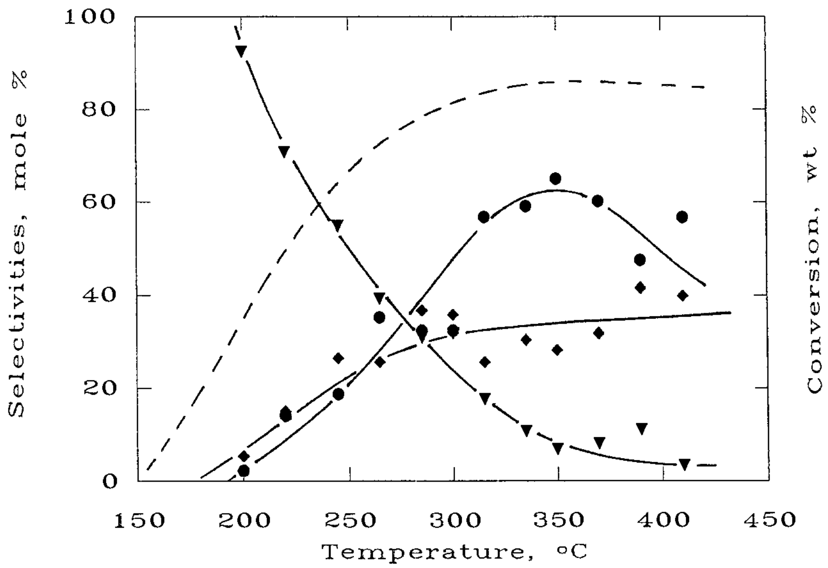

Fig. 2. Mole selectivities from methylcyclohexane over zeolite β as a function of temperature, WHSV = 0.68 h^{-1} after 1 h on stream. (●) Aromatics, (◆) C_2–C_6 alkanes, (▼) naphthenes, (— — —) conversion.

Pd/LaY faujasite were much smaller than ours. In contrast to methylcyclopentane, the product distribution in this case cannot be explained only in terms of disproportionation and isomerization (compare C_5 with C_9 and C_6 with C_8). One can observe that, in this case the product distribution is shifted to the lighter alkanes (C_3 and C_4), indicating the occurrence of higher cracking rates of the C_7-carbonium ion than with the previous feed. The smaller C_9 selectivities than those of C_5, are a result of the shape selectivity imposed by the zeolite pores to the transition state intermediates.

The increase in temperature has as a result the decrease of the naphthenes selectivities because of the transformation of the C_6 olefinic intermediates to the corresponding aromatics. A maximum in the selectivity for aromatics around 350°C was found. A noteworthy observation is that the toluene selectivity passes through a maximum around 350°C, reaching the value of 35 mol%. Other researchers [12] using methylcyclohexane over Pt/HZSM-5 reported that toluene generation starts at 330°C, but that at 350°C it was as small as 3%.

4. Conclusions

Pt impregnated β zeolite catalyzes reactions which result in molecules with higher octane numbers than those of the feed naphthenes. The enlargement of the C_5 cyclic ring of methylcyclopentane to a C_6 cyclic saturated or aromatic ring, as well as the dibranching and aromatization of methylcyclohexane are observed. The selectivity for these types of molecules is higher than those obtained over ZSM-5 and Y zeolites impregnated with Pt. A maximum for aromatic selectivities is observed around 350°C. The large amounts of naphthenes isomers produced at 200°C is an indication of the high isomerization capability of zeolite β.

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