The Effect of TCE Addition on the Performance of Catalytic Isomerization of n-Hexane

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Abstract

n-Hexane conversion enhancement was studied by adding TCE (Trichloro-ethylene) on feed stream using 0.3%Pt/HY zeolite catalyst. All experiments were achieved at atmospheric pressure and on a continuous laboratory unit with a fixed bed reactor at a temperature range 240-270◦C, LHSV 1-3h-1, H2/nC6 mole ratio 1-4.
By adding 435 ppm of TCE, 49.5 mole% conversion was achieved at LHSV 1h-1, temperature of 270ºC and H2/nC6 mole ratio of 4, while the conversion was 18.3 mol% on the same catalyst without adding TCE at the same conditions. The activation energy decreased from 98.18 for pure Pt/HY zeolite to 82.83 kJ/mole by adding TCE. Beside enhancement the activity, selectivity and product distribution enhanced by providing DMB (Dimethyl butane) which have higher octane number as compared with 0.3%Pt/HY zeolite. Indeed the increase of the 2.2-DMB/2,3DMB ratio with n-hexane conversion is more pronounced with TCE than with pure Pt/HY zeolite.

Introduction

Isomerization, cracking and alkylation are reactions that are catalyzed by acids. Considering the enormous oil consumption in the modern world (over 3.5 billion tons in 2005), it can be stated that acid catalyzed reactions of hydrocarbon are major importance nowadays and not surprising numerous studies have been devoted to the subject. However, important questions with regarded to the mechanism and to the effect of the catalyst pore structure on the activity and selectivity remain to be answered [1].

Regardless of reaction involved in the particular process it is very important that catalyst exhibits not only the capability to perform its specified functions initially but also perform them satisfactorily for prolonged period of time. The analytical terms employed in the art to measure how efficient a particular catalyst performs its intended functions in particular hydrocarbon conversion process are activity, selectivity and stability [2].

The most synthetic methods for zeolite modification are dealumination by means of steaming, leaching procedure and the modification with phosphorus compounds. Generally it is assumed that the acidic properties of zeolite govern their activity, which explains why many studies have devoted to determination of nature, the number and the strength of acid site [3, 4].

Lawrence Tuckerkass [5] studied the isomerization of cyclopropane to propylene over alumina containing 0-6% fluorine. The catalytic test was carried out at 127°C. The maximum isomerization rate occurs at 1.2%F and is about 5000 times that found for fluorine free alumina. At higher fluorine content, the rate constant decreased moderately to a value which was about 30% that at the maximum. The activation energy decreased sharply from 29 kcal/mol for pure alumina to a minimum of 13 kcal/mole. It is gradually increased to 16-18 kcal/mole for higher fluorine content.

Fan Van Lin et al.[6] studied the isomerization of n-hexane on both prepared and commercial Pt/Al2O3 as well as commercial Pt-Re/Al2O3.They studied the effects of chlorinated hydrocarbon addition (methylene chloride, trichloroethylene (TCE), chloroform and carbon tetrachloride) in the liquid feed on the activity. They concluded that chloroform show a most favourable chlorinating agent and they

indicate that upon chlorination the isomerization selectivity increased and the cyclization selectivity decreased.

Nattaporn et al. [7] studied the effect of various olefins addition (ethylene, propylene, 1-butylene and 1-pentene) on n-butane isomerization on sulfated zirconia (SZ) at 100ºC. The addition of butene was able to lower average surface resistance to active intermediate. The improve isobutene formation rate caused by addition of olefin was due to an increase concentration of surface intermediate leading to isobutene.

A problem that is encountered of in the isomerization of hydrocarbon is the rapid deactivation of isomerization catalyst that is because of the formation and accumulation of high molecular weight, carbon (coke) within the pore. In addition impurities presence in feed contributes to a rapid decrease in catalyst activity. Another option to elevate the deactivation is to operate the isomerization process at high hydrogen to hydrocarbon and at relatively high temperature. However activity may be enhanced by adding the effective amount of such organic chloride compound such a perchloro-ethylene (PCE) in isomerization feed stream. The concentration of organic chloride compound in the range of 0.01ppm to about 1000ppm gives an increase in activity and decrease in deactivation. One reaction mechanism that is believed to be occur in the process which helps to prevent the deactivation of catalyst is that the additive helps prevent high molecular weight hydrocarbons and impurities (such as sulfur compounds, olefins and aromatics) from adsorbing onto the catalyst surface at the reaction conditions of the isomerization process [6].

The objective of this work is to provide a method by which the activity of an isomerization can be enhanced during the use of acid catalysts in the isomerization of hydrocarbons.

Experimental work

Materials and catalyst

n-Hexane was supplied by BDH with 99% purity was used as feedstock for isomerization experiments. HY-zeolite (CBV 600) powder was supplied from Zeolyst International Company was used as support for catalyst preparation. For preparing catalyst, 100 g of HY zeolite powder was mixed with 30% montmorillonite clay as a binder as suggested by Murray [8]. The resulting were formulated and dried over night at 100ºC, then 0.3wt%Pt/HY zeolite was prepared by impregnation method with a proper solution of hexachloroplatinic acid containing of 0.1590g of hexachloroplatinic acid and 8ml deionized water for 20gm catalyst. The impregnated extrudates were dried at 110ºC then calcinated at 300ºC for 3hr in a furnace with dry air. The calcinated catalyst was then reduced with hydrogen at 350ºC for 3 hr [9].

Procedure and Equipment

The catalyst activity tests were carried out in a continuous fixed bed reaction unit. The reactor was a carbon steel tube with an outside diameter of 1.9 cm, 2 mm thick and 80 cm length. 30 cm3 of 0.3%Pt/HY catalyst was charged between two layers of inert materials (glass balls). The catalytic reactions were carried out in the temperature range of 240-270ºC, LHSV of 1-3 h-1, H2/nC6 mole ratio of 1-4 and atmospheric pressure. The partial pressure of hydrogen was kept at 0.57 bar while n-hexane partial pressure varied between 0.139-0.419 bar. Liquid products were trapped by condenser at -5ºC, collected periodically and analyzed by using gas chromatography. The gas chromatography model 438Aa-VSA supplied by Agilent Technologies Company was used for the analysis. This device equipped with column of 0.25mm diameter 100m length and FID detector.

For catalyst activity enhancement, 435 ppm, the preferred additive of TCE as noticed by Maha Al-hassani [10] of trichloroethylene ($CHCl:CCl_2$) was mixed with the feedstock stream during the activity tests.

RESULTS AND DISCUSSION

Catalyst Activity

Figures (1) to (4) show the change of n-hexane conversion and at different contact time (1/LHSV) and temperatures. As LHSV decreases n-hexane conversion increase. This means that increasing in the residence time, which leads to offer a plenty of contact time of feed stock with catalyst inside the reactor. All results indicate that low LHSV is favored for isomerization process, while with higher space velocities; conversions are lower, unless the temperature is raised. At 270◦C the conversion of n-hexane increases from 5.91 to 18.3% by LHSV decreasing from 3.0 to 1.0h-1, respectively. These observations are well agree with the previous investigation reported by Vu et al. [11] and Exner et al. [12].

The increase of isomerization reaction temperature at constant LHSV increases the conversion of n-hexane. This may be due to increasing of the number of active sites that can be used for the reaction.

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The conversion of n-hexane on 0.3wt%Pt/HY was enhanced from 18.3% to 49.5% after adding 435 TCE and at 1 LHSV and 270ºC.

The addition of TCE in feed stream is leads to increasing the concentration of surface intermediate loading to iso-hexane and this leads to increasing the activity, one reaction mechanism that is believed to be occurring in the process which helps to prevent the deactivation at the catalyst is that high molecular weight hydrocarbon, carbon and/or coke react with free chloride present in the additive instead of forming and accumulating within the pores of catalyst, particularly at the reaction sites within the catalyst. Another possible reaction mechanism is that the additive helps to prevent high molecular weight hydrocarbon such as aromatic and olefins from adsorbing onto the catalyst surface at the reaction condition of isomerizaton process.
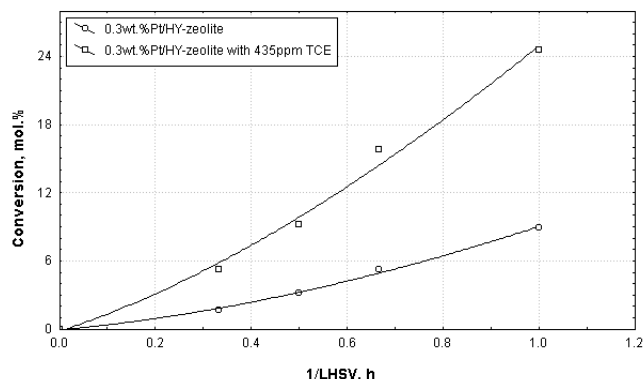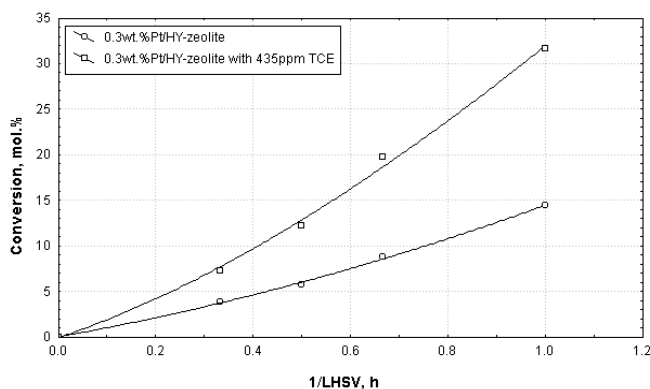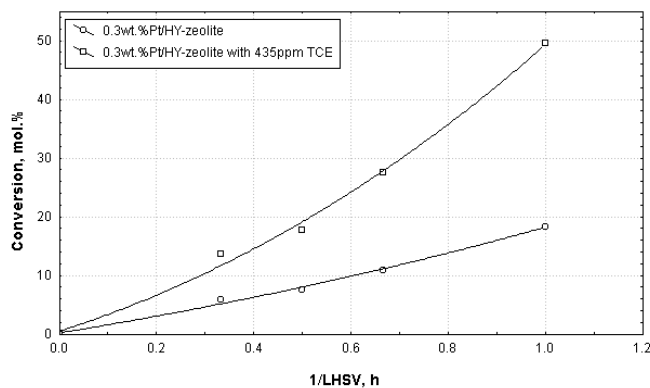

Fig.3: A comparison between n-hexane conversion with and without using of 435ppm of TCE over 0.3wt.%Pt/HY-zeolite catalyst at various contact time and at 260ºC.

Fig.1: A comparison between n-hexane conversion with and without using of 435ppm of TCE over 0.3wt.%Pt/HY-zeolite catalyst at various contact time and at 240ºC.

Fig.4: A comparison between n-hexane conversion with and without using of 435ppm of TCE over 0.3wt.%Pt/HY-zeolite catalyst at various contact time and at 270ºC.

The conversion of n-hexane was assumed to obey irreversible first order kinetic equation with negligible deviation from plug flow [13]. Plots of $\ln(1 - X_{nC_6})$ vs. 1/LHSV at different temperatures give straight lines with slops equal to rate constants as shown in figs. (5 and 6).The values of rate constant are tabulated in Table (1).

Fig.2: A comparison between n-hexane conversion with and without using of 435ppm of TCE over 0.3wt.%Pt/HY-zeolite catalyst at various contact time and at 250ºC.
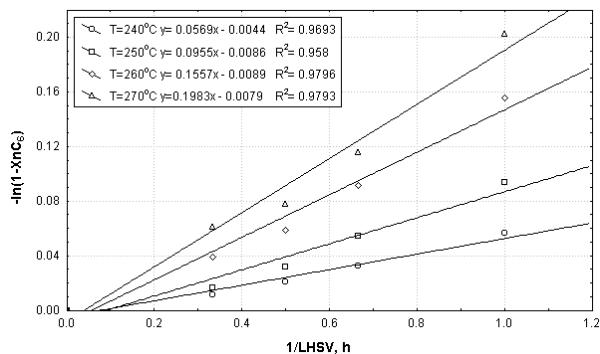
Fig.5: First order kinetic model for n-hexane conversion over 0.3wt.%Pt/HY-zeolite catalyst.
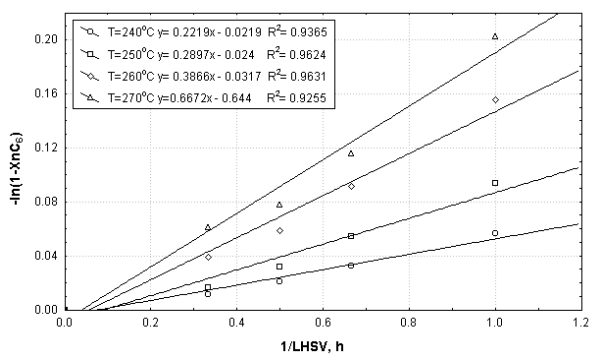

Fig.6: First order kinetic model for n-hexane conversion over 0.3wt.%Pt/HY-zeolite (with 435ppm TCE) catalyst.

Table 1 Results of rate constant measurements $nP_{H2}/nC_6=4$, Temperature range (240-270)°C.

Catalyst	K, h^{-1}			
	Temperature, °C			
	240	250	260	270
Pt/HY	0.0569	0.096	0.156	0.198
Pt/HY with adding TCE	0.222	0.290	0.397	0.667

The apparent activation energies for n-hexane conversion over 0.3wt.%Pt/Hy-zolite catalyst are calculated by using Arrhenius equation, which satisfies the relation between rate constant and the reaction temperature.

$$k = k_o e^{\left(\frac{-E_a}{RT}\right)} \qquad (1)$$

Plots of [(lnk) vs 1/T] gives a straight lines with slops equal to the ($\frac{-E_a}{RT}$) from which the activation energies were calculated. The results of the apparent activation energy estimated from fig. (7) are given in Table (2).

Table 2 Results of apparent activation energy measurements $nP_{H2}/nC_6=4$, Temperature range (240-270°C).

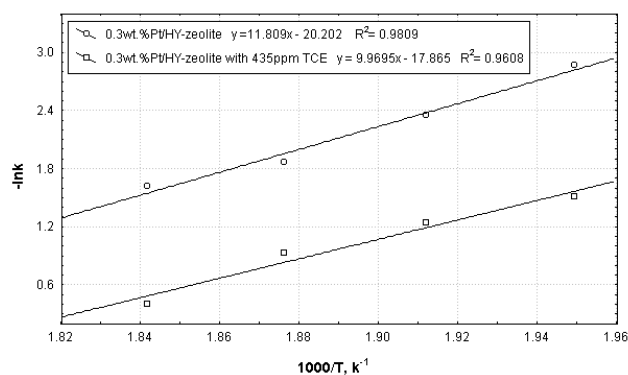| $E_{a, app}$ (kJ/mol)	Sample
98.18	Pt/HY
82.88	Pt/HY with adding TCE

Fig.7: Arrhenius plots for 0.3wt.%Pt/HY-zeolite and 0.3wt.%Pt/HY-zeolite (with 435ppm TCE) catalysts.

It was observed from data above that the activation energy of isomerization with adding 435 TCE is lower than that without adding TCE in hexane feed. The later catalyst related to the fact that the activity of 0.3wt%Pt/HY with adding TCE is higher than without adding and that the addition of TCE in feed stream. The addition of TCE in feed stream increases the number of the isomerization active sites and decrease the olefin content which leds to side reactions such as cracking. Also the addition of TCE in a feed stream serves to improve the selectivity to the desired product and aging properties of catalytic system. These observations are agreed well with the results reported by Jan-Ku et al. [14].

The main products of isomerization of n-hexane are 2 methyl pentane (2-MP), 3 methyl pentane (3-MP) ,2,2 dimethyl butane (2,2-DMB) and 2,3 dimethyl butane (2,3-DMB) for example only methyl pentane which has octane number 75 are formed from hexane when

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0.3 Pt/HY zeolite was charged while 2,2 DMB and 2,3 DMB which have octane number 95 were formed with adding 435 TCE to feed stream.

Figures (8) and (9) show the influence of temperature between 240-270°C on the isomerization selectivity and the product distribution. Only isomers formed at low conversion and a small amount of (C1-C4) products (<0.5%). The isomerization selectivity slightly increased with increasing temperature. The total isomerization selectivity was about (≥97%) over the Pt loaded catalyst.

The relation between the 2,2DMB/2,3DMB and 2MP/3MP ratios and conversion is shown in figs. 10 and 11 respectively. The ratio of 2.2DM/2.3DM on 0.3wt.%Pt/HY is very small while the ratio is higher where 0.3wt.%Pt/HY by adding TCE. Since, the branching is the limiting step of the bifunctional mechanism. With this mechanism 2MP and 3MP should be formed at a similar rate which can be observed, at low conversion however, the thermodynamics equilibrium between 2MP and 3MP is rapidly established because of their rapid isomerization through a methyl shift. Indeed the formation of 2,3DMB requires two successive branching PCP on the acid sites (equation 1 and 2). Since this branching is the limiting step of the bifunctional mechanism the formation of 2,3DMB should be consecutive to that of MP. Indeed methyl shift (A isomerization) is now to be faster than isomerization through PCP (B isomerization). Further more 2,3DMB should be formed more rapidly than 2,2DMB since 2,3DMB formation involves tertiary cation. These observations are in agreement with the results reported by Allain et al. (15) and Martens et al. (16).
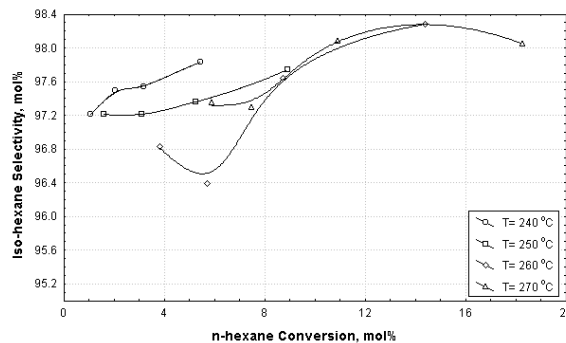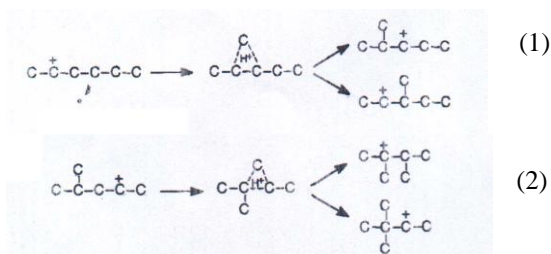

(1)

(2)

Fig.8: Isomerization selectivity as a function of conversion for 0.3wt.%Pt/HY-zeolite
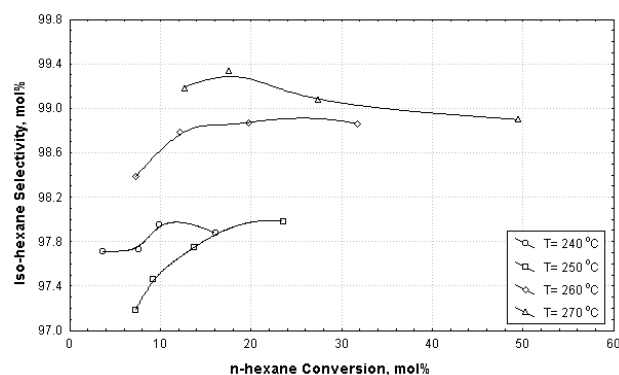

Fig.9: Isomerization selectivity as a function of conversion for 0.3wt.%Pt/HY-zeolite (with 435ppm TCE) catalyst.
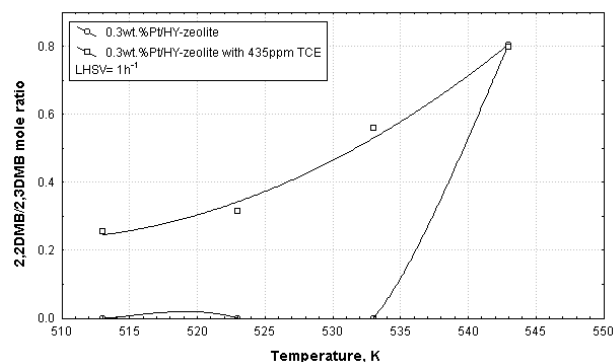

Fig.10: Products distribution as a function of conversion for 0.3wt.%Pt/HY-zeolite and 0.3wt.%Pt/HY -zeolite (with 435ppm TCE)catalysts.
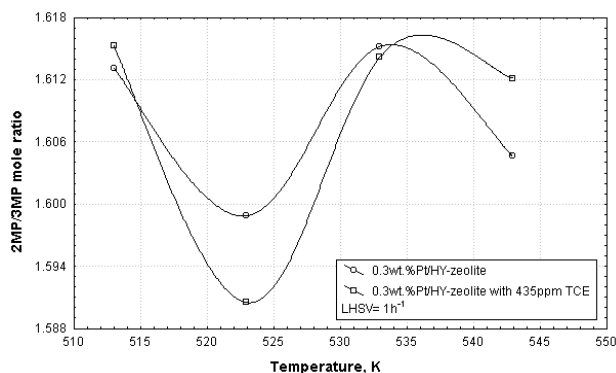
Fig.11: Products of distribution as a function of conversion for 0.3wt.%Pt/HY-zeolite and 0.3wt.%Pt/HY -zeolite (with 435ppm TCE) catalysts

CONCLUSIONS

1) n-Hexane conversion increases as the temperature is increasing from 240 to 270°C and decreases as the LHSV is increasing from 1 to 3 h-1. The highest n-hexane conversion 49.5 mol.% was achieved over 0.3 wt% Pt/HY zeolite catalyst with adding 435 ppm on feed stream at LHSV of 1 h-1, temperature of 270°C and H2/nC6 =4 mol ratio.

2) It was observed that the values of activation energy for hydroisomerization of n-hexane over the prepared catalysts take the following order:

3) Eact of 0.3wt% Pt/HY with adding TCE < Eact of 0.3wt% Pt/HY.

4) All the catalysts gave a high selectivity, and no significant change in the total isomerization selectivity was observed, while the product distribution is a decisive factor for catalyst activity evaluation. By adding TCE in a feed stream enhanced the selectivity toward 2,2MB and 2,3MB (higher octane number).

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