

Preparation and Catalytic Study of Selected Types of Zsm-zeolites

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Received on: 20/10/2010

Accepted on: 8/9/2011

Abstract

In present work experimental studies have been carried out on three types of crystalline zeolites were prepared and used as supports for platinum catalysts. All were synthesized in the laboratory (ZSM-5, -11, and -23) with SiO₂/Al₂O₃ ratio of 37, 86 and 94 respectively. N-Pentane is used as a feedstock for the process. The isomerization and cracking reaction were investigated to characterize the catalysts performance toward higher activity and selectivity to desired products. The performance of catalysts was studied under the following operating condition: liquid hour space velocity in the range of (1-2 hr⁻¹), reaction temperature in the range of (310-350 °C). The results showed that the prepared catalysts exhibit different activities toward n-Pentane isomerization and hydrocracking. These catalysts have high activity toward isomerization at low temperature while at high temperature the yield toward hydrocracking is increased. Also hydroconversion of n-Pentane decreases with increasing of liquid hour space velocity.

دراسة تحضير والحفازية لبعض أنواع الزيولايت المنقاة

الخلاصة

تضمن البحث اعداد دراسة شاملة عملية لثلاثة انواع من الزيولايتات واستخدمت كحوامل لمعدن البلاتين ، جميع هذه الانواع تم تحضيرها في المختبر وهي (ZSM-5, -11, and -23) ، حيث كانت نسبة السيلكا / الالومينا لهذه الانواع من الزيولايتات هي (37 ، 86 ، 94) على التوالي باستخدام مادة البنتان الاعتيادي كمادة أولية للعملية من اجل دراسة امكانية زيادة الكفاءة وتحسين الانتقائية للعوامل المساعدة. تم خلال البحث دراسة التفاعلات الرئيسية التي تحدث في العملية وهي (تفاعلات الازمرة وكذلك تفاعلات التكسير الحراري) بوجود الهيدروجين. تم دراسة اداء العوامل المساعدة الثنائية والثلاثية المعدن حسب الظروف التشغيلية التالية : السرعة الفراغية للغاز (1-2 ساعة⁻¹) ، درجة حرارة التفاعل تتراوح بين (310-350 م°). أظهرت النتائج للحفازات المحضرة سلوكا مختلفا تجاه تفاعلات الازمرة والتكسير للبنتان الاعتيادي. حيث بينت النتائج أن تأثير درجة الحرارة على فعالية الحفازات البلاتينية على جميع أنواع الزيولايتات ، ZSM-5, -11, and -23 أقوى وأشد مع تأثير تغير نسبة سرعة التدفق. حيث أن هذه الحفازات أظهرت فعالية أكبر تجاه الازمرة بدرجات الحرارة المنخفضة فيما يزداد التفاعل باتجاه التكسير عندما تزداد درجة الحرارة.

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Introduction

Reforming and isomerization can be considered as important processes, which are carried out on dual functional catalysts. These catalysts consist of noble metal dispersed on zeolite (hydrogenation-dehydrogenation components) supported on an active acidic support such as alumina, silica or amorphous silica-alumina [1].

It is well known that branched paraffin has higher octane value than linear paraffin, so that the isomerization reaction is important in gasoline reforming [2]. Isomerization reaction converts normal paraffins to iso-paraffins, the light naphtha stream from the crude tower, coker, and cracking units sent to isomerization unit to convert straight-chain paraffins into isomers that have higher octane numbers. Isomerization is a reversible reaction, and simply rearranges the molecule, with no appreciable loss in volume, or any gain or loss of hydrogen. The reason for trying to promote isomerization differs from paraffins and naphthenes. For example, n-pentane has an unleaded RON of 61.7 and isopentane has a rating of 92.3 [3, 4].

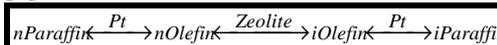
Several factors also make the study of paraffin isomerization on zeolite catalysts particularly interesting. The specific properties for zeolites catalysts such as ion exchange ability, high exchange capability, crystalline structure with regular pores of molecular size, quantity of cation and the silica/alumina ratio. A metal loading zeolite has a great

promise as catalyst in petroleum refining and in petrochemistry [5].

Isomerization reaction proposed generally has three stages [2, 3]:

1. Adsorption of n-paraffin molecule on dehydrogenation-hydrogenation site followed by dehydrogenation to n-olefins.
2. Desorption of n-olefin from the dehydrogenation sites and diffusion to a skeletal rearranging site, which converts n-olefin into iso-olefin.
3. Hydrogenation of iso-olefin into iso-paraffin molecule.

An atmosphere of hydrogen is used to minimize carbon deposits on the catalyst. Hydroisomerization of n-paraffin can occur through the bifunctional scheme shown below [6]:



Experimental Work

Materials and Chemical Compounds

Zeolites ZSM-5, ZSM-11 and ZSM-23 were synthesized in a hydrothermal system containing alumina source, silica source and an organic molecule, such as sulfuric acid, sodium hydroxide [7, 8]. Other chemicals are listed in Table (1).

b) Gases

Nitrogen was supplied from Dijlah factory, G.C. analysis for this gas shows that the purity is 99.9%.

Hydrogen was supplied from Al-Mansor plant; G.C. analysis of this gas shows that the purity is 99.9%, and hydrogen purified by passing it over molecular sieve type (5A) to drastically reduce oxygen and water impurities.

d) Catalysts and Support

Three different platinum supported types of zeolites, ZSM-5, ZSM-11 and ZSM-23 were prepared in sodium form. In some examples, sodium ions were exchanged by cesium ion and barium by using nitrate solution for catalytic studies.

Preparation of Zeolites Catalysts

1. Preparation of ZSM-5 Zeolite:

The sodium form of zeolite ZSM-5 was synthesized under conditions described in the literature [9]. The reaction mixture consisted of indigenous sodium aluminates, silica gel, and water and tetrapropyl ammonium hydroxide as template agent (specific structure-detecting). The resultant suspension was placed in a stainless steel autoclave in Figure. (1), and heated at 149°C with stirring for 6 days. The pressure was held constant at 8.7 bars.

The resultant liquor solution was cooled to room temperature, filtered off and the solid washed thoroughly with distilled water. The solid was left to dry at 110 °C for 24hr and then calcined at 538 °C for 16 hours.

A portion of this product was subjected to X-ray analysis, which was used to characterize the prepared ZSM-5 zeolite. The prepared ZSM-5, which was in powder form was sieved and mixed mechanically with montmorillonite clay (20 %) as a binder.

2. Preparation of ZSM-11 Zeolite

The sodium form of ZSM-11 was synthesized under conditions described in the literature [10]. The reaction mixture consisted of a silica solution, an acid alumina solution, benzyltrimethyl ammonium chloride and tetra butyl ammonium bromide. These two solutions were mixed in a stainless steel autoclave in Figure. (1). The resulting gel was whipped for one hour at room temperature with agitation, and then heated at 160 °C with stirring for 60 hours. The pressure was held constant at 7.5 bars.

The resultant liquor solution was cooled to room temperature, filtered off, and then solid washed thoroughly with distilled water. The solid was left to dry at 110 °C for 2 hours and then calcined at 538 °C for 16 hours.

A portion of this product was subjected to x-ray analysis, which was used to characterize the prepared ZSM-11 zeolite. The prepared ZSM-11, which was in powder form was sieved and mixed mechanically with montmorillonite clay (20 %) as a binder.

3. Preparation of ZSM-23 Zeolite:

The sodium form of ZSM-23 zeolite was synthesized under conditions described in the literature [11]. The reaction mixture consisted of sodium aluminates, colloidal silica and pyrrolidine. The resultant suspension was mixed in autoclave in Figure. (1) And heated at 177 °C with stirring for 2 days. The pressure was held constant at 17 bars.

The resultant liquor solution was cooled to room temperature, filtered

off and the solid was washed thoroughly with distilled water. The solid was left in oven to lessen all expected structural water at 110 °C for 24 hours and then calcined at 538 °C for 16 hours.

A portion of this product was subjected to x-ray analysis, which was used to characterize the prepared ZSM-23 zeolite. The prepared ZSM-23, which was in powder form was sieved and mixed mechanically with montmorillonite clay (20 %) as binder.

Preparation of Modified Zeolite by Cation Exchange for Catalytic Studies

1. Preparation of Cs-Zeolite Catalysts

Cesium zeolite was prepared by ion exchange of the sodium form of ZSM-5, -11, -23 with (0.5 N) cesium nitrate solution [12].

Thus 14.63 g of cesium nitrate in 150 ml distilled water was contacted with 30 g of zeolite at reflux condition with stirring for 2 hours at 100 °C; the procedure was repeated three times under the same condition. The exchange cesium zeolite was filtered off, washed with deionized water to be free of nitrate and dried, exchanged zeolites were then mixed with 20 % montmorillonite clays as binder, dried at 110 °C and calcined at 550 °C for 8hr.

2. Preparation of Ba-Zeolite Catalysts:

Barium form of zeolite was prepared by ion exchange of the original sodium form of each ZSM-5, ZSM-11 and ZSM-23 with (3 N) barium nitrate [13].

Thus 58.8 g of barium nitrate in 150 ml distilled water was contacted with 30 g of zeolite at reflux condition with stirring for 3 hours at 50 °C. The exchanged barium zeolite was filtered off, washed with deionized water to be free of nitrate and was dried overnight at 110 °C. The dried exchanged zeolites were then mixed with 20 % montmorillonite clay as binder, dried at 110 °C and calcined at 550 °C for 8 hours.

Preparation of Pt/Modified-Zeolite Catalysts

The ion-exchanged zeolites (which are modified in different ways) were loaded with 0.4 wt. % Pt by impregnation with aqueous solution of hexachloroplatinic acid. The platinum content of the catalysts was calculated from the weight of support and amount of the metal on impregnation solution [14].

Thus 0.1 g of hexachloroplatinic acid (40 wt. % Pt) was dissolved in 15 ml of distilled water. Then the solution was added to 10 g of each type zeolites sample as drop wise with mixing for 2 hours at 25 °C. The mixture was left for 24 hours at room temperature, and the resulting catalysts were dried for an additional 24 hours at 110 °C. All the zeolites were then mixed with 20 % montmorillonite clay as a binder and dried at 110 °C overnight. Calcined catalysts were modified as pellet (0.4 cm x 0.65 cm) and reduce with hydrogen gas at 350 °C for 3hr prior to utilization.

Catalysts Performance

The performance (activity, selectivity and yield) of three different platinum supported types of zeolites (ZSM-5,

ZSM-11 and ZSM-23) were tested in this study. The catalysts were originally in the form of extrudate, and then each type of catalyst was activated in the catalytic reactor, just before test runs, at 450 and 500 °C for 4 hr respectively in a current of hydrogen at 1 atm pressure with flow of (60 and 80 cm³/min).

Isomerization Unit

The experimental unit was designed and constructed in Research Laboratory (1) in Chemical Engineering Department / University of Technology, as shown in Figure (2).

Operating Procedure

n-Pentane was pumped to the top of the packing section using a calibrated dosing pump. Hydrogen passes through a flow meter; which was mixed with n-pentane before the reactor inlet. The mixture preheated before entering the reactor, the products are cooled by cooling system and collected in the separator in order to separate the uncondensed gases from the top to the atmosphere and the condensed liquid from bottom of the separator. Then the products samples are analyzed using gas chromatograph type Varian 6000 flow ionization detector.

The catalysts bed was tested under the operating temperature range Between (310, 320, 330, 340 and 350 °C), and under constant pressure fixed at 1 atm. The weight hour space velocity varied between (1, and 2 hr⁻¹), and H₂/H.C molar ratio was kept constant at 3:1. All types of catalysts were activated in the catalytic reactor before test runs for 4 hr in a current of hydrogen, also for

each test runs using fresh catalyst for each temperature and weight hour space velocity, therefore deactivation of catalysts will not need to study in this investigation.

Results and Discussion

1-X-Ray Diffraction of the Prepared Zeolites:

The zeolites of ZSM-5, -11, and -23 are known for its unusually high Si/Al ratio, high degree of thermal and acid stability, and high yield in certain catalytic conversion. All these properties make these types of zeolites suitable and important for industrial applications [15].

Figures (1, 2, and 3) show the XRD pattern for the prepared and standard zeolites (ZSM-5, -11, and -23).

The comparison of the heights of the main diffraction peaks to those characterizing best the corresponding pore reference zeolite indicate that the preparation method resulted in a material almost compatible with the crystal structure as ZSM-5, -11, and -23 zeolites. This leads to the conclusion that our preparation method gives an exact synthesized indigenous (ZSM-5, -11, and -23). Analysis of the chemical composition of prepared zeolites and reference zeolites are shown in table (2).

Table (2) indicates that SiO₂, Al₂O₃ and Na₂O are in wt. %. The SiO₂/Al₂O₃ molar ratio was 37.2, 84, and 94 for ZSM-5, -11, and -23 respectively which is typical for such types of zeolites [16].

2- Effect of Reaction Temperature

The activity and yield of prepared Pt/Ba⁺², and Pt/Cs zeolites catalysts were studied under the temperature

range between (310, 320, 330, 340, and 350 °C), the LHSV of (1hr^{-1}) in hydroconversion of n-Pentane.

Figures (6) to (11) show the results of the effect of operating temperature on n-Pentane hydroconversion (isomerization, and cracking reaction) of (Pt/Ba-ZSM-11, 23, and -5). Figures (6, 7, and 8) show that isomerization increases as temperature increase and reach maximum values at 350 °C. At higher temperatures the degree of isomerization decreases, which might be attributed to; firstly, the adsorption of hydrocarbon at the strong acid sites is hindered and secondly the decrease of isomerization is matched by an increase in cracking reaction.

The results in Figures (9, 10, and 11) indicate that maximum isomerization yield at 310 °C. As the temperature increase yield declines at 350 °C. This is apparently due to competitive hydrocracking character [16]. In addition, decreases the isomerization yield might be attributed to the production of cracked material at higher temperatures.

From the results it can be concluded that Pt/Ba-ZSM-11 is more active than Pt/Ba-ZSM-23 and the latter gives higher yield. The varying activity of the above two catalysts might be replomid as follows: firstly, the ion-exchange of ZSM-23 is smaller than that of Ba-ZSM-11 catalyst due to the low aluminum content and probably due to relative size of ZSM-23 pores and of the exchanging species. Secondly, the acidic sites, which are correlated quantitatively with the high Si/Al

ratio in ZSM-23, are considered very strong leading to high degree of yield for n-C₅ isomerization.

From the above results a conclusion could be made that Pt/Ba-ZSM-23 is more active than Pt/Ba-ZSM-5, which might be attributed to the difference in the Si/Al ratio. Since ZSM-23 is higher in Si/Al ratio than ZSM-5, which indicates the fact that high Si/Al ratio improves catalytic activity [17].

The activity and yield of prepared Pt/Cs ZSM-11, 23, and -5 can be observed from the results shown in Figures (12) to (17), similar general trend that degree of isomerization of n-Pentane increases with increasing temperature and goes up to maximum value at 350 °C, which total conversion is achieved at this temperature. The results show that cracked product reaches to maximum value at 350 °C. Also maximum isomerization yield at 310 °C. As the temperature increases the yield declines at 350 °C. This is apparently due to competitive hydrocracking character [17]. In addition, decreasing in the isomerization yield might be attributed to the production of cracked material at higher temperatures.

From the results obtained for both mono and di-valent zeolites one could notice that di-valent zeolites are more active than the mono-valent zeolites. This can be attributed to the mono-valent cation zeolites lack isomerization activity indicating that the strongly bonded mono-valent cation destroys the catalytic activity for ionic type hydrocarbon reaction. Polyvalent (di-valent) cationic with

high Si/Al ratio has high catalytic activity; it is assumed that the bonding of the di-valent cation is responsible for catalytic activity [18].

2. Effect of Liquid Hour Space Velocity (LHSV)

The activity and yield of prepared Pt on Ba⁺² zeolites catalyst were studied under different liquid hour space velocity (1 and 2 h⁻¹) in hydroconversion of n-pentane.

The results are shown in Figures. 18 to 23 for Pt/Ba-ZSM-11, -23, and -5. From Figures 18, 19, and 20 show that increasing the liquid hour space velocity leads to a decrease in the conversion of n-C₅ to reach maximum value and total conversion at LHSV of (1 h⁻¹) at 350 °C. This indicates that whenever the contact time decreases the chance of n-pentane reaction on the active site decreases. Therefore the conversion will decrease and the isomerization of n-pentane will consequently decrease, which is due to the fast rate of isomerization of n-pentane. Also these Figures indicate that cracked product also decreases when LHSV increases and it reaches maximum value at 350 °C.

Figures 21, 22, and 23 show that maximum degree of isomerization yield is at 310 °C, which is higher than at LHSV 1 h⁻¹, which indicate that as LHSV increases, yield increases.

The results shown in Figures. (24) to (26) indicate that when LHSV increases the conversion of n-pentane on Pt/Cs-ZSM-11, -23, and -5 decreases and it reaches a maximum

Nomenclature

Value at 350 °C. This might be ascribed to the reduction in contact time of reactant with the active sites in the catalyst and eventually reduce the conversion.

Figures. (27) to (29) show that the yield of isomerization increases as LHSV increases and its reach maximum value at 310 °C. The cracked products yield decreases as LHSV increases to reaches maximum value at 350 °C, because hydrocracking reaction rates are slow compared with isomerization reaction

Conclusions

1- The ion exchange technique and multi-steps (three time repeating) impregnation with the concentration of salt solution and short periods and times are more effective than chemical classical technique.

2- X-ray diffraction for ZMS-5, -11 and -23 points to the presence of high degree of crystallinity and surface structure stability. 3- The degree of isomerization of Ba-ZSM-11 reaches a maximum value of 29.21 % at 350 °C and LHSV of 1 h⁻¹, which is higher than ZSM-23 and ZSM-5. Maximum degree of isomerization yield for iso-pentane considered in Cs-ZSM-23 at LHSV (2 h⁻¹) is 98.35 % at 310 °C, which is higher than that for ZSM-11 and ZSM-5 at the same temperature.

4- Maximum yield for cracked products increases for Cs-ZSM-11; it increases as the reaction increases and it reaches 12 % at 350 °C, which is higher than that of ZSM-23 and ZSM-5 at the same temperature.

| Notation | Definition | Units | |
|---------------------|---|--------------------|---|
| GC | Gas chromatography | [-] | <i>Science and Catalysis</i> ", Vol. 49, Part B (1989). |
| H ₂ /H.C | Hydrogen to hydrocarbon ratio | [-] | [3]Raouf S. R., "Platinum Supported Zeolite Catalyst Preparation, Characterization and Catalytic Activity", Ph.D. Thesis, University of Technology, Baghdad (1994). |
| i-C ₅ | Iso-pentane | [-] | [4]Leach P. E., "Applied Industrial Catalyst" ; Vol 3, Academic press (1984). |
| I-C ₅ | Isomerization yield of pentane | [-] | [5]Jamali, J. S., Mutwali, F. S., and Mansour E. F., J. Eng. Tech., Special Issue of Proc. 2 nd Iraqi Conf. on Engineering, 6 (1988). |
| Kd | Distribution coefficient | [-] | [6]Rubae K. A., "Modelification and Characterization of Platinum Supported Zeolites Catalysts", M.Sc. Thesis, University of Technology, Baghdad (1996). |
| LHSV | Liquid hour space velocity | [h ⁻¹] | [7]Szostak R., "Molecular Sieves in Principles of Synthesis and Identifications", New York (1998). |
| Crac | Cracked product (C ₁ -C ₄) | [-] | [8]Thomas C. L., "Catalytic Processes and Proven Catalyst", Academic Press, New York, (1970). |
| T | Temperature | [°C] | [9]Argauer R. J., and Landolt G. R., U.S. Patent 3,702,886 (1972). |
| V | Volume of aqueous phase | [ml] | [10]Chu P. E., E.P.A H 2006 (1983), assigned to Mobil Oil. |
| XRD | X-ray diffraction analysis | [-] | [11]Plank G. A., Rosinski E. J., and Rubin M. K., U.S. Patent 4,076,842 (1978). |
| ZSM-11 | Group of pentasil zeolite number 11 | [-] | [12]John S., and Theodore U., "Adsorption and Ion Exchange Progress and Future Prospects", AIChE J., 80, No. 233 (1984). |
| ZSM-23 | Group of pentasil zeolite number 23 | [-] | [13]Vander G. F., Janson J. C., and van Bekkumm H., Proceeding sixth International Zeolite Conference, Reno (1983). |
| ZSM-5 | Group of pentasil zeolite number 5 | [-] | |

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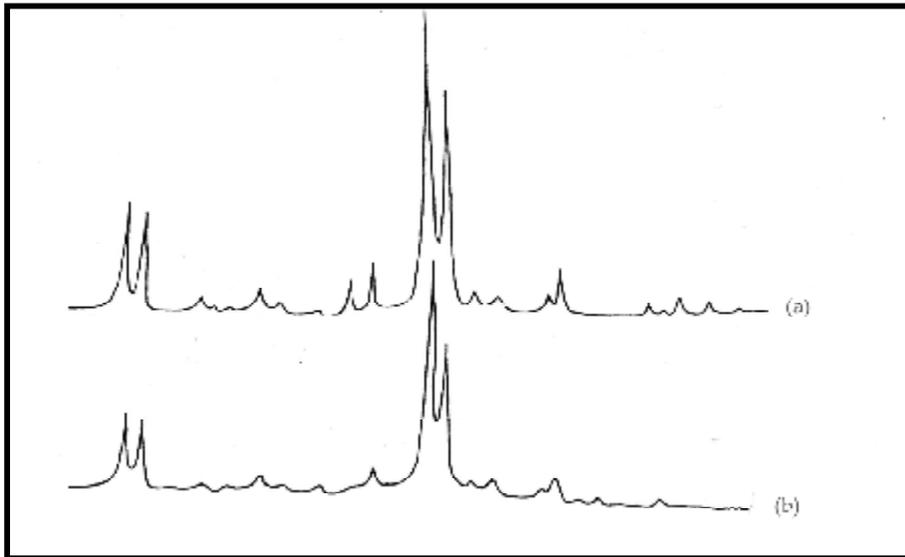
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Table (1) Chemical Components

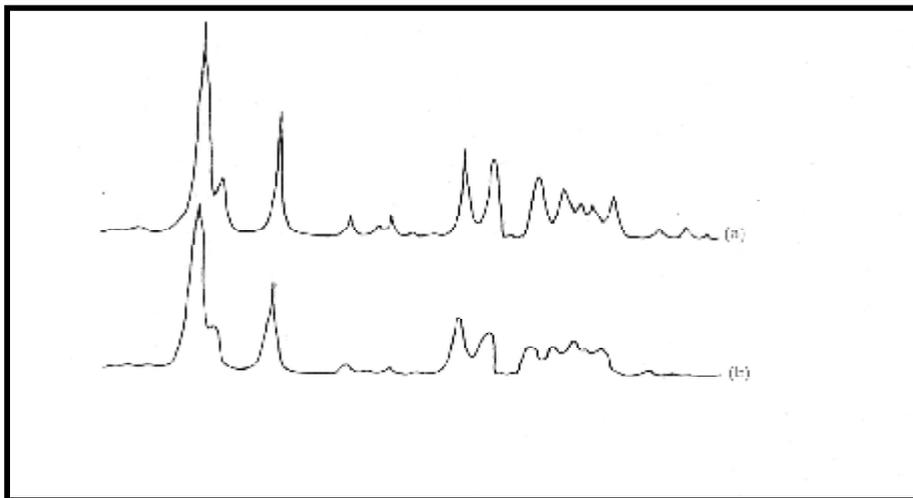
| No. | Compound | Purity | Company |
|-----|----------------------------------|--------|-----------------|
| 1 | Aluminum oxide | 99% | Brussel-Belgium |
| 2 | Hexachloroplatinic acid | 40% | Fluka |
| 3 | Cesium nitrate | 99.99% | Fluka |
| 4 | Nitric acid | 67% | Fluka |
| 5 | Potassium nitrate | 99.9% | Fluka |
| 6 | Strontium nitrate | 99.9% | Fluka |
| 7 | Tetrapropylammonium hydroxide | 10% | Fluka |
| 8 | Tetrabutylammonium bromide | 40% | Fluka |
| 9 | Pyrrolidone | >98% | Fluka |
| 10 | H ₂ gas | 99.98% | Mansour company |
| 11 | n-pentane | 99.9% | Merch-Germany |
| 12 | Silica gel | 100% | Riedeh-Dehlaen |
| 13 | Sodium hydroxide | 99.99% | Riedeh-Dehlaen |
| 14 | Sulfuric acid | 99.9% | Riedeh-Dehlaen |
| 15 | Lithium nitrate | 99% | Riedeh-Dehlaen |
| 16 | Barium nitrate | 99.9% | Riedeh-Dehlaen |
| 17 | Benzyltrimethylammonium chloride | 60% | Riedeh-Dehlaen |
| 18 | Sodium silicate | 98% | Riedeh-Dehlaen |

Table (2): Analysis of the Chemical Composition of Prepared and Reference Zeolites.

| Chemical Composition wt% | Prepared | Reference |
|---------------------------------|---|---|
| ZSM-5 | | |
| Oxide formula | Na ₂ O.Al ₂ O ₃ .5-100 SiO ₂ . ZH ₂ O | 0.9±0.2 Na ₂ O.Al ₂ O ₃ .5-100 SiO ₂ . ZH ₂ O |
| SiO ₂ | 91.1 | 93.5 |
| Al ₂ O ₃ | 4.16 | 4.9 |
| Na ₂ O | 1.27 | 1.6 |
| ZSM-11 | | |
| Oxide formula | Na ₂ O.Al ₂ O ₃ .10-150 SiO ₂ . ZH ₂ O | 0.9±0.3 Na ₂ O.Al ₂ O ₃ .10-150 SiO ₂ . ZH ₂ O |
| SiO ₂ | 95.52 | 97.96 |
| Al ₂ O ₃ | 1.91 | 2.216 |
| Na ₂ O | 0.057 | 0.07 |
| ZSM-23 | | |
| Oxide formula | Na ₂ O.Al ₂ O ₃ .40-250 SiO ₂ . ZH ₂ O | 0.5±3.4 Na ₂ O.Al ₂ O ₃ .40-250 SiO ₂ . ZH ₂ O |
| SiO ₂ | 94.78 | 96.9 |
| Al ₂ O ₃ | 1.61 | 1.65 |
| Na ₂ O | 0.19 | 0.27 |



**Figure (1) XRD Pattern of Prepared and Standard Zeolite (ZSM-5)
(a) Standard and (b) Prepared.**



**Figure (2) XRD of Prepared and Standard Zeolite (ZSM-11) Standard and
(b) Prepared.**



Figure (3) XRD of Prepared and Standard Zeolite (ZSM-23)
(a) Standard and (b) Prepared.

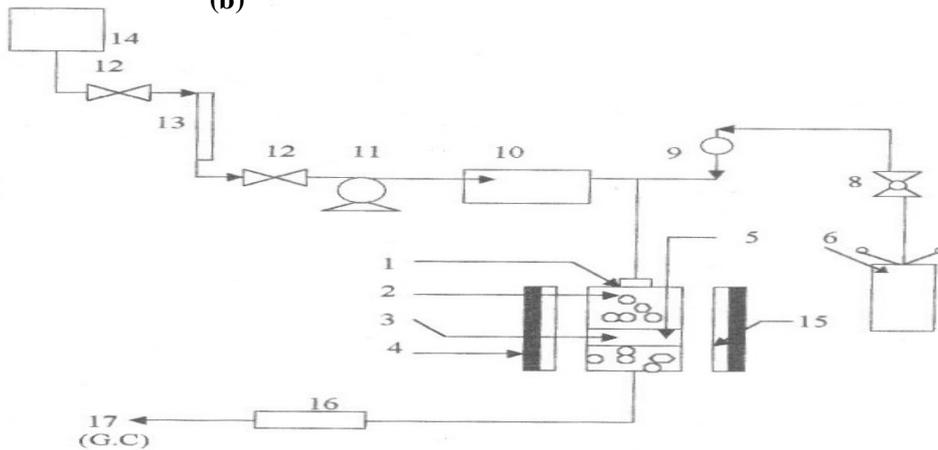


Figure (4) the Stainless Steel Autoclave.

| | |
|--|-----------------------|
| 1-Reactor | 11-Feed pump |
| 2-glass packed | 12-Valve |
| 3-Catalyst bed | 13-Metering burette |
| 4-Insulation | 14- Feed tank |
| 5-Thermocouple and temperature indicator | 15-Heater |
| 6-H ₂ gas cylinder | 16-Gas sample trap |
| 7-Pressure regulator | 17-Gas chromatography |
| 8-Needle valve | |
| 9-Flow meter | |
| 10 -One way valve | |

Figure (5) Schematic Flow Diagram of Catalytic Experimental Rig.

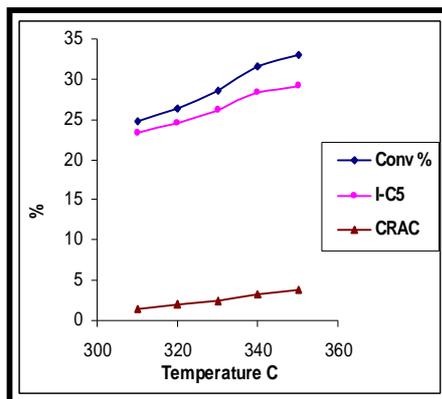


Figure (6) Hydroconversion of n-Pentane on Pt/Ba ZSM-23 Catalyst at LHSV =1/h

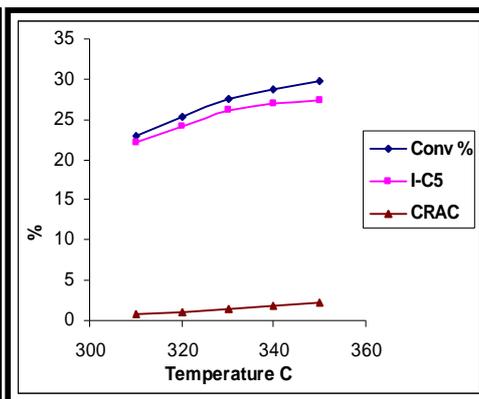


Figure (7) Hydroconversion of n-Pentane on Pt/Ba ZSM-11 Catalyst at LHSV =1/h.

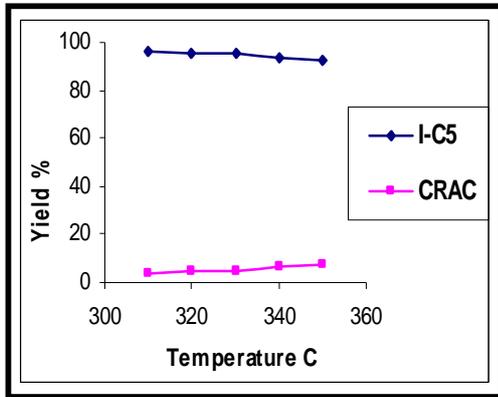


Figure (8) Hydroconversion of n-Pentane on Pt/Ba ZSM-5 Catalyst at LHSV =1/h.

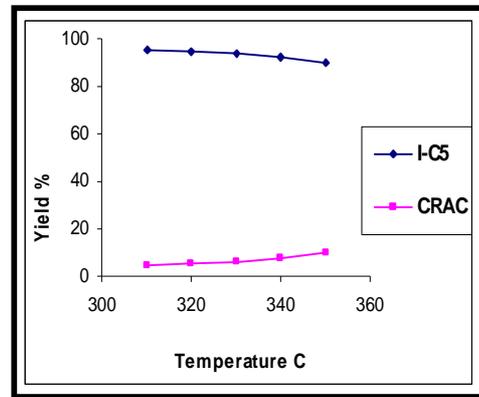


Figure (9) Yield of Pt/Ba ZSM-11 Catalyst on n-Pentane Hydroconversion at LHSV =1/h.

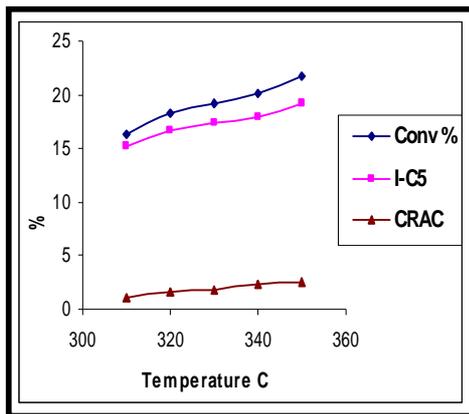


Figure (10) Yield of Pt/Ba ZSM-23 Catalyst on n-Pentane Hydroconversion at LHSV =1/h.

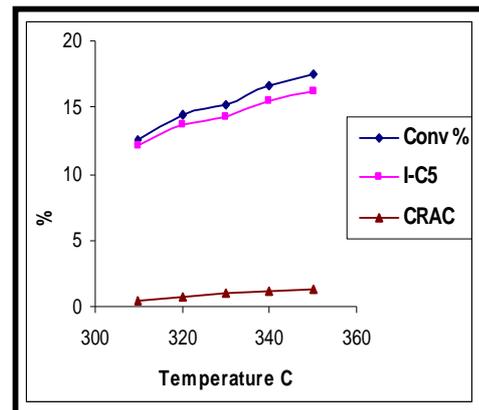


Figure (11) Yield of Pt/Ba ZSM-5 Catalyst on n-Pentane Hydroconversion at LHSV =1/h.

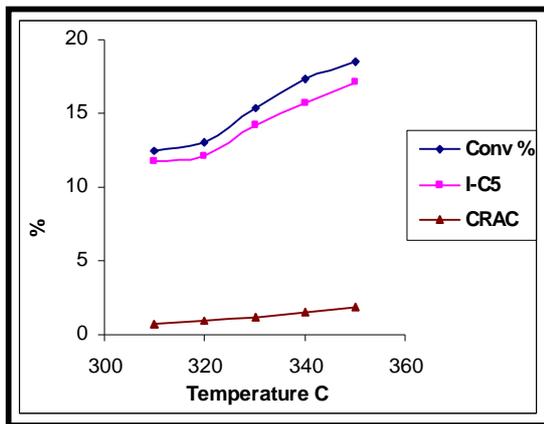


Figure (12) Hydroconversion of n-Pentane on Pt/Cs ZSM-11 Catalyst at LHSV =1/h.

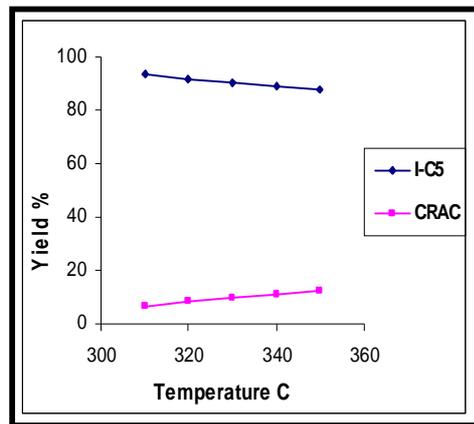


Figure (13) Hydroconversion of n-Pentane on Pt/Cs ZSM-23 Catalyst at LHSV =1/h.

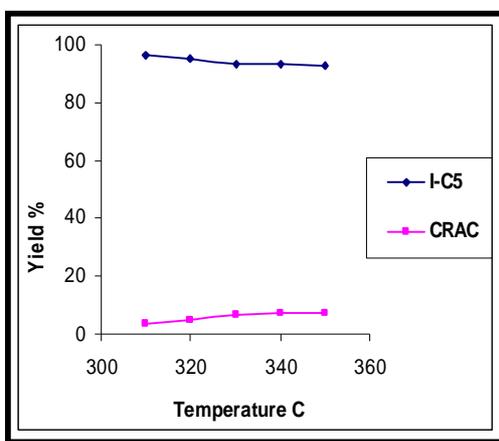


Figure (14) Hydroconversion of n-Pentane on Pt/Cs ZSM-5 Catalyst at LHSV =1/h.

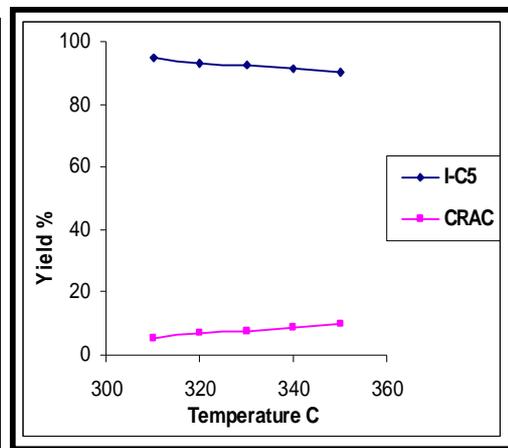


Figure (15) Yield of Pt/Ba ZSM-11 Catalyst on n-Pentane Hydroconversion at LHSV =1/h.

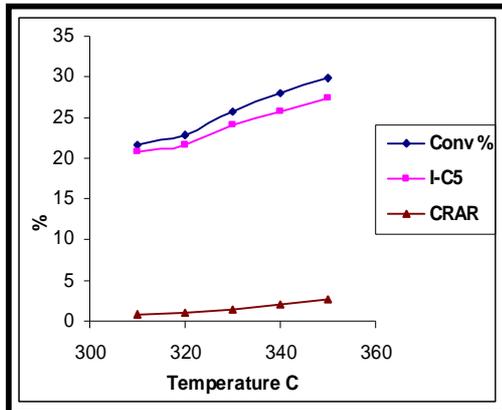


Figure (16) Yield of Pt/Cs ZSM-23 Catalyst on n-Pentane Hydroconversion at LHSV =1/h.

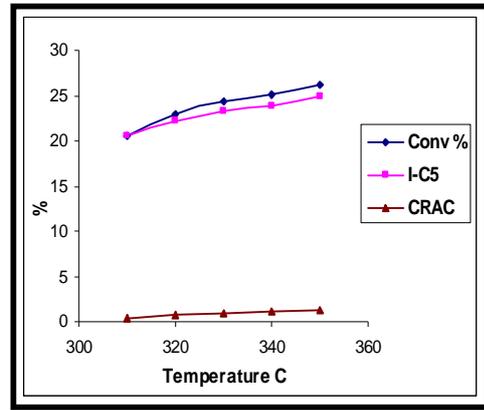


Figure (17) Yield of Pt/Cs ZSM-5 Catalyst on n-Pentane Hydroconversion at LHSV =1/h.

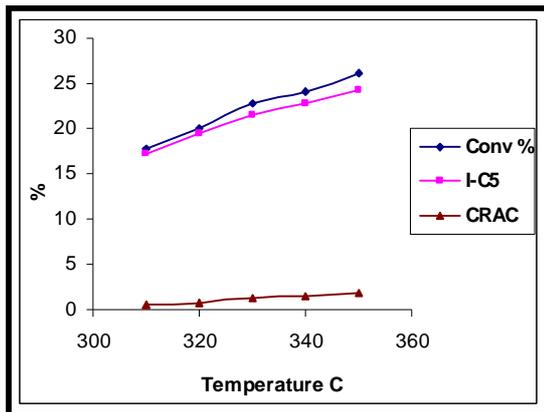


Figure (18) Hydroconversion of n-Pentane on Pt/Ba ZSM-11 Catalyst at LHSV =2/h.

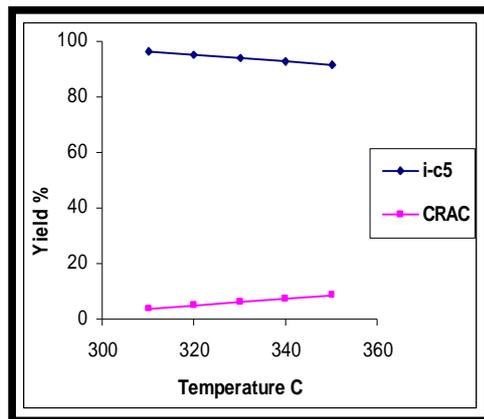


Figure (19) Hydroconversion of n-Pentane on Pt/Ba ZSM-23 Catalyst at LHSV =2/h.

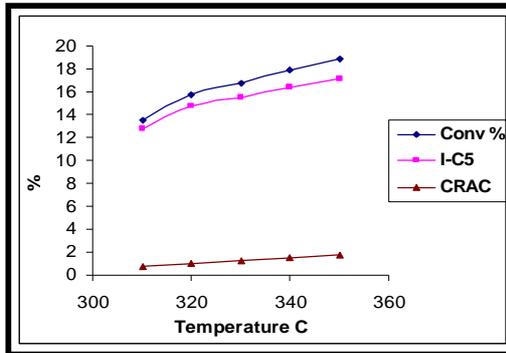


Figure (20) Hydroconversion of n-Pentane on Pt/Ba ZSM-5 Catalyst at LHSV =2/h.

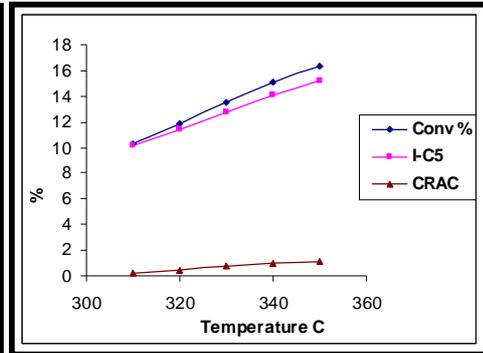


Figure (21) Yield of Pt/Ba ZSM-11 Catalyst on N-Pentane Hydroconversion at LHSV =2/h.

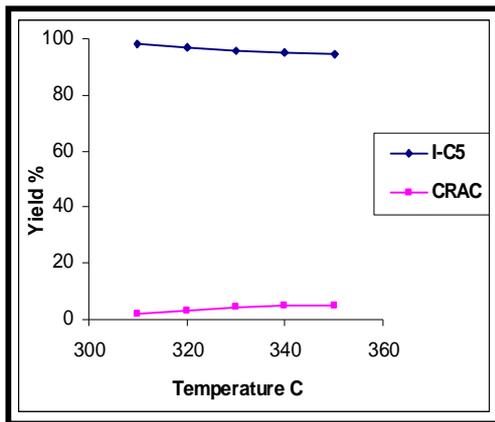


Figure (22) Yield of Pt/Ba ZSM-23 Catalyst on n-Pentane Hydroconversion at LHSV =2/h.

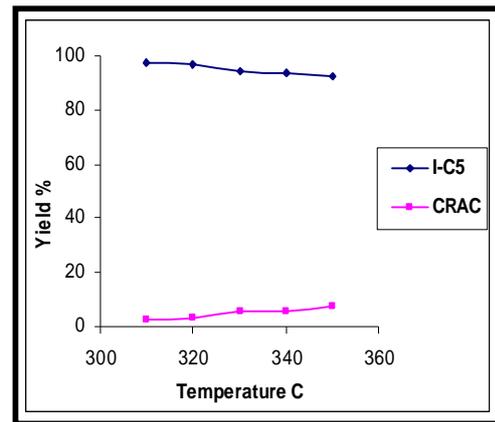


Figure (23) Yield of Pt/Ba ZSM-5 Catalyst on n-Pentane Hydroconversion at LHSV =2/h.

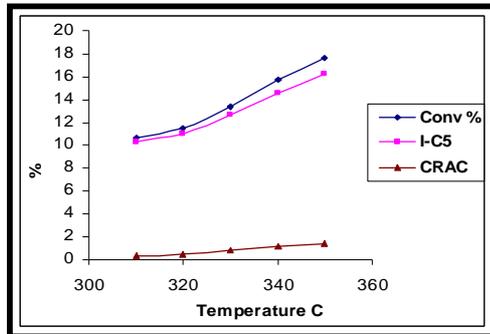


Figure (24) Hydroconversion of n-Pentane on Pt/Cs ZSM-11 Catalyst at LHSV =2/h.

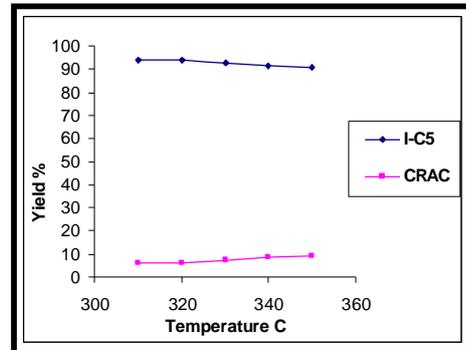


Figure (25) Hydroconversion of n-Pentane on Pt/Cs ZSM-23 Catalyst at LHSV 2/h.

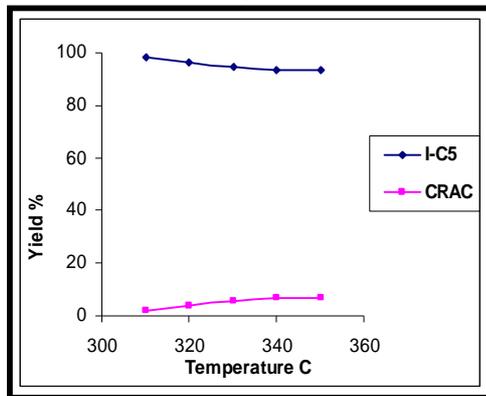


Figure (26) Hydroconversion of n-Pentane on Pt/Cs ZSM-5 Catalyst at LHSV =2/h.

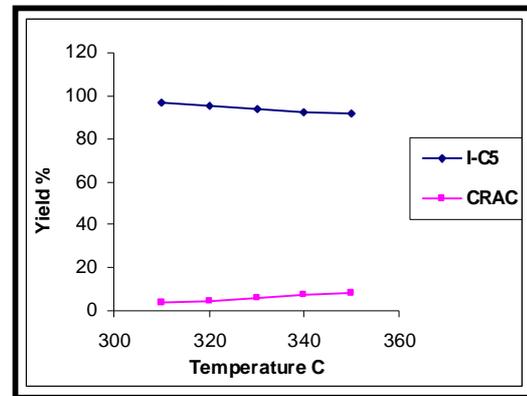


Figure (27) Yield of Pt/Cs ZSM-11 Catalyst on n-Pentane Hydroconversion at LHSV =2/h.

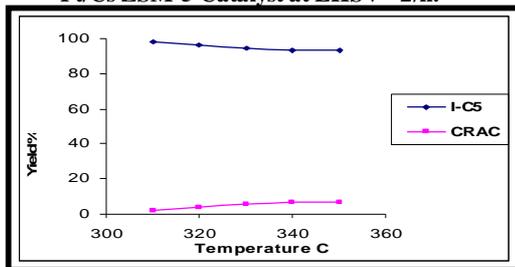


Figure (28) Yield of Pt/Cs ZSM-23 Catalyst on n-Pentane Hydroconversion at LHSV =2/h.

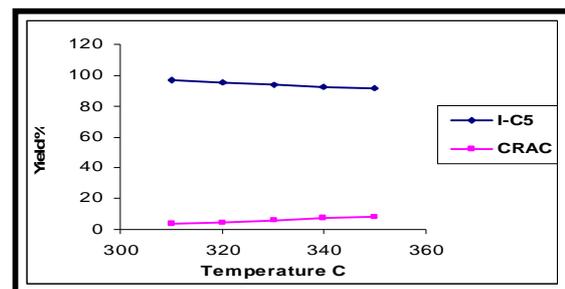


Figure (29) Yield of Pt/Cs ZSM-5 Catalyst on n-Pentane Hydroconversion at LHSV =2/h.