Catalytic treatment of Kerosene (180-260) °C over Bentonite rich alumina silicate and oxidation over prepared Silver catalyst supported on calcinated CaCO3

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Abstract

In this research work , two types of catalysts were prepared from Bentonite . The Bentonite was purified from inactive components such as carbonate, bicarbonate , dolomite .... etc

In the first catalytic treatment, kerosene was passed over the bentonite catalyst at 500 ° C at constant flow rate aiming to obtain some reactive linkages for the second treatment . The second catalyst was prepared by supporting silver metal over calcium carbonate and used to react with materials from the above step . Analysis of the hydrocarbon chemical composition indicate a reduction in the n-paraffinic content which could be due to cracking reactions , The amount of olefinic hydrocarbons are increased too in the two treatments . The two catalysts activate reactions accurated in the treatment according to the temperature employed and probably the hydrocarbon structure .The (IR) spectrum showed increase the aromatic system in some treated samples.

Keywords : Kerosene , catalyst , alumina silicate

Introduction

Heterogeneous catalysts is have along history , dating back to the early studies of the dehydration of alcohol over alumina and alcohol oxidation over platinum metal in the prev. century (١) .

Industrial catalysts can be manufactured employing many methods and technologies . In the industry, usually they concentrate in the shape and size that gave a large surface area for chemical reaction . Also some times the shape and size are a design requirements for the process and the reactor employed (2 ,3).

Catalytic processes and catalysts play important role in the petroleum industry in comparison to the chemical industries. The variation and the goal of the petroleum industry and efforts conducted by the producer and the consumer to obtain the profitable units. The catalysts used in the petroleum industry were modified to give a valuable product from the original crude oil . In addition to those used in the modification (e.g., isomerization , oligmerization , reforming ….. etc) and finishing of the cut and the products.

In recent years the petroleum industry was highly engaged with development of the production of catalysts heterogeneous and homogeneous that have a great ability to increase the octane number of the gasoline which is a problem of the automobile engines developed and the environmental regulations. These methods may be of a catalytic type cracking , catalytic reforming and catalytic isomerization . …… etc . (4).

The increase in the use of catalysts to the catalytic treatment of kerosene and heavy naphtha was greatly improved , this is because kerosene and heavy naphtha are produced in a large amounts and there a little uses in modern civilization , also these fractions have a high boiling point and a large range of petroleum hydrocarbons . Kerosene fraction obtain from crude oil by distillation under atmospheric pressure , kerosene has a boiling point of (176-250)° C , contains a various types of hydrocarbons which present in the paraffinic , isoparaffinic , naphthenic and substituted mono alkyl benzene and to a less extent all containing hydrocarbons (sulfur , nitrogen and oxygen compounds) . Usually and from analysis point of view , kerosene contains hydrocarbons having a carbon number (C9 – C15) (5).

The paraffinic hydrocarbons are mainly (C9 – C13) which is suitable for further upgrading processes . Looking back at the literatures we found many methods using numerous raw materials in the production of catalysts and some of them are give below.

Ugtterhoeven et al .(6) , described a certain procedure for the preparation of a metallic catalyst having a catalytically active metal as Pt . The catalyst produced is has various surface area and pores.

Joyner et al .(7) , were prepared catalyst containing Pd, alkali metals , earth metals , and/or lanthanide. The metal supported on active carbon which gave a certain area . The catalyst was employed to methanol conversion into H2O and CO2 (Synthesis gas) which suitable in Fisher-Tropsch processes.

On the other hand , Mul, . et al .(8) prepared epoxide from alkane using lanthanide-promoted silver catalyst , especially, convert propane to propylene oxide using silver nitrate and lanthanum nitrate – on BaCO3 as support.

Mamedov, et al .(9) prepared catalyst system for oxidative dehydrogenation of paraffins, the catalyst consists of two kind of metal, the first is alkali or alkali earth metal and the second is bismuth or Gallium , niobium , tin and neodymium.

Gaffney et al . (10) was using precious metal catalyst such as silver and gold supported on the whole or in substantial part of an alkaline earth metal carbonate such as potassium carbonate to produce propylene oxide from propylene in presence of oxygen , this method used currently for commercial production of ethylene oxide.

Deshpande , et al .(11) used a palladium complex as catalyst for the oxidation of linear alkanes with employing of molecular oxygen as the oxidant to produce secondary alcohols and ketones in high selectivity , the said catalyst is a single and does not requires the use of any co-catalyst or solvent .

Experimental

1- Preparation of Catalysts :

A- Preparation of treated Bentonite Catalyst :-

(100) gm of bentonite refluxed with (300) ml of (10%) HCl for 3 hr., Bentonite free acidic component was converted to granular form by mixing it with a little amount of water. The bentonite slurry was passed through suitable syringe then were dropped over paper to dry on air , Finally the grains was thermally treated between 120 °C for 3 hr. , then at 300 °C and finally at 750°C to remove all kinds of water to give the catalyst hardness and retained carbonates.

B- Preparation of Silver Catalyst supported on Calcium Carbonate (10) :-

(20.7) gm of ethylene diamine was dissolved in (20.4) gm of distilled water . Then add (15.0) gm of oxalic acid dihydrate , (26.0) gm of pure silver and (7.2) gm of ethanol amine were added to the mixture . Addition of potassium nitrate dissolved in (5.0) gm of distilled water to the above mixture , finally (34.0) gm of calcium carbonate was added to the total mixture , The resultant mixture, was converted to granular form and dried at 110 °C for 2 hr. and calcined at 400 °C for 3 hr.

2- Catalytic Cracking :

A- Catalytic Cracking by Granular Bentonite:-

(30) gm of catalyst was placed in silica tube was previously placed in tube furnace of total carbon analyzer (100 – 1600 °C) . Kerosene vapor was passed over the catalyst at a flow rate of (6-7) drops/minute at 500 °C . The cracked materials were collected in ice cooled traps . The gases were left to flow outside . The resultant materials were kept in dry closed container to be used in the second step.

B- Catalytic Cracking by Silver Catalyst :-

The experimental was repeated as in (step –2) with exception of using (250 , 300 and 350 °C).

3- Study of the n-paraffins component of parent Kerosene and all Cracked Samples using Urea Adduction :

(8) gm of urea was dissolved in 20 ml of absolute methanol in pre dried conical flask to which (10) gm of kerosene was added . The mixture was shacked at (25°C) until the adduct was formed . The solvent was filtered and the adduct was washed by cold methanol and kept to dry at room temperature for 3 hr. Decomposition of the adduct was conducted by adding (25) ml of distilled water with slight heating until clear solution of the two layers were separated . The isolated n-paraffins were weighted and its percentage was accounted.

4- Determination of Unsaturated hydrocarbons :Bromine solution (0.1 N) was added from burette to a conical flask containing 10 gm of the kerosene and the addition continued till the color of bromine reserved . The volume was counted and the unsaturated compounds were determined.

5- Measurement of Refractive Index :

1-2 drops of kerosene was placed over the pellet of instrument (ATAGO , JAPAN) at 20 °C .

6-Measurment of Infrared Spectroscopy (IR):

1-2 drops of the samples was placed in a NaCl cell unit and the spectrum was measured (Bruker , Tenser 70 , Germany).

Discussion

Kerosene is considered one of low cost , low values and low uses in the 20th century and after . Kerosene contains-from chemical point of view from n-paraffins (C8-C15) , branched chains , bicyclic naphthenes (Dekalin derivatives) and aromatic hydrocarbons , Moreover , It may contains Olefinic hydrocarbons , Sulphur , Nitrogen and some Oxygen compounds .

In this study treatment of kerosene was conducted in the vapor phase of constant flow rate of (15-20) drops/minute (outside from reactor) over carbonate free bentonite previously placed in silica tube placed in tube furnace of temperature range from (100 - 1500) °C .

The treatment was conducted at 500 °C aiming to produce olefins and low molecules weight reactive species . The treatment showed increase of the olefinic hydrocarbons from (0.2% to 3.29%) . The paraffinic content of the parent kerosene was (17.81%) compared to (3.01%) in the treated kerosene . The results indicate that carbonate free bentonite which prepared, calcined and activated at 600 °C for 3 hr is highly effective in conducting cracking reactions , which appeared from the paraffinic values .

Employing feedstock prepared in the step (at 500 °C) to the prepared silver catalyst supported over calcium carbonate (using U.S.P. No with modifications in experimental section) at the same flow rate in gas phase and using (250,300 and 350) °C for treatment .

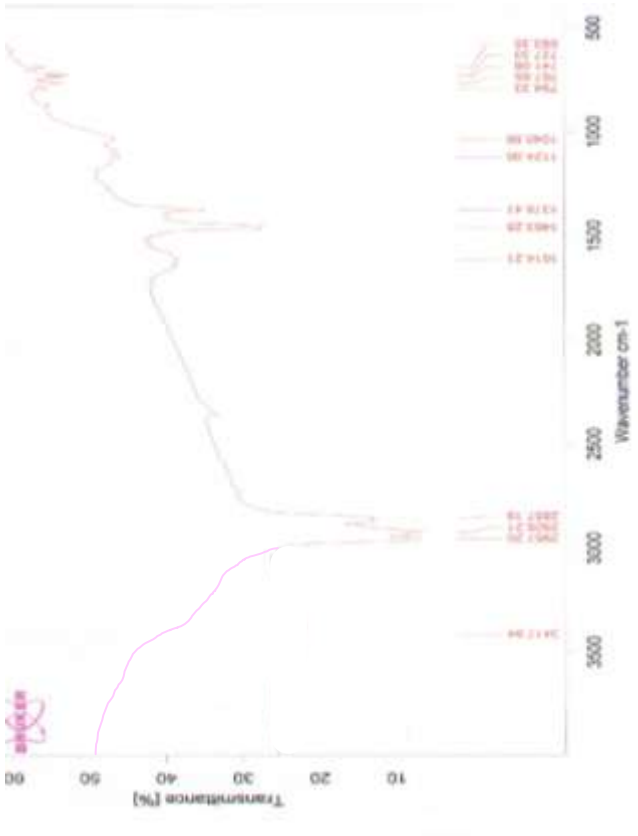
The results indicate that a decrease in the amount of paraffins in all temperatures used .

The infrared spectroscopy (IR) measurement of untreated and treated kerosene samples is showed the increase of aromatic system in treated sample especially at 250 °C that can be observed it approximately at a wave number (1400-1600) cm -1. The result of (IR) indicated the formation of oxygenated hydrocarbon that observed clearly at (3418) cm -1 and (3147) cm -1 in treated samples (500 °C by bentonite clay and 350 °C by silver catalyst) consecutively.

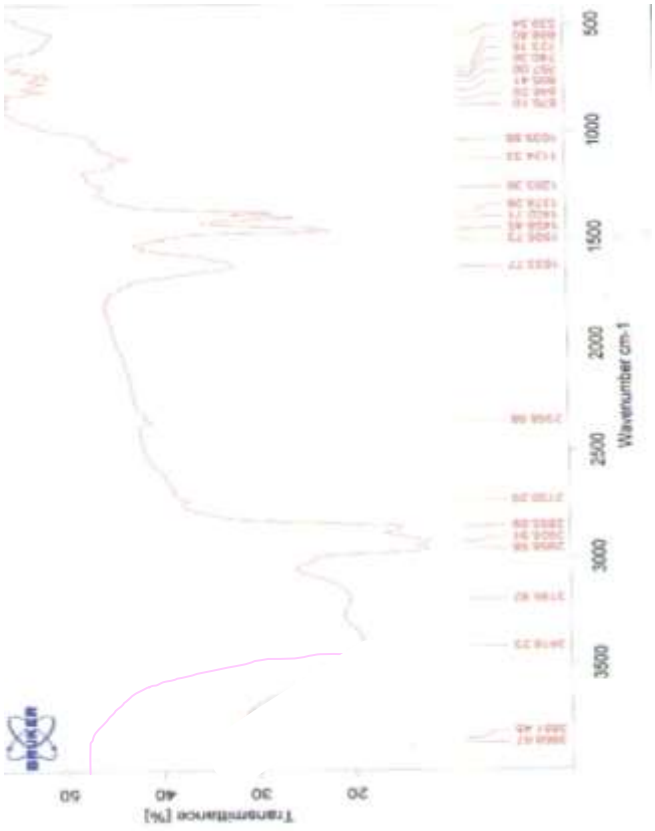
The silver catalyst as expected from silver oxide catalyst analog expected to oxidize the weak linkages at the feedstock used. But what happen is indicating that silver catalyst help recombination reactions and oxide of the double bond oxide. The results are given in table (1) and the figures (1,2,3,4and 5).

Table (1) Results of treated and untreated Kerosene samples measurements

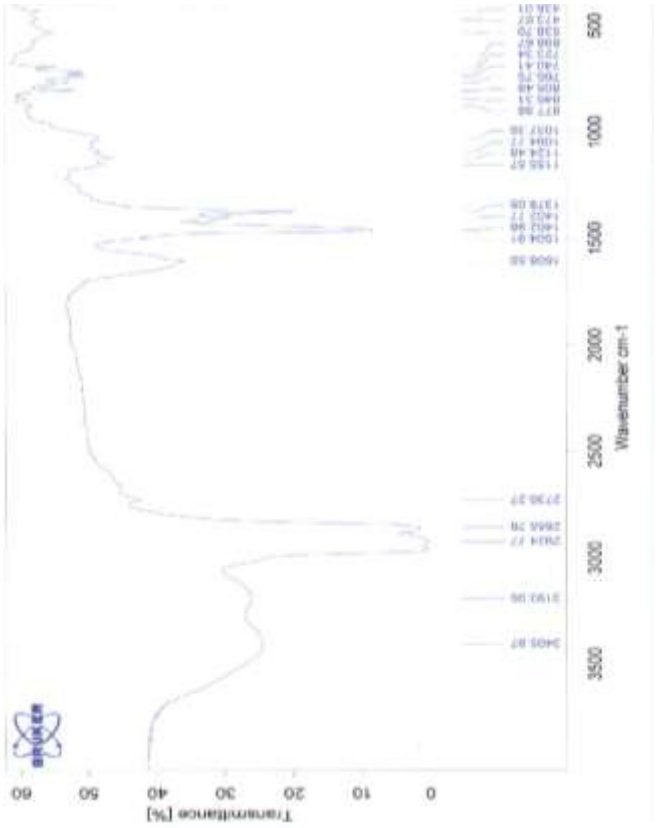
Catalyst type	Temperature	Paraffins %	Olefins %	Refractive Index
Untreated Kerosene	___	17.8	0.211	1.438557
Bentonite	500	3.01	3.295	1.437580
Silver	250	8.7	2.696	1.434567
Silver	300	8.1	2.297	1.43677
Silver	350	5.68	2.996	1.436575



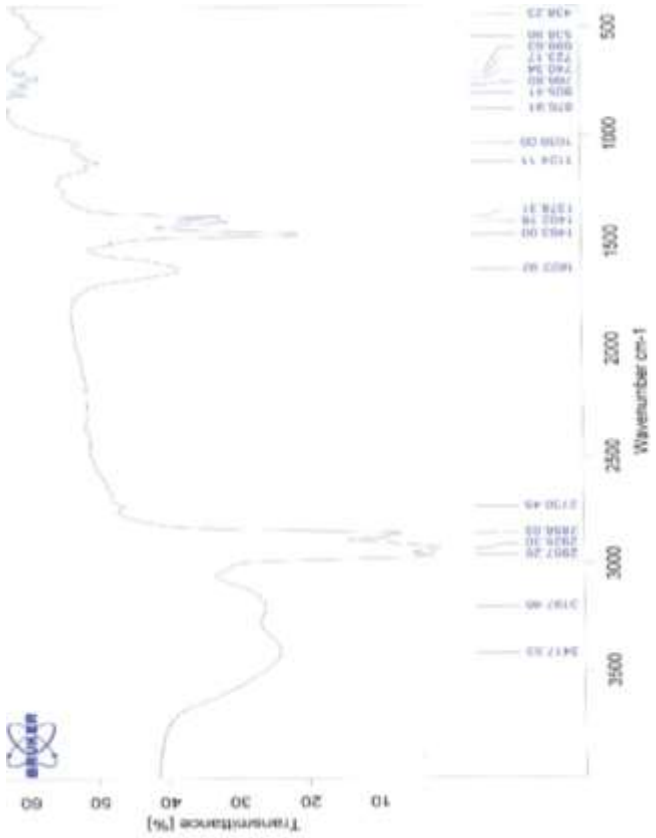
Figures (1) infrared spectroscopy (IR) of untreated kerosene sample



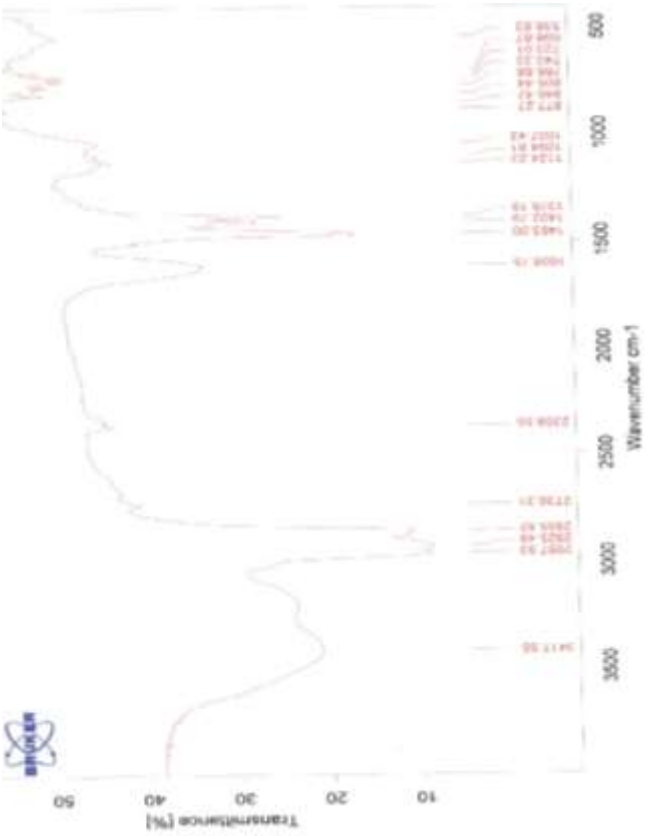
Figures (2) infrared spectroscopy (IR) of treated kerosene sample at 500° C by Bentonite Catalyst



Figures (3) infrared spectroscopy (IR) of treated kerosene sample at 250˚ C by sliver Catalyst



Figures (4) infrared spectroscopy (IR) of treated kerosene sample at 300˚ C by sliver Catalyst



Figures (5) infrared spectroscopy (IR) of treated kerosene sample at 350° C by sliver Catalyst

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الخلاصة

تم في هذه الدراسة تحضير حفازان ، الأول تم تحضيره من خام البنتونايت المزالة منه المواد الخاملة والحفاز الثاني تم تحضيره من الفضة المستندة على كاربونات الكالسيوم ، إذ مرر الكيروسين بالحالة البخارية على الحفاز الأول بدرجة حرارة (٥٠٠) م° ثم مرر ناتج المعاملة الأولى على الحفاز الثاني بدرجات حرارية (٢٥٠ و ٣٠٠ و ٣٥٠) م° وتم دراسة نماذج الكيروسين المعاملة بالحفازين للتعرف على التغيرات التركيبية لمحتوى الكيروسين، وقد اظهر الحفازان نقصان في نسبة المركبات البارافينية المستقيمة ، واظهر الحفازان زيادة في نسبة المحتوى الاوليفيني . وبصورة عامة فان الحفازين لهما القدرة على عمليات التكسير والازمرة واتضح من خلال طيف الأشعة تحت الحمراء أن هناك زيادة في النظام الاروماتي في بعض النماذج المعاملة.