Application of Dodeca Tungesta Phosphoric Acid Supported on Zirconia's To The Catalytically Treated Decalin Over Alumina Silicate Derived From Bentonite

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Abstract

This work involves preparation of a catalyst from bentonite ore. The ore was purified from carbonate and bicarbonate . The carbonate free bentonite (alumina silicate) was used to Catalytically treated decalin at 600 ° C. A second step was the treatment of the product from bentonite catalyst over more selective cracking catalyst (W/ZrO_2) at 300, 400 and 500 °C at constant flow rate for all treatment. The product from the treatment was analyzed chemically and spectroscopicaly using IR, refractive index and gas-liquid chromatography (UOP 744). The result indicated the conversion of decalin to alkyl cyclohexane and alkyl benzene.

Keywords : Decalin , catalyst , Tungesta, alumina silicate

Introduction

Catalytic dehydrogenation is an important means of manufacturing unsaturated hydrocarbons which are not available in sufficient quantities in any petroleum fractions. It is also used in the production of aromatic hydrocarbons from n-paraffins and naphthenes via catalytic dehydrocyclisation and dehydroaromatisation[1].

Supported catalysts represent the largest group of catalysts (Heterogeneous) which are of major economic importantance, especially in petroleum refining and petrochemical industries. Supported catalysts are prepared by adding small amount of the active materials, especially metal oxides …. etc. to the surface of the porous solid support. The most important solid supports are alumina oxides, silica gel, MgO, TiO_2, ZrO_2, alumina silicates, zeolite , activated carbon and ceramics[2]. The supported catalysts have a special forms such as; pellets, rings, extradites, and granules[3]

Zirconia supported catalyst is very stable during catalytic treatment processes. It has a surface endowed with weakly acidic and basic sites. The catalyst is able to maintain a high specific surface area upto about look, if transition metals ions are present. Supported oxide catalysts are generally prepared by copercipitation or impregnation processes[4]. At the Many methods using various materials were employed in the production of catalysts and some of them are given below;

Houzvicka et al., prepared catalyst from; alumina, tungsten, zirconium and palladium[5]. for the isomerization of C_4 paraffins, aromatics and cycloparaffins. Johnson et al ., used chromium supported over aluminum phosphate to isomerize olefinic hydrocarbons[6]. Hayes et al ., used platinum group metals as a support for the dehydrogenation and hydrogenation of hydrocarbons[7]. Mamdove et al ., prepared a dual metal catalyst, from alkali or alkali earth metal and bismuth or gallium and tin for the oxidative dehydrogenation of paraffins[8]. Sabry, prepared a catalyst from bentonite ($Al_2O_3.SiO_2.H_2O$) and used it for the catalytic treatment of naphtha. The hydrocarbon composition of the treated naphtha samples were studied by determining the amount of n-paraffins, aromatics and olefinics compounds[9]. Ramadhan et al., prepared two types of catalysts, the first was used to treat kerosene at (300-500°C). The second catalyst was prepared by supporting silver oxide over calcium carbonate. Analysis of the hydrocarbon chemical composition indicated a reduction in the n-paraffinic content which may be due to cracking reactions. The amount of olefinic hydrocarbon are increased to in the two treatment[10].

Experimental

1- Preparation of Catalysts:

A- Preparation of treated Bentonite Catalyst :-

100 gm of bentonite ore was refluxed with 300 ml of 10% HCl for 3 hrs. The free bentonite was converted to granules by mixing it with a little amount of water. The bentonite slurry was converted to pellet and kept to dry on air. Finally the grains were thermally treated at 120 °C for 3 hrs. and to accept at 300°C for 2 hrs. latterly at 700°C for 3hr in order to remove all kinds of water present in the structure and to enable the catalyst hard to be and thermal stable.

B. Preparation of tungsten catalyst supported on Zirconia[11] :-

300 ml (water and hydrogen peroxide 35%) from tungstic acid compound and add every 10 g zirconia in 150 ml of tungstic acid solution . The mixture is agitated at room temperature for 15 hr and filtered . The catalyst slurry was converted to small pellets and kept to dry on air. Finally the grains thermally treated at 100-120 ºC for 4 hrs, then at 600º C for 3 hrs.

2- Catalytic Cracking:

A- Catalytic cracking by Granular Bentonite :-

The placed 30 gm catalyst was placed in silica tube previously placed in tube furnace of total carbon analyzer (100–1600°C). Decalin vapor was passed over the catalyst at a flow rate of 0.5 ml per minute at 600°C . The cracked materials were collected in an ice cooled traps water. The gases were left to flow outside. The resultant materials were kept in dry closed container to be used in the second step.

B. Calytic Cracking by tungsten Catalyst:-

The experiment was repeated as in (step –2A) except using (300, 400 and 500°C).

3- Study of the n-paraffins parent Decalin 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 10gm of decalin was added. The mixture was shacked at 25-30°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 hrs. Decomposition of the adduct was conducted by adding 25 ml of distilled water with slight heating until a clear solution of the two layers was separated. The isolated n-paraffins were weighted and their percentage were accounted.

4- Determination of Unsaturated Hydrocarbons:

Bromine solution (0.1 N) was added from burette to a conical flask containing 10gm of the decalin 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 decalin were placed over the pellet of instrument (ATAGO, JAPAN) at 20° C.

6-Measurment of Infrared Spectroscopy (IR):

1-2 drops of the samples were placed over NaCl cell disc and the spectrum was recorded (Bruker , Tenser 70, Ger.

Results and Discussion

The IR spectra of the decalin over purified bentonite (hydrated alumina silicate) indicate increasing volatility of which fraction which may be due a certain catalytic cracking and/or dehydrogenation reaction. On the other hand, treatments of product from alumina silicate at 600ºC over a selective cracking catalyst (WO_3/ZrO_2) enhance cracking reactions which could not be evaluated by the IR spectra. This access to study the refractive index of treated fraction at 300, 400 and 500 ºC, which may help to follow the reaction pathway. Analysis of the aromatic hydrocarbon formed, unsaturated and paraffine hydrocarbons. The results are given in Table 1.

Table (1): Results of treated and untreated decalin samples measurements

Sample	**Paraffins %**	**Aromatics %**	**unsaturated %**	**Naphthenes % + gases**	**Refractive Index**
decalin	0.00	0.00	0.00	100.00	1.472727
decalin 600 ºC (bentonite)	0.00	5.04	5.99	88.97	1.478750
decalin 300 ºC (Zrw)	0.00	10.174	5.193	84.63	1.476743
decalin 400 ºC (Zrw)	0.00	12.89	5.692	81.42	1.477500
Decalin 500 ºC (Zrw)	0.00	18.773	7.490	73.74	1.479754

However study of the chemical analysis of treated decalin did not give the identity of the reactions processed. Analysis of the product using gas chromatograph and employing UOP (744) with some modification to suit our case.

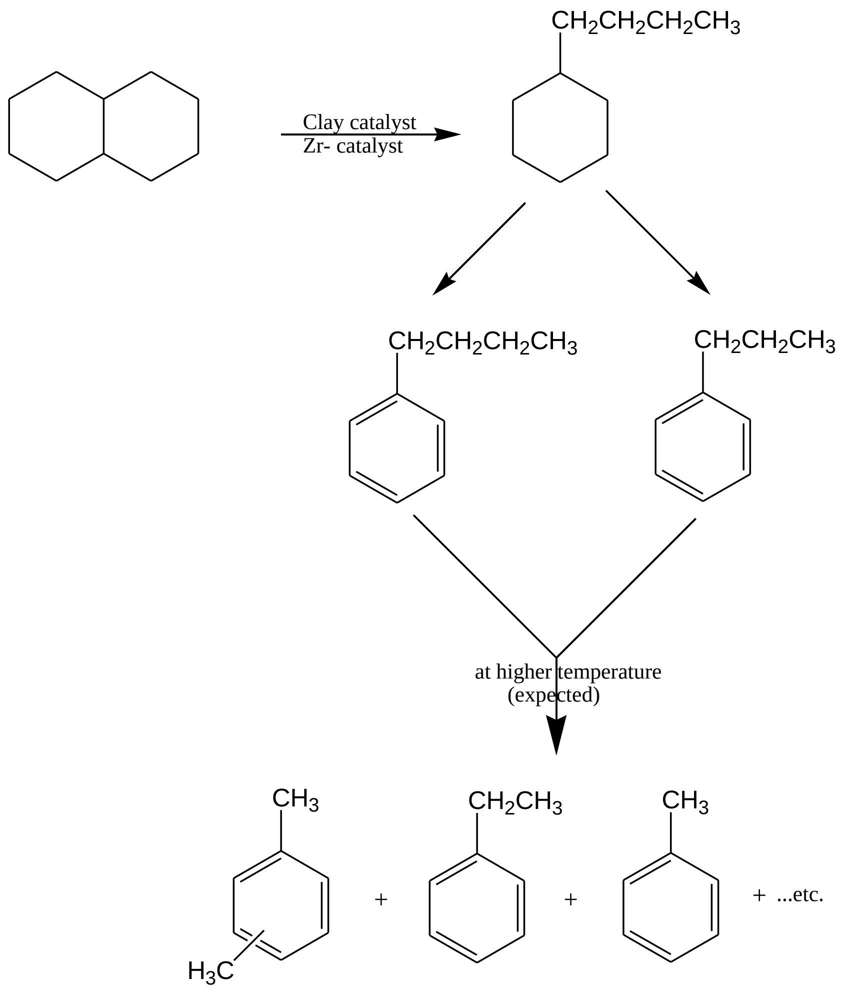
The results of the GC are given in Table 2.

Table (2): Results of treated decalin samples measurements by GC

Samples	Butyl Cyclohexane	Cis decalin	Trans decalin	Butyl Benzene	Propyl Benzene	Gases lost
decalin 600 ºC (bentonite)	15.18	24.78	45.41	2.05	2.05	1.53
decalin 300 ºC (Zrw)	8.18	30.67	47.94	4.92	6.08	2.21
decalin 400 ºC (Zrw)	6.88	34.35	45.36	4.55	6.90	1.96
Decalin 500 ºC (Zrw)	14.47	24.27	42.99	8.43	7.62	2.22

The results given in table indicated that purified clay have a good catalytic properties and the second catalyst (Zr catalyst) showed cracking ability, dehydrogenation and aromatization and the reactions are mainly dependant on the temperature and catalyst.

The suggested reaction pathway is as follow:



Comparing the GC of the untreated decalin with the treated once at 600°C over the natural purified clay and that of the prepared catalyst of 300, 400,500°C and depending on the retention time and the area of each peak compared to that of the untreated sample.

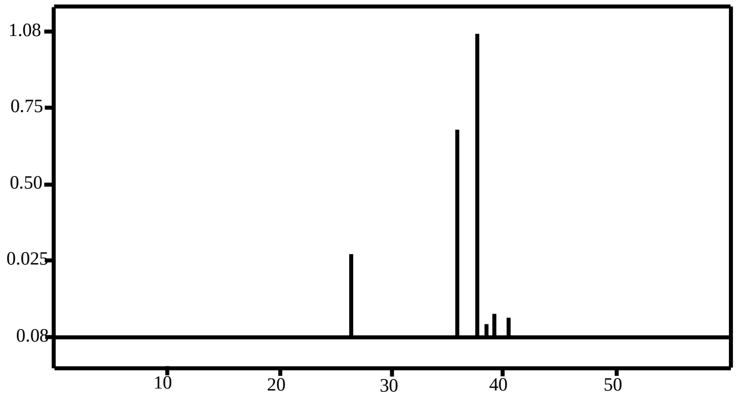


Figure (1): GC of untreated decalin sample

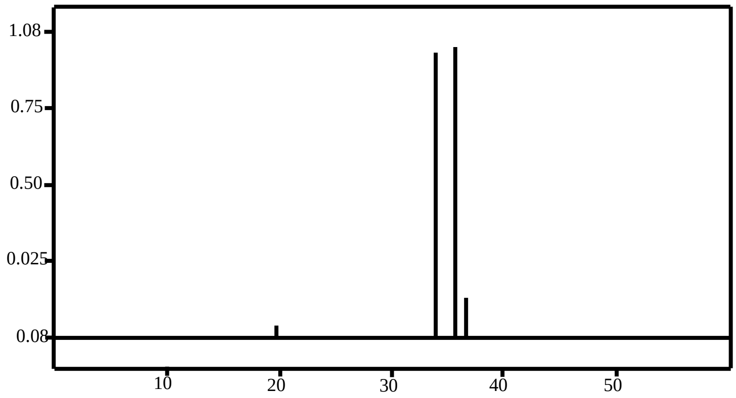


Figure (2): GC of treated decalin sample at 600° C by Bentonite Catalyst

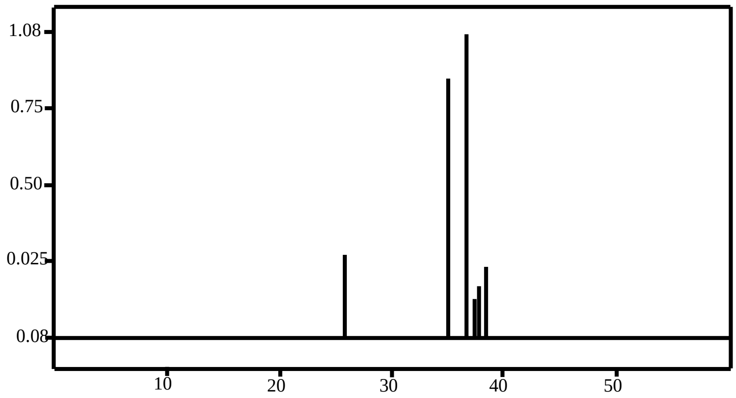


Figure (3): GC of treated decalin sample at 300° C by WO_3/ZrO_2 Catalyst

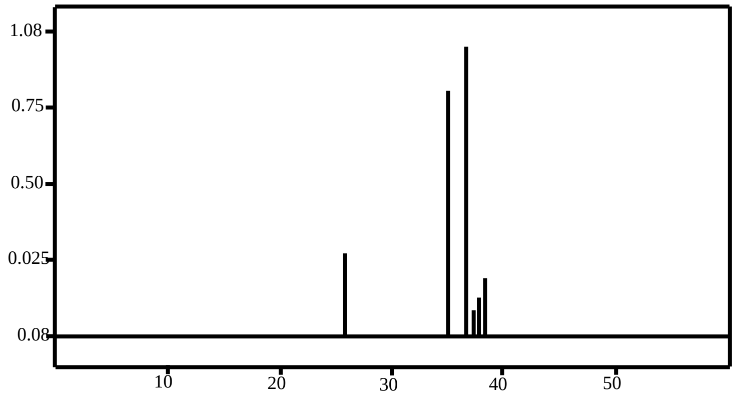


Figure (4): GC of treated decalin sample at 400° C by WO_3/ZrO_2 Catalyst

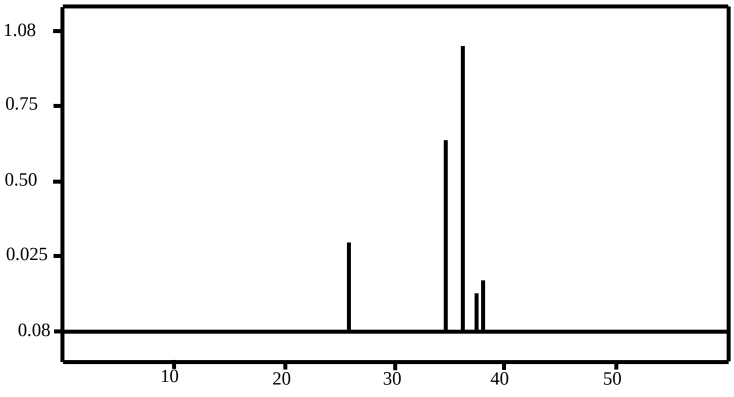
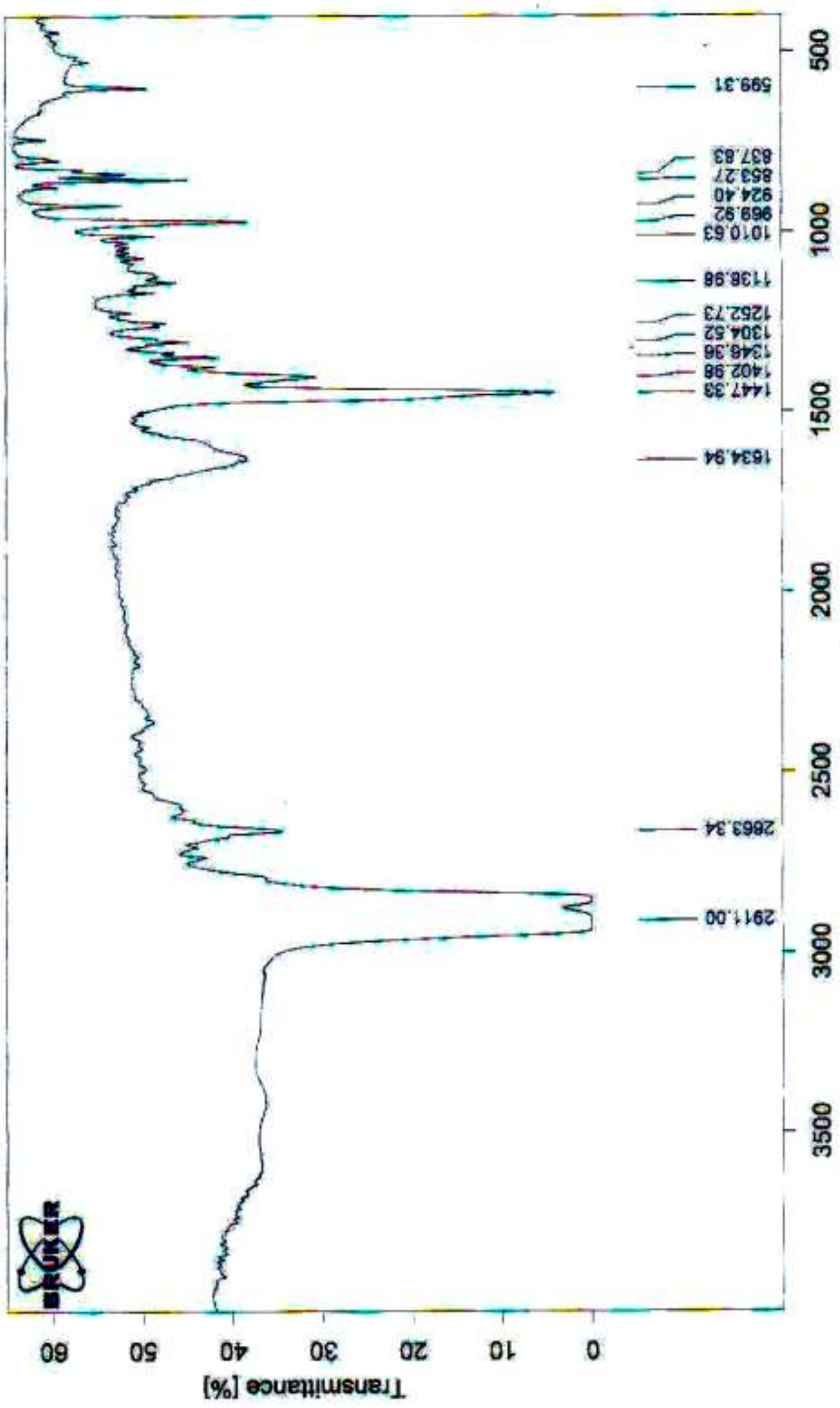
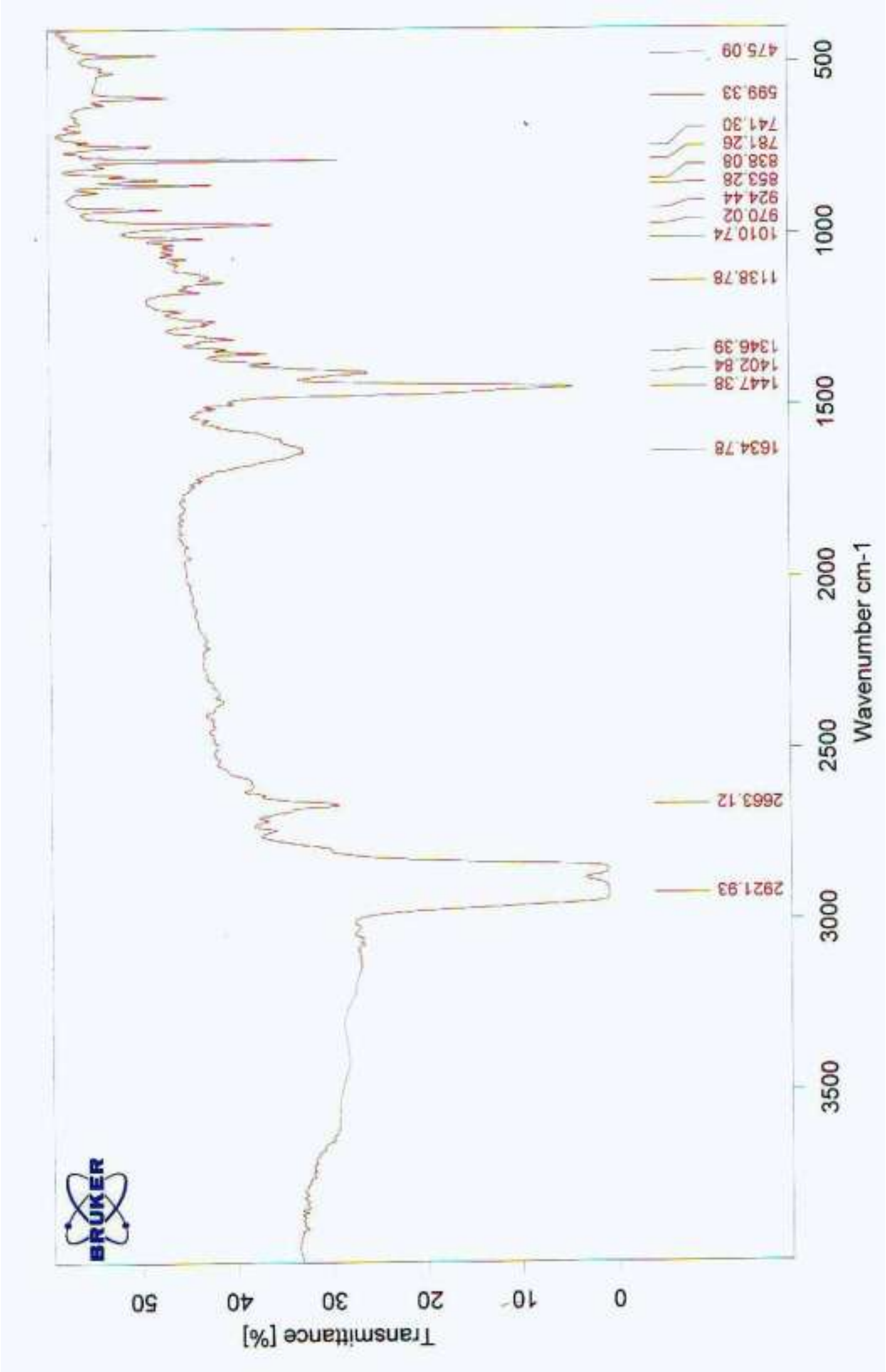


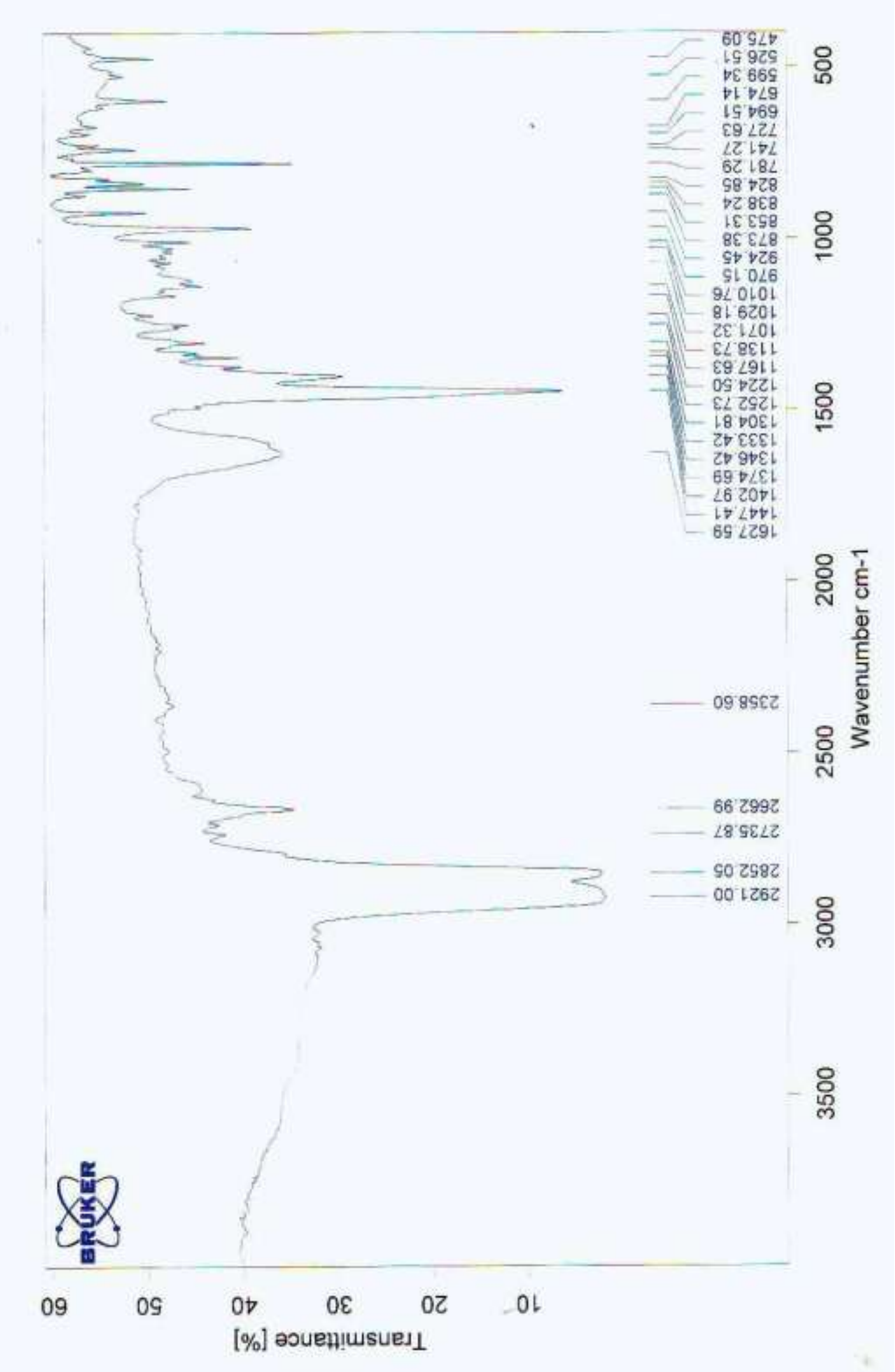
Figure (5): GC of treated decalin sample at 500° C by WO_3/ZrO_2 Catalyst



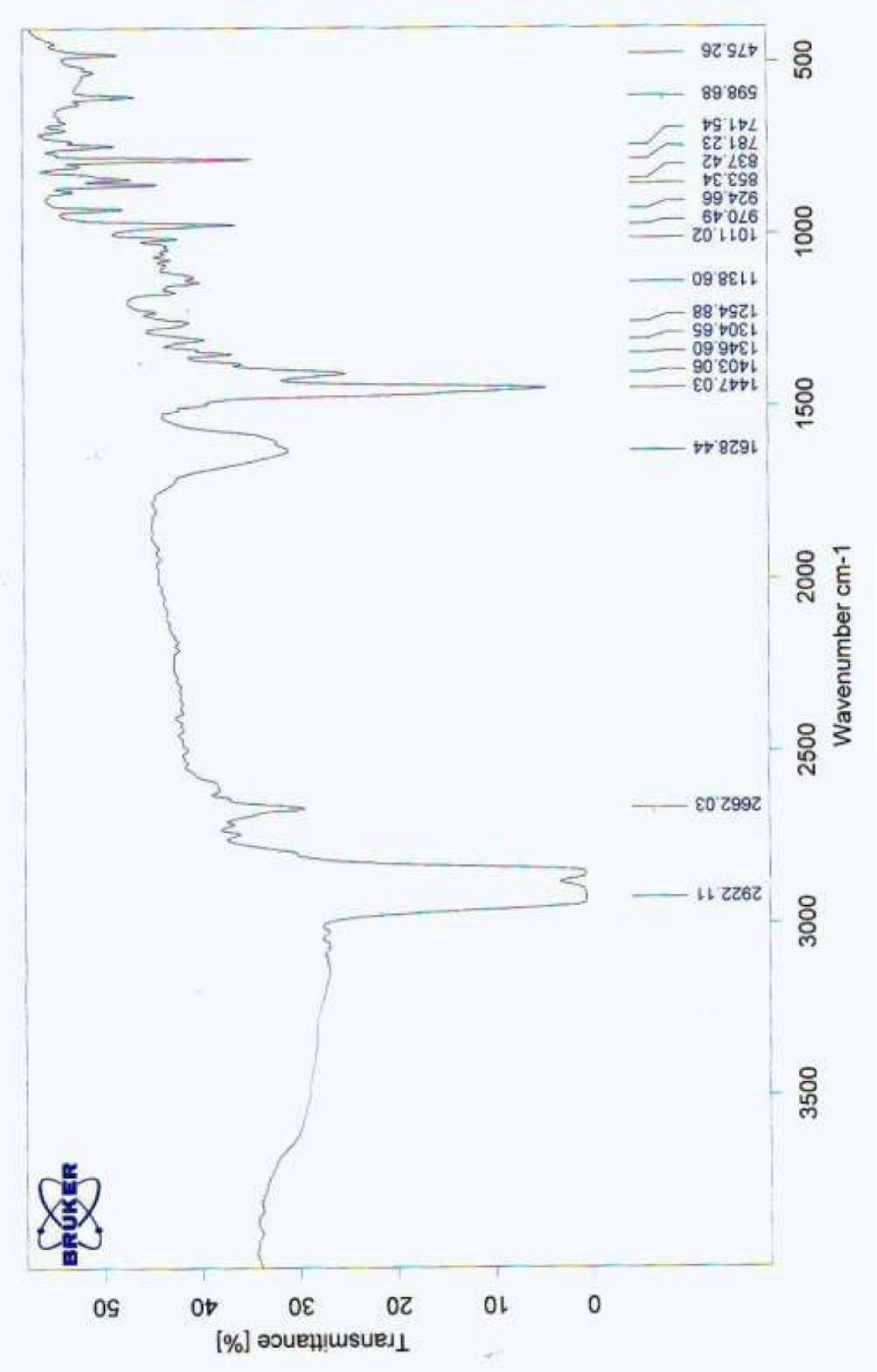
Figures (6) infrared spectroscopy (IR) of untreated decalin sample



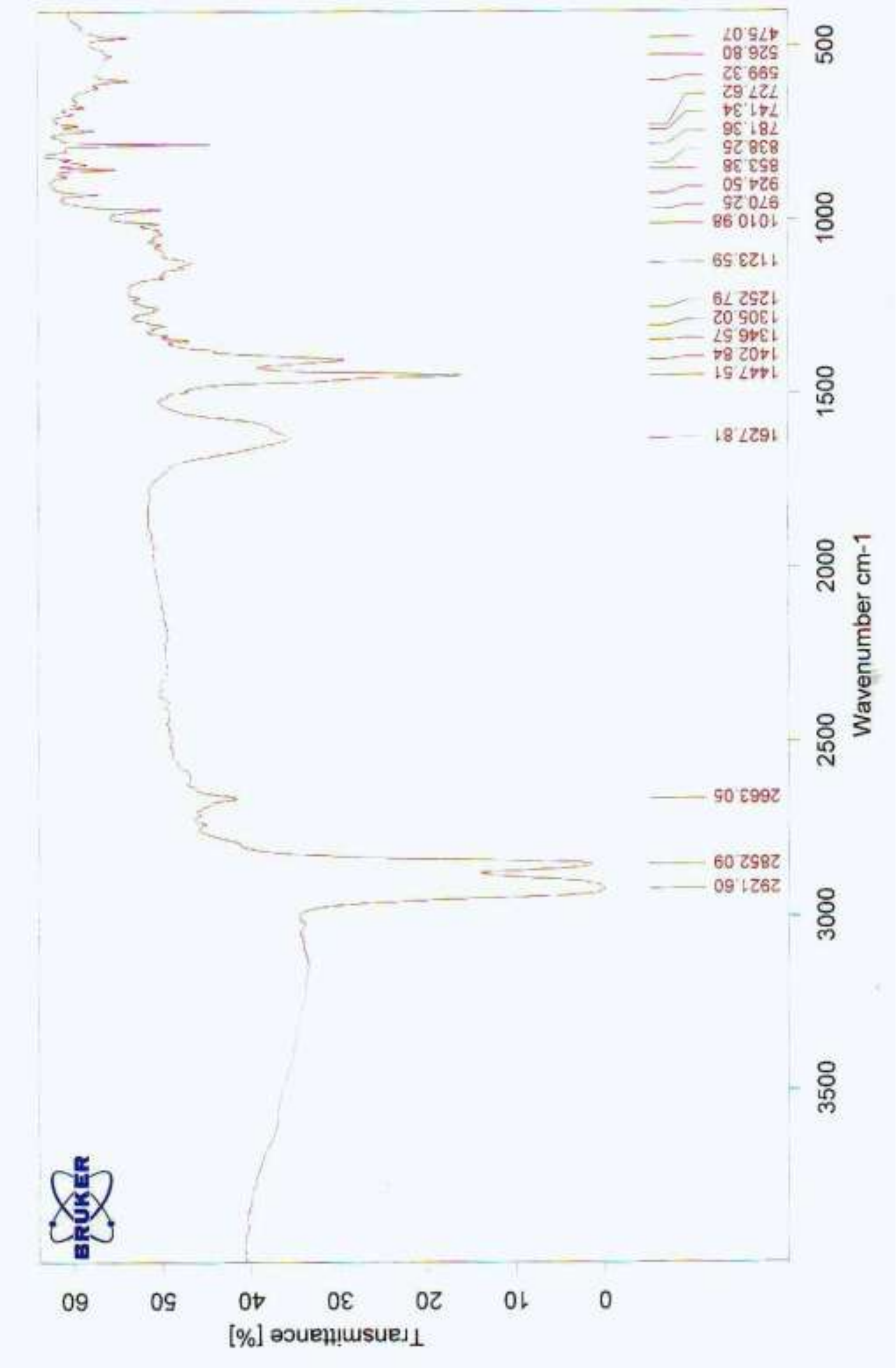
Figures (7) infrared spectroscopy (IR) of treated decalin sample at 600° C by Bentonite Catalyst



Figures (8) infrared spectroscopy (IR) of treated decalin sample at 300° C by WO_3/ZrO_2 Catalyst



Figures (9) infrared spectroscopy (IR) of treated decalin sample at 400° C by WO_3/ZrO_2 Catalyst



Figures (10) infrared spectroscopy (IR) of treated decalin sample at 500° C by WO_3/ZrO_2 Catalyst

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تطبيق للدوديكا تنكستا حامض الفسفوريك المسند على الزركونا للديكالين المعامل بالعوامل المساعدة على سليكات الالومينا والمشتقة من البنتونايت

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الملخص

تضمن هذا البحث تحضير حفاز من خام البنتونايت الخالي من الكاربونات والبيكاربونات مرر عليه الدكالين بالحالة البخارية بدرجة حرارة ٦٠٠ °م ، ثم مرر ناتج الخطوة الاولى على حفاز اوكسيد التنكستن المستند على الزركونيوم بدرجات حرارية (٣٠٠ و ٤٠٠ و٥٠٠) °م.تم دراسة نماذج الدكالين بالحفازين بوساطة الاشعة تحت الحمراء ومعامل الانكسار وكروماتوغرافيا الغاز–السائل (UOP-744) فضلاً عن التحليلات المختبرية للتعرف على التغيرات التركيبية للدكالين وتشير النتائج الى تحول الدكالين الى الكيل سايكلوهكسان والكيل البنزين.