Preparation of Catalyst and its Application in Thermal and Photo Vapor Phase ammoxidation of Toluene.

Ghanim Abdulnabi Kadhim , Mousa Umran Kadhum

Department of Chemistry, Faculty of Education for Girls , University of Kufa, Najaf, Iraq.

mk220@inbox.ru

الخلاصة :-

تم تحضير عامل مساعد (MoO_3-CdO) ودراسة كفاءته في عملية الأمكسدة الحرارية بالطور الغازي بنسب وزنية مختلفة(0:3 3:0,3:1,3:3,1:3) وتم تحميلها بطريقة التحميل (Loading Method)على اطيان الكاوؤلين بواسطة جهاز التبخير المفرغ (vacuum evaporation technique) بدرجة حرارة (343) كلفن وتم تشخيص العامل المساعد المحضر من خلال مطيافية FTIR . درست بعض الخواص الفيزيائية للعامل المساعد مثل المسامية (Porosity) , حجم المسام (Pore Size), الكثافة (Density) , والمساحة السطحية (Surface Area),التوصيلية الكهربائية (Electrical Conductivity). كذلك درست فعالية العامل المساعد المحضر لاستخدامه بعملية الأمكسدة الحرارية للتلوين بدرجة حرارة مابين 280 و 300 درجة مئوية وتم دراسة النواتج المتكونة بتقنية كروموتوغرافيا الغاز .

Abstract

Catalyst was prepared from composed (MoO_3-CdO)by loading method in different ratios(3:0,1:3,3:3,3:1 and0:3) and supported on granulated kaolin clay with different sizes by the thermal vacuum evaporation technique was at temperature(343)k .Characteristic catalyst was prepared by. Fourire transformsin spectroscopy (FT-IR) and studied some physical properties for catalyst such as particles size, Surface area, porosity , pores size, electrical conductivity and density . Also studied the activity of prepared catalyst by thermal ammoxidation for Toluene(573-553)K The products were studied by gas chromatography technique .

keyword: *pores size, Ammoxidation, Catalyst*

1-Introduction:-

The catalyst:-

A Catalyst is a chemical that increases the speed of a specific chemical reaction by directing the chemical reaction to the thermodynamic balance state, where it is involved in the reaction without any significant change in its chemical structure(1). It can also be defined as the substance that changes the kinetic properties of the system without share in the chemical equation (2).

The catalyst does not remain as it is during the reaction but gets a structural or vacuum change at the intermediate stage of the interaction. At the end of the reaction, however, the total amount of the catalyst remains constant (1). The catalysts are categorized as positive catalysts and negative catalysts. The first one increases the speed of the reaction while the other reduces the speed of the reaction if it used in reactions that include the formation or disappearance of free radicals (3). The catalyst was first used in 1835 as the catalyst reduces the activation energy as show in the Figure(1-1).

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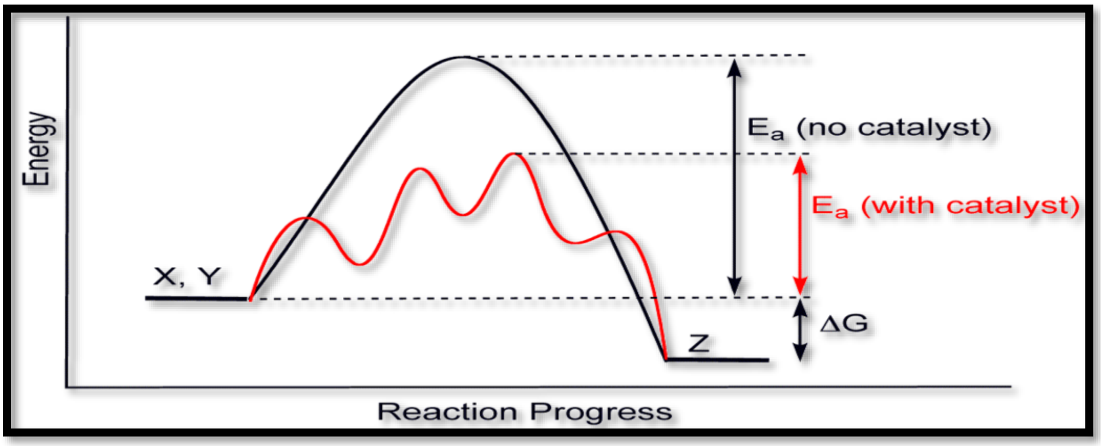

Figure (1-1): The role of the catalyst

The Catalysts are used in the chemical industry, where more than 90% of the products have been produced depends on the use of catalysts and is not limited to the chemical industry as it plays a central role during the processing of raw materials in refineries, and during the production of energy such as fuel cells and batteries as well as in the protection of the environment [4]. They are used in the manufacture of ammonia, methanol, nitric incubation, as well as in petrochemicals and automobiles, in refining and in removing hydrocarbons in consumer emissions and minimizing waste to prevent environmental pollution[5,6] . In recent years, catalyst have developed rapidly through many new applications. Assisting factors are key to the success and development of many new processes in various industries. They reduce the amount of waste and emissions in cars and fuel stations and assist factors in many interactions The most important reactions are oxidation, ammoxidation, and estrae [8,7].

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2-Experimental

2-1 Instrumentals

All chemicals were used supplied by Aldrich and Merch with high purity 98%.

2-2 Apparatus

Gas Chromatography- Dani -2013,. Fourier transforms infrared spectrophotometer -8400S Shemadzu..Kethley 2400 Source meter. Muffle Furnace Size –Two Gallenkamp. Oven Bs Size Two England Gallenkamp. Reactor used in ammoxidation reaction was designing research in my laboratory. Rotary evaporator UAOR RES2A. Japan**.**

2-3 Preparation of catalysts

The catalyst was prepared by mixing MoO_3 and CdO with different ratios(3:0,3:0,3:3,1:3 and0:3) and supported on granulated kaolin clay . The thermal vacuum evaporation technique was used at (343)K to removal the solvent and the as prepared catalysts were calcinated at 823K into furnace for 3 hours. The catalyst was determined by FTIR spectrum. The results were tabulated in Table(3-2) and plotted in Figure(3-5),(3-6) and(3-7). Also porosity pores size, particle size; density and electrical conductivity were studied. The results were tabulated in Table (3-1) and seen in Figure(3-1),(3-2),(3-3) and(3-4). The activity of prepared catalyst was studied by thermal ammoxidation of Toluene at (573-553)k. The products were studied by gas chromatography technique.

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2-4 Methods

Thermal ammoxidation of Toluene was carried out over heating glass spheres at (573 -553) K in Pyrex reactor to converted to vapor phase. The substance in vapor phase was flowed over catalyst (MoO_3-CdO)/ kaolin clay) 3cm high. The air pressure and speed supplied oxygen were 12 psi and 9ml/sec respectively these conditions used in all experiments. the concentration of product was determining by gas chromatography also the results were tabulated in Table(3-3) ,(3-4) and plotted in Figure(3-8),(3-9) ,(3-10) ,(3-11) ,(3-12). Figure (2-1) shows the reactor system**.**

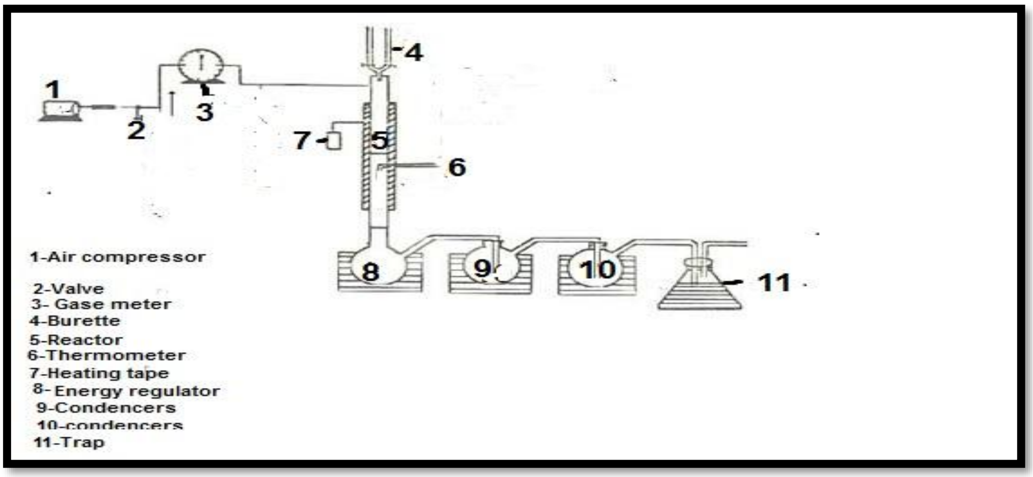


Figure (2-1): The designed system had been applied to thermal catalytic vapor phase Ammoxidation.

3- Results and Discussion

3-1- Characterization of catalyst

Physical properties: The Physical properties were tabulated in Table (3-1) and plotted in Figure (3-1), (3-2), (3-3)and (3 -4).

Table(3- 1) : physical properties of Catalys

Weight ratio ofMoO$_3$:CdO (g)	*Percentage %*	*Porosity X100*	*Pore size Cm^3/gm*	*Density Gm/c*	*electrical conductivity*
3:0	%100	46.8	0.237	3.88	0.508
3:1	%75	63.1	0.261	3.18	0.631
3:3	%50	67.3	0.540	2.61	1.463
3:1	%25	56	0.322	3.11	0.995
0:3	%0	48.5	0.298	3.35	0861

3-1-1-Porosity:- The porosity is the one significant physical properties of catalyst was determined by liquid impregnation method [9]. and tabulated in Table 1 and plotted in Figure (3-1).

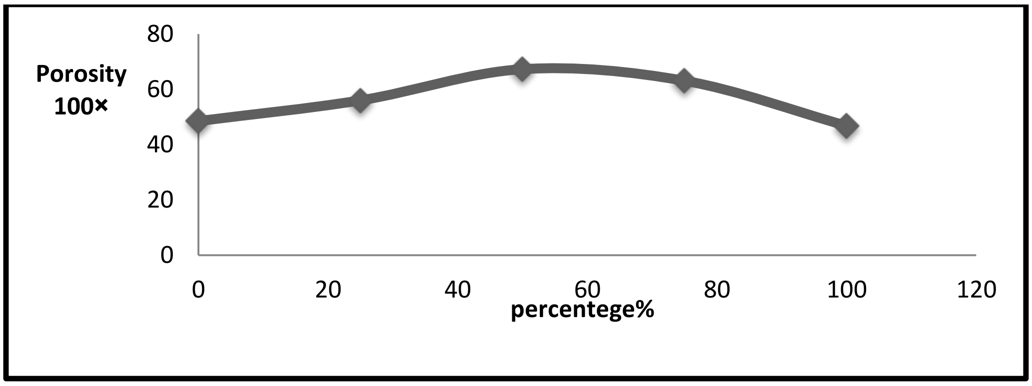
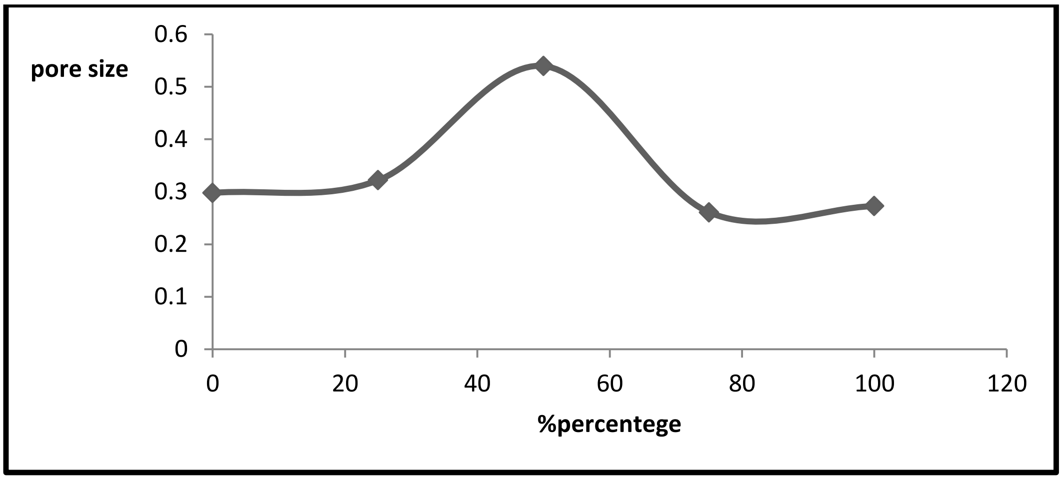


Figure (3-1): Effect of weight percentage on porosity for MoO_3-CdO catalyst

Figure (3-1) shows that the porosity of catalyst (MoO_3-CdO)/) kaolin clay in different percentage (0, 25%, 50%, 75% and 100%) was increase until (67.3) in ratio (50%) and decrease in the other percentages. The above Figure shows that the maximum porosity of the mixed catalyst occurs at 50%, by mixing equal weight of both metal oxides (3.0 gram of each one). This might be clarified that the addition successive weight of oxides was increased removing water of crystallization,carbon dioxide and another volatile materials that leave many porous in material which can absorb much fluid . Also the different between crystal system phases for oxides cause random aggregation for grain oxides therefore the porous formed [10].

3-1-2-Pore size: The pore sizes of catalyst was limited by liquid impregnation method and tabulated in Table 1 and plotted in Figure(3 - 2).



Figure(.3-2): Effect of weight percentage on pore size for MoO_3-CdO catalyst

Figure (3-2) shows that the pores size of catalyst (MoO_3-CdO)/ kaolin clay in different percentages. (0, 25%, 50%, 75% and 100%) were increase until(0.540)in ratio (50%) and decrease in the other percentages. The above Figure shows that the maximum pores sizes of mixed catalyst (3.0 gram of each one), which may be due to fusion between different particles are fewest that cause access in pores size between different particles, which increasing the ability of the analyst molecule to penetrate inside the particle and interact with its inner surface and may get a high activity of the catalysts[11] .

3-1-3-Density: The density of catalyst was determined by liquid impregnation method and tabulated in Table 1 and plotted in Figure(3-3) . .

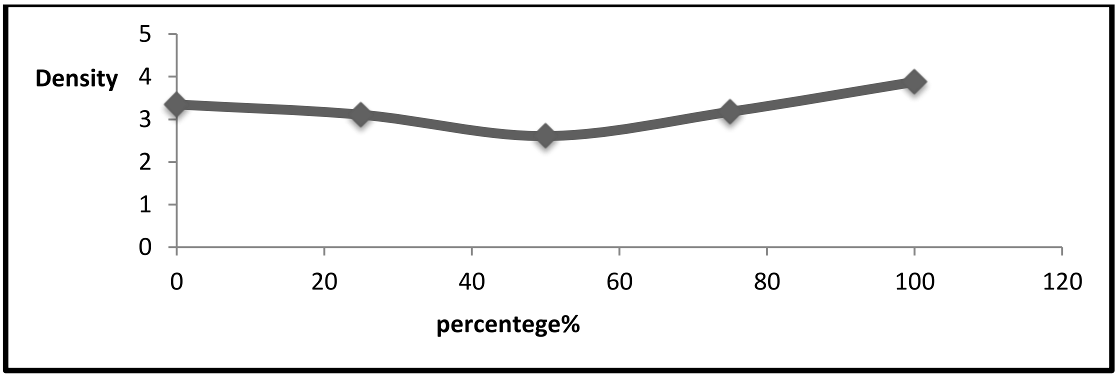


Figure (3-3): Effect of weight percentage on density for MoO_3-CdO catalyst.

Figure (3-3) shows that the density of catalyst(MoO_3-CdO)/ kaolin clay in different percentages (0, 25%,50%,75% and 100%) were decrease until(2.6 1)in ratio(50) and increase in the other percentages. The above Figure shows that the minimum density of the mixed catalyst occur by mixing equal weights of both catalyst (3.0 gram of each one), which may be due to fusion between different grains are fewest that cause excess in porosity and pore size, therefore; increase the volume of the sample for a constant weight which leads to decrease of density [12].

Electrical Conductivity: The electrical conductivity of catalyst was determined by conductivity measure apparatus and tabulated in Table 1 and plotted in Figure(3-4).

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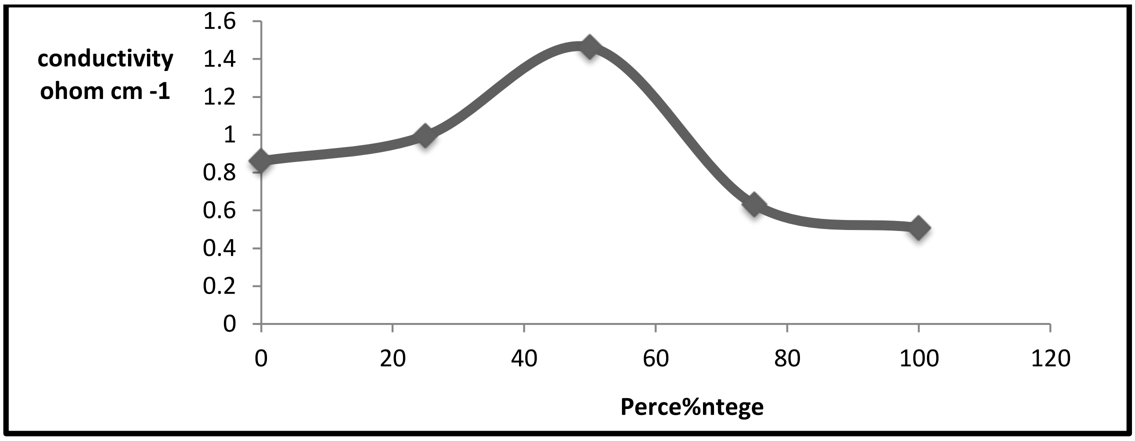

Figure (3-4): Effect of weight percentage of metal oxides (MoO_3-CdO) on the electrical conductivity.

Figure (3-4) shows that the electrical conductivity of catalyst in different percentages (0, 25%, 50%, 75% and 100%) were increase until (1.46) in ratio (50) and decrease in the other percentages. The above Figure shows that the maximum electrical conductivity of the mixed catalyst occur by mixing equal weight of both metal oxides (3.0 gram of each one).This might be explain that the degree of doping in solid state semiconductors make a large difference in conductivity , more doping leads to higher conductivity [13].

3-2 Spectroscopic studies

FTIR spectroscopy of pureMoO3, pure CdO and the prepared catalysts MoO3-CdO in Table(3-2) .

Table(3-2): Peak of the pure catalysts and the prepared catalysts

Compound	λ (cm)$^{-1}$					
MoO_3	3439.27	1637.56	1039.63	671.23	486.06	
CdO	3437.12	3009.23	1415.89	1345.34	1021.42	669.86
MoO_3-Cd	3442.94	2920.23	1681.93	1554.63	1427.32	993.34

The above Table shows new peak. With high intensity which return to the new bonded between crystal lattice of both oxide as in Figure(3-5),(3-6) and (3-7). .

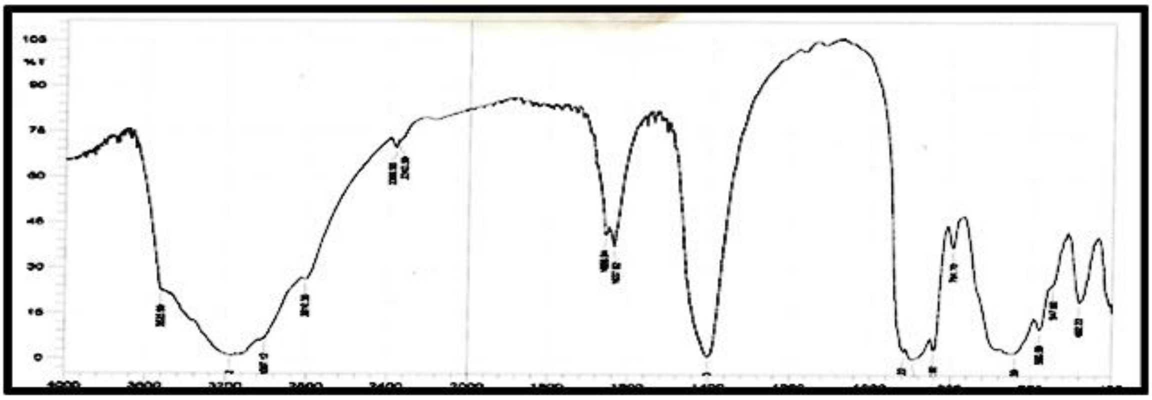

Figure (3-5): FTIR with high intensity to pur MoO_3

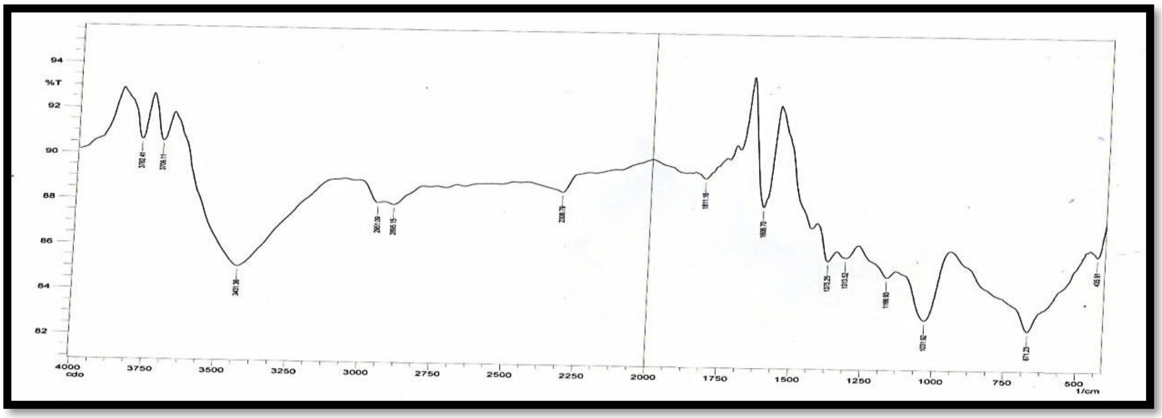

Figure (3-6): FTIR with high intensity of pur CdO.

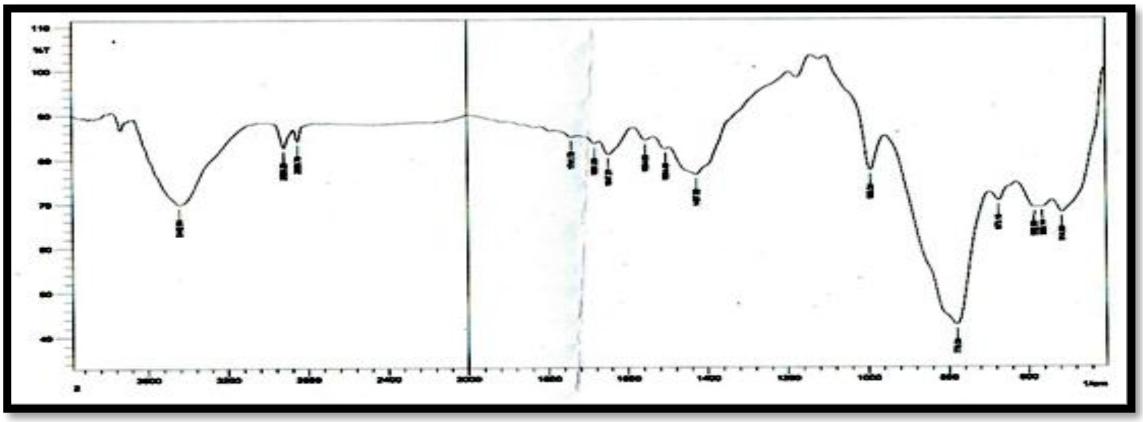

Figure (3-7): FTIR with high intensity of prepared catalyst MoO_3-CdO which return to the new bonded between crystal lattice of both oxides .

3-3 Analysis of the results by Gas chromatography (GC)

The effect of the heating time in the Toluene ammoxidation was calculated by using the MoO_3-CdO in the optimum percentage (50%). The pressure and velocity of the airflow inside the reactor was 12pascal, 9cm3 / sec and the size of the catalyst ranged between (4-3) mm and the use of (20gm) of the catalyst respectively for (6,4,2) hours. the concentration of product was determining by gas chromatography Using Table(3- 3) and the followin equationg.

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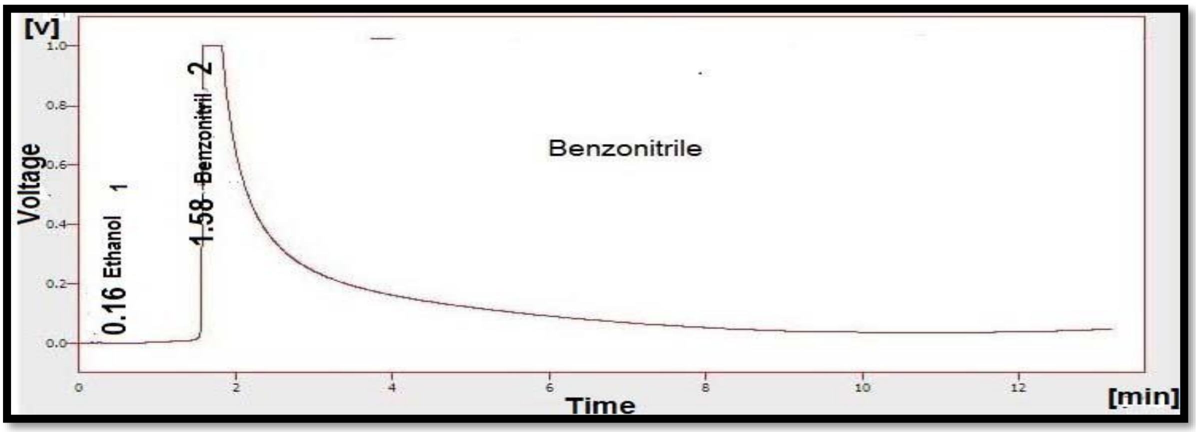
Conc.sample=Conc.of Standard x Area of Sample/Area of Standard [14].

Also the results were tabulated in Table 4 and plotted in Figure(3-8),(3-9) ,(3-10) ,(3-11) ,(3-12),(3-13)).

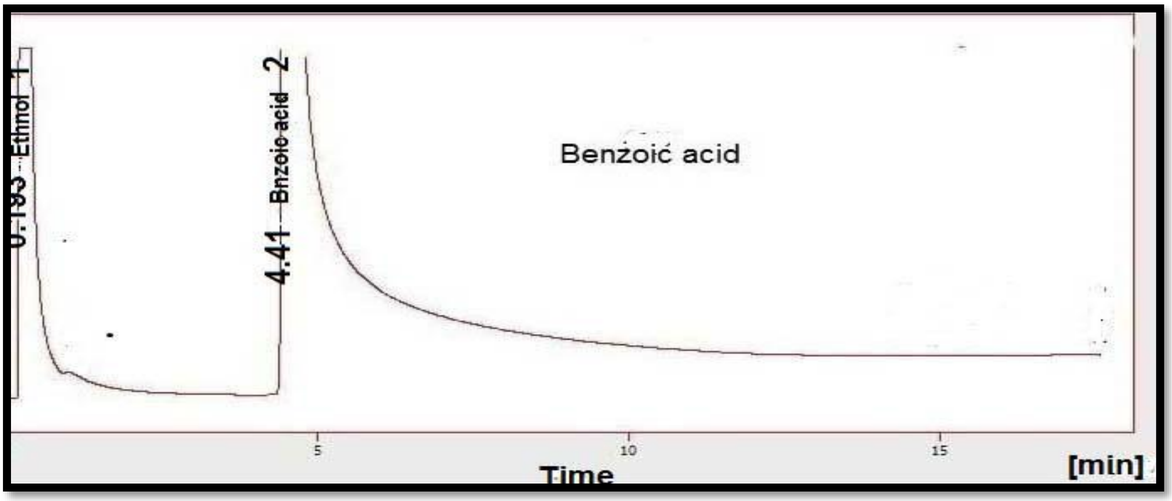
Table(3-3):The Areas and concretions of standard Benzonitrile and Benzoic Acid.

standard substance	*Conc. Mol/L*	*Area*
Benzonitrile	4 M	*77057.475*
Benzoic Acid	2M	*108847.150*



	Reten. Tim [min]	***Area [mv.S]***	***Height [mv]***	***Compund Name***
1	**0.163**	**22536.978**	**3.777**	***Benzonitril***
2	**1.577**	**77057.475**	**994.407**	
	Total	**77062.075**	**998.184**	

Figure.(3-8): chromatogram of standard Benzonitrile



	Reten .Tim [min]	*Area [mv.S]*	*Height [mv]*	*Compund Name*
1	**0.193**	**19947.18**	**995.480**	***Benzoic Acid***
2	**4.410**	**108847.150**	**985.904**	
	Total	**29876.876**	**996.654**	

Figure (3-9) chromatogram of standard Benzoic acid .

These Tables shows thermal catalytic ammoxidation of Toluene to benzoic acid and benzonitrile over ((MoO_3-CdO)/ kaolin clay in ratio (50%) because it gave proportion high from another ratios at (573-553)k .

Table(3-4): Thermal catalytic vapor phase ammoxidation of Toluene over catalyst MoO_3-CdO in ratio (3:3) g at(573-553)K .

Area	Conc. Bnzoic acid	Area	Conc. Benzonitrile	Time h
36805.130	0.676	44589.116	2.32	**2**
77281.476	0.1.42	58000.815	3.01	**4**
101227.849	1.86	68000.609	3.52	**6**

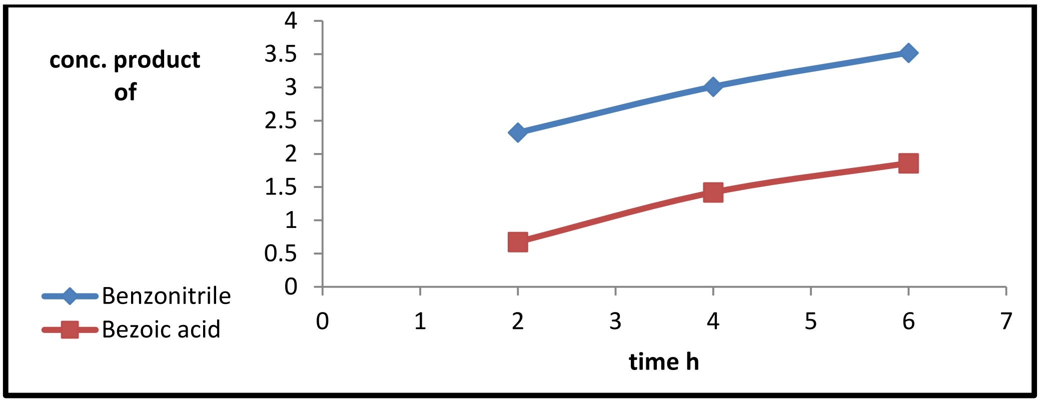
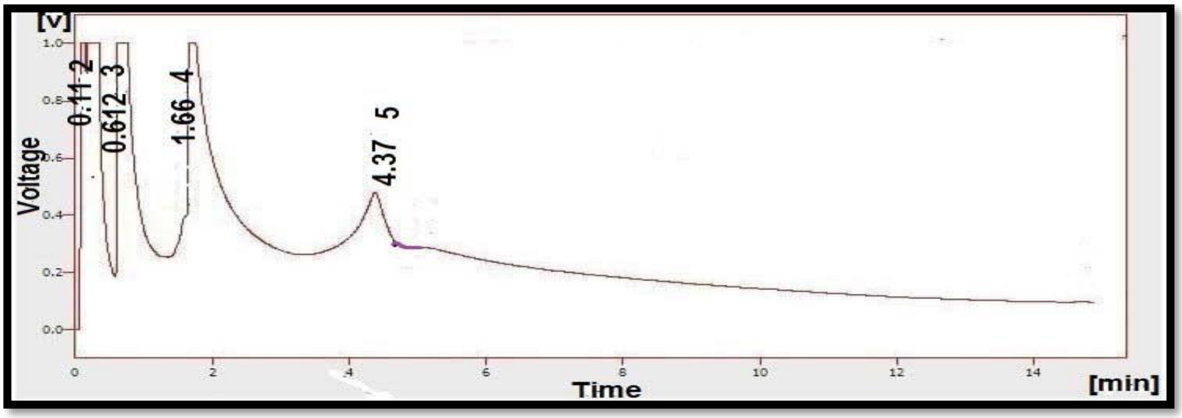


Figure (3-10): The concentration of production to benzoic acid and benzonitrile was increasing with excess reaction time in thermal catalytic vapor phase ammxidation .



	Reten. Tim [min]	*Area [mv.S]*	*Height [mv]*	*Compund Name*
1	0.767	546.486	985.142	*B1*
2	0.11	1529.181	894.532	
3	0.612	24518.306	942.532	
4	1.66	44589.116	867.042	
5	4.37	36805.130	437.909	
	Total	178630.90	4061.903	

Figure (3-11): The thermal vapor phase ammoxidation of Toluene tobenzoic acid and benzonitril in2, hours in Gas chromatography

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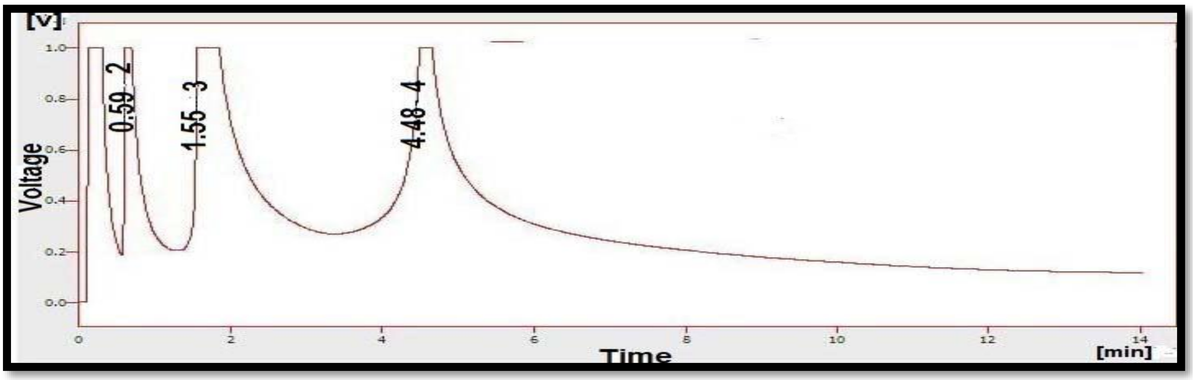

	Reten. Tim [min]	Area [mv.S]	Height [mv]	Compund Name
1	0.116	17699.982	995.432	B2
2	0.597	19257.547	991.567	
3	0.155	58000.815	983.808	
4	4.480	77281.476	960.046	
	Total	204335.16	3930.850	

Figure (3-12): The thermal vapor phase ammoxidation of Toluene tobenzoic acid and benzonitril in4, hours in Gas chrom atography .

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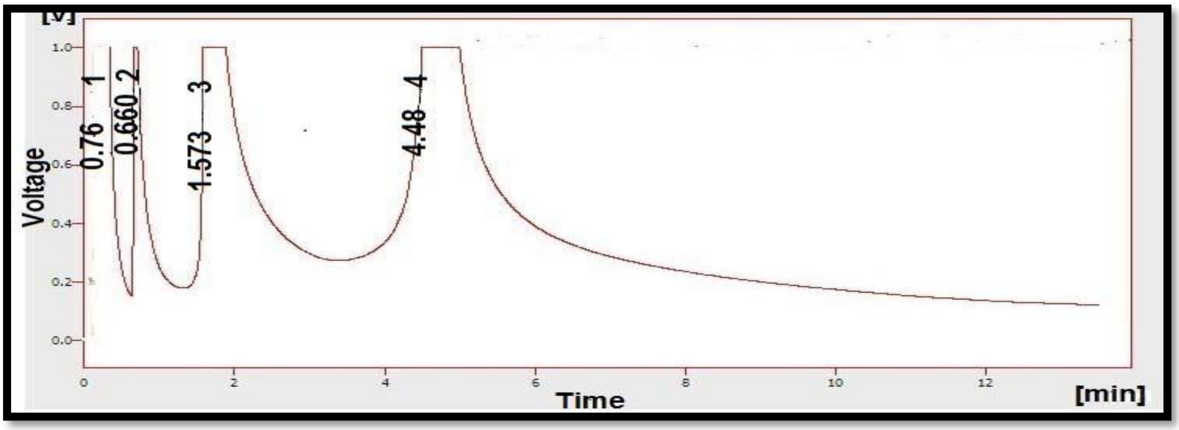

	Reten .Tim	Area	Height	Compund

	[min]	[mv.S]	[mv]	Name
1	0.67	17717.159	994.968	B3
2	0.660	15361.525	990.55	
3	1.573	68000.609	982.704	
4	4.483	101227.89	957.689	
	Total	224140.82	3925.916	

Figure (3-13): The thermal vapor phase ammoxidation of Toluene tobenzoic acid and benzonitril in6, hours in Gas chromatography .

From these results it is found that, the concentration of the produced Benzoic acid and Benzonitrile was increased with the time as a result of progress of reaction with the time under reaction conditions.

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