Study the Effect of Hydrophily Changing Silicate Catalytic (MCM-41) on Interaction in the Aqueous Medium

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Abstract

A silicate catalyst prepared which has a mezopore type (MCM-41) ,by manner that condensation where the interaction between Tetra Ethyl Ortho Silicate (TEOS) with 3-Mercapto Propyl Tri-methoxy Silane (MPTS), in the presence of superficial active substance {Cetyl Trimethyl Ammonium Bromide(C_{16} TAB)}at room temperature.The process of changing the surface hydophilic of the catalyst has done by using substance(Hexa methyl disilazane), which symbolized by the symbol (HMDS).Then some measurements made for catalyst, which is prepared in this research before and after changing the hydrophilic. calibration results had shown that the number of acidic sites equals (0,633m mol/lit), the specific surface is equal to (1500m^2/gr),the graph lines belonging to the adsorption and desorption of nitrogen showed: decreasing the voleume of adsorbed nitrogen with increasing applied pressure whenever sample hydrophilic increased. {7}Then we prepared a compound 5-hydroxy methyl furfural according to the reference method, as a model for the interaction in an aqueous medium, by using catalyst which prepared in this research before and after changing its hydrophilic {12}.

Keywords: Polar silicate catalysts, Hexa methyl disilazane, hydrophilic, acidic effective sites,MCM41, 5-hydroxy methyl furfural.

1-The theoretical part:

1-1- The theoretical introduction:

The catalyst word created by Burleios researcher at year 1835.

There are two types of catalyst ,catalyst homogeneous and heterogeneous , heterogeneous catalysts characterized easily separated from the reactants and products materials, and reused for many cycles,

One type of heterogeneous catalysts is called mezoporous molecular sieves, which symbolized by the symbol{MMS}. {1}

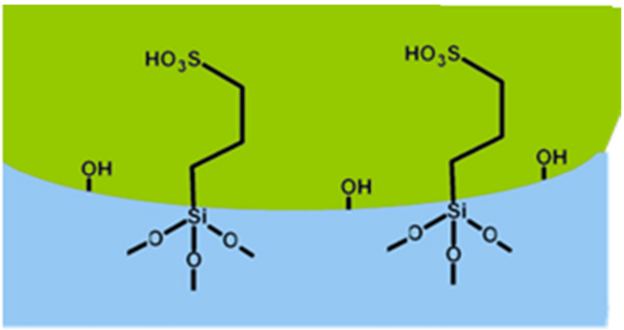
1-2-Reference study:

1-2-1-Features silicate catalysts:

-The preparation of homogeneous catalyst is guarantees controlling by all effective factions on the surface of the catalyst, as well as to control the surface space of the catalyst and, pore size , all these things have led to increased interest in mezoporous molecular sieves, which symbolized by the symbol{MMS} as a silicate catalysts, which has regular structure , fixed thermally, and qualitative surface area of up to (1500 m^2/gr).

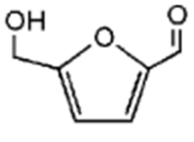
It has a follicular diameter of single distributed located in the range (2-50 nm),and this pores in the order of interstitial like channels, because of formaing it on the micelle's effective surface of material surface{2}.

- These catalysts and MCM-41 catalyst, which is one of it's kinds Characterized with high superficial hydrophilic, because there are hydroxyl factions (OH), which is hydrophilic on the surface of the silicate support . This is illustrated as follows:



1-2-2-Hydrophilic of the silicate support of the catalyst reduces the quality of his performance in the aquatic reactions:

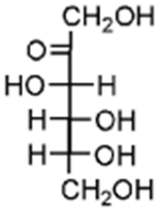
The chemical formula of the compound 5-hydroxy methyl furfural is:



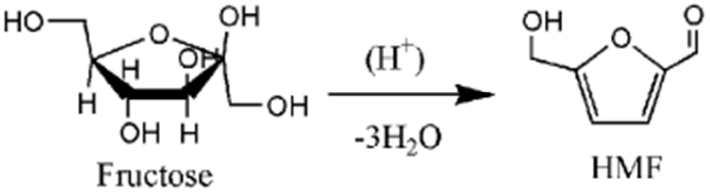
HMF

And the chemical formula of fructose is:

Fructose



Both have a clique or factions hydroxyl(OH) , which is hydrophilic that hampering the work of the catalytic, especially its surface hydrophily , Leads to the difficulty desorption out products, as well as the solution used in the preparation of(5-hydroxy methyl furfural) from fructose is water in according to the following reaction:



1-3-Definitions:

-Catalyst: it is asubstance change the speed of the reactionon condition that it doesn't consume this substance in the reaction, and doesn't change the dynamics ,but it changes its speed and its rank sometimes.{1}

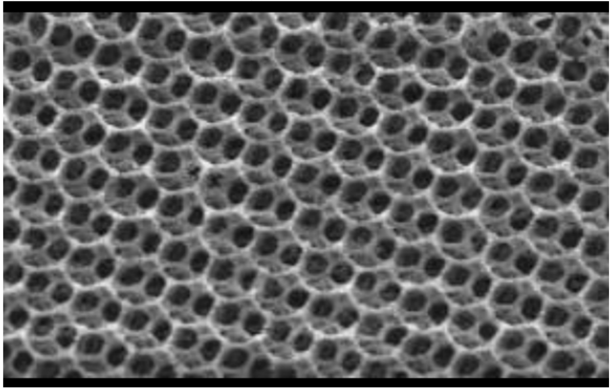
-Silylation: it is a process to replace hydroxyl factions with methyl(CH_3) factions to lose silicate support hydrophilic of catalyst. {1}

-The Hydrophilic: it expresses how much love of the chemical to the water, and thus the extent of adhesion or aversion this substance to the water, and losed catalyst hydrophily in this research improved performance of the catalyst in aqueous mediums.

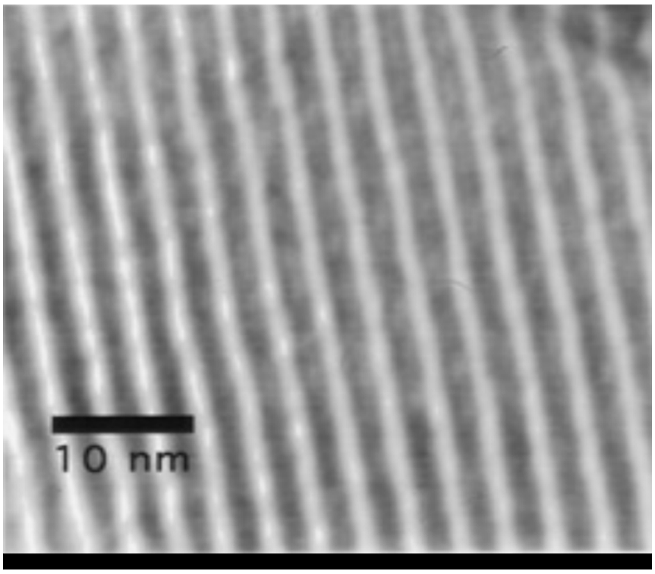
1-4- (MCM-41) as example of catalysts MMS:

There are many kinds of MMC catalysts, but it's first synthesis was in 1992, when a superficially effective substance, which is (C_{16}TAB) was used to form cylindrical micelle (hexagonal), that is used as control factor for the composition, where a silane Condenses on it's surface to get what is called (MCM-41),{2}.

and there are many kinds of (MCM) like (MCM-48)cubic micelle that have the form:



And lamellar micelle (MCM-50) as the following:



And (MCM-41) which we made changing in its hydrophilic, which we will show in this article.

2-Aim of the research:

1-the research aims to prepare a solid catalyst (MCM-41) to make it easier to be separated from the solvents in the medium of interaction, in addition to it has large number of active sites (Acidic cliques which numbered{0,633m Mol/gr}),also features include a large area of qualitative surface up to (1500cm^2/gr),this reduces the amount of consumed catalyst in interactions compared to other catalysts, and those led to less economic cost.

2-Catalytic hydrophilic loses a significant impact on improving the quality of its performance ,because of the most important reactions of (MCM-41) are reactions to dehydration for many compounds ,since these silicate catalysts have prepared in characterized by high hydrophilic, because of the hydroxyl factions on the surface of the catalyst , the study of changing hydrophilic support silicate for this catalyst has a very important role in improving the performance, and increase the speed of reaction in the aqueous medium, or dehydration reactions, and the possibility of reactivate the catalyst is more easily in order to repeat use it again in other reactions to five times .the reference, [12][11].

3. using catalyst in reaction to prepared 5-hydroxy methyl furfural, which symbolized by symbol(5-HMF), by deleting three water molecules from fructose as an application on using this catalyst by different degrees hydrophobic, and demonstrate its impact on the gross amount of the product,[12].

3- Equipment and substances used in this research:

3-1- used devices:

In addition to the various laboratory instruments , electric drying oven ,mechanical engine , magnetical engine and heater, used the following devices:

-Reactor consists of container made of teflon material provider by a metal lid tightly.
-An electronic balance type (As 220/92) model RADWAG 2008 it's accuracy (0.0001 gr).
-A measure of the degree of acidity PH type consort model (C830).
-A device for measuring infrared spectrum(infrared spectroscopy) (from company Jasco FTIR-4100 type A)
-Specific surface measuring device of the company Micromeritice.
-Electric ashtray temperatures of up to 1100 type carbolit.
-Scanning electronic microscope(SEM)of the company FEI model Quanta200.

3-2- Materials used:

Table 1. the information about materials put in it

The name of manufacturer	density g/ml	Molecular weight g/mol	Purity	Symbol	Material name
Merck	0.94	208.3	>98%	TEOS	Tetra ethyl ortho silicate
Merck	1.05	196.4	≥95%	MPTS	3-Mercaptopropyl tri methoxy silane
Merck	-	364.5	>97%	C_{16}TAB	Hexa decyltrimethy lammonium bromides
-	-	-	-	HMDS	Hexa methyl disilazane
laboratory supplies Poole	-	180,16	-	fructose	Fructose (D-fructose)

All materials are described above

-Indicators:

1-Phenolphthalein ethanolic (W/ V = 1%)

2-Methyl orange.

Calibration standards:

-Borax($Na_2B_4O_7$.H2o) prepared in concentration (0,1N).

-Hydrochloric acid (HCL) prepared in concentration (0,1N),and make sure standard.

-Potassium hydroxide(KOH) prepared in concentration (0,1N), and make sure standard.

4- A method of work:

4-1- Synthesis of silicate catalyst(MCM-41): {10,8}

We dissolve (3,33gr) from (C_{16}TAB) in (200 ml) of mix (MeOH:H_2O ,70:30) ,and control the temperature of the mix at (25± 1°C).

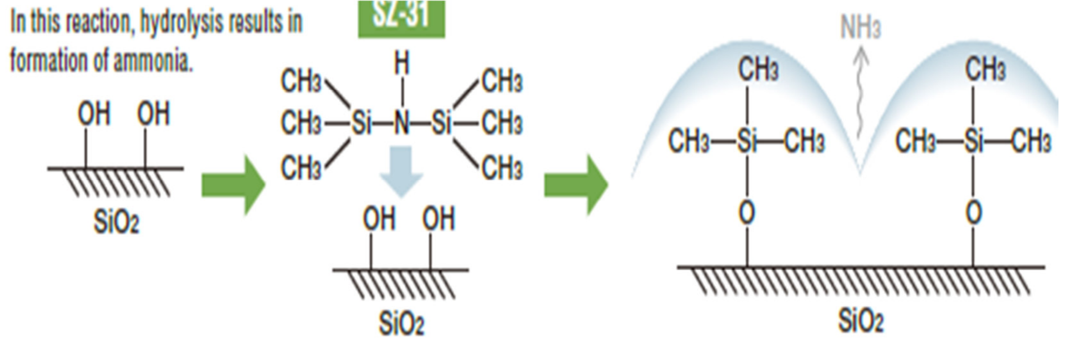
mix up (18,7gr) from (TEOS) with (1,96gr) (MPTS) in a separated beaker, then it is added to the previous mixture slowly with intense mechanical stirring for an hour, and then add about (10ml) from NaOH (2,7N) (ph≈10 almost), leading to constituted a white precipitate, and then continue with the intense mechanical stirring, and temperature was controlled at (25±1°C) for 24 hours. The interaction mixture placed in the teflon autoclave, closed mightily, and put it in the oven at temperature (105-110 °C) for four days, and then the precipitate was filtrated on suppress Ghosh, and was washed several times with distilled water, and was dried in the oven at temperature (*40±5°C*) for 24 hours.

The resulting precipitate is treated with a mixture from (ETOH :HCl , 10:l) in the rate of (255 ml) for every (1,5 g) of dried precipitate, in order to remove the remnants of the superficial active substance(C_{16}TAB). processing was in a distillation apostate device, with stirring for 24 hours ,washing the precipitate several times to suppress Ghosh, with hot distilled water until the removal superficial active substance entirely, then we dried precipitate (catalyst) at temperature (50°C).

4-2- Losing the surface hydrophilic of the silicate support:

Keep in flask (1000 mg) of silicate catalyst with (100 ml) toluene with stirring for (15 min), even all catalytic dispersion in toluene, and then add (20 ml) from (HMDS) with continuing stirring, and heating to a constant temperature (110°C) in presence of distillation apostate device, and repeats the process for the four samples from the same catalyst for periods time is (1h-2h-3h-4h).

where the quotient interaction:



Then we filter to suppress Gush using discharge flask, that connect to with pumper, and then wash flask by toluene to ensure there is no loss of the amount of catalyst, after that we wash the catalyst with acetone ,and dried it at a temperature (60°C) for (24h).Ref [2,3,6].

-we chose Hexa methyl disilazane material is symbolized by the symbol (HMDS) to lose hydrophilic of silicate surface, because it is cost cheap material , easy to dealing ,commercially available, chemically stable, and much using to silylation hydroxyl groups Ref[9].
After drying the four samples of the catalyst, as well as the sample number(0) which untreated with (HMDS) material , acidic function is calibrated by inverse calibration as follows:
-Standardization HCl (0,1N) prepared by borax (0,1N), with the help of methyl orange indicator .
-Standardization (10ml) from (KOH) by (HCl) standard, with help of phenolphthalein indicator.
-we dispersal (0,03gr) of catalyst in (10ml) From (KOH), then we calibration surplus from (KOH)by (HCL),so also with the help of phenolphthalein indicator.

4-3-Preparing 5-hydroxy methyl furfural (5-HMF):
Practical way:
We dissolved (0,69 gr)from fructose in (1,5 ml)distilled water , added (0,108 gr)of catalyst with continuing magnetic stirring ,then added (4ml)from ethyl acetate, and then raise the temperature to(130^oC) in the presence of reflex cooler.
we set interaction time at (3hours),then filtrate to separate the catalyst, and separate the filtrating by using suppression separated to get two phases watery and organic. then we drain off organic phase that containing the desired product at temperature (70^oC)to get rid of ethyl acetate.

5-Results and discussion:
5-1- Measuring the specific surface of the catalyst:
the results is put in it. Table 2.

Figure tridimensional	Pore diameter (nm)	Specific surface (cm^2/gr)	The noun	Abbreviation
Hexagonal	1,5-10	1500	Mobil Composition of Matter-41	MCM-41

Description for the above table:Measuring the specific surface of the catalyst and pore diameter by using Micromeritice device in a way B.E.T.

5-2-Calibration of acidic function:
Table 3. which shows the results of the calibration acidic function.

Sample number	The time it takes to change the hydrophilic (**h**)	Sample weight (**gr**)	HCl size needed to calibrate the surplus of(KOH) **ml**)(	HCl size needed to calibrate acidic function in catalyst(**ml**)	Number of moles of the acidic site(10ml**)** **(mol/10ml)**	Number of effective sites estimated (**m mol /gr**)
0	0	0,03	23,5	0,50	$0{,}019\ .10^{-3}$	0,633
1	1	0,03	23,5	0,50	$0{,}019\ .10^{-3}$	0,633
2	2	0,03	23,5	0,50	$0{,}019\ .10^{-3}$	0,633
3	3	0,03	23,53	0,40	$0{,}0152\ .10^{-3}$	0,5066
4	4	0,03	23,6	0,40	$0{,}0152\ .10^{-3}$	0,5066

The standardization of (HCL) by borax shows that concentration of ([HCL]=(0,038Mol/Lit).
where the volume of(HCL) required for the calibration of (10ml) from (KOH) free of catalyst was (24ml).
it has been calculating the number of active sites in the following way:-
An example of the sample number (3)

$(N\ .\ V\ )_{catalyst} = (N'\ .\ V'\ )_{HCl} \Rightarrow$

$n\times 10\ ml = 0{,}038\ mol/ml \times 0{,}40\ ml \Rightarrow N = \frac{0.038\times 0{,}40}{10} = 0{,}00152\ mol\ /\ lit$

$= 1{,}52\ .10^{-5}\ mol\ /\ 10ml$

-Every (10ml) contain (0.03 gr) catalyst and ($1{,}52\ .10^{-5}$) effective site
Every (1 gr) catalyst has **X** effective sites -

$X = \frac{1{,}52\ .10^{-5}}{0{,}03} = 0{,}5066\ .10^{-3} mol\ /\ gr$

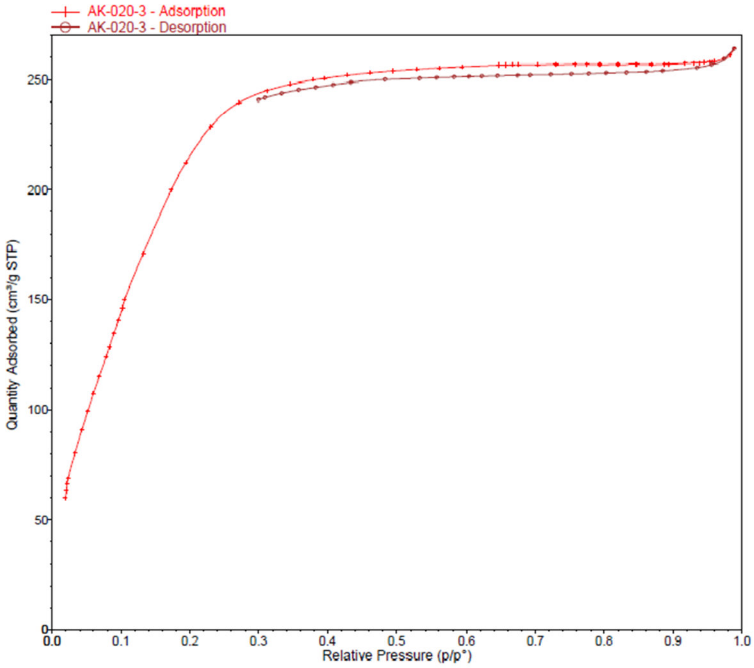
$= 0{,}5066\ m\ mol\ /\ gr.$

- In the same way it was accounts for the rest of the samples .

We note starting from sample number (3) , decrease number of acidic effective sites , because of the particles (HMDS)are larger than the size of particles (OH) which leads to cover some of the active sites

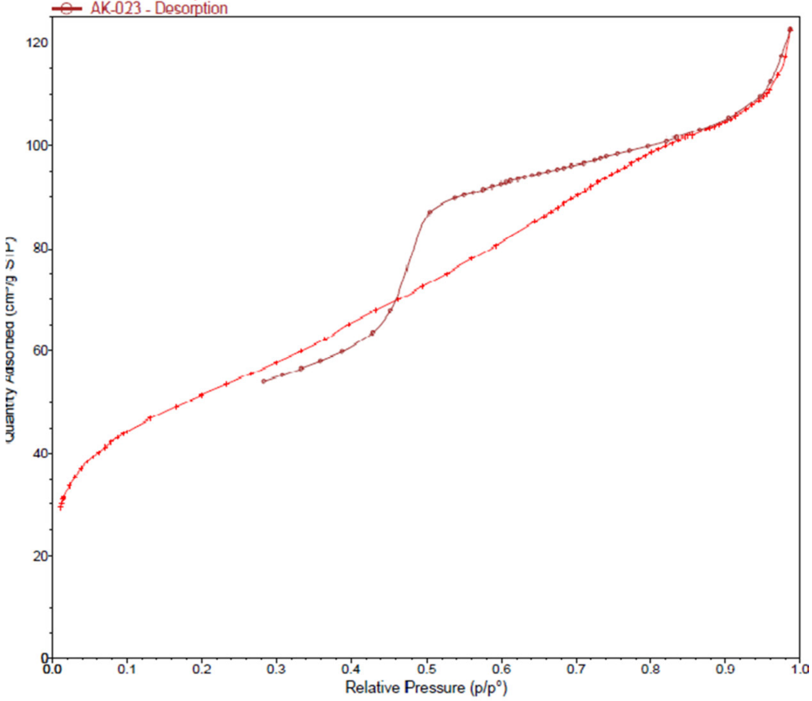
5-3- Graphs for the adsorption and desorption nitrogen:

The following presentation graph lines for adsorption and desorption nitrogen [estimated by measuring unit (cm^3/gr)] with increase the applied pressure to the a maximum value (1mmHg) for samples of catalyst (MCM-41) with different hydrophily proportion:



Graphs of the sample number 0 figure 1.

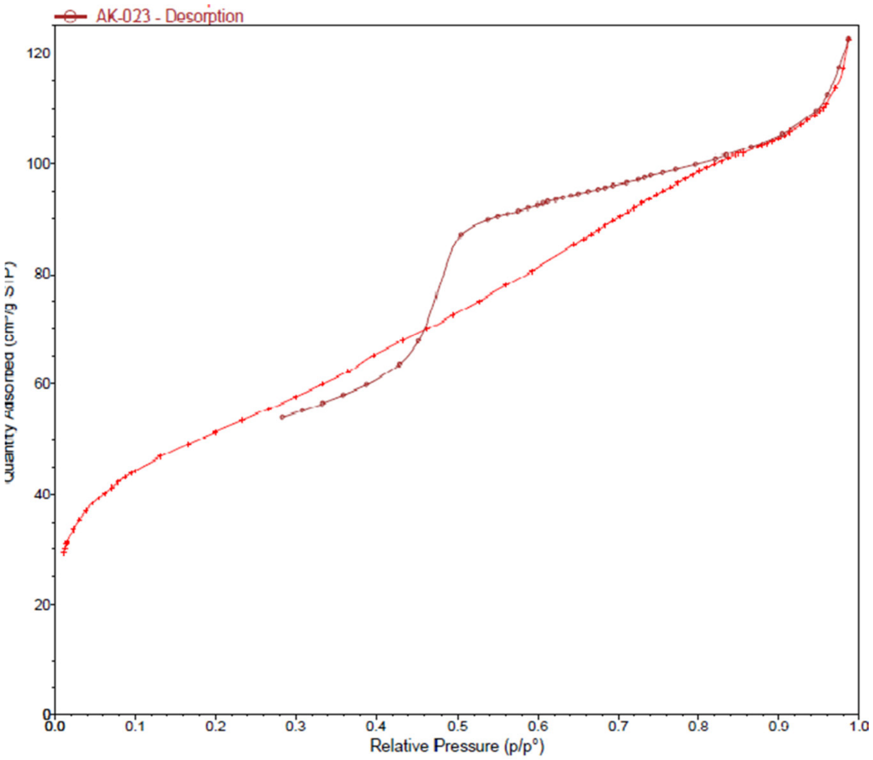
Reached the size of adsorbed nitrogen gas on a catalyst in this sample (240 cm^3/gr), and corresponding to a pressure value equal to the (0.3 mmHg).



Graphs of the sample number 3 figure2.

in this case nitrogen gas volume was adsorbed on a catalyst in this sample (56 cm^3/gr), and corresponding to a pressure value equal to the (0.3 mmHg)

While size of adsorbed nitrogen gas (120 cm^3/gr) when the applied pressure maximum value equal to (1mmHg).



Graphs of the sample number 4 figure3.

in this case nitrogen gas volume was adsorbed on a catalyst in this sample (32 cm^3/gr) and corresponding to a value equal to the pressure (0.3 mmHg)

While size adsorbed nitrogen (77 cm^3/gr) when the applied pressure reached maximum value equal to (1mmHg).

Where we conclude decrease the amount of the adsorbent material by increase the sample hydrophobic as a result of the deposition of molecules tri methyl silane, which is large sized particles on the silicate surface [4,5,7]

5-4- spectroscope results IR :

Hereafter the IR spectroscopy pictures to previous samples

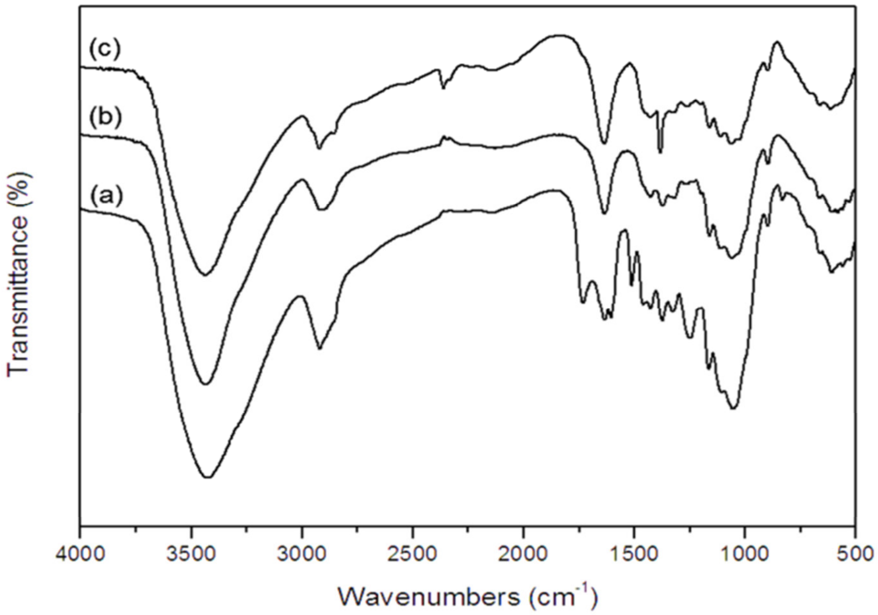


Figure 4.

-A line graph (C) stand for sample number 0, which didn't treat with (HMDS) substance.

-A line graph (B) stand for sample was treated with (HMDS) substance for 2h.
-A line graph (A) stand for sample was treated with (HMDS) substance for 4h.
-Note the increasing the sharp of the peak in the range (2850-2950 cm^{-}), which is belonging to the faction (CH_3) as a result of deposition tri methyl silane molecules on the surface of the silicate support.
- Spectrum IR of a compound resulting from the interaction dehydration fructose appeared on the following figure:

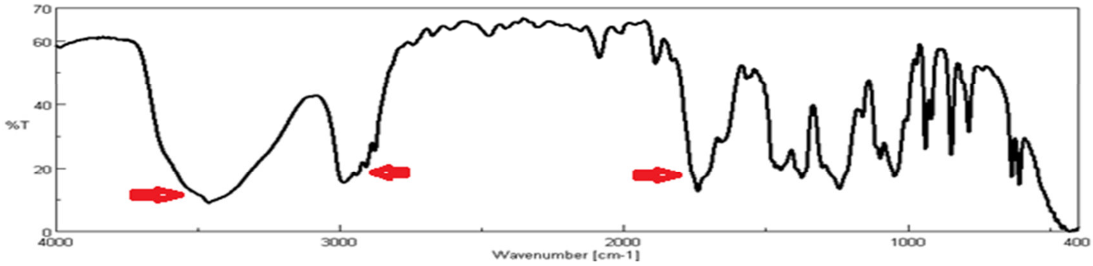
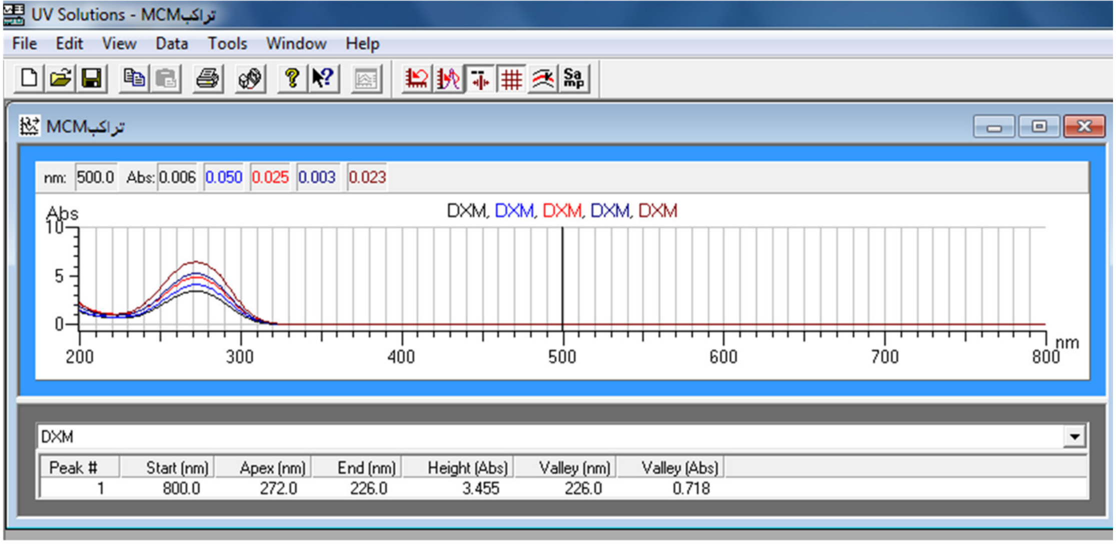


Figure 5. Spectrum IR of a compound resulting and It is very similar to a spectrum of compound (5-HMF) Reference.

5-5- Spectrums UV results:
Following spectrums back to a compound 5-HMF, which is prepared by using catalyst [MCM-41], where the absorbency of this compound at (272nm), and we find that the intensity of the absorption is gradually increased with increasing hydrophobic of catalyst .



nm: 500.0 Abs: 0.006 0.050 0.025 0.003 0.023

DXM

Peak #	Start (nm)	Apex (nm)	End (nm)	Height (Abs)	Valley (nm)	Valley (Abs)
1	800.0	272.0	226.0	3.455	226.0	0.718

Figure 6. Spectrums UV of 5-HMF

We conclude that the shades UV to outputs previous catalytic tests have shown to increase the amount of product 5-HMF by increased catalyst hydrophobic.

6- conclusions

-We prepared the catalyst (MCM-41) with a surface area (1500 cm^2/gr), and the pore diameter (1.5-10-nm).
-We identified a number of acidic sites in a manner reverse calibration was equal to (0.633 mol/gr).
-(HMDS) hexa methyl disilazane substance proved successful in silylation process, where the groups of hydroxyl have been replaced by groups of tri-methyl silane ,
-We proved with the help of graph lines for the adsorption and desorption of nitrogen decrease the amount of adsorbent nitrogen, estimated (cm^3/gr) by sample hydrophobic increase due to the deposition of of molecules tri methyl silane, which is large sized particles(compared with groups of hydroxyl) on the silicate surface.
-Spectrums (UV) of the outputs of the previous catalytic tests, showed increase the amount of product (5-HMF)by increase catalyst hydrophobic.

7-Recommendations

- Useing other materials to increase the hydrophobic, and compared their results with the results we have obtained with the use of HMDS.
-Circulating the idea of increasing the hydrophobic on many other substances, such as paints and industrial leather, which protects it from pollution with many liquid materials which is high hydrophilic, also prevents

wetted them: (paints and industrial leathers….etc) with water.

8-References

1, Dr. Mikhail, S. (1981).Physical Chemistry 4 Faculty of Science. University of Aleppo, (Chapter 1).

2. Guidotti,M., Gener, I.B., Gianotti, E., Marchese, L., Mignard, S., Psaro, R., Sgobba, M., Ravasio, N. (2008). The Effect of Silylation on Titanium Molecules. Mecropours and Mesoporous Materials,111, 39-47
3. Arreche, R.A., Blanco, M.N., Martin, M. Vazquez, B.,G. (2012). Structural Synthesis of Hydrophilic and Hydrophopic Silica for its Use in Food Packaging Films. Procedia Materials Science, 1, 572-579
4. Kim, J.M., Kwak, J.H., Jun, S., Ryoo, R. (1995). Ion Exchange and Thermal Stability of MCM-41. Phys Chem, 99 (45), 16742-16747
5. Sushil, K.R.P., Carl, R.F.L. (2011). Formation and Growth of Humins via Aldol Addition and Condensation during Acid_catalyzed Conversion(5-Hydroxymethylfurfural). Energy Fuels, 25(10), 4745-4755
6. shln-etsuchemicalco,ltd. [Online] Available: http://www.shinetsusilicone-global.com/silicone@ligomershttp
7. Kruk, M., Jaronic, M. (1997). Application of Large Pore MCM-41 Molecular Sieves to Improve Pore Size Analysis Using Nitrogen Adsorption Measurements. Langmuir, 13,(23), 6267-6273
8. Nemati, F., Heravi M. M., Rad S. R. (2012). Nano-Fe3o4 Encapsulated-Silica Particles Bearing Sulfonic Acid Groups as Magnetically Separable Catalyst for Highly Reactions of Aromatic Aldehydes with 1,3-Cyclic Diketones, Chin.J.Catal., 33, 1825-1831
9. Daryoush Z.,Revaneh A.,Mohammad A.K. (2011). Silylation of Alcohols and Phenols with Hexamethyldisilazane over Highly Reuseable Propyl Sulfonic Acid Functionalized Nanostructured SBA-15,Chinese Journal of Catalysis , 12, 1864-1868
10. Yi-Chia L.,Yi-Hsin L.,Yann H.,Xiao-Yan L., Chung-Yuan M. (2013). Mesoporous Silica Supported Cobalt Catalysts for Hydrogen Generation in Hydrolysis of Ammonia Borane, International Journal of Hydrogen Energy,38, 7280-7290
11. Claudia B., Karine De Oliveira V., Mariana S., Nicolas B., Luis M., Paula F.,Francois J. (2014). Catalytic Dehydration of Fructose to HMF over Sulfonic Acid Functionalized Periodic Mesoporous Organosilicas:Role of The Acid Density, The Royal society of Chemisry.
12. Gholam Hossien M.,Mohammad Mehdi G., Hamid S., Fatemeh K. (2010). MCM-41 Functionalized Sulfonic acid Catalyzed One-pot Synthesis of 1,8-dioxo-octahydroxanthenes,J.Iran.Chem.Res.,3, 117-120
13. Hiromi Y.,Yuu H.,Sadaharu I.,Shinichiro N. ,Norikazu N.,Kohsuke M. (2008). Surface Hydrophilic-Hydrophopic Property on Transparent Mesoporous Silica Thin Films Containing Chromium Oxide Single-site Photocatalyst , Catalysis Today ,132, 146-152
14. Babak K.,Behzad G.(2000). Mild and Highly Efficient Method for the Silylation of Alcohols Using Hexamethyldisilazane Catalyzed by Iodine under Nearly Neutral Reaction Conditions, J. Org. Chem., 65 (21),7228–7230