Increase Hydrophily of silicate catalytic using TCMS to Improving performance in Fischer esterification

Bana IK

Doi: 10.21608/ajsr.2020.177502

IK, Bana (2020). Increase Hydrophily of silicate catalytic using TCMS to Improving performance in Fischer esterification. ***The Arab Journal of Scientific Research***, AIESA, Vol. 4 Issue 4.

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. {11,9}. The process of changing the surface hydophilic of the catalyst has done by using substance(trimethylchlorosilane), which symbolized by the symbol (TCMS). calibration results had shown that the number of acidic sites equals (0,633mmol/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. {8}Then we applied The Fischer esterification reaction between a carboxylic acid(Benzoic Acid) and an alcohol(Mythanol) to give an ester (benzoate). 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 (13).

Kay words :silicate catalysts; hydrophilic; acidic effective sites; MCM-41; Fischer esterification; mezopore; benzoate; channels.

1-The theoretical part:

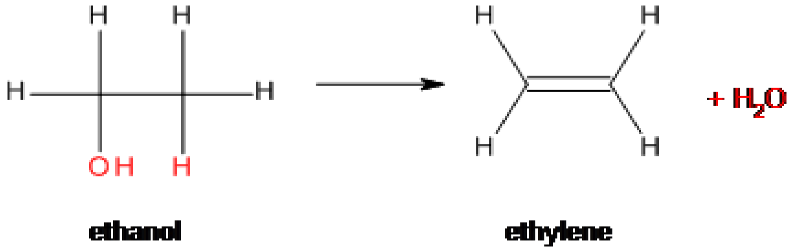
1-1- The theoretical introduction:

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}.And One type of catalysts is called mezoporous molecular sieves, which symbolized by the symbol{MMS}. {4,1}

1-2-Reference study:

1-2-1-Examples of Dehydration Reactions {3}:

The one thing that dehydration reactions have in common is that they start with a single molecule and produce a new molecule, plus a molecule of water. These reactions occur frequently in organic chemistry. One of the most common dehydration reactions involves the conversion of an alcohol to an alkene, as shown here, for the dehydration of ethanol to produce ethylene, also known as ethane. Notice that one hydrogen atom in the water molecule came from one carbon in ethanol, and the oxygen atom and the second hydrogen atom come from a different carbon.

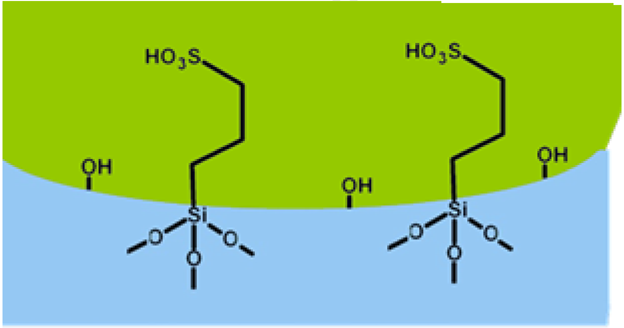


1-2-2-Features silicate catalysts:

-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) {5}.

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 forming 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 {5}

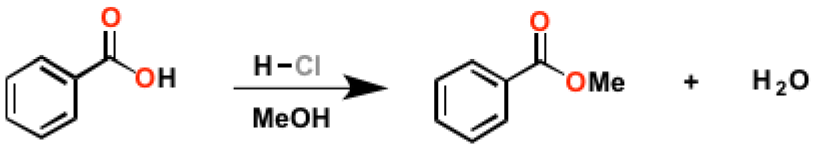


1-2-3-Hydrophilic of the silicate support of the catalyst reduces the quality of his performance in the aquatic reactions (The reason you using alcohol as solvent):

Ethanol undergoes a dehydration reaction to form ethylene and a molecule of water**.**

The Fischer esterification is the reaction between a carboxylic acid and an alcohol to give an ester. You typically run the reaction by dissolving the carboxylic acid in the alcohol you want to make the ester with (e.g. ethanol to make the ethyl ester). The reason you do this is that it's an equilibrium reaction: your product is water, so by using your alcohol as solvent, you effectively drown out the reverse reaction, which is hydrolysis of the ester to give you back the acid. The final step of setting up the reaction is the addition of a strong acid (like HCl) and commencing heating. After an hour or two at reflux, you strip off the solvent, and voila – you have your ester.{6}

Fischer esterification example



Observation: Without the acid catalyst, the reaction is painfully slow.

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.{7}

And the Figure number 1 explaine silylation Attached at the end of the search.

-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.{10}

-Fischer esterification: is the reaction between a carboxylic acid and an alcohol to give an ester

2-Aim of the research:

1-the research aims to prepare a catalyst (MCM-41),which 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, in addition to it has large number of active sites (Acidic cliques which numbered{0,633 m Mol/gr}

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, [13][12].

3-Using this solid catalyst in Fischer esterfication instated of liquid acidics, to make it easier to be separated from the solvents in the medium of reaction.

3- Equipments 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 Jascol 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***:

  Attached in Table 1

-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:

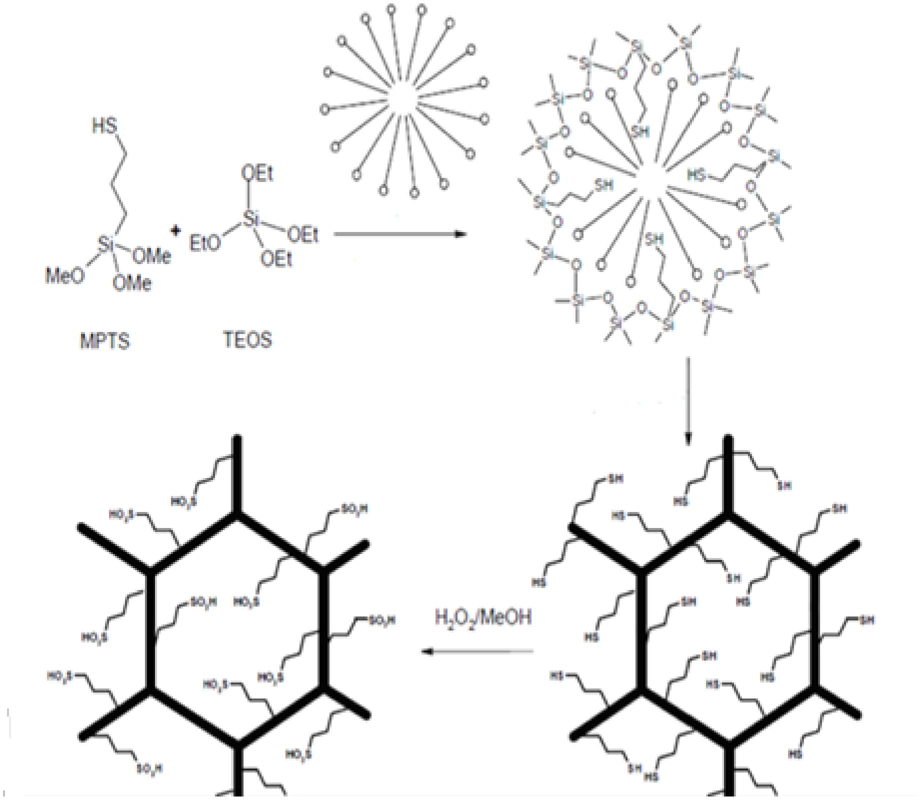
4-1- Synthesis of silicate catalyst(MCM-41): {11,9}

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^oC).

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 controled at (25±1^oC) for 24 hours. The interaction mixture placed in the teflon autoclave, closed mightily, and put it in the oven at temperature (105-110 ^oC) 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 ($40\pm5^{o}C$) 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^{o}C).

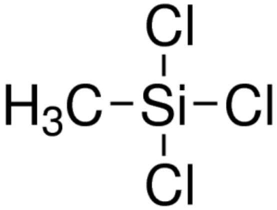
This is the synthesis reaction:



And the Photo number 1 of the catalyst that has been Synthesised in laboratory Attached at the end of the search

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 (TCMS) with continuing stirring, and heating to a constant temperature ($110^{O}C$) 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).{7}



CH_3SiCl_3

TCMS Chemical formula

4-3- Conditions of esterification reactions and results:

Esterification Experiments.-All operations were carried out in glass apparatus fitted with interchangeable ground joints. Esterification experiments were carried out in the thermostat kept at 24.93 * 0.02'. Twenty-five cc. samples of reaction mixture were pipetted for recovery of the water, and from these the methanol, water and a small amount of the methyl benzoate were distilled in vacuo at room temperature. This initial process took thirty minutes at a maximum, thus causing a negligible error in the reaction time recorded. The distillate was then fractionated at atmospheric pressure, the water and methyl benzoate remaining behind. In the final step, the water was distilled off in vacuo from the methyl benzoate. The water samples obtained by this method were always contaminated by small amounts of methanol and methyl benzoate; these impurities can have no effect on the results obtained by the method of analysis given above. The amount of exchange of the benzoic acid was determined as follows: 102 cc. of a reaction mixture, having the composition originally given, was set up, using ordinary benzoic acid, ordinary methyl alcohol and water containing 0.509% catalyst, This reaction was done using the hydrophilic Unchangeable catalyst and we obtained results that were placed in the table number 2

Time (hours)	reaction%	mole H_2O formed	(the original catalyst)
0	0	0	no catalyst
94	24.5	0.674	0.509%
206	39.9	0.1098	0.509%
378	54.7	0.1505	0.509%

table number 2

The same reaction was repeated for 3 hours only, The comparison between the hydrophilic modulator catalysts and the results were summarized in the table number 3

Time of reaction(hours)	Duration of hydrophilic modulator for catalyst(hours)	Reaction %
3	0	3.4
3	1	7.58
3	2	14.46
3	3	24.97

table number 3

5- 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).

- (TCMS) trimethylchlorosilane substance proved successful in silylation process, where the groups of hydroxyl have been replaced by groups of methyl silane
- At the reaction time of(206) hours, the reaction rate was (39.9 %) using a non-modified hydrophilic catalyst
- While we repeated the same reaction, conditions and for a period of (3) hours only, obtained a rate of (24.97%) to run of the interaction using hydrophilic changeable catalysts.

References:

1-, Dr. Mikhail Samaan, 1981,Physical Chemistry 4 Faculty of Science, University of Aleppo,.

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- U. K. Das, S. Chakraborty, Y. Diskin-Posner, and D. Milstein,(2018), **Direct Conversion of Alcohols into Alkenes by Dehydrogenative Coupling with Hydrazine/Hydrazone Catalyzed by Manganese**, Chem. Int. Ed.Vol. 57, 13444 – 13448

4- 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

5- Dıaz I., Marquez-Alvarez C., Mohino F., Pérez-Pariente J., Sastre E., (2000), **Combined Alkyl and Sulfonic Acid Functionalization of MCM-41-Type Silica Part 1: Synthesis and Characterization,** Journal of Catalysis,Vol 193, 283-294.

6- Sakdinun N. ,Toshiyuki Y. , Takashi T. , Chawalit N.,(2016), **Enhanced esterification of carboxylic acids with ethanol using propylsulfonic acid-functionalized natural rubber/hexagonal mesoporous silica nanocomposites,** Catalysis Communications**,** Vol 80, 5-9.

7--Daryoush Z.,Revaneh A.,Mohammad A.K., (2011), **Silylation of Alcohols and Phenols with Hexamethyl disilazane over Highly Reuseable Propyl Sulfonic Acid Functionalized Nanostructured SBA-15,**Chinese Journal of Catalysis ,Vol 12, 1864-1868.

8.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),pp 6267-6273.

9.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.

10- Hiromi Y.,Yuu H.,Sadaharu I.,Shinichiro N. ,Norikazu N., (2008), Kohsuke M., **Surface Hydrophilic-Hydrophopic Property on Transparent Mesoporous Silica Thin Films Containing Chromium Oxide Single-site Photocatalyst** , Catalysis Today ,132, 146-152.

11.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

12.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.

13.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

table number 1

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
	0.856	108.66	-	TCMS	Trimethylchlorosilane
Merck	1.321	122.12	-	-	Benzoic acid

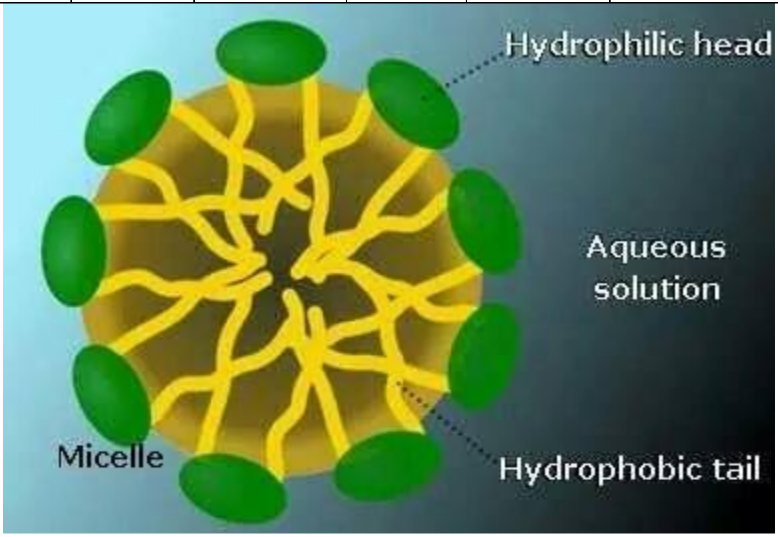


Figure 1

Photo number 1