



PHENOL OXIDATION AS A TEST REACTION FOR TI INCORPORATION IN MODIFIED FORMS OF Y- ZEOLITES

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Abstract:

The Phenol oxidation is considered as a test reaction in confirmation of the framework incorporation of Ti in the zeolite as per the reported methods. The applications of the zeolites can be changed depending upon the modification of the zeolite without much disturbing its crystallinity. The position of the incorporated active metal inside the zeolite also affects its characteristics. The zeolite-Y is the single largest used zeolite even today in refining and petrochemical industries due to its 3D pore structure. Most of the zeolites are unstable and lose their activity at higher temperature and in hydrothermal conditions. The Synthesized highly crystalline Na-Y zeolite in pure form is obtained from Union Carbide Corporation, USA (Linde, SK-40) with Si/Al = 2.4 as a original sample for further modification. It is convert into NH₄-Y form by using Ammonium Nitrate solution at 1000C using reflux method and calcined at 5000C, The process were repeated three times to convert it in to highly crystalline form of low silica H-Y zeolite. The H-Y zeolite is stabilized by treating carefully under controlled hydrothermal conditions at 5500C for 4h and then gradually cooling at the rate of 20C/min. carefully to obtain the final product. This high silica H-USY 500, sample was used for insertion of Ti in oxidized form in to the stable H-USY-500 Zeolite and It is modified to Ti-USY-500 zeolite products. The incorporated Ti in the zeolite changes their catalytic activity and selectivity of the products and the reactants. These samples are characterized by XRD, AAS, XRF and NMR techniques etc. For the confirmation of incorporation of Ti at the framework location of the H-USY zeolite The Phenol oxidation as a test reaction is carried out with the samples prepared. The details of the reaction, are discussed in the present paper.

KEYWORDS:

(1) potassium titanium oxalate as a Ti-source(2)controlled Steam chamber(3) Synthesized Faujasite Na-Y zeolite.

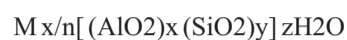
INTRODUCTION:-

What are Zeolites?

Zeolites are crystalline hydrated alumino- silicates having rigid three dimensional infinitely extended framework structure. It encloses the cavities and channels of molecular dimensions . The framework structure contains corner sharing of [SiO₄]-4 and [AlO₄]-5 Tetrahedral linked through common oxygen atoms as the primary building units. The general empirical crystallographic unit cell formula of zeolite is expressed as

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where

M= charge compensating cations of valency.

x and y represents the no. of moles of SiO₂ & AlO₂ where y > x and

z= no. of water molecules.

Most of the zeolites are very unstable and lose their catalytic activity easily under the severe conditions of catalytic reactions and hydrothermal conditions at high temperatures. By large dealumination of zeolite framework may leads to collapse Its structure. To overcome this problem synthesized zeolites are dealuminated in a very carefully controlled manner under hydrothermal conditions. Which is found to be a best method for increasing catalytic activity as well as stability of the zeolite. The extra lattice aluminum species formed are removed by acid leaching. Abundant literature is available on Y type zeolite as it is most promising zeolite due to its 3D pore structure. it is best suited to produce large numbers of petrochemicals. Such zeolites are treated under steam at different temperatures and are called as ultra stable Y zeolite. The zeolite fujasite type-Y is low silica, large 3D pore zeolite, hence can be easily synthesized in the laboratory and in the industry. The unit cell of Y type zeolite is cubic with a large dimension of 250Å and contains 192(Si, Al) O₄ tetrahedral, has remarkably stable and rigid framework structure with largest void space, which amounts to be nearly 40% by volume of the dehydrated crystal.

Experimental:

10g of Na-Y was added in to 200 ml 2N NH₄NO₃ to ion exchange it for the Preparation of NH₄-Y zeolite from it. The Solution was taken in a round bottom flask. This mixture was heated at 100°C by stirring it for 12h by using reflux method. The sample was then filtered, washed several times with hot de-ionized water till free from any traces of nitrate ions and dried at 100°C over night, the above procedure was repeated at list three times to obtain more than 90% of NH₄-Y from Na-Y by above method. As Sodium was added to the zeolite the total no. of acid sites was reduced. Effect of sodium poisoning was found to be dramatic over the entire range of Si/Al ratio examined. one sodium atom could effectively poison 5 non frame work acidic Al atoms which found to reduce the catalytic activity of the zeolite. The amount of Ti incorporated into the Frame work is found to be increased as the presence of Na (alkali metals) in the jell decreased. In view of this report Na-Y was converted into NH₄-Y zeolite and was used for Ti incorporation in it. Still It was used in the Synthesis of zeolite, because it can be easily ion exchanged with any metal.

Procedure of Preparation of Different samples of Ti-USY zeolites by using NH₄-Y and K₂TiO(C₂O₄)₂·2H₂O with different methods:

Preparation of USY zeolites;

Most of the zeolites are very unstable and lose their catalytic activity easily under the severe conditions of catalytic reactions and in hydrothermal conditions. Due to large dealumination of zeolite framework which leads to collapse of zeolite structure to overcome this problem synthesized zeolites are dealuminated in controlled manner and extra lattice aluminum species formed were removed by acid leaching. The NH₄-Y zeolite prepared was further dealuminated under carefully controlled steam in the cylindrical reactor by keeping the sample in the silica sample holder to increase hydrothermal severity at 550 °C for 4 h. There after the sample is kept for cooling very slowly till its temperature reaches to 100°C then the steam passing over the sample is stopped it takes about 3h to reach to 100°C from 550°C temperature. The sample holder is taken out of the reactor at a temperature about 50-60°C. Then it is transefered in to the conical flask containing 2N NH₄NO₃ solution in proportionate to about 20ml of it for 1gm of the sample. All the samples prepared were ion exchanged with 2N NH₄ NO₃ as per above procedure and finally the sample was calcined at 500 °C to obtain H-USY zeolite. The Final sample prepared was treated with K₂TiO(C₂O₄)₂·2H₂O by different mole fraction of it. This Ti treated different samples at different temperatures as mentioned in the table are used for Phenol oxidation. As Ti incorporated in to the frame work location increases the Phenol oxidation. Hence it is considered as the conformation Of Ti incorporation in to the frame work location of the Modified zeolites. All the Ti treated samples are ion exchanged with 0.001N normal HCl to make its blokages free (i.e. its void volumes and channels) at 100°C for 4h by reflux method. The procedure for preparation of different samples is narrated in the table -1

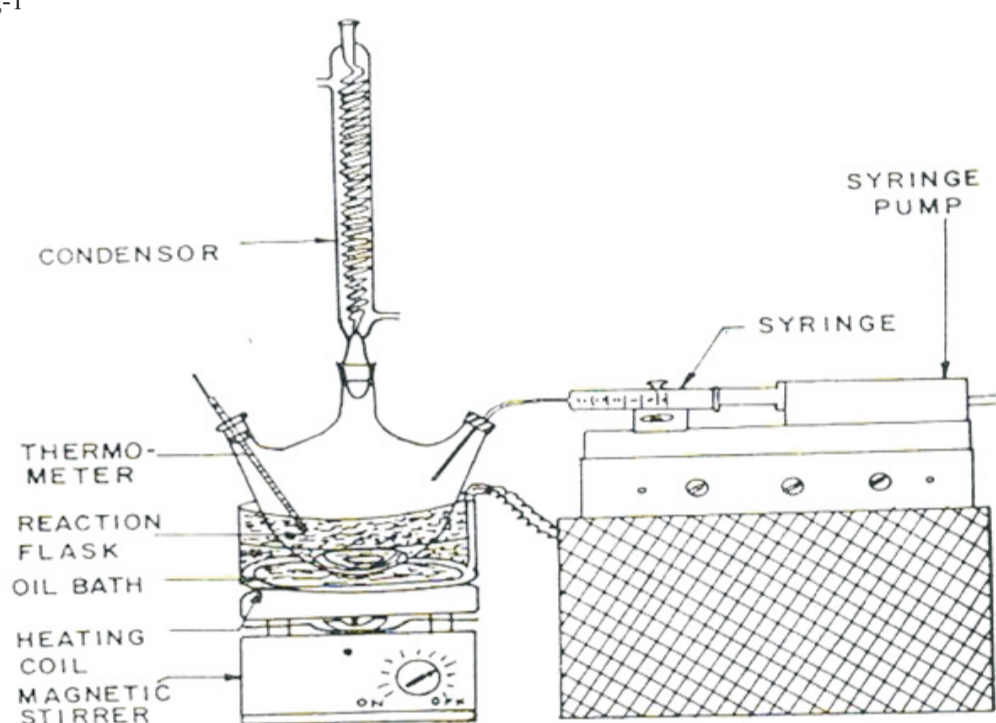
Liquid Phase reaction for oxidation of phenol:

In the present study the following catalyst are used NH₄-Y, HUSY-1, HUSY-2, HUSY-3 samples are used for phenol oxidation with H₂O₂ as oxidising agent in liquid phase reaction.

Reaction Composition;

catalyst used in each reaction is 200mg, Reaction condition,
 Phenol mole = 5, catalyst used in each reaction = 200mg, Phenol = 1 gm, H₂O₂ 30% = 1.2ml
 H₂O₂
 Solvent used for sample NH₄-Y = 20 ml of water, Temperature of reaction = 85°C.
 Apparatus used for liquid phase reaction for oxidation of phenol is shown in Fig-1

Fig-1



This total mixture was taken inside the triple necked 100ml capacity capacity of round bottom flask as shown in fig-1. This flask is put into the oil bath at temperature 85°C one end of the condenser is inserted in to its vertical mouth and cold water is circulated inside the condenser to avoid the loss of water at that temperature. The thermometer was inserted through the rubber cork in its second mouth. When the temperature of the mixture rises to 85°C then phenol was inserted in the three necked bottle through its third mouth by the syringe as shown in fig-1. The mixture is stirred during the course of reaction by using magnetic stirrer apparatus and magnetic needle. The products are collected by the syringe after required time interval and are analysed by using G.C. analysis. From the result of the analysis it was clear that the catalytic activity of Ti- treated sample for oxidation of phenol was 56.4% greater than the catalyst without Titanium incorporation. The result of the G.C. analysis is shown in the table -2. After phenol oxidation the three major products were found to be produced. These products as per G.C. analysis were Benzo-quinone, Catechol and hydroquinone. Which supports the frame incorporation of the titanium of the catalyst. The product Benzoquinone was formed comparatively in small amount as compared to catechol and hydroquinone. The phenol itself was hydroxylated to form catechol and hydroquinone.

Reaction Mechanism: Fig-1

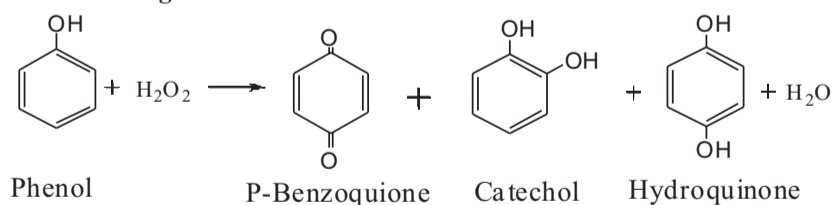


Table-1
Preparation of different Ti- USY samples used for phenol oxidation in liquid phase reaction.

S. N.	Name of the sample	Steaming temperature	Ion Exchange with 2N NH ₄ NO ₃	Calcined at 500 ⁰ C	IonExch. with 0.001NH Cl	Mol.fraction of K ₂ TiO(C ₂ O ₄) ₂ 2H ₂ O and temp.of tretment
1	NH ₄ -Y original sample	-	-	-	-	-
2	H-USY- 1	550 ⁰ C	3times	4 times	yes	0.06, 100C
3	H-USY- 2	550 ⁰ C	3times	4 times	Yes	0.08, 100 ⁰ C
4	H-USY- 3	550 ⁰ C	3times	4 times	yes	0.1, 100 ⁰ C

The catechol was formed on the surface of the zeolite due to its surface activity, where as hydroquinone was formed inside the channels of the zeolite. Hence in initial 0.5h The percentage of catechol formed as a product was more than Hydroquinone. There after the surface activity of the catalyst was practically Stopped. The change in the surface activity of the catalyst was either by catechol itself or by secondary products formed as a result of the hydrogen peroxide with dihydroxyBenzene.

Table-2 Phenol oxidation with H₂O₂ and its products formed. Temp. of reaction=850C, Solvent used Water.

S. N.	Name of the sample	Time on stream in hours	%conversion	% B.Q.	%H. Q.	%catechol
1	NH ₄ -Y original sample	1h	2.2	21.18	26.17	52.65
		1 ½ h	2.46	20.08	56.22	34.7
2	H-USY- 1	1h	43.6	2.64	52.34	45.12
		1 ½ h	51.33	2.19	56.34	41.46
3	H-USY- 2	1h	47.9	0.41	44.24	54.47
		1 ½ h	58.648	0.31	48.41	50.39
4	H-USY- 3	1h	49.8	1.68	56.2	42.03
		1 ½ h	60.02	1.41	58.4	40.08

The hydroquinone formation was not affected as it was mainly produced inside the zeolite channels. Hence after 0.5h The formation of hydroquinone was more than the catechol as shown in the table-2

Conclusions:

1, The substitution of Ti at the framework location of the H- USY Zeolites was confirmed by the phenol. Oxidation as per the reported method as the results of the reaction are matching with it (2) Succeed in framework incorporation of Ti in to the modified H-USY zeolites.

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