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FTIR SPECTRA OF ADSORBED PYRIDINE ON H- USY-550-700 ZEOLITE AND STUDY OF METHYLATION OF O-TOLUIDINE OVER IT.

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Abstract:

The methylation of *o*-toluidine on USY zeolite- is very complex and consisting of both parallel combination of *N* alkylation and *C* alkylation together. The study of effect of different modification of synthesized zeolite on the chemical reaction is studied in the present paper. The USY zeolite is highly stable .For its preparation, synthesized Na -Y zeolite is unstable at higher temperature and under hydrothermal reaction conditions hence its modification is necessary. This zeolite is ion exchanged to convert into NH4-Y using reflux method at 1000C with Ammonium Nitrate solution then filtered, washed with hot deionized water, several times to remove all the traces of NO3 from it , The sample prepared.is then dried at 1000C for 12h. The sample is further stabilized by treating carefully under controlled hydrothermal conditions at 550OC for 4h and then gradually cooling at the rate of 20C/min. carefully to obtain the final product. and it is calcined it at 5000C,The process are repeated three times to convert it in to highly crystalline high silica H-Ultra stable-Y zeolite. The sample H-USY is then further treated carefully under controlled hydrothermal conditions at 700OC for 4h and then gradually cooling at the rate of 20C/min. carefully to obtain the final product-USY-550-700. After each steam treatment the samples are ion exchanged thrice with NH4NO3 as per the above procedure. The USY-550-700 final sample is used for FTIR Spectra of adsorbed pyridine to study the type of acidity produced on the sample prepared. This sample is also tested in the chemical reaction as a catalyst to study the effect of acidity developed on it in the chemical reaction. The study of methylation of *O*-toluidine by methanol at different temperatures over the sample USY-550-700. produced..

KEY WORDS:

(1) controlled Steam chamber(2) Synthesized Faujasite Na-Y zeolite

INTRODUCTION

What are Zeolites?

Zeolites are crystalline hydrated aluminosilicates having rigid three dimensional infinitely extended framework structure. It encloses the cavities and channels of molecular dimensions . The framework structure contains corner sharing of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral linked through common oxygen atoms as the primary building units. The general empirical crystallographic unit cell formula of zeolite is expressed as

$M_x/n[(\text{AlO}_2)_x(\text{SiO}_2)_y]z\text{H}_2\text{O}$

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where

M= charge compensating cat ions of valency.

x and y represents the no. of moles of SiO_2 & AlO_2 where y \propto x and z= no. of water molecules.

Experimental: The 10g of Na-Y is added in to 200 ml 2N NH_4NO_3 i.e. 20ml of solution for 1gm of sample. This Solution is taken in a round bottom flask. This mixture is heated at 1000C for ion exchange it by stirring the mixture for 16 h by using reflux method. The sample is then filtered, washed repeatedly with hot de-ionized water till it is free from the traces of nitrate ions and dried at 1000C over night, the above procedure is repeated several times to obtain more than 90% of $\text{NH}_4\text{-Y}$ by the above method. As Sodium is added to the zeolite it reduces all its acid sites. This effect of sodium poisoning is 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 and found to reduce the catalytic activity of the zeolite. In view of this report, Na-Y is converted into $\text{NH}_4\text{-Y}$. But still It is used in the Synthesis of zeolite, because it can be easily ion exchanged with any of the metal. This sample is calcined at 500oC over night and final produt H-Y Zeolite is used for hydrothermal treatment at two different temperatureone after the other. As Most of the zeolites are very unstable and lose their catalytic activity and stability easily under the severe conditions of catalytic reactions temperature and in hydrothermal conditions. Due to large dealumination of zeolite framework in the reaction Its sturecture gets collapsed. To overcome this problem synthesized zeolites are dealuminated in controlled manner. The H -Y zeolite prepared is treated carefully under controlled steam in the cylindrical reactor by keeping the sample in the silica sample holder to increase hydrothermal severity at 550 OC for 4 h. There after the sample is kept for cooling very slowly till its temperature reaches to 1000C then the steam passing over the sample was stopped, it takes about 3h to reach to 1000C from 5500C temperature. The sample holder is taken out of the reactor at a temperature about 50-600C. Then it is transferred in to the conical flask containing 2N NH_4NO_3 solution in proportionate to about 20ml for 1gm of the sample. All the samples prepared are ion exchanged with 2N NH_4NO_3 as per above procedure and finally sample is calcined at 500 OC to obtain H-USY. This zeolite H-USY is further dealuminated under carefully controlled steam in the cylindrical reactor to increase hydrothermal severity at 700 OC for 4 h, in succession by using the previous sample as the mother sample for the next sample. After hydrothermal treatment at each temperature interval the samples are ion exchanged with 2N NH_4NO_3 as per the above procedure and finally sample is calcined at 500 OC to obtain H-USY-550-700 zeolite. The above condition of the samples is standardized. The ir spectroscopy of adsorbed pyridine has been used as a characteristic tool to detect and measure the presence of Bronsted and Lewise acid centers on the H-USY 550-7000C solid surfaces. The ir bands are of interest to study the C-H and N-H stretching as well as the C-C and the C-N stretching in the pyridine ring. n. The FTIR spectra of adsorbed pyridine at 1000C, 2000C, 3000C, 4000C on the samples listed in the table-1 are depicted. The spectra were normalized with respect to 5 mg/cm² weight of the wafer and the relative concentration of Bronsted and Lewis acid sites are presented in the table-2

Observations:

- 1) Acid site density decreases monotonically with the severity of hydrothermal treatment due to hydroxylation and dealumination.
- 2) Hydrothermally dealuminated : H-Y(USY) samples have greater number of Bronsted acid sites than Lewis acid sites at all higher temperatures other than at 1000C
- 3). Most of the zeolites are unstable and lose their catalytic activity under the severe conditions of catalytic reactions and hydrothermal conditions at high temperatures. By large dealumination of zeolite framework hence leads to collapse of zeolite structure. To overcome this problem synthesized zeolites are dealuminated in a very controlled manner under hydrothermal conditions Which is found to be a best method for increasing catalytic activity as well as stability of the zeolite-Y

Wave number Cm-1 FTIR Spectra of adsorbed pyridine on USY-550-700 Sample. Zeolite-Y due to its 3D pore structure is maximum used in the USY form in production of petrochemicals. Such zeolites are called as ultra stable Y zeolite. The zeolite fujasite type-Y can be easily synthesized in the laboratory and in the industry. unit cell of Y type zeolite is cubic with a large dimension of 250A and contains 192(Si, Al) O₄ tetrahedra, and has quite stable and rigid framework structure with largest void space, which amounts to be about 40% by volume of the calcined crystal.

Fig-1

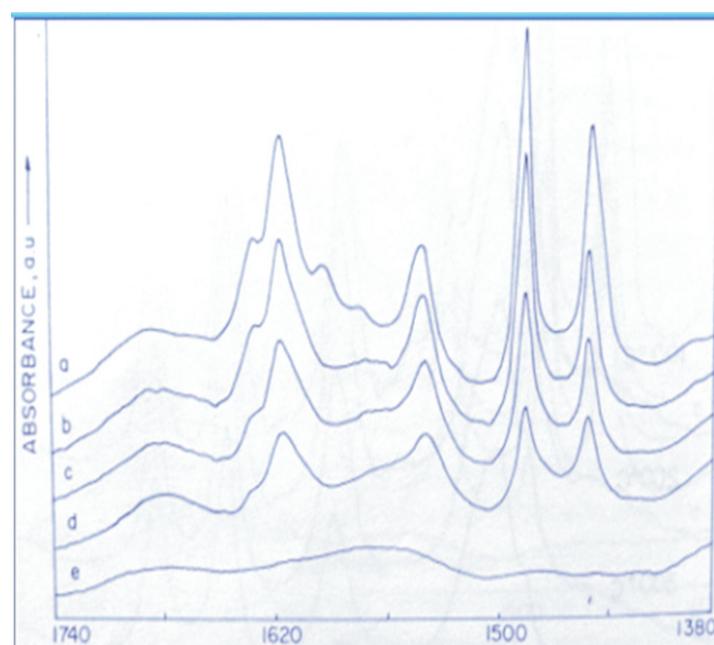
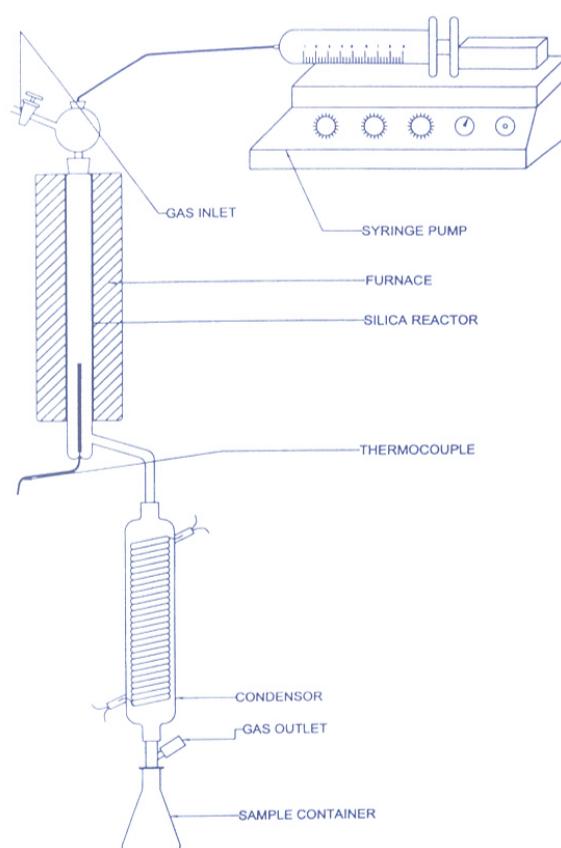


Fig-2



Gas phase reaction apparatus used to carry out the gas phase reaction is as shown in fig-2.
 Table-1 Influence of reactant mol ratio (methanol : O-toluidine) on O-toluidine conversion and product distribution and yields over USY-550-700,
 Reaction conditions; temp.3500C, Time on stream=2h WHSV=1h-

Mol ratio(O-toluidine:NH ₃ OH)	10	7	5	2	1	0.5	0.2
o-toluidine conversion(wt%)	100	100	100	99.9	99.9	46.2	24.8
Selectivity(%)	1.1	0.5	1.3	1.6	0.8	1.9	1.6
Lower boilers, Aniline	0	0	0	0	0	4.8	10.1
N,N-dimethyl -O-toluidine	7.7	6.1	9.8	8.1	37.7	0	0
N,N-dimethyl xylidine	58.8	55.9	0.2	0.1	0.2	0	0.1
N-methyl-O-toluidine	0.7	0.5	0.2	6.4	0.1	0.02	0
2,4-xylidine	0.8	1.1	39.6	37.4	42.3	83.9	83.3
N,N-dimethyl-2,4,6-trymethyl aniline	8.8	8.6	0.2	0.07	0.09	0.01	0.02
N-methyl-xylidine	14.9	17.5	2.5	10.5	0.1	0.03	0
2,4,6--trymethyl aniline.	1.3	2.4	39.3	32.3	6.3	7.2	2
Others	5.6	7.2	6.8	3.4	12	1.9	2.8

The reaction consisting of parallel C-alkylation and N-alkylation and net work of consecutive reactions involving both C-and N-dialkylation, disproportion, and N to C transformations. The mechanism of methylation of O-toluidine over Bronsted and Lewis acid sites over different types of USY can be represented as follows.*

1)O-toluidine alkylation over Bronsted and Lewis acid sites:

Toluidine being a stronger base than methanol, is preferentially adsorbed on Lewis acid sites, while oxygen of methanol forms strong hydrogen bonds with Bronsted acid protons. The methyl carbocation formed by protonation of methanol on Bronsted acid sites reacts with the conjugate base of Bronsted acid site giving ether of carbocation on the surface. Aniline preferentially gets adsorbed on the Lewis sites through loan pair of electrons on aniline group, then loses a proton to balance the positive charge developed on the Nitrogen. The high electro negativity of oxygen in either linkage develops a partial positive charge on alkyl side chain. This initiates the heterolytic cleavage of polar O-C bond and the shift of Nitrogen.

Table-2 : Influence of WHSV on O-toluidine conversion and product Selectivity over USY-550-700, Reaction condition; Temp.3500C, Time on stream= 2h=const. Feed O-toluidine : methonal=1:2,

WHSV(h ⁻¹)	5	3.3	2	1	0.2
O-toluidine conversion(wt%)	83.3	92.1	95.1	99.9	83.3
Selectivity %	0.4	1.3	0.9	1.6	3.9
Lower boilers					
<i>N,N</i> -dimethyl- <i>o</i> -toluidine	3	2.1	2.1	1.1	0.2
<i>N,N</i> dimethyl xylidine	0.02	0.2	0.04	0.1	0.4
<i>N</i> -methyl- <i>o</i> -toluidine	25	12.9	7.8	6.4	1.2
2,4-xylidine	35.5	37.7	38.8	44.4	52.6
<i>N,N</i> -dimethyl 2,4,6--try methyl aniline.	0.1	1.2	0.6	0.07	0.2
<i>N</i> ,methyl -xylidine	20.2	25.6	23.9	10.5	0.3
2,4,6--try methyl aniline.	13.9	16.9	22.8	32.3	33.5
others	1.8	2.1	3	3.4	7.7

**Table-3
Influence of Time on stream on O-toluidine conversion and product yields over USY-550-700, Reaction condition; Temp.3500C, WHSV 1h-1 , Feed O-toluidine : methonal=1:2,**

time on stream	5h	3.3h	2h	1h	0.2h
O-toluidine conversion(wt%)	83.3	92.1	95.1	99.9	83.3
Selectivity %	0.4	1.3	0.9	1.6	3.9
Lower boilers					
<i>N,N</i> -dimethyl- <i>o</i> -toluidine	3	2.1	2.1	1.1	0.2
<i>N,N</i> dimethyl xylidine	0.02	0.2	0.04	0.1	0.4
<i>N</i> -methyl- <i>o</i> -toluidine	25	12.9	7.8	6.4	1.2
2,4-xylidine	35.5	37.7	38.8	44.4	52.6
<i>N,N</i> -dimethyl 2,4,6--try methyl aniline.	0.1	1.2	0.6	0.07	0.2
<i>N</i> ,methyl -xylidine	20.2	25.6	23.9	10.5	0.3
2,4,6--try methyl aniline.	13.9	16.9	22.8	32.3	33.5
Others	1.8	2.1	3	3.4	7.7

Fig-3

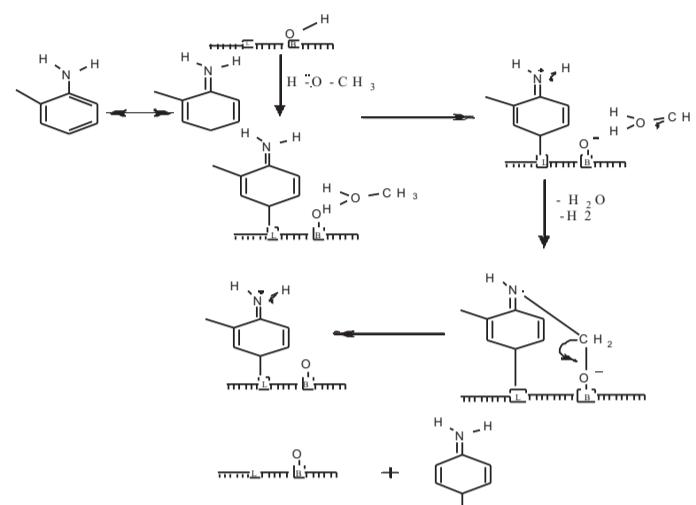
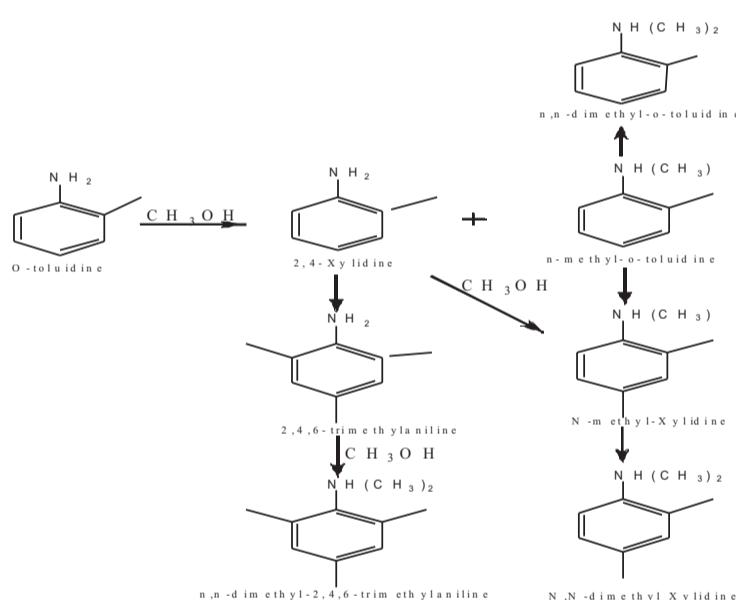


Fig-4



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