Vol 2 Issue 11 May 2013

Impact Factor : 0.1870

ISSN No :2231-5063

Monthly Multidisciplinary Research Journal

GoldenResearch Thoughts

IMPACT FACTOR : 0.2105

Welcome to ISRJ

RNI MAHMUL/2011/38595 **ISSN No.2230-7850**

Indian Streams Research Journal is a multidisciplinary research journal, published monthly in English, Hindi & Marathi Language. All research papers submitted to the journal will be double - blind peer reviewed referred by members of the editorial Board readers will include investigator in universities, research institutes government and industry with research interest in the general subjects.

International Advisory Board

Editorial Board

Address:-Ashok Yakkaldevi 258/34, Raviwar Peth, Solapur - 413 005 Maharashtra, India
Cell : 9595 359 435, Ph No: 02172372010 Email: ayisrj@yahoo.in Website: www.isrj.net

Golden Research Thoughts
Volume 2, Issue. 11, May. 2013
ISSN:-2231-5063
Available online at www.aygrt.isrj.net

ORIGINAL ARTICLE

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

K.U.GORE

Head ,Department of Physics, NSB college, Nanded, Maharashtra ,India.

Abstract:

The methalation of o-toulidine 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 zewolite 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 2oC/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 2oC/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-toludine by methenol at different temperatures over the sample USY-550-700. produced..

KEYWORDS:

(1) controlled Steam chamber(2) 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

$M\ x/n[\ (AlO2)x\ (SiO2)y]\ zH2O$

Title : FTIR SPECTRA OF ADSORBED PYRIDINE ON H- USY-550-700 ZEOLITE AND STUDY OF METHYLATION OF O-TOLUIDINE OVER IT. Source:Golden Research Thoughts [2231-5063] K.U.GORE yr:2013 vol:2 iss:11

where

M= charge compensating cat ions of valency.
x and y represents the no. of moles of SiO2 & AlO2j where y≥x and z= no. of water molecules.

Experimental: The 10g of Na-Y is added in to 200 ml 2N NH4NO3 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 NH4-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 NH4-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 NH4NO3 solution in proportionate to about 20ml for 1gm of the sample. All the samples prepared are ion exchanged with 2N NH4NO3 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 NH4NO3 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 band s 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 at1000C, 2000C, 3000C,4000C on the samples listed in the table-1 are depicted. The spectra were normalized with respect to 5 mg/cm2weight 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-550-700Sample. Zeolite-Y due to its 3D pore structure is maximum used in the USYform 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

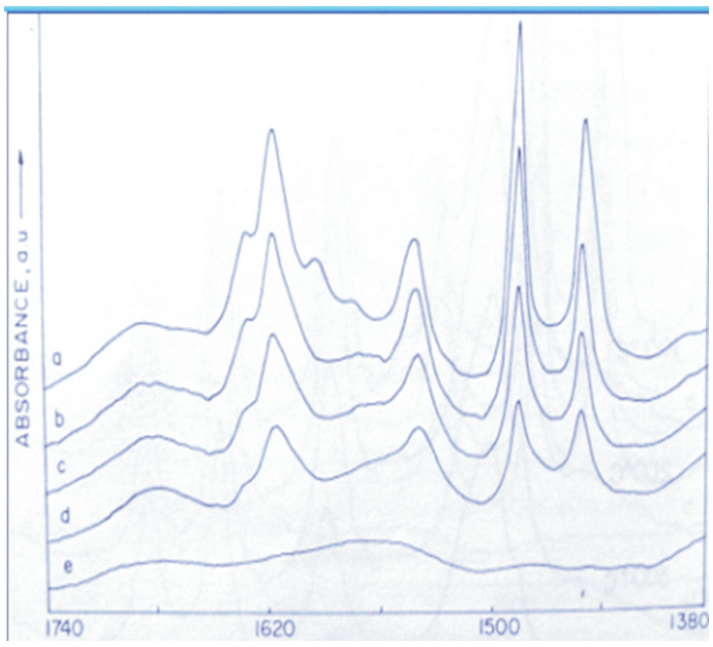
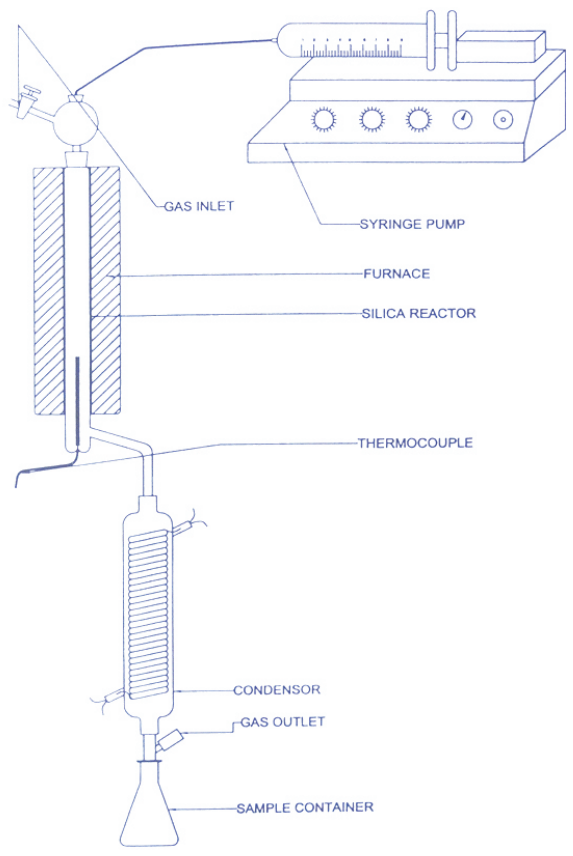

ABSORBANCE, a u
a
b
c
d
e
1740
1620
1500
1380

Fig-2


GAS INLET
SYRINGE PUMP
FURNACE
SILICA REACTOR
THERMOCOUPLE
CONDENSOR
GAS OUTLET
SAMPLE CONTAINER

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 (methnol : O-toulidine) 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_3OH)	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 methonal, is preferentially adsorbed on Lewis acid sites, while oxygen of methonal forms strong hydrogen bonds with Bronsted acid protons. The methyl carbo-cation formed by proto-nation of methonal 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 looses 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 hetrolytic 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 % *Lower boilers*	0.4	1.3	0.9	1.6	3.9
N,N-dimethyl-o-toluidine	3	2.1	2.1	1.1	0.2
N,N dimethyl xylidine	0.02	0.2	0.04	0.1	0.4
N-methyl-o-toluidine	25	12.9	7.8	6.4	1.2
2,4-xylidine	35.5	37.7	38.8	44.4	52.6
N,N-dimethyl 2,4,6--trymethyl aniline.	*0.1*	*1.2*	*0.6*	*0.07*	*0.2*
N,methyl -xylidine	20.2	25.6	23.9	10.5	0.3
2,4,6--trymethyl aniline.	13.9	16.9	22.8	32.3	33.5
others	1.8	2.1	3	3.4	7.7

Table-3
Influnce 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 % Lower boilers	0.4	1.3	0.9	1.6	3.9
N,N-dimethyl-o-toluidine	3	2.1	2.1	1.1	0.2
N,N dimethyl xylidine	0.02	0.2	0.04	0.1	0.4
N-methyl-o-toluidine	25	12.9	7.8	6.4	1.2
2,4-xylidine	35.5	37.7	38.8	44.4	52.6
N,N-dimethyl 2,4,6--trymethyl aniline.	0.1	1.2	0.6	0.07	0.2
N,methyl –xylidine	20.2	25.6	23.9	10.5	0.3
2,4,6--trymethyl aniline.	13.9	16.9	22.8	32.3	33.5
Others	1.8	2.1	3	3.4	7.7

Fig-3

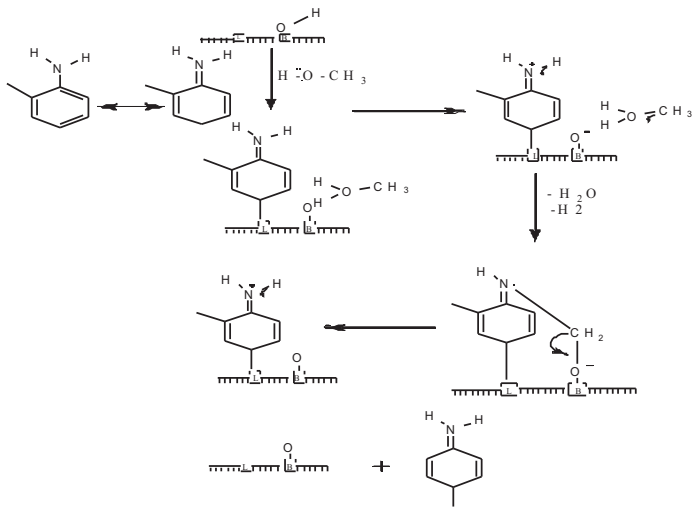
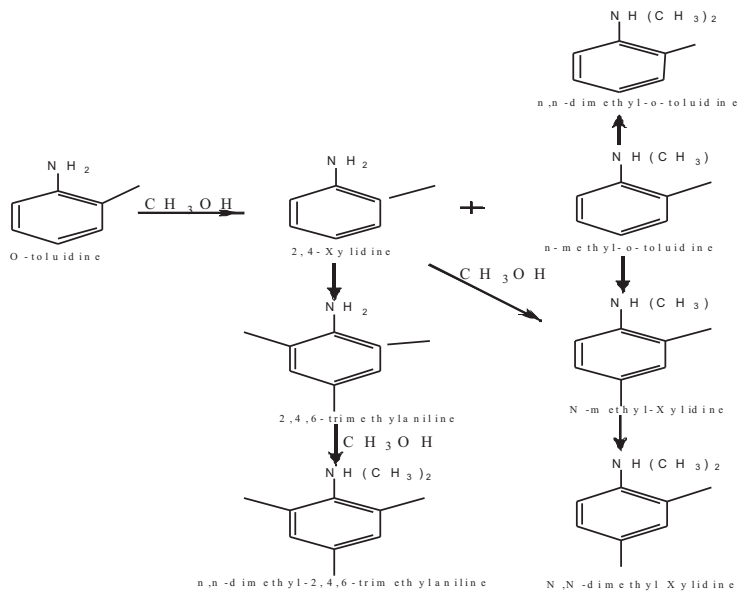


Fig-4



ACKNOWLEDGEMENT:

1)Thanks to the director of National chemical research laboratory, Pune for providing the research facility in NCL.
2) Thanks to the Dr. S.G. Hegde Scientist in National chemical research laboratory, Pune for providing his valuable guidance in my stay NCL.

REFERENCES:

1) Bo Wang,† Chul Wee Lee, Tian-Xi Cai,† and Sang-Eon Park*2. M. A. Sanchez-Castillo, N. Agarwal, C. Miller, R. D. Cortright, R. J. Madon, and J. A. Dumesic, 056 Bull. Korean Chem. Soc. 2001, Vol. 22, No. 9 Notes

2) M. A. Sanchez-Castillo, N. Agarwal, C. Miller, R. D. Cortright, R. J. Madon, and J. A. Dumesic, J. Catal., 205 (2002) 672.
3) Conghua Liu a,b,∗, Xionghou Gaob, Zhongdong Zhang b, Haitao Zhang b, Shuhong Sunb, Youquan Denga Applied Catalysis A: General 264 (2004) 225–228
(4)Joachim Klass, Glinter Schulz-Ekloff and Nils Jager , J.Phys. Chem.B 101 P1305-1311 (1997)
(5) Dr. K.U. Gore, Structural det.and physic. Chem.. studies of zeolites, Ph. D. Thesis,(2002)
(6) Mu Mu htay,Mya MyaOo, World academy of science, Engineering and technology 48,2008
(7) Myat Myat. Ph.D. Thesis Department of Eng. Chemistry, Yangon Technological university Mynmar (2003)
(8) Stefan H.Bossmann et al. and Nicholas J.Turro. Photochem.Photobiol. sci :2003, 2,p-477-486.
(9)Nidhi Dubey et al. Applied catalysis A General303 March2006 p152-157.
(10) Pham T.H. et..al., Studies in surface science and catalysis Vol. 159 p-197-200, 2006 (1990).
(11) Myat Myat. Ph.D. Thesis Department of Eng. Chemistry, Yangon Technological university Mynmar (2003)
(12) Nitin Labhshetwar et.al; and H. haneda. Current Science, Vol.95, No.6, 25 Sep. (2008)
(13)Yangdong Wang, Aimin Zhang ,Qinhue Xu, RanzhangChen , Applied Catalysis A: General 214 167-177 (2001)
(14)conghua Liu, et; Al. Applied catalysis A General264 (2004) p225-228.