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Highlights for review

- ✓ Zeolitic pore formation in montmorillonite upon PDSA treatment.
- ✓ Cycloisomerization of alkynylamide to oxazole is enhanced by zeolitic pore.
- There is a good correlation between VAF and oxazole formed.
 VAF is a term which is a product of acidity and micropore volume.

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Graphical Abstract:



Manifestation of Zeolitic pore characteristics of modified montmorillonite in oxazole synthesis by

propargylation and cycloisomerization reactions

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Abstract:

Zeolitic micropores are found to be developed on montmorillonite clay by treatment with phenoldisulphonic acid (PDSA). The micropores developed have the ability to enhance the cycloisomerization of the alkynylamide to form oxazole product. Pore characteristics by surface measurement techniques and acidity by pyridine adsorption using FTIR were evaluated. Surface measurements showed significant increase in the surface area, acidity and the micropore volume but neither of them correlated well with the cycloisomerization activity. Variation in Brønsted and Lewis acidity and pore volume by surface coverage using Brønsted (B) and Lewis (L) acid compounds, caused variation in cycloisomerization activity. Best correlation with the amount of oxazole formed was observed when volume accessibility factor (VAF), a product of micropore volume and ratio of B to L aciditywere considered. Based on this, a reaction scheme for cycloisomerization is proposed involving both B and L sites within themicropores.

Keywords: montmorillonite, phenoldisulfonic acid, propargylation, cycloisomerization, zeoliticpore.

1. Introduction:

Nucleophilic substitution and cyclization are two major reactions adopted in chemical industries[1-4]. Cycloisomerization reactions are important routes for the synthesis of heterocyclic compounds. These

compounds being specialty chemicals find applications in pharmaceutical industry[4-6].Generally, heterocyclic compounds are prepared by condensation of amines and carbonyl compounds such as acid, ester, anhydrides and acid chloridesin the presence of homogeneous catalysts like, HCl, H₂SO₄, H₃PO₄, TFA, p-TSA, BF₃, acetic acid and pyridine in acetic acid[7-10].Metal complexes such as Cp*RuCl(µ2-SMe)₂RuCp*Cl]/AuCl₃/NH4BF₄[11] and Zn(OTf)₂/ pRuPPh₃(CH₃CN)₂PF₆[12] have also been tried to catalyze the cycloisomerization.

More powerful and useful transformations are possible when nucleophilic substitution and cyclization are combined in a one-pot procedure. Propargylic substitution and subsequent cycloisomerization are good examples of such transformations[1,13-16].

Solid acid catalysts are widely used in industrial practices for their easy handling, less cost, eco-friendly and easy modification[5,17].In recent times, inorganic solid acid-catalyzed organic transformations are gaining much attention due to the proven advantage of heterogeneous catalysts, like simplified product isolation, mild reaction conditions, high selectivity, ease in recovery, reuse of the catalysts and reduction in the generation of waste by products[18–20]. In this context, we have been investigating various industrially important organic reactions aimed at adopting solvent-lesssingle step techniques and replacing toxic and corrosive reagents with innocuous chemicals in presence of environmentally benign solid acid catalysts[5].Over the past few years, the modified solid acids have been receiving much attention, among other solid acids such as zeolites, heteropolyacids,ion exchange resins andmetal oxides, due to their superior catalytic activity for hydrocarbon conversions[3, 21, 22].

Emphasis of preset work is on to modify the montmorillonite clay by treatment with phenoldisulfonic acid (PDSA) and with an objective to study its performance as a bi-functional catalyst for propargylation and subsequent cycloisomerization to form substituted oxazole product.

2. Experimental

2.1Catalyst preparation

Montmorillonite clay obtained from Bhuj area, Gujarath was supplied to us by Ashapura Group of Industries, India[23]. The parent clay was converted to homoionicby treatment with 1M NaCl solution, and idealized structural formulaSi₄[Al_{1.432}Fe_{0.416}Mg_{0.266}] $O_{10}(OH)_2Na_{(0.318)}$ was evaluated using ICP elemental analysis. This clay sample was used further for treatment with PDSA to improve the surface area and acidity.

The modification was done by following reported procedure [23-25], 100ml of 1M PDSA solution was taken in 250ml round bottom flask. In this,10g of montmorillonite clay was dispersed completely and the mixture was subjected to microwave irradiation for 30min at 110^oC by applying 800 watt energy.After cooling, the mixture was centrifuged and the solid was repeatedly washed to completely remove PDSA, dried at 120^oC ground and then sieved with mesh size 0.075mm. Similarly, samples were also prepared by treating with 0.1M and 0.5M PDSA. The treated samples were designated as 0.1PDSA, 0.5PDSA and 1PDSA.

The 1PDSA-clay was further loaded with 5-20 % PDSA by wet impregnation method[26]. The procedure briefly involved dispersing 5 g of the 1PDSA sample in 100 ml of water with required amount of PDSA dissolved. The mixture was stirred using a magnetic stirrer overnight, water was evaporated on a hot plate to get the PDSA-loaded solid catalyst samples. These were designated as 1PDSA(5%), 1PDSA(10%), 1PDSA(15%) and 1PDSA(20%).

2.2 Characterization

The prepared catalysts were characterized using pyridine-FT-IR, NH₃-TPD, XRD, SEM and BET surface area and Magic Angle Spin ²⁷Al - NMR.

Acidity was measured by FT-IR spectroscopy using pyridine as probe molecule. All the samples were activated by degassing at 120° C for 2 h and then saturated with pyridine. The catalyst samples were then evacuated at 115° C for 30min to remove physisorbed pyridine. FT-IR spectra of the samples were then

recorded in the range 1400–1600 cm⁻¹ using IRAffinity-1 spectrophotometer having resolution of 4 cm⁻¹ with 40 scans[7,23].

Surface area and porosity measurements were done using Quantachrome Nova-1000 surface analyzer under liquid nitrogen temperature. N_2 adsorption-desorption isotherm measurements at -193 0 C were carried out in order to study the evolution of porosity and textural properties of the acid treated clay samples. Pore size distribution was calculated from adsorption data by inferring pore geometry and using deBoer t-plot and BJH method[9, 23].

Structural integrity of the catalyst samples after the reaction was checked by powder XRD. The data were recorded by step scanning at 2θ = 0.020⁰ per step from 3^oto 12^o on Shimadzu MAXima_X XRD-7000 X-ray diffractometer with graphite monochromatized Cu K α radiation (λ =1.5406 Å)[2,3].

The NH₃-TPD measurements were performed on the catalyst samples. In a typical experiment, 0.1 g of catalyst was taken in a U-shaped, flow through, quartz sample tube. Prior to measurements, the catalyst was pretreated inHe (30 cm³/min) at 150 $^{\circ}$ C for 2 h. A mixture of NH₃ in He (10%)was passed (30 cm³/min) at 60 $^{\circ}$ C for 30 min. Then, the sample was subsequently flushed with He(30 cm³/min) at 60 $^{\circ}$ C for 1 h.The TPD measurements were carried out in the range 100–700 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min. Ammonia concentration in the effluent was monitored with a gold-plated, filament thermal conductivity detector[24,27].

Morphology of parent, 1PDSA-clay and 1PDSA (5%) clay were recorded using JEOL JSM-6490 Scanning Electron Microscope (SEM) under high vacuum mode.

²⁷Al-MAS NMR pattern were recorded using single pulse Jeol ECX-2 400MHz solid state magic angle spin nuclear magnetic resonance spectrometer with 4mm rotor of spinning speed 10⁴. The standard used in the measurement was Aluminium nitrate.

The amount of interlayer aluminium was estimated by the method reported elsewhere [27]. It involved stirring 2 g of clay sample with 0.1M HCl for 60min at 60 $^{\circ}$ C. Then the mixture was centrifuged and the residue was repeatedly washed with deionized water. The centrifugate was used to estimate Al by aluminon reagent method spectrophotometrically using Chemito UV-2100 Spectrophotometer[23,24, 28].

2.3 Catalytic activity

The activity of catalyst samples was studied under microwave irradiation, using microwave lab station for synthesis, "START-S" model from Milestone, Italy, having software which enables the control of reaction mixture temperature with aid of infrared sensor by regulation of microwave power output in such a way that, the reaction mixture was exactly in line with infrared sensor that monitors the temperature. Variable power up to 1200W was applied by microprocessor-controlled single-magnetron system[2,3].

Ten mmol of Propargyl alcohol (PA) and ten mmol of amide were mixed with the catalyst in a microwave reactor vessel with magnetic stirring bar. The vessel was kept in microwave reactor and an initial power of 1200 W was applied for 1 minute to attain the reaction temperature of 150^oC. The reaction temperature was then maintained for 29 minutes to get maximum conversion. The reaction mixture was then cooled for 10 minutes and extracted by stirring with 5 mL of ethanol for 5 minutes and filtered to remove the catalyst. The ethanol extract containing the product and the unused reactants were analyzed using Chemito GC-1000 gas chromatograph with TR-Wax capillary column of length 30m, 0.32mm thickness and 0.55µm internal diameter with flame ionization detector[3,23]. The products were also confirmed by GC-MS.

Catalyst characteristics and activity measurement were performed three times on each sample and the mean of the measurements were used for calculating the standard deviation.



Scheme 1 Reaction between PA and amide to form Oxazole in presence of PDSA-clay.

Oxazole formation involves two steps, first step being condensation between propargyl alcohol and acetamide(propargylation) forming alkynyl amide as primary product. In the second step, primary product on contact with acidic sites gets cycloisomerized to form oxazole as secondary product.

3. Results and discussion:

3.1PDSA treatment of montmorillonite; zeolitic pores

Surface measurement values and other properties of the catalyst samples are given in Table 1.

Table.1 CEC, surface area, average pore diameter and micropore volume of unmodified, Al-clay and PDSA treated clays.

Clay samples	CEC	\mathbf{S}_{BET}	APD	\mathbf{V}_m	\mathbf{V}_{tm}	Interlayer
	(meq/g)	(m^2/g)	(Å)	(cm^3/g)	(cm^3/g)	Al (meq/g)
Untreated clay	0.83	27	50.3	0.011	0.067	-
Al-clay	0.83	27	50.3	0.011	0.067	0.83
0.1 PDSA	0.79	109.14	44.13	0.026	0.074	0.49
0.5 PDSA	0.75	196.09	33.34	0.064	0.132	0.62
1PDSA	0.71	276.44	26.04	0.203	0.14	0.70

*S_{BET}-BET surface area, APD-average pore diameter, V_m - total pore volume, V_{tm} - micropore volume by t-plot method.

Untreated and Al- exchange clays had similar physico-chemical characteristics, a CEC of 0.83-0.85meq/g, surface area of 28-32 m²/g, average pore diameter (50.27 Å) and micropore volume (0.011 cm³/g) with the exception in the interlayer Al content. On the other hand, PDSA treatment of montmorillonite clay samples showed differences in physico-chemical characteristics such as (i) surface area, (ii) pore sizeand pore volume (iii) CEC and (iv) interlayer Al and acidity in relation with both parent and ion-exchange clay samples. It is reported that organic acids and chelating agents remove the structural Al, Fe and Mg from the octahedral layer of the parent clay resulting in micropores onthe clay surface enhancing its surface area[23,24]. The structural elements get dislodged by forming complex species which get hydrolyzed on subsequent washing and release a part of the cations into the interlayer. The hydrated Al and Fe ions, which displace the sodium ions in the interlayer act as acid sites, thus enhancing the acidity[23,24]. Removal of structural elements would create voids in the structure resulting inincrease in microporosity, micropore volume and surface area. It is known that when structural aluminium is

removed, there is no reduction inCEC, while the removal of isomorphously replaced Fe and Mg causes a reduction in CEC.

Fig. 1 (a) and (b) show the BJH curves and the t-plots for the untreated and PDSA treated clays at different concentrations, respectively. The two plots reveal an increase in surface area, formation of micropores and decrease in average pore diameter compared to untreated clay.

The ²⁷Al MAS NMR spectra of the clay samples treated with PDSA of different concentrations. Decrease in intensity of chemical shift value at 6ppm with respect to standard[31] indicates the removal of octahedral aluminium from the treated clay samples as the concentration of PDSA increases from 0.1M to





Fig 1(a) and (b) BJH curves and t-plots of untreated, 0.1, 0.5 and 1M PDSA treated montmorillonite clay.

3.1.1 Acidity: Acidity was measured by FTIR technique using pyridine as probe molecule. The results are shown in Fig. 2. Treatment with increased amounts of PDSA exhibited an increase in the Brønsted (1545 cm⁻¹) and Lewis acidity (1445 cm⁻¹) of the clay samples. This is attributed to the removal of increased amounts of structural Al from the octahedral layer, part of them replacing the interlayer Na ions [23,24]. Clay sample treated with 1 M PDSA had almost the same acidity as Al-clay.



Fig.2 FT-IR spectra of adsorbed pyridine on (a) Al-clay, (b) 1PDSA, (c) 0.5 PDSA and (d) 0.1 PDSA.

3.2 Propargylation of acetamide under microwave heating

The reaction conditions were optimized by varying parameters like reaction time, temperature, mole ratio of reactants and catalyst amount for the propargylation and cycloisomerization of PA with acetamide (AA). Maximum conversion was observed at mole ratio of PA:AA of 1:2 with 1PDSA-clay. Under the experimental conditions, interphase and intraparticle heat and mass transfer as calculated using Koros-Novak, Mears and Weisz- Prater criteria were negligible [31, 32].

3.2.1 Effect of catalyst amount.

In the absence of catalyst, no reaction was observed between PA and AA. Fig. 3 shows conversion of PA to the products alkynyl amide and oxazole under the specified conditions when the catalyst amount was varied from 0.1 to 1 g. The product formed increased with the increase in the catalyst quantity showing equimolar concentrations of the products when the catalyst used was 0.6 to 0.7 g. With lower catalyst amount, (<0.3 g), lower conversion of PA was observed; most of the conversion was towards the condensation product (alkynylamide) with less yield of cyclized product (oxazole). Increase in the

catalyst amount to 1 g showed an increase in PA conversion to 65% comprising of 40% oxazole and 25% alkynyl amide. It could be clearly seen that the formation of the condensation product alkynyl amide is favored at lower catalyst amounts and the cycloisomerized oxazole formation enhanced at higher catalyst amounts.



Fig .3 Effect of catalyst amount on the propargylation and cycloisomerization of PA and AA Reaction conditions: reaction time; 60 min, reaction temperature 150°C; reactants molar ratio PA:AA; 1:2.

3.2.2 Effect of temperature.

Fig.4 shows that temperature had a significant effect on the PA conversion which ranged from 11% to 70% when the temperature is raised from 80 °C to 170 °C. At lower temperature of 80°C, 11% of PA conversion was observed with 9% alkynyl amide, rest being oxazole. Further increase in temperature showed increase of PA conversion with formation of equimolar amounts of the products at 140°C. Beyond 140 °C the amount of alkynyl amide decreased with proportionate increase in the oxazole. It appears that the condensation is more selective to form alkynyl amide at lower temperature and cyclisation of alkynyl amide to form oxazole predominates at higher temperatures.



Fig .4 Effect of temperature on the propargylation and cycloisomerization of PA and AA. Reaction conditions: catalyst amount; 1 g, reaction time; 60min, reactants molar ratio PA: AA; 1:2.

3.2.3 Effect of reaction time.

Reaction time as a function of conversion of PA under optimized reaction conditions are shown in Fig.5. Initially, conversion of PA was observed to be 15%. As the reaction proceeds, the conversion of PA gradually increased reaching a maximum of 65% at 60 min. Further increase in irradiation time, resulted in no significant change in the conversion. At reaction time between 10 and 40 minutes, the reaction mixture was found to contain more amount of alkynyl amide (28%) with 17% oxazole. Further increase in reaction time, resulted in the increase in oxazole amount and at the end of 240 min, the yield of oxazole was nearly 50%, rest being alkynyl amide. Apparently, cycloisomerization to form the oxazole product is facilitated by the surface of the catalyst with progress in time.





3.3 Comparison of PDSA treated and Al-exchange catalyst samples

Reactions were conducted under the chosen conditions which yielded maximum amount of the Oxazole product. This involved use of 1 g catalyst, 150 °C, PA:AA mole ratio of 1:2, reaction time 60 minutes under MW irradiation. Results are given in Table2.

Catalyst	TPD-NH ₃	% PA	%	% yield	\mathbf{V}_{tm}	Average	$\mathbf{S}_{BET}(\mathbf{m}^2/\mathbf{g})$
	(µmol/g)	conversion	Alkynyl	of	(cm ³ /g)	TOF)
			amide	Oxazole		(\min^{-1})	
Al-Clay	250	46	36	10	0.011	0.066	27
0.1PDSA	78	30	18	12	0.026	0.256	109
0.5 PDSA	196	44	20	24	0.064	0.256	196
1 PDSA	236	65	25	40	0.203	0.282	276
BEA	500	70	15	55	0.305	0.432	552
1PDSA (5%)	228	67	21	46	0.104	0.365	213
1PDSA (10%)	248	70	20	50	0.064	0.348	146
1PDSA (15%)	262	60	28	32	0.019	0.154	106
1PDSA (20%)	232	48	36	12	0.004	0.10	70

Table2 Comparison of TPD-NH₃ acidity, conversion of PA and yield of products with Al-clay, PDSA treated, BEA zeolite and different PDSA loaded clay catalyst samples.

Reaction conditions: catalyst amount; 1 g, reaction temperature 150° C; reactants molar ratio PA:AA; 1:2, reaction time 60min. *S_{BET}-BET surface area, V_{im}-micropore volume by t-plot method.

It could be seen from Table 2 that the catalytic activity for the conversion of PA increased with the increase in concentration of PDSA used for treatment from 0.1 to 1M. A corresponding increase in the alkynyl amide and the oxazole products was observed. This is attributed to the increase in the acidity of the PDSA treated samples as measured by pyridine FTIR method (Fig 2). Al-clay although had comparable acidity with 1PDSA, showed lower propargylation and cycloisomerization products. The enhanced catalytic activity of 1PDSA having relatively large pore volumes and insignificant cycloisomerized product in the case of Al-exchange clay having very low micropore volume could be attributed to the combined effect of acidity and micropore volume. Further investigation was made to relate the role of micropores and acidity with the amount of oxazole formed.

3.4 Maximization of the oxazole product:

To study the role of Brønsted and Lewis acid sites on the oxazole formation, we impregnated 5 % of PDSA (Brønsted acid) and 5% each of ZnCl₂ and FeCl₃ (Lewis acids) on 10 g of 1PDSA-clay separately. Results are presented in Table 3. The results show that the formation of oxazole decreased on loading with the Lewis acids, ZnCl₂ and FeCl₃, while there was a substantial increase in the formation of oxazole when loaded with 5 % PDSA. Apparently, the Lewis and Brønsted acid centers on the surface are playing an important role in the formation of oxazole. Scanning electron micrographs(Fig.6) show morphological changes after acid treatment in1PDSAclay and its partial surface coverage when loaded with 5% PDSA. Increased loading beyond 15% PDSA on 1PDSA clay showed a decrease in the formation of cycloisomerized product. This is attributed to enhanced coverage of the micropores upon loading with more and more amounts of PDSA. This suggests an increase in Brønsted sites within the pores by the added PDSA, which also accounts for reduction in the pore volume. Apparently, the cycloisomerization requires the presence of both Brønsted and Lewis acids in the micropores formed. The effect of ratio of Brønsted to Lewis acidity and micropore volume on the cycloisomerization was further investigated by correlating the various parameters with the yield of oxazole. Combination of micropore volume and acidity as explained by volume accessibility factor (VAF) was used [23]. Briefly, the term volume accessibility factor is related to the product of micropore volume and acidity. VAF has been used to

explain reactions involving Brønsted and Lewis acids that take place exclusively in micropores. In the present study, cycloisomerization is observed to take place on the clay catalyst surfaces only when micropores which facilitate access to the acid sites are generated. Treatment with organic acids, such as PDSA displaces structural Al atoms in the clay matrix, thus creating micropores which provide access to the acid sites. The factor VAF provides a measure of this accessibility for orientation of the molecules to reach out to the acid sites. It thus determines the ease with which the transformation is brought out within the micropores and aids the molecule to properly extend to reach out to the acid sites.XRD patterns of 1PDSA claysafter the reaction did not show any d(001) reflection change indicating there is no layer swelling by intercalation of reactant or product molecules in the interlayer.

The results are given in Table3 which shows correlation results (r^2 value) between mesopore volume, total pore volume and volume accessibility factor and oxazole yield. Very poor correlation with oxazole yield was observed for Brønsted (B), Lewis (L), (B + L) and (B/L). VAF values obtained by multiplying with micropore volume showed slightly improved correlations for B, L and (B+L). Best correlation ($r^2 = 0.911$) was seen for B/L. Both Al-exchange clay with low micropore volume and Lewis acid treated 1PDSA clays having relatively high micropore volumes showed lower oxazole formation. On the other hand, 1PDSA loaded with 15 and 20% PDSA having high B/L values also exhibited decreased oxazole formation. Neither an increase in Brønsted acidity nor in the Lewis acidity on the clay surface showed a proportionate increase in the oxazole formation. Apparently, an appropriate combination of micropore volume and B/L ratio facilitates maximum yield of oxazole. In the present study, 5 to 10 % loaded 1PDSA samples havea right combination of micropore volume and B/L ratio. The VAF(B/L) value of 0.15 and beyond show the best results under the conditions of the experiment.





Fig.6 SEM images of (a) Untreated (b) 1 PDSA and (c) 1 PDSA (5%).

Table3 Correlation b	between v	olume a	accessibility	factors	and y	vields	of c	oxazole	for the	different	catalyst
samples					-						-

Catalyst	% PA	% yield	\mathbf{V}_{tm}	\mathbf{B}	\mathbf{L}	B+L	B/L	Volu	Volume Accessibility Factor			
	conver		(cm/g)	(µmor/g)	(µmor/g)				()	Ar)		
	sion	Oxazole						Py	ridine F	T-IR aci	idity	
								В	L	B+L	B/L	
1PDSA (5%)	67	46	0.104	92	58	150	1.59	9.48	5.97	15.45	0.16	
1PDSA (10%)	70	50	0.064	112	49	161	2.29	7.17	3.14	10.30	0.15	
1PDSA (15%)	60	32	0.019	123	38	161	3.24	2.34	0.72	3.06	0.06	
1PDSA (20%)	48	12	0.004	133	28	161	4.75	0.53	0.11	0.64	0.02	
1PDSA (Zn-5%)	54	16	0.106	61	86	147	0.71	6.47	9.12	15.58	0.07	
1PDSA (Fe-5%)	61	16	0.099	56	92	148	0.61	5.54	9.11	14.65	0.06	
Al-clay	46	10	0.011	74	70	144	1.06	0.81	0.77	1.58	0.01	
0.1PDSA	30	12	0.026	34	44	78	0.77	0.88	1.14	2.02	0.02	
0.5PDSA	44	24	0.064	52	50	102	1.04	3.23	3.2	6.53	0.07	
Correlation factor, r ²			0.207	0.096	0.014	0.077	0.002	0.61	0.03	0.252	0.911	

*VAF = Micropore volume × Acidity (Example VAF(B) = $0.103 \times 92 = 9.48$. B-Brønsted acidity, L-Lewis acidity.V_{tm}-micropore volume by t-plot method.

Reaction conditions: catalyst amount, 1 g, reaction temperature 150°C; reactants molar ratio, PA:AA; 1:2; reaction time, 60min.

Catalyst	% PA conversion	% yield of	V_{meso} (cm ³ /g)	V_m (cm ³ /g)	Volume mesopo	Volume Accessibility Factor for mesopore volume, (VAF) _{meso}					
		Oxazole	× 0,	× 0,	Pyridir	ne FT-IR	acidity	, meso			
					В	L	B/L	B+L			
1PDSA (5%)	67	46	0.150	0.253	13.8	8.70	0.28	22.50			
1PDSA (10%)	70	50	0.135	0.199	15.12	6.61	0.31	21.74			
1PDSA (15%)	60	32	0.136	0.155	16.73	5.17	0.44	21.90			
1PDSA (20%)	48	12	0.117	0.121	15.56	3.28	0.55	18.84			
1PDSA (Zn-5%)	54	16	0.155	0.261	9.45	13.33	0.11	22.76			
1PDSA (Fe-5%)	61	16	0.160	0.259	8.96	14.72	0.10	23.68			
Al-clay	46	10	0.067	0.078	4.96	4.69	0.07	9.65			
0.1PDSA	30	12	0.094	0.121	3.19	4.14	0.07	7.33			
0.5PDSA	44	24	0.132	0.196	6.86	6.60	0.17	13.46			
Correlation factor r^2			0.196	0.216	0.240	0.001	0.020	0.102			

Table4 Correlation between yield of oxazole formed with mesopore volume, total pore volume and volume accessibility factor for mesopore volume(VAF)_{meso}

Correlation factor, r²0.1860.2160.2400.0010.0290.193Reaction conditions: catalyst amount; 1 g, reaction temperature 150°C; reactants molar ratio PA:AA; 1:2, reaction time 60min.

*V_{tm}-micropore volume by t-plot method, V_{meso}-mesopore volume.

Table4 shows the $(VAF)_{meso}$ values obtained by multiplying the different acidity values with mesopore volumes. The results show a very poor correlation with the oxazole yield indicating insignificant role of mesopores in the cycloisomerization reaction.

3.5 Zeolitic behavior of the modified clay samples: The transformation of alkynyl amide to oxazole is facilitated by the Brønsted and Lewis acid sites accessed through micropores. To know whether such transformation could be brought about in zeolites which are known to possess Brønsted and Lewis acidities within the micropores, the propargylation reaction was studied on a sample of BEA(H-beta) zeolite. The sample of zeolite having a relatively large micropore volume of 0.305 cm³ g⁻¹ and a B/L ratio of 2.39[22,33] and a VAF value of 0.72 showed an enhanced oxazole formation (Table 2). This confirms the role played by zeolitic pores in the modified clay samples used in this study and also the applicability of VAF to zeolitic systems.

3.6 Plausible Reaction Mechanism

The reaction studied involves two steps (i) propargylation to form propargyl amide and (ii) cycloisomerization of the amide to form the oxazole product. First step is favored by both L and B sites. Other workers who have studied propargylation have also seen that the increase in either the B or L sites favor the reaction [1]. Even in the system studied, clay treated with PDSA and also the Al-exchange clay having both B and L sites show activity for propargylation. Mechanism of step 1 as shown in scheme 2 involves the protonation of the alcohol and nucleophilic attack of the protonated alcohol on the amide group.

Cycloisomerization, on the other hand, requires both acid sites in such a way that an optimum ratio of B to L is needed. Mechanism for cycloisomerization step therefore involves both the B and L sites in close proximity. Such an availability of both B and L sites can happen only in a micropore.

The probability of the reactant molecules to position themselves on B and L sites as shown in scheme 2 is greater within a pore. Enriching the number of one site over the other will only decrease the step 2. An optimum ratio of B to L is thus required and is seen within the pores generated due to acid treatment. Alclay is not effective in cycloisomerization due to the fact that the requirement of B and L in close proximity is not fulfilled. It appears that beta zeolite also has such pores with optimum B to L ratio in close proximity.



Scheme 2.Possible reaction mechanism for the propargylation and cycloisomerization.

4. Conclusion: Zeolitic micropores develop on the surface of montmorillonite clay by treatment with organic acids. The micropores thus developed on the modified clay have the ability to enhance the cycloisomerization of the intermediate alkynylamide to form valuable oxazole products. Micropores provide an access to the acid centers for the intermediate product to undergo transformation to the final product. Variation of Brønsted and Lewis acidity and pore volume on the modified clay surface showed variation in the oxazole formed. The combinative role of micropore volume and acidity is expressed by a factor called volume accessibility factor, VAF which is a product of micropore volume and acidity. Best correlation for the oxazole formation was obtained with VAF (B/L) which indicates an optimal combination of micropore volume and B/L ratio for higher rate of oxazole formation under the experimental conditions studied. Thus manifestation of zeolitic pores on the surface of clays by organic acid treatment can accelerate the transformation of reaction intermediates into value added products. Furthermore, the VAF component of the micropore could possibly find application in zeolite catalysis.

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References :

- [1] Y. Pan, F. Zheng, H. Lin, Z. Zhan, J.Org.Chem. 74 (2009) 3148-3151.
- [2] S.Ramesh, B. S. JaiPrakash, Y. S. Bhat, Appl.Catal.A. 41 (2012) 157-162.
- [3] N. J. Venkatesha, B.M. Chandrashekara, B.S. JaiPrakash, Y.S. Bhat, J.Mol.Catal.A. 392 (2014) 181-187.
- [4] M. Campanati, A. Vaccari, O. Piccolo, Catal. Today. 60 (2000) 289-295.
- [5] B.M. Reddy, P.M. Sreekanth, P. Lakshmanan, J.Mol.Catal.A. 237 (2005) 93-100.

- [6]Y. J.Yang, Y. N.Yang, J. S.Jiang, Z. M.Feng, H. Y. Liu, X. D. Pan, P. C. Zhang, Chin.Chem.Lett. 21 (2010) 902-904.
- [7] G. P.Romanelli, J. C.Autino, J. Org. Chem. 6 (2009) 359-366.
- [8] N.Narender, K.S. K. Reddy, M.A. Kumar, C.N. Rohitha, S.J. Kulkarni. Catal.Let. 134 (2009) 175-178.
- [9] M. Miyashita, A. Yoshikoshi, P.A Grieco, J.Org.Chem. 42 (1977) 3772-3774.
- [10] M.J. Gregory, J.Chem.Soc.B. (1970) 1201-1207.
- [11] M. D. Milton, Y. Inada, Y. Nishibayashi, S. Uemura, Chem. Com. 23 (2004) 2712-2713.
- [12] M. P. Kumar, R. S. Liu, J.Org.Chem. 71 (2006) 4951-4955.
- [13] E. Bustelo, P. H. Dixneuf, Adv.Synth.Catal. 349 (2007) 933-942.
- [14] A. Arcadi, S. Cacchi, L.Cascia, G. Fabrizi, F. Marinelli, Org.Lett. 3 (2001) 2501-2504.
- [15] V. Cadierno, J. Gimeno, N. Nebra, Adv. Synth. Catal. 349 (2007) 382-394.
- [16] Z. Zhan, J. Yu, H. Liu, Y. Cui, R. Yang, W. Yang, J. Li, J.Org. Chem. 71 (2006) 8298-8301.
- [17] K. Wilson, J.H. Clark, Pure.Appl.Chem. 72 (2000) 1313-1319.
- [18] J.H. Clark, Acc.Chem. Res. 35 (2002) 791-797.
- [19] A. Corma, Chem.Rev. 95 (1995) 559-614.
- [20] T. Okuhara, Chem.Rev. 102 (2002) 3641-3666.
- [21] P. Wipf, Y. Aoyama, T. E. Benedum, Org.Lett. 6 (2004) 3593-3595.
- [22] R. J. Kalbasi, A. R. Massah, A. Shafiei, J.Mol.Catal.A. 335 (2011) 51-59.
- [23] N. J Venkatesha, B. S Jai Prakash, Y. S Bhat, 'Active Site Accessibility Aspect in Montmorillonite for Ketone Yield in Ester Rearrangement' Catal.Sci.Technol.(2014) DOI: 10.1039/C4CY01356E
- [24] S. Ramesh, Y.S. Bhat, B.S. Jai Prakash, Clay. Miner. 47 (2012) 231-242.
- [25] U. Flessner, D.J. Jones, J. Roziere, J. Zajac, L. Storaro, M. Lenarda, M. Pavan, A. J. Lopez, E.R Castellon, M. Tro mbetta, G. Busca, J.Mol.Cat.A. 168 (2001) 247-256.
- [26] A. Jha, A.C. Garade, M. Shirai, C.V. Rode. Appl.Clay.Sci. 74 (2013) 141-146.

- [27] E. B. Sandel, Colorimetric Determination of Traces of Metals, 3rd edition. Interscience Publishers, New York, 1959.
- [28] S. Selvaraj, B. V. Mohan, K. N. Krishna, B. S. Jai Prakash, Appl.Clay.Sci. 10 (1996) 439-450.
- [29] S. Ramesh, B. S. Jai Prakash, Y. S. Bhat, Appl.Clay.Sci. 48 (2010) 159-163.
- [30] I. Tkac, P. Kodamel, D. Muller, Clay.Miner. 29 (1994) 11-19.
- [31] M. Cobo, A. Quintero, C.M. de Correa, Catal. Today. 133 (2008) 509-519.
- [32] S. T. Oyama, X. Zhang, J. Lu, Y. Gud, T. Fujitani, J.Catal. 257 (2008) 1-4.
- [33] B.M. Chandra Shekara, B.S. Jai Prakash, Y.S. Bhat, ACS. Catal. 1 (2011) 193-199.

Figures:



Fig 1(a) and (b) BJH curves and t-plots of untreated, 0.1, 0.5 and 1M PDSA treated montmorillonite clay.



Fig.2 FT-IR spectra of adsorbed pyridine on (a) Al-clay, (b) 1PDSA, (c) 0.5 PDSA and (d) 0.1 PDSA.



Fig .3 Effect of catalyst amount on the propargylation and cycloisomerization of PA and AA Reaction conditions: reaction time; 60 min, reaction temperature 150°C; reactants molar ratio PA:AA; 1:2.



Fig .4 Effect of temperature on the propargylation and cycloisomerization of PA and AA. Reaction conditions: catalyst amount; 1 g, reaction time; 60min, reactants molar ratio PA: AA; 1:2.

Fig .5 Effect of Reaction time on the propargylation and cycloisomerization of PA and AA Reaction conditions: catalyst amount; 1 g, reaction temperature 150°C; reactants molar ratio PA:AA; 1:2.

Fig.6 SEM images of (a) Untreated (b) 1 PDSA and (c) 1 PDSA (5%).

Tables:

Table.1 CEC, surface area, average pore diameter and micropore volume of unmodified, Al-clay and PDSA treated clays.

Clay samples	CEC	\mathbf{S}_{BET}	APD	\mathbf{V}_m	\mathbf{V}_{tm}	Interlayer
	(meq/g)	(m^2/g)	(Å)	(cm^3/g)	(cm^3/g)	Al (meq/g)
Untreated clay	0.83	27	50.3	0.011	0.067	-
Al-clay	0.83	27	50.3	0.011	0.067	0.83
0.1 PDSA	0.79	109.14	44.13	0.026	0.074	0.49
0.5 PDSA	0.75	196.09	33.34	0.064	0.132	0.62
1PDSA	0.71	276.44	26.04	0.203	0.14	0.70

*S_{BET}-BET surface area, APD-average pore diameter, V_m-total pore volume, V_m-micropore volume by t-plot method.

Catalyst	TPD-NH ₃ $(umol/g)$	% PA conversion	% Alkynyl	% yield of	\mathbf{V}_{tm}	Average TOF	\mathbf{S}_{BET} $(\mathbf{m}^2/\mathbf{q})$
	(pinor, 8)	0011101010	amide	Oxazole	(01175)	(\min^{-1})	(1117g)
Al-Clay	250	46	36	10	0.011	0.066	27
0.1PDSA	78	30	18	12	0.026	0.256	109.14
0.5 PDSA	196	44	20	24	0.064	0.256	196.09
1 PDSA	236	65	25	40	0.203	0.282	276.44
BEA	500	70	15	55	0.305	0.432	552
1PDSA (5%)	228	67	21	46	0.104	0.365	213
1PDSA (10%)	248	70	20	50	0.064	0.348	146
1PDSA (15%)	262	60	28	32	0.019	0.154	106
1PDSA (20%)	232	48	36	12	0.004	0.10	70

Table2 Comparison of TPD-NH₃ acidity, conversion of PA and yield of products with Al-clay, PDSA treated, BEA zeolite and different PDSA amount loaded clay catalyst samples.

Reaction conditions: catalyst amount; 1 g, reaction temperature 150° C; reactants molar ratio PA:AA; 1:2, reaction time 60 min.*S_{*BET*}-BET surface area, V_{*im*}-micropore volume by t-plot method.

Table3 Correlation between volume accessibility factors and yields of oxazole for the different catalyst samples

Catalyst	% PA	% yield	\mathbf{V}_{tm}	В	L	B+L	B/L	Volu	Volume Accessibility Factor			
	conver	of	(cm³/g)	(µmol/g)	(µmol/g)				(V	(AF) [*]		
	sion	Oxazole						Py	Pyridine FT-IR acidit		idity	
								В	L	B+L	B/L	
1PDSA (5%)	67	46	0.104	92	58	150	1.59	9.48	5.97	15.45	0.16	
1PDSA (10%)	70	50	0.064	112	49	161	2.29	7.17	3.14	10.30	0.15	
1PDSA (15%)	60	32	0.019	123	38	161	3.24	2.34	0.72	3.06	0.06	
1PDSA (20%)	48	12	0.004	133	28	161	4.75	0.53	0.11	0.64	0.02	
1PDSA (Zn-5%)	54	16	0.106	61	86	147	0.71	6.47	9.12	15.58	0.07	
1PDSA (Fe-5%)	61	16	0.099	56	92	148	0.61	5.54	9.11	14.65	0.06	
Al-clay	46	10	0.011	74	70	144	1.06	0.81	0.77	1.58	0.01	
0.1PDSA	30	12	0.026	34	44	78	0.77	0.88	1.14	2.02	0.02	
0.5PDSA	44	24	0.064	52	50	102	1.04	3.23	3.2	6.53	0.07	
Correlation factor, r ²		N.	0.207	0.096	0.014	0.077	0.002	0.61	0.03	0.252	0.911	

*VAF = Micropore volume × Acidity (Example VAF(B) = $0.103 \times 92 = 9.48$.

B-Brønsted acidity, L-Lewis acidity.V_{tm}-micropore volume by t-plot method.

Reaction conditions: catalyst amount, 1 g, reaction temperature 150°C; reactants molar ratio, PA:AA; 1:2; reaction time, 60 min.

Table4	Correlation	between	yield	of	oxazole	formed	with	mesopore	volume,	total	pore	volume	and
volume	accessibility	factor for	r mesc	por	e volum	e(VAF) _n	neso						

Catalyst	% PA conversion	% yield of	V_{meso} (cm ³ /g)	V_m (cm ³ /g)	Volume Accessibility Factor for mesopore volume, (VAF) _{meso}					
		Oxazole			Pyridir	ne FT-IR	acidity			
					В	L	B/L	B+L		
1PDSA (5%)	67	46	0.150	0.253	13.8	8.70	0.28	22.50		
1PDSA (10%)	70	50	0.135	0.199	15.12	6.61	0.31	21.74		
1PDSA (15%)	60	32	0.136	0.155	16.73	5.17	0.44	21.90		
1PDSA (20%)	48	12	0.117	0.121	15.56	3.28	0.55	18.84		
1PDSA (Zn-5%)	54	16	0.155	0.261	9.45	13.33	0.11	22.76		
1PDSA (Fe-5%)	61	16	0.160	0.259	8.96	14.72	0.10	23.68		
Al-clay	46	10	0.067	0.078	4.96	4.69	0.07	9.65		
0.1PDSA	30	12	0.094	0.121	3.19	4.14	0.07	7.33		
0.5PDSA	44	24	0.132	0.196	6.86	6.60	0.17	13.46		
Correlation factor, r ²			0.186	0.216	0.240	0.001	0.029	0.193		

Reaction conditions: catalyst amount; 1 g, reaction temperature 150°C; reactants molar ratio PA:AA; 1:2, reaction time 60 min.

 V_{tm} -micropore volume by t-plot method, V_{meso} -mesopore volume.

Scheme:

Scheme 1 Reaction between PA and amide to form Oxazole in presence of PDSA-clay.

Scheme 2 Possible reaction mechanism for the propargylation and cycloisomerization.