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Enhancement in activity and shape selectivity of zeolite BEA by phosphate treatment for 2-methoxynaphthalene acylation

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Pore-engineering of large pores of zeolite BEA by phosphate treatment effectively narrowed the pores with a creation of new acid sites. Phosphate modification of BEA with lower loading was more effective in pore modification without affecting the zeolite structure. Pyrophosphates and polyphosphates are mainly responsible for the narrowing of the zeolite pores. Both the activity and shape selectivity for 2-acetyl-6-methoxynaphthalene were enhanced in acylation of 2-methoxynaphthalene. At higher concentration of phosphates, conversion and selectivity decreased due to dealumination. 1% P loading was found to be optimum for acylation of 2-methoxynaphthalene. With the optimized phosphate modification of BEA, high selectivity of 78% to 2-acetyl-6-methoxynaphthalene was achieved with 77% conversion.

Introduction

The alkylation and acylation reactions are important C-C bond forming chemical reactions practiced in industries. For these reactions, all possible regio-isomers are observed as products. To improve shape-selectivity to the desired product, pore-size engineering was widely reported for medium pore zeolites.¹ For molecules with mono-nuclear aromatic rings, medium pore zeolites are widely studied and for bi-nuclear aromatics, large pore zeolites are preferred. There are also few reports on pore-size engineering of large pore zeolites. Pore size engineering of zeolites with large pore is carried out by coating zeolite with bulkier organo-silanes.²⁻⁶ Organo-silanes are expensive and method of silica coating over zeolite is tricky as it involves multiple steps of coating, work-up and calcination steps which makes it difficult to scale-up and commercialize. However, phosphate modification is an easy and inexpensive technique which has better commercial prospects.

During acylation of 2-methoxynaphthalene (2MN), due to the increased electron density at β position on naphthalene ring, formation of 1-acetyl-2-methoxynaphthalene (1,2MNAC) is kinetically preferred to other isomers. On the other hand, 2acetyl-6-methoxynaphthalene (2,6MNAC) is an important intermediate for the synthesis of anti-inflammatory drug naproxen. 2,6MNAC has a wider application and demand compared to its other isomers. Current manufacture process of naproxen,⁷ does not comply with the principle of green chemistry process due to non-selective synthesis, lesser atom economy and use of hazardous chemicals which can overcome by the application of selective heterogeneous catalyst.

Plausible mechanism of acylation of 2-MN with acetic anhydride over acid homogeneous catalyst is represented in Scheme S1. Over microporous catalysts, product distribution can change depending on the molecular dimensions of the products. 2MN being binuclear aromatic compound, its molecular dimension is closer to the pore dimensions of large pore zeolites. Hence, large pore zeolites are better catalysts for acylation of 2MN.⁸ To improve the selectivity towards 2,6MNAC, ion exchanged large pore zeolites are widely studied using acyl halides as acylating agents over ion-exchanged zeolites.⁹ Among all the reported catalysts, highest selectivity of 70 % to 2,6MNAC was achieved with zeolite BEA polymorph C (with yield of \approx 24.5 %), whereas Al-ITQ-7 was reported to give highest yield of ≈39 % (with 65 % selectivity).^{8,10,11} Hence, these reported catalysts could give low yields for the desired product.

Phosphate modification of ZSM-5 has been widely studied previously to modify the pores but mostly the modification resulted in decrease in catalytic activity.¹²⁻¹⁶ Shanbhag and coworkers have recently reported phosphate modified ZSM-5 with the novel introduction of water treatment step for removing the ionic phosphate generated during phosphate modification.¹⁷⁻¹⁹ However, phosphate modification of large pore zeolites like BEA is not studied for increasing the activity and shape selectivity for organic transformations so far.

In the present study, zeolite BEA was selected for this reaction because the molecular dimensions of two acylated products are close to the pore size of BEA. We thought that the selectivity for 2,6MNAC can be enhanced by pore size regulation and passivation of external surface acid sites of zeolite BEA. Pore-size regulation with phosphate modification is studied for zeolite BEA for acylation reactions for the first time. Phosphate modified zeolite BEA was characterized by

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XRD, N₂ sorption, MAS NMR, TPD-NH₃, FTIR, Py-FTIR and FESEM. Due to dealumination property of phosphate modification, performance of the catalyst was compared with that of H-BEA modified by mild dealuminating agents.

Results and Discussion

XRD of phosphate modified catalyst shows structural integrity at lower amount of phosphate loading and decrease in crystallinity with increase in phosphate loading (Fig. 1). Decrease in peak intensity can be observed with progressive increase in phosphate loading from 3 to 14 %. At 14 % P loading (as phosphates), zeolite BEA loses almost all of its crystallinity. Loss of crystallinity could be due to interaction of phosphate with Al and subsequent removal of framework Al during water treatment and calcinations steps. Removal of Al increases with increase in phosphate content resulting in loss of BEA structure at 14 % P loading as phosphates (Fig. 1A). XRD of modified BEA with mild dealuminating agents did not show any considerable change in BEA structure (Fig. 1B).

FTIR of framework shows T-O-T asymmetric stretching vibrations at 1095 and 1220 cm⁻¹, symmetric stretching vibrations at 820 cm⁻¹ and double rings at 560 cm⁻¹. For 1PBEA, peak at 1095 cm⁻¹ shifted to lower frequency indicating some amount of phosphate incorporation in the zeolite framework.²⁰ With increase in phosphate loading >1% P, frequency of these vibrations shifted to higher frequency indicating dealumination of BEA. Collapse of zeolite structure at higher phosphate loadings is supported by XRD and FTIR (Fig. 2 A).

In Pyridine FTIR spectra (Fig 2 B), area under the curve was calculated for Brönsted (B) and Lewis (L) acid sites and their ratio gives the relative change in acid sites (Table 1.). For unmodified BEA, B/L was 3.43, whereas with 1 % P (as phosphate) it increased to 4.04 indicating increase of B sites and decrease of L sites. For 3 % P, B/L was 4.48, where both B and L increased which is possible by the removal of 'Al' acid sites and generation of new phosphate based acid sites (Scheme 1). With further increase in phosphate content from 5 to 14 % P, there was a progressive decrease in intensity of both B and L peaks showing the decrease in acidity due to dealumination. The Brönsted acidity for 1PBEA was lower than 3PBEA and 5PBEA due to lower amount of phosphates in the zeolite. From 3PBEA, peak area of Brönsted acid sites decreased with increase in phosphate loading due to increase in dealumination and also due to decrease in the acid sites corresponding to phosphates in the framework.

Nitrogen sorption study shows that with addition of 1 % P, specific surface area decreased marginally from 577 to 553 m^2/g and after water treatment, surface area of 1 % P modified BEA decreased slightly to 526 m^2/g (Table 1). With

further increase in P addition, surface area drastically decreased (3 P – 398.1 m²/g, 5 P – 195.9 m²/g, 14 P – 115.8 m²/g). Pore volume of unmodified and modified BEA remained similar for 1 % P (0.30 – 0.32 cc/g) but further increase in P decreased pore volume to 0.20 cc/g for 3 P. Pore volume for higher loadings 5 P and 14 P were low and there was no difference between the two (0.07 cc/g). Initial decrease in surface area and marginal increase in pore volume could be attributed to pore narrowing by phosphates, whereas greater decrease in surface area and pore volume at higher concentrations of P could be attributed to dealumination.

Temperature programmed desorption (TPD) of unmodified H-BEA showed a typical trace of BEA with 0.91 mmol of acid sites per gram of catalyst (Fig. 3). With addition of 1 % P, acidity decreased to 0.7 mmol/g and with increase of P from 3 to 5 %, acidity was similar (0.73 and 0.75 mmol/g). However, acidity considerably decreased to 0.53 and 0.45 mmol/g for 7 and 10 % P respectively. The acidity decreased marginally with further increase to 14 P (0.42 mmol/g).







Scheme 1. Phosphate interaction with zeolite framework as adopted from A, 21 B, 22 C, 23 D, 24 E, 23

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Fig. 2. (A) Framework FTIR of zeolite BEA before and after modification (B) FTIR of pyridine adsorbed zeolite BEA before and after modification



Decrease in acidity up to 3 % P loading can be attributed to the formation of phosphate ester with acid sites (Scheme 1.), whereas for drastic decrease in the acidity after 7 % P addition could be due to the removal of acid sites by structure collapse as seen by XRD and FTIR studies.

Water treatment after phosphate modification is essential for the removal of soluble ionic phosphates which can block the pores and also leach out easily in presence of polar medium. Hence, water treatment of P-modified BEA was carried out after P-loading and calcination. Therefore, phosphorous (as phosphate) was estimated after water treatment to know the amount of phosphorous that is covalently bound to the zeolite matrix.

Table 1	Specific surface	area and	nore volume	changes	with D	modification
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Catalyst	Specific surface area (m ² /g)	Pore volume (cc/g)	B (area)	L (area)	B/L
H-BEA	576.8	0.30	4.08	1.19	3.43
1PBEA	526.5	0.31	4.57	1.13	4.04
3PBEA	398.1	0.20	6.34	1.31	4.84
5PBEA	195.9	0.07	5.42	0.45	12.04
7PBEA	-	-	0.67	0.06	11.17
14PBEA	115.8	0.07	-	-	-

P remaining (as phosphate) in BEA after water treatment increases with increase in P addition (Fig. 4.). A plot of P remaining (wt %) v/s the P added (wt %) shows a linear correlation with 2 different slopes indicating two types of interactions of phosphates are possible with the BEA framework. At lower concentration of phosphates, they react to form esters of P with acid site and at higher concentration, they tend to form polyphosphates and aluminophosphates with the loss of BEA framework.

²⁷Al MAS NMR studies (Fig. 5.) showed that H-BEA before modification contained most of Al in the tetrahedral form and only small amount of extra framework Al was present. After modification with 1 % P, most of the Al in the zeolite framework is intact as there is only a marginal increase in octahedral Al. For 14 % P modified H-BEA, all of the tetrahedral aluminium is dealuminated to form the aluminophosphates which can be seen at -15.55 ppm.



Fig. 4. Estimation of P remaining as a function of P added



Fig. 5. 27AI MAS NMR of A) H-BEA B) 1P H-BEA C) 14P H-BEA

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with 5 % P, the morphology and particle size did not change to noticeable extent. This shows that phosphate modification, calcination and water treatment steps did not affect the morphology and particle size.

Initial catalyst screening (Table 2.) was carried out with wellknown solid acid catalysts and results are compared with H-BEA. Montmorillonite K10 and amberlyst-15 (65.31 and 72.43% conversion respectively) gave kinetically preferred 1,2MNAC as major product (97.7 and 84% respectively). Over microporous zeolite catalysts, selectivity to 1,2MNAC was low, whereas selectivity to 2,6MNAC increased in the order; HY (6.0%) <mordenite (38.5%) < H-BEA (65.0%). Increase in selectivity to 2,6MNAC is consistent with the decrease in the pore diameters (Table 2.). Thus, increase in selectivity to 2,6MNAC can be attributed to shape selective property of zeolites. Even though 1,2MNAC is kinetically preferred product, its formation can be restricted by the application of microporous solids because of its bulkier molecular size compared with 2,6MNAC. For HY zeolite, selectivity to 1,2MNAC was higher than the other isomer. Molecular diameter of 1,2MNAC is 7.3 Å, whereas kinetic diameter at the reaction temperature is less than that. As the super cage pore width of HY is larger than 1,2MNAC, it predominantly catalyzes the non-selective reaction. In case of mordenite, only one channel can be accessed by the molecules in one dimension as the channel dimension is comparable to molecular dimensions (1,2MNAC and 2,6MNAC) and therefore, increase in the selectivity of 2,6MNAC (38.5 %) was observed. Zeolite H-BEA gave better conversion of 2-MN due to its 3-dimensional channel system with large pores, where reactants and products can diffuse easily. Selectivity towards 2,6MNAC increased due to easy access to active site inside the pores and shape selective catalysis. Non shape-selective and kinetically preferred product can be formed on the acid sites on the external surface. Hence, zeolite H-BEA was taken for further pore modification to improve activity and shape selectivity for the desired 2,6-MNAC.

Dealuminated H-BEA was studied for this reaction based on the assumption that dealumination can remove the external acid sites of zeolite and hence decreases the non selective product improving selectivity for desired 2,6-MNAC. However, selection of proper dealuminating agent is important as dealumination also changes other properties of the catalyst. Hence, mild dealuminating agents such as organic acids are preferred which do not decrease acidity to a great extent. Dealumination of zeolite with tartaric acid and methane sulphonic acid increased the pore volume and decreased the diffusion limitation to reactants and products. Hence, increase in conversion and increase in kinetically preferred product can be observed. H-BEA dealuminated with tartaric acid gave 48.01 % 2MN conversion with 55.4 % selectivity to 2,6MNAC. Moreover, for catalyst dealuminated with methane sulphonic acid, 62.6 % 2MN conversion with 53.1 % selectivity to 2,6MNAC was obtained. Hence, treatment of H-BEA with tartaric acid and methane sulphonic acid improved the conversion but decreased selectivity for the desired 2.6MNAC.



Fig. 6. 31P MAS NMR of A) 1PH-BEA B) 5PH-BEA C) 14PH-BEA

³¹P MAS NMR studies (Fig. 6.) show that 1 % P addition forms several types of polyphosphates, orthophosphate mono ester as seen at 3.8 ppm, polyphosphates (-21.0 ppm) and glassy type polyphosphates (-51.3 ppm).²⁵ 5 % P loaded BEA showed more of aluminophosphate (-30.92 ppm) species and glassy type polyphosphates (-55.7 ppm). With increase of phosphate to 14 % P, orthophosphate ester (-0.03 ppm), polyphosphates (-11.7) and AIPO were observed (-39.9 ppm). Orthophosphate mono esters generate new moderately acidic acid sites in phosphate modified BEA zeolite.



Fig. 7. FESEM Images A) HBEA B) 5PHBEA

FESEM images (Fig. 7.) showed spherical particles of H-BEA with an average particle size of 110 nm. After P-modification

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Table 2. Performance of unmodified catalysts

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Catalyst	Surface area m²/g	Acidity mmol/g	Pore diameter Å	Conversion 2MN wt%	1,2MNAC selectivity	2,6MNAC selectivity	Others wt %	2,6MNAC Yield
					wt %	wt %		wt %
K10	242	1.1	~14*	65.31	97.7	2.3	0	1.5
A-15	53	4.7	300	72.43	84.0	16.0	0	11.5
H-Y	600	1.6	7.4 x 7.4	11.65	81.9	6.0	2.1	0.7
H-MOR	234	2.0	6.5 x 7.0	14.71	61.5	38.5	0	5.7
H-BEA	576	0.91	6.6 x 6.7 and 5.6 x 5.6	42.67	28.15	65.0	6.9	27.7
****		420.00.0						

*Interlayer distance; Temperature = 130 °C, 2MN : $(Ac)_2O = 1:1$, Time = 6 h



Scheme 2. 2-Methoxynaphthalene acylation over a) Zeolite BEA; b) P-modified BEA. 1) Acetic anhydride; 2) 2-Methoxynaphthalene; 3' & 4') Transition states of respective products; 3) 1-Acetyl-2-methoxynaphthalene 4) 2-Acetyl-6-methoxynaphthalene.

Table 3. Performance of modified H-BEA catalysts

Catalyst	Conversion 2MN %	1,2MNAC selectivity	2,6MNAC selectivity	Others wt %	2,6MNAC Yield
		wt %	wt %		wt %
H-BEA	42.67	28.15	65.0	6.9	27.7
With 1M TA	48.01	36	55.4	8.6	26.6
Al : EDTA = 1 : 1	32.92	22.6	71.1	6.3	23.4
Al : EDTA = 1 : 2	68.89	33.6	56.2	10.2	38.7
0.1 M MeSO₃H	62.61	42.1	53.1	4.8	33.2
0.5P HBEA	42.74	23.6	67.7	8.7	28.9
1P HBEA	76.15	15.8	77.1	7.1	58.7
2P HBEA	80.86	22.6	70.1	7.3	56.6
3P HBEA	50.88	36	57.4	6.6	29.2
5P HBEA	47.04	36.8	52.4	10.8	24.6
7P HBEA	43.88	29.9	48.2	8.7	21.1
14P HBEA	15.18	79.7	20.3	0	3.1

But with EDTA as dealuminating agent (AI:EDTA = 1:1), dealumination occurs only at the external surface of the zeolite, because size of EDTA is bigger than the pore size of H-BEA.

As the acid sites are removed, conversion decreased, whereas selectivity towards 2,6MNAC increased (71.1 %) which indicates that shape selective reaction takes place inside the pores. Increased concentration of EDTA (AI : EDTA = 1 : 2) resulted in increase of non selective acid sites similar to other dealuminated catalysts because of higher dealumination. Decrease in pore volume creates a barrier for the formation and diffusion of bulkier products like 1,2MNAC and thus imparts shape selectivity for smaller 2,6MNAC molecule.

Phosphate modification decreases the acidic strength with a creation of new moderately acidic acid sites and also decreases pore volume and hence, initial loading increased selectivity of 2,6MNAC. At 1 % loading, all acidic sites may not be accessible which are within channels of different dimensions of zeolite BEA. Moreover, due to the decrease in pore volume, there was an increase in the selectivity towards 2,6MNAC from 65 to 77 % (yield increased from 27.7 to 58.7 %) (Table 3.).

The increase in product yield after phosphate modification could be attributed to the new acid sites created by phosphate modification which are highly efficient to catalyze this reaction. Further increase in phosphate content to 2 % increased the conversion (80.86 %) but decreased the selectivity (70.1 %) and thus decreased the overall yield (56.6 %) for 2,6MNAC. With further increase in phosphate content to 3, 5 and 7 % P, conversion gradually decreased to 50.8, 47, 43.8 % respectively with gradual decrease in selectivity to 2,6MNAC (57.4, 52.4 and 48.2 % respectively).

Conversion decreased with increase in phosphate content due to a decrease in acid sites. Decrease in selectivity is due to the loss of zeolite structure with phosphate modification which decreases the diffusion limitation and hence, increase in conversion and decrease in selectivity was observed. When phosphorus was increased to 14 % (as its oxide), selectivity of the catalyst became similar to nonporous catalyst. This is due to complete collapse of the BEA structure as seen from XRD. Hence, 1PBEA was taken further to study the effect of reaction temperature, mole ratio and reaction time on catalytic activity.

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Increase in conversion with increase in reaction temperature is due to increase in the reaction rates. But marginal increase in selectivity is due to the increase in diffusivity inside pores with increase in temperature. (Fig. 8A.). This shows that 2,6-MNAC product formation is not kinetically controlled and truly due to shape selectivity exhibited by modified BEA pores (Scheme 2). With increase in temperature from 110 to 120 °C, 2MN conversion marginally increased (68.3 to 71 %) with marginal increase in the selectivity of 2,6MNAC (from 76.6 to 78.6 %). Further increase in temperature to 130 °C increased 2MN conversion to 76.2 % with 77.1 % selectivity to 2,6MNAC. At 140 °C, conversion of 2MN increased marginally to 78.8 % and selectivity to 2,6MNAC remained almost unchanged (77.8 %).

Increase in concentration of $(AC)_2O$ in the reaction mixture increased the conversion up to mole ratio of 1 : 2 (MN: $(AC)_2O$). Further increase in $(AC)_2O$ concentration did not have any effect on conversion (Fig. 8 B.). Interestingly, at lower concentration of $(AC)_2O$, the selectivity of 2,6MNAC was highest with 77.7 %. At lower concentrations, reaction is limited within the pores, whereas at higher concentration, reaction can occur in both inside and outside the pores. Kinetically preferred non-selective reaction can occur outside the pores to form 1,2MNAC²⁶ resulting in the decrease of 2,6MNAC.



Fig. 9. Variation of product distribution with respect to time with catalyst 1PBEA

Effect of reaction time on activity was studied by sampling the reaction mixture with an interval of 0.5 h. Conversion of 2,6MNAC increased linearly and reached the maximum of 77 % and remained constant during the study of 4 h (Fig. 9). Product distribution did not change during the study. This indicates that the reaction occurs inside the pores forming the thermodynamically more stable product due to pore narrowing. Kinetically preferred product is formed mainly outside the pores. Studies on operating parameters show that it has a negligible effect on selectivity of 2,6MNAC. This means that the increase in selectivity is truly due to the increase in shape selectivity due to pore modification by phosphates.

Conclusion

Higher selectivity for 2,6MNAC for zeolite BEA is due to its shape selective property, which enhanced further after P modification and by selective removal of acid sites from the external surface. Phosphate impregnation in smaller quantity regulates the pore of zeolite BEA and in higher quantities of phosphates, dealumination of zeolite BEA with collapse of framework was observed. Phosphates react with the zeolite framework and forms phosphate esters and polyphosphates inside the zeolite pores which increases the shape selectivity of zeolites. Phosphate modification enhanced both 2MN conversion and selectivity to 2,6MNAC which could be attributed to the creation of new acid sites by phosphate modification with pore narrowing. Studies show that reaction parameters have negligible effect on selectivity and increase in selectivity is due to decrease in the pore size.

Experimental Section

Catalyst modification

K10 was purchased from Sigma Aldrich, amberlyst-15 from Alfa-Aeser. Zeolite BEA (H-BEA), zeolite mordenite (H-MOR), and zeolite Y (H-Y) were gratefully received from Süd-Chemie India Pvt. Ltd. Dealumination of zeolite BEA was carried with different dealuminating agents according to the reported optimized conditions.²⁷⁻²⁹ Dealumination of H-BEA with tartaric acid; 100 ml of 1 M tartaric acid was added to 2 g of zeolite and refluxed for 1 h, filtered, washed with water, dried at 120 °C followed by calcination at 550 °C for 6 h^[23] (With 1M TA). Dealumination of zeolite BEA with EDTA; To 2 g of zeolite slurry, EDTA (0.25 g) corresponding to stoichiometric amount of aluminium present in the zeolite was added and refluxed for 24 h, filtered, washed, dried at 120 °C followed by calcination at 550 °C for 6 h (AI : EDTA = 1 : 1). Same procedure was followed with 0.5 g of $EDTA^{[23]}$ (AI : EDTA = 1 : 2). Dealumination of zeolite BEA with MeSO₃H was carried as follows. 100 ml of 0.1 M MeSO₃H with 2 g of zeolite was refluxed for 4 h, filtered, washed, dried in an oven at 120 °C followed by calcination at 550 °C for 6 h^{28} (0.1 M MeSO₃H).

The H-BEA was modified post synthetically by wet impregnation method by treatment with phosphorous reagent. In a typical procedure, required amount of $NH_4H_2PO_4$ was dissolved in 20 ml water at 60 °C to which 5 g of zeolite

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was added with stirring followed by solvent evaporation at 90 °C. It was then dried at 120 °C for 4 h and calcined initially at 330 °C for 3 h and then at 560 °C for 10 h. To remove water soluble phosphates, the calcined sample was cooled to room temperature and stirred in water at 80 °C for 12 h (mentioned as water treatment), then filtered, dried and calcined at 500 °C for 4 h.¹⁸

Catalyst characterization

X-ray diffraction studies were performed with Bruker D2 Phaser diffractometer equipped with Cu Ka source. X-ray diffraction data collected was from 5 to 50° Bragg angle with steps of 0.02 with an interval of 0.5 sec. Framework FTIR was measured by KBR wafer technique. About 0.5 mg of zeolite was thoroughly mixed with 500 mg of KBR and pressed into a transparent pellet. Data was collected as an average of 32 scans with 4 cm⁻¹ resolution. Pyridine FTIR was measured by adsorbing pyridine on self-supporting wafers. In a typical procedure, about 30 mg of catalyst was pressed in a hydraulic press to get self-supporting wafers. These wafers were calcined at 550 °C for 2 h and cooled in a desiccator. Pyridine drops were placed on wafer in a perfectly ventilated fume hood. After evaporation of added pyridine in fume hood, wafers were placed in an oven for 30 min maintained at 200 °C to remove all physisorbed pyridine. Data was collected as an average of 32 scans with 4 cm⁻¹ resolution. Nitrogen sorption measurements were carried out over Autosorb-1C (Quantachrome, USA) unit. The isotherms were measured at 77 K after degassing samples below 10^{-3} torr at 300 °C for 4 h. The BET specific surface area was estimated using adsorption data as per the ASTM method 4365 applicable for microporous solids. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.95. The acidity of the catalysts was measured by temperature programmed desorption (TPD) of NH₃. In a typical procedure, 0.1 g of sample was taken in a quartz tube of ¼ inch packed with silica wool from both sides to remove dead volume and sample was dehydrated at 550 °C for 1 h. The temperature was decreased to 100 °C and NH₃ was adsorbed by passing a stream of 10% NH₃ in He through catalyst for 1 h. Physisorbed NH₃ was then purged by dry He for another 1 h. The desorption of NH₃ was carried out in He flow (30 ml min⁻¹) by increasing the temperature to 550 °C at 10 °C min⁻¹ using TCD detector. Solid state nuclear magnetic resonance with magic angle spinning (MAS NMR) was performed in VARIAN Mercury Plus 300MHz using standard procedure. Sample was placed in a 5 mm probe and was spun at 5 KHz. Chemical shifts were plotted with respect to reference standards, $NH_4H_2PO_4$ and $Al(NO_3)_3$ for ³¹P and ²⁷Al nuclei respectively. Phosphorus content in the modified catalyst was estimated by colorimetry.^[18] In a typical procedure, catalyst was digested with a mixture of 1 g of HCl, 0.5 g HF and 1 g HNO₃. The mixture was then neutralized with H₃BO₃ and this mixture was diluted to 200 ml. 2 ml of this solution was taken in 50 ml volumetric flask and 5 ml of 2M H_2SO_4 was added followed by 5 ml of 0.01 M ammonium paramolybdate. To this solution, 4 ml of mixed reagent (1:1

mixture of freshly prepared 10 % ascorbic acid : 0.004 M antimony potassium tartrate solution) was added to get intense blue color. After 10 min, optical density (OD) was measured at 890 nm in Perkin Flmer UV-Vis spectrophotometer. Similar method was followed to make NH₄H₂PO₄ standard solutions and phosphorus was estimated in the catalyst samples using 5 point calibration curve obtained from standard solutions. Morphology of the catalysts were studied with FESEM. In a typical procedure, a small amount of catalyst was smeared on carbon tape glued to the stage, degassed in vacuum for 24 h, sputtered with gold for 1 min and image was collected in Zeiss instrument with different magnifications.

Catalyst evaluation: acylation of 2-methoxynaphthalene

In a typical experimental procedure, 5 mmol of 2methoxynaphthalene (2MN), 5 mmol of acetic anhydride $((Ac)_2O)$ were taken in a 2-necked glass reactor along with 3 g of chlorobenzene as a solvent and 1 mmol of nitrobenzene as internal standard. To this solution, 400 mg of catalyst preactivated at 500 °C was added. Glass reactor was fitted with a condenser and whole setup was evacuated and maintained with nitrogen blanket throughout the reaction time to avoid the decomposition of acetic anhydride by moisture. Reaction was carried out at 130 °C for catalyst screening. After 6 h of reaction time, reaction mixture was cooled to room temperature and 10 g of ethanol as diluent was added. This mixture was analyzed by gas chromatograph equipped with FID detector and RTX-5 capillary column. Products were identified by GCMS and quantified by internal standard method using software provided with gas chromatograph. Yield (wt%) was calculated by the formula

 $\frac{conversion(wt\%) \times selectivity(wt\%)}{100}$

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