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Short Communication

# Phosphoric acid modified montmorillonite clay: A new heterogeneous catalyst for nitration of arenes $\overset{\vartriangle}{\succ}$

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# ABSTRACT

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### 1. Introduction

Heterogeneous catalysis is receiving significant interest over homogeneous counterpart due to the advantages like a) good dispersion of active sites, b) easier and safer handling, c) easier separation from the reaction mixture, and d) reusability [1]. Among heterogeneous catalysis, solid acids, prepared by adsorbing mineral acids onto a solid surface, are introduced mainly to replace highly corrosive mineral acids in the reaction medium and used in many important large-scale industrial processes [2]. In this regard, nitration of organic compounds is one of the most important industrial reactions and nitro-derivatives are extensively utilized as a chemical feedstock for wide range of useful materials [3]. However, nitration of organic compounds is still being done by using fuming nitric and concentrated sulfuric acids in the industry. Hence, development of an efficient and eco-friendly protocol for nitration of organic compounds without using sulfuric acid is still desirable. Very recently, advances in sulfuric acid free toluene nitration are briefly reviewed [4]. Although a large number of reagents and catalysts are known [4–14], they suffer from limitations like longer reaction time, tedious work-up procedure and involvement of huge expenses for cleaning up. In an effort to develop environmentally

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benign catalyst for nitration reactions, solid acids are found to be more efficient. Several solid acid catalysts such as sulfonated polyorganosiloxanes [15], acidic resins [16], zeolites [17] and supported sulfuric acids [18] are used in nitration reactions. Regioselectivity in nitration reaction is observed while using polyoxometalates (POMs) or heteropolyacids [19–22]. Modification of solid oxides such as TiO<sub>2</sub>, SiO<sub>2</sub>, and MoO<sub>3</sub> with phosphoric acids was reported [23–25] and the modified MoO<sub>3</sub> in the presence of silica support was applied for toluene nitration [25]. Also 'phosphate impregnated titania or alumina' catalyst was prepared and found to be efficient in nitration of various organic compounds [26-29]. Many acidic zeolites have been used for paraselective vapor phase nitration of toluene. However, the process could not be commercialized due to deactivation of catalyst. In order to achieve efficient and selective process zeolites are modified, for instance, ZSM-5 was modified with phosphoric acid and found to be highly selective for vapor phase nitration of toluene [30]. The impact of modification of ZSM-5 with phosphoric acid was also studied [31]. Although, there was no change in the hydrothermal stability of the zeolite, variation on the Brønsted acid site was observed which is responsible for the efficient catalytic activity [31]. Para-selectivity in nitration of toluene was also achieved by using montmorillonite clay as catalyst [32]. The clay minerals have been modified with acid as well as other reagent and applied in various organic transformations [33,34]. However, to the best of our knowledge, no report related to modification of montmorillonite clay with phosphoric acid and its application is available. Herein, the modification of montmorillonite clay with phosphoric acid and its efficacy in catalytic nitration of various aromatic compounds are reported.

The easily available montmorillonite clay is treated with phosphoric acid and 10 wt.% is found to be the optimum

concentration of phosphoric acid that can be adsorbed chemically on the surface of the clay. Acidity of this

phosphoric acid treated montmorillonite clay (PAM) is determined by volumetric as well as potentiometric

titration and characterized. Catalytic efficacy of PAM in nitration of various aromatic compounds is reported.





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 $<sup>\</sup>stackrel{\stackrel{}_{\scriptstyle \rm T}}{\rightarrow}$  Dedicated to Prof. M. K. Chaudhuri, Vice Chancellor, Tezpur University, India on occasion of his 67th birthday.

Table 1	
Nitration of various organic compounds in the presence of PAM-10.	



[a] The unit of the given in square bracket is hour, [b] isolated yield, [c] the ratio of isomer calculated from NMR and GCMS analysis, [d] reaction at 50  $^{\circ}$ C, [e] reaction in 10 g scale.

## 2. Experimental

Montmorillonite K10 (MK10) was obtained from Sigma-Aldrich. Reagent grade 85% phosphoric acid [Merck] was used as purchased. Solvents were distilled before used. Organic substrates for nitration reaction were used as purchased. IR spectra (4000–250 cm<sup>-1</sup>) were recorded on a Shimadzu Prestige-21 FTIR spectrophotometer. TG analyses were done in Perkin Elmer Pyris Diamond TG/DTA instrument. The BET surface area was determined by using Quantachrome Autosorb IQ equipment. The melting points of the solid products were determined using Buchi B450 melting point apparatus. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker Avance II 400 NMR spectrometer.

# 2.1. Preparation of catalyst

500 mg of montmorillonite clay was taken in a round bottomed flask fitted with a reflux condenser. To this, a known amount (5–100 wt.%, abbreviated as PAM-5, PAM-10, PAM-100, etc.) of phosphoric acid and 5 mL of toluene was added. Then the mixture was refluxed for 5 h and the toluene was distilled off. The "acid treated clay" was then dried in an oven (110–120 °C). PAM-10 indicates 10 mg of phosphoric acid was used for 100 mg of montmorillonite clay.

For the determination of chemically adsorbed phosphoric acid onto the clay, the samples (50 mg) were taken in the water (10 mL) and vigorously stirred for 10 min at room temperature, filtered and dried in the oven (110–120  $^{\circ}$ C).

# 2.2. Determination of acidity

The acidity of the acid treated clay was determined by acid-base titration as well as thermo gravimetric analysis (TGA). To 50 mg of the catalyst, 10 mL of standardized NaOH (0.01 M) solution was added and stirred for 10 min. Then it was filtered and filtrate was titrated against standardized  $H_2SO_4$  solution.

# 2.3. Catalytic nitration reaction

In a typical experiment, bromobenzene (1.5 g, 1 mL, 10 mmol) and PAM-10 (75 mg, 5 wt.% to the bromobenzene) were taken in a round-bottomed flask. Then nitric acid (70%) (1.35 mL, 15 mmol) was added and stirred at room temperature for the specified time period (Table 1). The reaction was monitored by TLC. On completion of reaction, the product was extracted with ethyl acetate, washed sequentially with 5% aqueous solution of sodium bicarbonate (2.5 mL), and water (5 mL), and then dried with anhydrous  $Na_2SO_4$ . Evaporation of the solvent, followed by column chromatography of the crude mixture on silica gel using *n*-hexane and ethyl acetate (95:5) as eluent, afforded 2-nitro toluene and 4-nitro toluene in the ratio of 44:56 in pure form. The overall yield was 97%. In cases of solid substrates, acetonitrile (3–5 mL) was used as the solvent.

#### 3. Results and discussion

#### 3.1. Preparation and characterization of catalyst

Initially, various amounts of phosphoric acid were refluxed with 500 mg of montmorillonite clay in toluene to evaluate the maximum amount of acid adsorbed on the clay. It was observed that after treating with 80 wt.% of acid the product became sticky which was washed with diethylether to obtain the solid product. Toluene was chosen as solvent because of its higher boiling point than water. Hence, water from phosphoric acid as well as produced in the reaction will be distilled off with toluene to give better modified clay with a minimum of water content. MK10 was also treated with other mineral acids such as sulphuric and perchloric acids. However, refluxing the MK10 with sulphuric and perchloric acids in toluene resulted in a black material which indicates the destruction of layered structure.

The acidity of these modified montmorillonite clay (PAM) was obtained by determining the amount of NaOH consumed with standardized  $H_2SO_4$  by using phenolphthalein indicator. The results are depicted in Fig. 1. The acid equivalent is found to be approximately in accordance with the phosphoric acid used in preparation. Further, the



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**Fig. 1.** The determination of acid equivalent of the catalyst prepared by using different amounts of phosphoric acid, (a) green = the amount of acid used in preparation, (b) blue = acid equivalent, and (c) brown = acid equivalent after water.

acidity of water-washed PAM is also determined and the values are shown in Fig. 1. Surprisingly, the acid equivalent obtained after washing is found to be different from that without washing for all the composition. However, PAM-10 (10 wt.% phosphoric acid), shows minimum loss of acid equivalent after washing. Hence it can be concluded that physically adsorbed phosphoric acids are washed out with water and 10 wt.% is the maximum amount of phosphoric acid that was chemically adsorbed on the clay surface. Therefore we selected the PAM-10 catalyst for further studies. In order to study the effect of solvent in the preparation of catalyst, another reaction was carried out in ethanol (PAM-10 Et) instead of toluene and the acidity was found to be lower than that of PAM-10 (Fig. 1). This might be due to the lower boiling point of ethanol compared to toluene as well as may be the possibility of formation of hydrogen bonding with the protic solvent. Further loss of acid strength was observed while heating the catalyst in furnace at 300 °C for 3 h (PAM-30F and PAM-40F, Fig. 1) which might be due to destruction of layered structure at a higher temperature. The acidity of the PAM-10 is also determined by FTIR and TGA by adsorbing pyridine and the results are found in accordance with that obtained from volumetric titrations.

The acid strength of PAM-10 was determined potentiometrically and compared with free phosphoric acid. The pH of the PAM-10 and phosphoric acid was recorded by adding 0.2 mL of standardized NaOH (0.01 N) solution. The derivatives of the pH value against the volume of NaOH added are plotted and shown in Fig. 2. It is observed that the dissociation constant of the first proton of PAM-10, i.e. phosphoric



Fig. 2. Derivative plot of potentiometric titration indicating the first dissociation point.



Fig. 3. XRD pattern of PAM-10.

acid bound to the clay surface, is comparatively lower than that of free phosphoric acid. This might be due to electron withdrawing effect of silicon present in PAM-10. The dissociation of the second proton of PAM-10 did not lead to sharp peaks as compared to phosphoric acid (Fig. 2). This could be explained by the fact that the attachment on the surface may impart some stability to the monoanionic species.

FTIR spectrum of PAM-10 shows no significant changes compared to MK10, however, a shoulder peak is observed around 1050 cm<sup>-1</sup> which can be assigned for P-O bond (see supporting Information). Also, a shift from 1061 cm<sup>-1</sup> to 1064 cm<sup>-1</sup> for Si–O vibration is observed for PAM-10. The peak observed around 780  $\text{cm}^{-1}$  is due to symmetric stretching vibration of alumina octahedra. Thermogravimetric analysis was done to examine the stability of the acid modified clay and it is observed that both MK10 and PAM-10 show loss of surface and interlayer water below 140 °C (see supporting information). A minor weight loss at around 570 °C is observed which is due to irreversible dehydroxylation of silane in case of unmodified clay, whereas the same weight loss is not observed for PAM-10. Differential thermal analysis shows an endothermic peak at around 335 °C due to structural change (see supporting information). The BET analysis shows significant decrease of surface area in PAM-10 (69.67  $m^2/g$ ) as compared to that of montmorillonite  $(210 \text{ m}^2/\text{g})$  thereby indicating acid adsorption.

The XRD pattern of PAM-10 with the *hkl* values of highly intense peaks is shown in Fig. 3. Although there was no significant difference between the XRD pattern of PAM-10 with that of MK10, the decrease in intensity for basal (001) peaks indicates the alteration of layered structure upon acid treatment. The retention of other clay related peaks with minimum shift of 2 $\theta$  values observed at 19.84(003), 20.90(020), 26.68(003) and other peaks indicated conservation of two-dimensional lattice.

Hence the above experiments for characterization of the phosphoric acid modified montmorillonite clay corroborate chemical adsorption of acid on the surface. Our next aim was to study the efficiency of this





newly prepared modified clay in acid-demanding nitration reaction instead of sulfuric acid.

#### 3.2. Nitration of different aromatic compounds

In order to examine the efficacy of the catalyst for nitration of aromatic compounds several reactions were carried out with bromobenzene. Although the reaction of bromobenzene took longer time, it has been considered as model substrate for optimization of the reaction conditions assuming that once this can be nitrated in the presence of the catalyst, other substrate with electron-donating substituent might undergo nitration easily. An amount of 5 wt.% of catalyst (with respect to substrate) and 1.2 equivalent of HNO<sub>3</sub> are found to be the optimum experimental conditions for nitration reaction. Thereafter several aromatic substrates were nitrated and the results are summarized in Table 1.

As expected, aromatic compounds with electron donating substituent gave corresponding nitro compounds with excellent yields in a very short time (entries 2 and 3, Table 1). In case of aniline, some oxidized polymeric byproducts were obtained, thereby decreasing the yield of desired nitro-aniline (entry 4, Table 1). The para selectivity in the present case is found to be higher than general nitration with H<sub>2</sub>SO<sub>4</sub>. Similar observation was observed in the case of unmodified montmorillonite [32], phosphate impregnated titania [26], aluminium tris(dihydrogen phosphate) [27], and modified MoO<sub>3</sub> [25]. Benzene also yielded nitrobenzene efficiently (entry 1, Table 1). Moderately activated aromatic compound such as acetanilide afforded orthoand para-nitro acetanilide in good yields (entry 6, Table 1). The paranitroacetanilide was observed as major product due to the bulkiness of the acetanilide group. Most interestingly, chlorobenzene underwent nitration in the presence of PAM-10 and gave 35% of corresponding nitrochlorobenzene.

Notably, several previously reported catalysts failed to nitrate chlorobenzene [12,26,27]. Due to higher electronegativity of chlorine than that of bromine, the aromatic ring is more deactivated towards electrophilic substitution reaction, thereby providing low or almost no yield. Several polyaromatic hydrocarbons, viz, naphthalene (entry 8, Table 1) and anthracene (entry 9, Table 1), underwent regioselective nitration under the same reaction condition. In addition, the presence of a hydroxyl group, e.g. in 1-naphthol (entry 10, Table 1) further facilitates the nitration reaction. With the present reaction condition, we observed some undesired product in the nitration reaction of 1naphthol, hence the yield of the reaction is found to be slightly lower than that of naphthalene (entry 8, Table 1). Nitration reaction with pyridine yielded pyridine-n-oxide instead of nitro-pyridine (entry 11, Table 1). Due to the presence of non-delocalized lone pair of electron on the nitrogen, pyridine prefers oxidation to give pyridine-n-oxide rather than 3-nitro pyridine with the present reaction condition. A preparative scale reaction performed with 10 g of bromobenzene worked well and gave isolated yield of 72% (entry 5, Table 1).

The usefulness of the present catalyst is demonstrated by conducting different control experiments and the results are depicted in Table 2. Reactions were conducted with bromobenzene and nitric acid in the presence of a) no catalyst (entry 1, Table 2) b) 5 wt.% montmorillonite (entry 2, Table 2), c) 5 wt.% phosphoric acid (entry 3, Table 2) and

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Reusability of catalyst for nitration of bromobenzene.

Reaction run	Yield (%)				
	Catalyst is reused after filtration	Catalyst is reused after evaporating the aq. layer	Catalyst is regenerated by refluxing with phosphoric acid		
1st	20	55	65		
2nd	18	44	62		
3rd	15	40	63		
4th	15	38	62		

#### Table 4

Comparison of catalytic efficiency of PAM-10 with other catalysts in terms of regioselectivity of nitration of toluene.

Catalyst	Temp. (°C)	Yield (%)	O/P ratio	Ref.
Phosphate impregnated titania	RT	87	0.92	[26]
Al(H <sub>2</sub> PO <sub>4</sub> ) <sub>3</sub>	RT	90	1.22	[27]
Montmorillonite	200	72	0.78	[32]
Present catalyst (PAM-10)	RT	97	0.78	This work

d) 5 wt.% montmorillonite and phosphoric acid (entry 4, Table 2), separately. The conversion in each case was comparatively far less which demonstrates that neither of them is effective to forward the desired reaction.

#### 3.2.1. Reusability of the catalyst

The reusability of the catalyst was studied for nitration of bromobenzene and the results are incorporated in Table 3. After completion of reaction, the products were extracted with ethyl acetate  $(\times 3)$  and the remaining aqueous suspension of catalyst was filtered, washed with water, and finally heated in oven at 100-120 °C. This dried used-catalyst was reused for nitration reaction with fresh bromobenzene and nitric acid. The efficiency of the catalyst was found to decrease significantly and gave 20 and 18% yield in 2nd and 3rd run respectively. However, when the aqueous suspension was directly evaporated by heating at 100-120 °C and reused, we obtained 55 and 44% of conversion in 2nd and 3rd run respectively. Thereafter, the efficiency of the catalyst was lost and very less conversion was observed. This is due to leaching of phosphate group from the surface of clay which was confirmed by gravimetric determination. However, the efficiency can be easily regenerated by refluxing the used catalyst with 10 wt.% phosphoric acid.

In order to evaluate the efficiency of the present catalyst, we have compared the results of the nitration of toluene with those of other catalysts and shown in the Table 4. It is observed that the yields are almost similar in case of 'phosphate impregnated titania',  $AI(H_2PO_4)_3$  and PAM-10, whereas montmorillonite gives comparatively low yield at high temperature. Montmorillonite and the PAM-10 show similar selectivity, which is higher than the other two catalysts, indicating clearly that the present catalyst gives higher yield and better selectivity at room temperature.

# 4. Conclusions

A heterogeneous solid acid catalyst is developed by adsorbing phosphoric acid on montmorillonite clay. 10 wt.% of phosphoric acid with respect to the weight of clay is found to adsorb chemically with minimum loss upon water treatment. The phosphoric acid modified clay is found to be an efficient catalyst for nitration of organic compounds with nitric acid and a wide range of such compounds have been nitrated by avoiding the use of sulfuric acid and this is one of the most significant advantages of the present process. Although the reusability of the catalyst is poor, it is compensated by efficacy, ease of handling and scalability which render this protocol very attractive and useful. Further we hope that gas phase nitration will provide regio-selective nitration due to layered structure of the clay which will be carried out in due course. This PAM-10 has been found to efficiently catalyze several organic transformations, which will be communicated elsewhere.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2014.08.019.

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