



Short Communication

Phosphoric acid modified montmorillonite clay: A new heterogeneous catalyst for nitration of arenes[☆]Saitanya K. Bharadwaj^{a,b,*}, Purna K. Boruah^b, Pradip K. Gogoi^b^a Department of Chemistry, Pragjyotish College, Guwahati, 781009 Assam, India^b Department of Chemistry, Dibrugarh University, Dibrugarh, 786004 Assam, India

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ABSTRACT

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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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


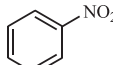
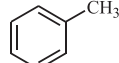
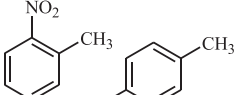
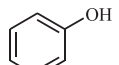
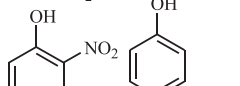
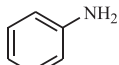
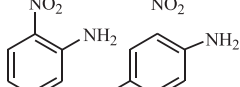
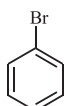
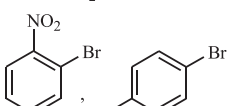
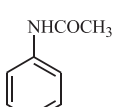
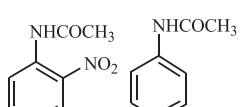
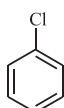
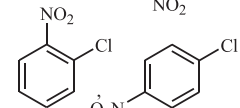
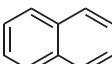
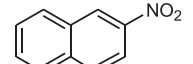
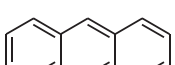
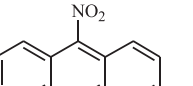
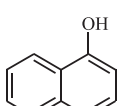
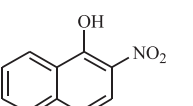


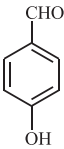
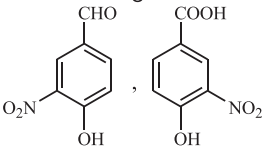
benign catalyst for nitration reactions, solid acids are found to be more efficient. Several solid acid catalysts such as sulfonated polyorganosiloxanes [15], acidic resins [16], zeolites [17] and supported sulfuric acids [18] are used in nitration reactions. Regioselectivity in nitration reaction is observed while using polyoxometalates (POMs) or heteropolyacids [19–22]. Modification of solid oxides such as TiO₂, SiO₂, and MoO₃ with phosphoric acids was reported [23–25] and the modified MoO₃ 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 *para*-selective 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.

[☆] Dedicated to Prof. M. K. Chaudhuri, Vice Chancellor, Tezpur University, India on occasion of his 67th birthday.

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

Entry	Substrate	Time min ^[a]	Product	Yield (%) ^[b] (O/P ratio) ^[c]
1		30, 5 ^[d]		90
2		5		97 (0.78)
3		5		92 (0.92)
4		10		42 (0.84)
5		[24]		68,72 ^[e] (0.17)
6		[15]		73 (0.11)
7		[15]		35 (0.25)
8		15		80
9		10		85
10		30		75
11		[15]		76
12		30		68 (30, 70)

[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 °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⁻¹) 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 ¹H and ¹³C NMR spectra were recorded in CDCl₃ 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 °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 H₂SO₄ 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 Na₂SO₄. 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 H₂SO₄ 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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