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Structure–activity studies of dodecatungstophosphoric acid impregnated bentonite clay catalyst in hydroxyalkylation of *p*-cresol

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ABSTRACT

Bentonite clay impregnated with dodecatungstophosphoric acid (20% DTP/BNT) showed an excellent activity, selectivity and stability [95% product yield with 94% selectivity to 2, 2′-methylenebis (4-methylphenol), DAM] for the hydroxyalkylation of *p*-cresol with formaldehyde at 353 K and for a mole ratio of 5. Ammonia-TPD results showed that an increase in total concentration of acid sites from 4.9 of parent bentonite to 11.6 micromoles per surface area NH_3 ($\mu molS^{-1}$ NH_3) of 20% DTP/BNT was due to a strong interaction of protons of bulk DTP with surface hydroxyl groups of BNT as evidenced by ^{31}P NMR studies.

1. Introduction

Activity of catalysts concomitant with their structures is frequently tuned by modifying their surface properties [1–3]. Surface properties and thereby activity of the catalysts for a particular reaction can be tailored by adopting different methods of preparation and post-synthesis treatments [4–6]. Among various organic transformations, hydroxyalkylation of phenols is an industrially important reaction whose end product e.g. dihydroxydiarylmethane is widely used as chemical intermediate in plastic and rubber industries [7]. Several solid acid catalysts have been reported by researchers [8–11] for replacing the conventional toxic and corrosive reagents which often create serious environmental and operational problems in the hydroxyalkylation of phenols. Among various catalysts, zeolites are widely used for the hydroxyalkylation reaction of various aromatics compounds [12,13]. A major problem associated with these catalysts is their small pore size which restricts diffusion of reactants and products through their voids. Secondly, bulky and high molecular weight condensation products formed during the progress of a reaction poison the catalyst, thereby decreasing its activity [14]. Recently, we have also reported dodecatungstophosphoric acid (DTP) impregnated on various supports, as catalysts for the hydroxyalkylation of phenol where we observed variation in catalyst activity as a function of supports under similar DTP loadings [15,16]. This was mainly due to the difference in textural properties of supports and the extent of interactions of various supports with bulk DTP affecting the acidity of the solid acid catalysts which is a fundamental property governing the activity and selectivity pattern in hydroxyalkylation reactions [17,18]. Supports like silica interact with DTP and forms $(SiOH_2)^+(H_2PW_{12}O_{40})^-$ species which enhanced activity of silica for various organic transformations while other supports like MgO and Al_2O_3 tend to decompose heteropolyacids [19,20] hence the proper choice of support for impregnation of DTP is very crucial. In this context, we thought that bentonite clay is a good alternative due to its inherent acidity which can be further modified by DTP impregnation to create highly active acidic centers [21]. In the present study we report for the first time, surface modified bentonite (BNT) impregnated with DTP as a highly active, selective and reusable catalyst for the hydroxyalkylation of *p*-cresol to form 2, 2′-methylenebis (4-methylphenol) [DAM] as shown in Scheme 1. Activity comparison with bulk DTP, H-β-zeolite ($SiO_2/Al_2O_3 = 25$) and montmorillonite KSF/O was also studied for the hydroxyalkylation of *p*-cresol. All the catalysts were characterized by BET surface area measurements, NH_3-TPD, and by ^{31}P-CPMAS NMR. The reusability and stability of the catalyst were studied by catalyst recycle experiments.

2. Experimental

2.1. Materials

p-Cresol, formaldehyde, toluene and DTP were purchased from Loba Chemie, Mumbai, India. Bentonite was obtained from Ashapura, India. Montmorillonite KSF/O was purchased from Fluka, India. H-β-zeolite ($SiO_2/Al_2O_3 = 25$) was available from Catalysis Pilot Plant, National Chemical Laboratory, Pune India.

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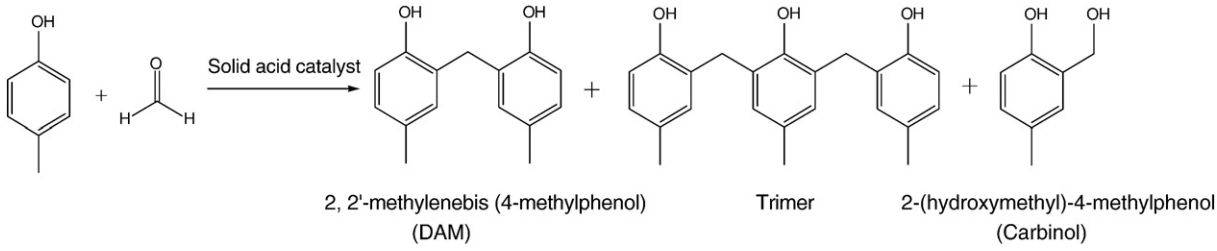

Scheme 1. Hydroxyalkylation of *p*-cresol to 2, 2′-methylenebis (4-methylphenol).

2.2. Catalyst preparation

Surface modified bentonite impregnated with 20% dodecatungstophosphoric acid (20% DTP/BNT) catalyst was prepared by a wet impregnation method. Four g of BNT was weighed and added slowly to the solution of 1 g of DTP in 50 mL methanol with constant stirring over a period of 20 min. The slurry was stirred for 8 h at room temperature and the solvent was evaporated under vacuum. The catalyst formed was dried in an oven at 393 K for 2 h and then calcined at 573 K for 5 h.

2.3. Characterization

X-ray powder diffraction patterns have been recorded on a Rigaku, D-Max III VC model, using nickel-filtered CuKα radiation. The samples were scanned in the 2θ range of 1.5–80°. BET surface areas have been measured by means of N_2 adsorption at 77 K preformed on a Quantachrome CHEMBET 3000 instrument. TPD measurements were carried out on a Quantachrome CHEMBET 3000 TPR/TPD instrument. TPD measurements were carried out by: (i) pre-treating the samples from room temperature to 473 K in a flow of nitrogen; (ii) adsorption of ammonia at room temperature; (iii) desorption of adsorbed ammonia at 10 K min^{-1} starting from the adsorption temperature to 973 K. Brønsted and Lewis acid sites were determined by ex-situ FT-IR spectroscopy with chemisorbed pyridine. For this purpose, catalyst samples were dried at 473 K for 2 h and then saturated with pyridine vapors in a desiccator containing pyridine. Physically adsorbed pyridine was removed by heating the samples at 393 K for 2 h in a continuous flow of nitrogen. FT-IR spectra of the samples were recorded on a Shimadzu (Model-820 PC) spectrophotometer under DRIFT (diffuse reflectance infrared Fourier transform) mode. ^{31}P-CPMAS NMR spectra were measured at room temperature on a Bruker TOPSPIN AVANCE-300 spectrometer equipped with a Bruker MAS-4 BLCP probe using phosphoric acid as a reference compound for the calibration in NMR. The probe head, rotor (4 mm diameter), and sample tubes were made totally moisture free and 0.1 g samples of catalysts were weighted separately and 300 Mz ^{31}P-CPMAS NMR was recorded. Data acquisition and processing were done by using TOPSPIN software provided by Bruker.

2.4. Activity measurement

The hydroxyalkylation of *p*-cresol with formaldehyde was carried out in a magnetically stirred glass reactor (capacity 50 mL) fitted with a reflux condenser and an arrangement for temperature control. In a typical experiment, *p*-cresol (42.5 mmol), formaldehyde (8.5 mmol), toluene (12 cm^3) and catalyst (0.03 g/cm^3) were added to the reactor, which was then heated to a 353 K for 1 h. The product yield (sum of DAM and trimer based on formaldehyde) and selectivity were determined with an HP6890 series GC System (Hewlett Packard) coupled with FID detector and capillary column (HP-1 capillary column, 30 m length × 0.32 mm i.d.). The products were identified by ^{1}H-NMR, ^{13}C-NMR and by GC-MS.

Catalyst recycle experiments were carried out as follows. After the first hydroxyalkylation run, the used catalyst was filtered and washed several times with dichloromethane. Then the catalyst was dried at 383 K for 2 h and reused for the subsequent run. The procedure was followed for three subsequent hydroxyalkylation experiments.

3. Results and discussion

3.1. Catalyst characterization

Both parent BNT and 20% DTP/BNT samples showed XRD pattern which is a characteristic of amorphous material. 20% DTP/BNT sample did not show any crystalline phase of bulk DTP, indicating an excellent dispersion of DNT on BNT after impregnation.

Table 1 presents BET surface areas and NH_3-TPD results of various solid acid catalysts. As can be seen from Table 1, BET surface area of bulk DTP obtained was 8 m^2/g while that of BNT was 242 m^2/g which decreased to 151 m^2/g after impregnation of 20% DTP. This confirmed that DTP was well dispersed (non-porous material) on BNT support after impregnation. The BET surface areas of various catalysts decreased in the following order: H-β-zeolite > BNT > 20% DTP/BNT > montmorillonite KSF/O > DTP.

Fig. 1(a–c) shows the NH_3-TPD profiles of BNT, 20% DTP/BNT and bulk DTP catalysts, while FT-IR pyridine adsorption spectra of various solid acid catalysts are presented in Fig. 2. Among various catalysts, bulk DTP showed the highest concentration of acid sites [163.8 micromoles NH_3 per surface area (μmol$S^{-1}NH_3$), Table 1] having a very sharp desorption peak of strongly chemisorbed ammonia at 925 K [22]. Since bulk DTP exhibit purely Brønsted acidity [23], the peak appeared at 925 K having high acid strength could be assigned to Brønsted acid sites. This was further confirmed by FT-IR pyridine adsorption spectrum of bulk DTP (Fig. 2c) which showed a peak at 1545 cm^{-1} corresponding to Brønsted acidity. NH_3-TPD of parent BNT also showed two signals appearing as low (425 K) and high (825 K) temperature peaks, which could be assigned to Brønsted and Lewis acid sites respectively [24] and total concentration of acid sites was estimated as 4.9 μmol$S^{-1}NH_3$. Interestingly, the total concentration of acid sites of parent BNT increased significantly from 4.9 to 11.6 μmol$S^{-1}NH_3$ after impregnation of 20% DTP loading

Table 1
Textural properties of solid acid catalysts.

Catalysts	S_{BET} (m^2/g)	NH_3 adsorbed (μmolS^{-1})	TPD of NH_3 (%) distribution of acid sites	
			Region I (LT-peaks)	Region II (HT-peaks)
BNT	242	4.9	38	62
20% DTP/BNT	151	11.6	40	60
DTP	8	163.8	35	65
Montmorillonite KSF/O	131	15.5	25	75
H-β-zeolite	650	11.8	63	37