Catalysis Communications 11 (2010) 942–945

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

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

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ARTICLE INFO

Article history:
Received 1 February 2010
Received in revised form 7 April 2010
Accepted 13 April 2010
Available online 24 April 2010

Keywords:
Hydroxyalkylation
Surface modification
Bentonite
p-Cresol
^{31}P CPMAS NMR

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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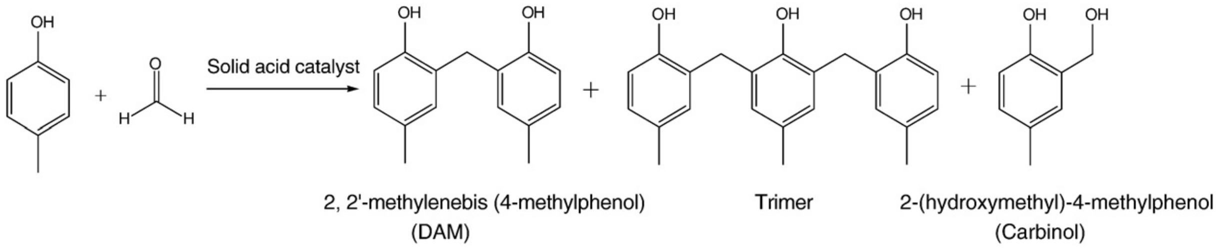
doi:10.1016/j.catcom.2010.04.008



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 (μmolS^{-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 μmolS^{-1}NH$_3$. Interestingly, the total concentration of acid sites of parent BNT increased significantly from 4.9 to 11.6 μmolS^{-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

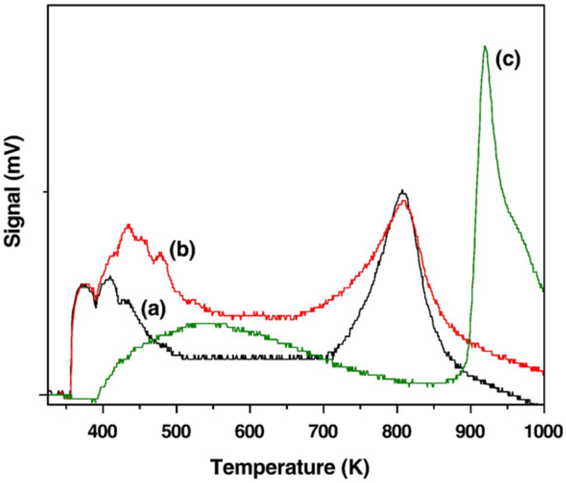


Fig. 1. Ammonia-TPD profile of (a) BNT (b) 20% DTP/BNT and (c) DTP.

(Figs. 1b and 2b), mainly due to the enhancement of Brønsted acid sites that was also evident from a very intense peak appearing at 1545 cm^{-1} as compared to a weak peak at 1445 cm^{-1} corresponding to Lewis acidity. This alteration in acidity could be due to the surface modification of BNT by interaction of bulk DTP with its surface hydroxyl groups similar to that of silica [25,26] which was further confirmed by ^{31}P-CPMAS NMR analysis as discussed later.

Montmorillonite KSF/O also showed two types of acid sites having maxima at 425 K and 675 K with highest total acid sites concentration as 15.5 $\mu molS^{-1}NH_3$ (Table 1). In case of montmorillonite KSF/O, concentration of acid sites at 675 K was 3 times (75%) higher than that of weak acid sites (25%) at 425 K. As can be seen from Fig. 2d, montmorillonite KSF/O showed a single pyridine desorption peak at 1545 cm^{-1} corresponding to purely Brønsted acid sites. This indicates that two desorption peaks at 425 K and 675 K observed in ammonia-TPD plot of montmorillonite KSF/O were due to the Brønsted acid sites having different acid strengths. H-β-zeolite showed higher concentration of acid sites (63%) in a low temperature region (425 K) having total concentration of acid sites of 11.8 $\mu molS^{-1}$ NH_3. These acidic sites in a low temperature region could be due to Lewis acidity [27] which was further confirmed by pyridine-IR analysis of H-β-zeolite which showed a very intense peak at 1445 cm^{-1} (Fig. 2e).

Fig. 3(a, b) shows ^{31}P-CPMAS NMR of DTP and 20% DTP/BNT. DTP showed a sharp signal at −15.61 ppm that corresponds to tetrahedral co-ordination of PO_4 in the Keggin unit [28,29]. Interestingly, 20% DTP/BNT showed a broad signal which shifted towards downfield from −15.61 to −13.7 ppm after impregnation of 20% DTP on it. This broadening and downfield shifting of signal could be due to the strong interaction of protons of bulk DTP with surface hydroxyl groups of BNT similar to that observed in case of silica and alumina [30–32]. This interaction leads to the localization of DTP protons thereby increasing their proximity to the Keggin anion because of the decrease in proton mobility [30]. Such surface as well as acidity modification of BNT due to DTP impregnation enhanced its catalyst activity as discussed below.

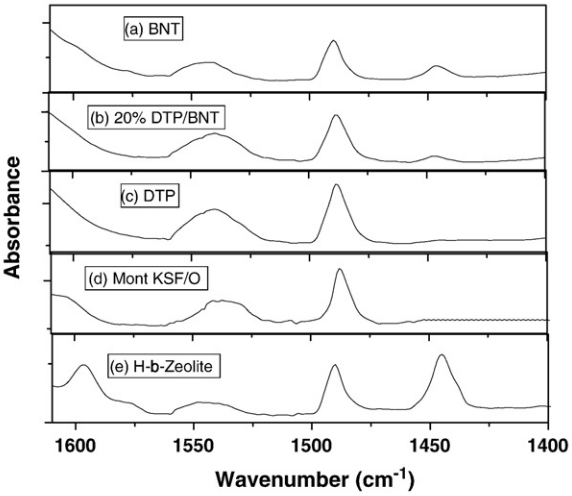


Fig. 2. FT-IR pyridine adsorption spectra of various percentages of various solid acid catalysts.

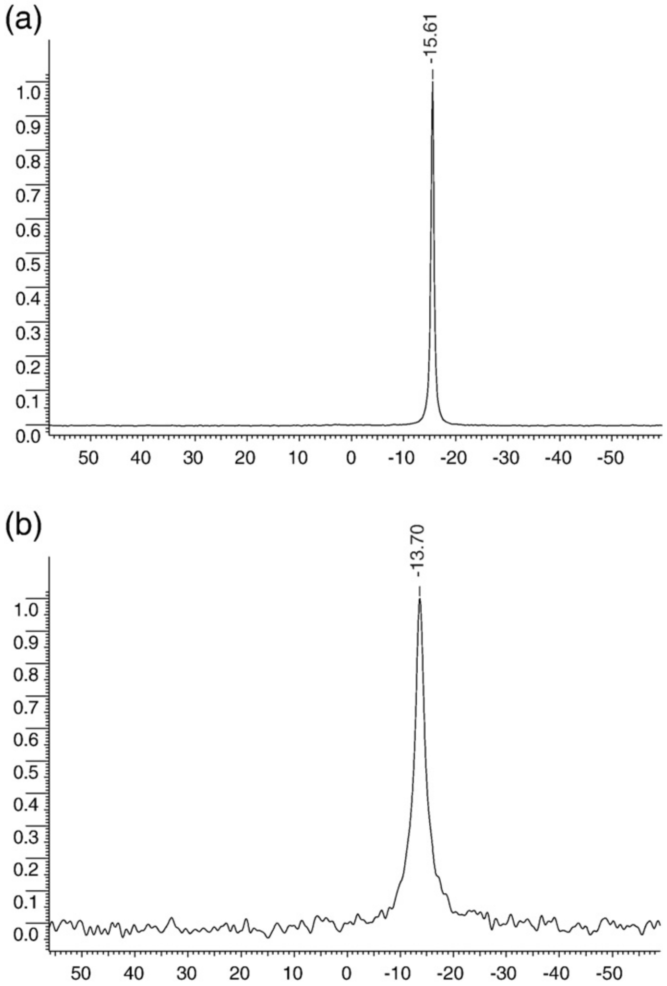


Fig. 3. ^{31}P-CPMAS NMR of (a) DTP and (b) 20% DTP/BNT.

3.2. Catalyst activity

In all the activity measurement experiments, the molar ratio of *p*-cresol to formaldehyde was kept at 5 which was found to be optimum, according to our earlier work [18]. Among the various catalysts studied for the hydroxyalkylation of *p*-cresol (Fig. 4), parent BNT showed 49% product yield with 96% and 4% selectivity to DAM and carbinol respectively, while bulk DTP showed 72% product yield with 65% selectivity to DAM. The lower DAM selectivity with bulk DTP was due to its high acidity (163.8 $\mu molS^{-1}$ NH_3) as well as due to presence of only Brønsted acid sites having high strength (65%) in a high temperature region which facilitates the formation of a trimer by reaction of initially formed DAM with formaldehyde followed by *p*-cresol. Some undetected tarry products were also observed with bulk DTP which resulted into lowering in the mass balance (80–85%). Interestingly, surface modified 20% DTP/BNT catalyst showed the highest product yield (95%) with 94% selectivity

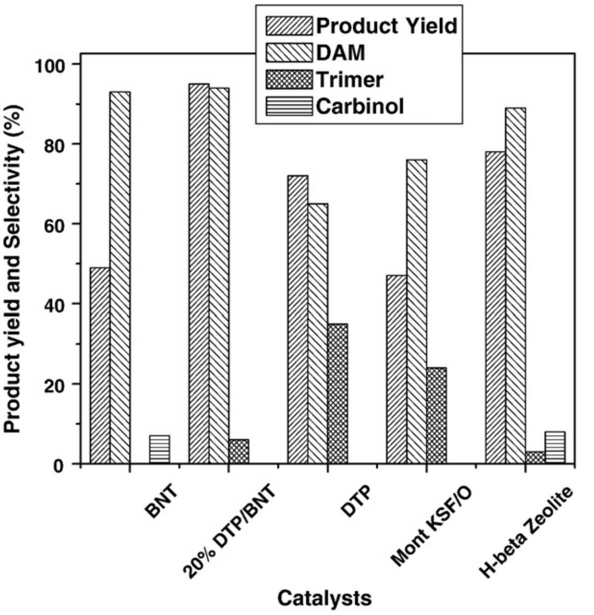


Fig. 4. Catalyst screening for hydroxyalkylation of *p*-cresol. Reaction conditions: *p*-cresol, 42.5 mmol; formaldehyde, 8.5 mmol; mole ratio of *p*-cresol to formaldehyde, 5; catalyst concentration, 0.03 g/cm^3; temperature, 353 K; time, 1 h; solvent, toluene (12 cm^3).

to DAM. The highest product yield with 20% DTP/BNT catalyst was due to the increase in the total concentration of acid sites especially that of Brønsted acid sites, from 4.9 to 11.6 $\mu molS^{-1}$ NH_3 and the stabilization of intermediate carbocation formed during the reaction of heteropolyanion of DTP that also facilitates the formation of DAM [33]. Montmorillonite KSF/O showed 47% product yield, with a lower selectivity (76%) to DAM due to the predominant formation of a trimer (24%) facilitated by its high acidity (15.5 $\mu molS^{-1}$ NH_3) and the presence of Brønsted acid sites (75%) in a high temperature region. Although, H-β-zeolite showed the total acid sites concentration (11.8 $\mu molS^{-1}$ NH_3) similar to 20% DTP/BNT, however lower product yield (78%) with 89% selectivity to DAM was observed with a substantial formation of carbinol (8%) due to the presence of more Lewis acid sites (63%) in a low temperature region. Catalyst activity results showed that Brønsted acid sites in optimal concentration are necessary for achieving highest selectivity to DAM than Lewis acid sites.

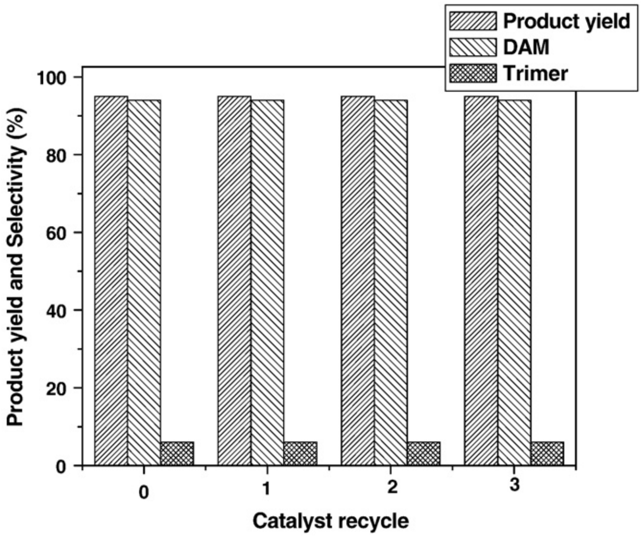


Fig. 5. Catalyst recycle experiment. Reaction conditions: *p*-cresol, 42.5 mmol; formaldehyde, 8.5 mmol; mole ratio of *p*-cresol to formaldehyde, 5; catalyst concentration, 0.03 g/cm^3; temperature, 353 K; time, 1 h; solvent, toluene (12 cm^3).

Catalyst recycle experiments were carried out at 353 K with *p*-cresol to formaldehyde mole ratio of 5 using 20% DTP/BNT catalyst and the results obtained are presented in Fig. 5. The catalyst was found to retain its activity even after the third recycle experiment showing 95% product yield. The selectivity to DAM (94%) remained constant for all the three recycle experiments.

4. Conclusions

Among various solid acid catalysts studied, surface modified BNT (20% DTP/BNT) catalyst showed an excellent activity (95% product yield with 94% selectivity to DAM) for the hydroxyalkylation of *p*-cresol. The increase in total acid sites concentration especially Brønsted acid sites of 20% DTP/BNT from 4.9 to 11.6 $\mu molS^{-1}$ NH_3 was found to be responsible for its high activity and selectivity. ^{31}P (CPMAS) NMR studies showed the broadening and downfield shifting of signal from −15.61 to −13.7 ppm after impregnation of 20% DTP on BNT due to a strong interaction of protons of bulk DTP with surface hydroxyl groups of BNT. The 20% DTP/BNT catalyst was found to retain its original activity even after 3rd recycle experiment.

Acknowledgment

One of the authors (ACG) thanks the University Grant Commission (UGC) New Delhi, for the award of a senior research fellowship.

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