



## Acidity tuning of montmorillonite K10 by impregnation with dodecatungstophosphoric acid and hydroxyalkylation of phenol

A.C. Garade<sup>a</sup>, V.S. Kshirsagar<sup>a</sup>, R.B. Mane<sup>a</sup>, A.A. Ghalwadkar<sup>a</sup>, U.D. Joshi<sup>b</sup>, C.V. Rode<sup>a,\*</sup>

<sup>a</sup> Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune 411008, India

<sup>b</sup> Netaji SubhashChandra Bose College, NANDED 431 601, India

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### ABSTRACT

Acidity tuning of montmorillonite K10 (mont K10) was achieved by impregnating with dodecatungstophosphoric acid (DTP). The effect on the hydroxyalkylation of phenol was studied at 353 K with phenol to formaldehyde molar ratio of 5. The nature and strength of acid sites were determined by NH<sub>3</sub>-TPD measurement while the distribution of Brønsted and Lewis acid sites expressed as B/L ratio, was determined by pyridine IR technique. Among various loadings of DTP (5–60%) studied for the hydroxyalkylation of phenol, 20% DTP/mont K10 showed the highest catalyst activity (90% selectivity to bisphenol F with 28% conversion of phenol). Both total concentration of acid sites and the distribution of acid sites in a high temperature region were required for the high bisphenol F selectivity. Our catalyst (20% DTP/Mont K10) could be recycled three times.

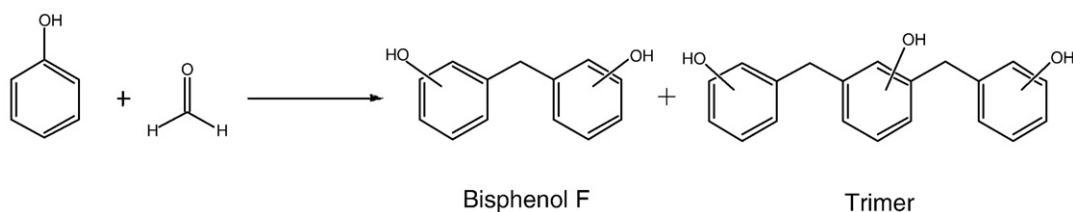
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### 1. Introduction

Due to their specific catalyst activity and recyclability as compared to the conventional acidic reagents, the use of solid acid catalysts has tremendously increased in the fine chemical industry (Corma et al., 2001; Okuhara, 2002; Garade et al., 2009a,b,c; Modrogan et al., 2009; Rode et al., 2009). Owing to its inherent advantages like low toxicity and corrosive nature over conventional reagents, several industrial processes based on the use of acidic reagents in the stoichiometric amount were replaced by the solid acid catalyzed processes (Bhure et al., 2007, 2008; Kozhevnikov, 1998; Misono, 2001). Hydroxyalkylation of phenol to bisphenol F is one such important reaction widely used in the fine chemical industry (De Angelis et al., 2004; Jana et al., 2004, 2005). Since the synthesis of bisphenols is a consecutive reaction, controlling the product selectivity particularly to bisphenol F is a challenging task in the field of catalysis. For the catalyst having lower acidity and acid strength, the predominant formation of carbinol was observed which decreases the bisphenols selectivity while for the catalyst having higher acidity and acid strength, the predominant formation of trimers was observed (Garade et al., 2009a). Hence, developing the catalyst with appropriate acidity and strength to give higher activity

and selectivity to bisphenols is highly desirable. Several solid catalysts such as zeolites, clay minerals, ion exchange resins and amorphous aluminosilicates have been reported for the hydroxyalkylation reaction (Perego et al., 2000; Barthel et al., 2000; Alvaro et al., 1998, 2003; Yadav and Kirthivasan, 1997; Reincker and Gates, 1974; Das et al., 2001). In this context, heteropolyacids are also a good alternative due to its stronger acidity (Mizuno and Misono, 1998; Hou and Okuhara, 2003). However, heteropolyacids have very low (<8 m<sup>2</sup>/g) surface area and very high acidity which generally decreased bisphenols selectivity due to the formation of unwanted side products (trimers and its higher homologue) (Garade et al., 2009a). Hence, better dispersion of heteropolyacids on a suitable support is highly imperative for the hydroxyalkylation of phenol. Although, mesoporous silica is widely used as support (Kuang et al., 2003; Izumi, et al., 1995; Yadav and Manyar, 2003), montmorillonite clays are also a good alternative due its high surface area. In this paper, we report the effect of acidity tuning of montmorillonite K10 (mont K10) on the hydroxyalkylation of phenol to bisphenol F (Scheme 1). The acidity of mont K10 was tuned by dispersing dodecatungstophosphoric acid (DTP) on mont K10 support by wet impregnation method. Among various solid acid catalysts screened, 20% DTP/Mont K10 was found to be the most active catalyst for the hydroxyalkylation of phenol. Ammonia TPD studies of various catalysts showed that the acid sites present in a high temperature region are highly desirable for the high catalyst activity and bisphenol F selectivity. The catalyst was successfully recycled for three times.

\* Corresponding author. Tel.: +91 20 2590 2349; fax: +91 20 2590 2620.  
E-mail address: [cv.rode@ncl.res.in](mailto:cv.rode@ncl.res.in) (C.V. Rode).



**Scheme 1.** Hydroxyalkylation of phenol to bisphenol F.

## 2. Experimental

### 2.1. Materials

Phenol (99%), aqueous formaldehyde (37%), toluene (99%) and DTP were purchased from Loba chemie, Mumbai, India. Mont K10 was purchased from Sigma-Aldrich, Bangalore, India.

### 2.2. Catalysts preparation

DTP impregnation of mont K10 (20% DTP/Mont K10) was performed by dispersing 4 g of mont K10 in a solution of 1 g of DTP in 100 mL methanol with constant stirring over a period of 20 min. The dispersion was stirred for 24 h at room temperature and the solvent was evaporated under vacuum. The catalyst was dried at 383 K for 2 h and then calcined at 573 K for 6 h. 5, 10, 40 and 60% DTP/Mont K10 catalysts were also prepared by similar method.

### 2.3. Characterization

X-ray powder diffraction patterns were recorded on a Rigaku, D-Max III VC model, nickel filtered  $\text{CuK}\alpha$  radiation. BET surface area measurements were carried out by  $\text{N}_2$  adsorption at 77 K (Quantachrome CHEMBET 3000). Ammonia temperature programmed desorption (TPD) was also done on Quantachrome CHEMBET 3000 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 with a heating rate  $10 \text{ K min}^{-1}$  starting from the adsorption temperature to 998 K. The Brønsted and Lewis acid sites were determined by ex-situ FT-IR spectroscopy with chemisorbed pyridine. For this purpose, catalyst samples were dried at 383 K for 1 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.

The chemical composition of the sample was determined by energy-dispersive X-ray (EDX) (JEOL JSM 500) analysis.

### 2.4. Reaction procedure

The hydroxyalkylation of phenol with formaldehyde was carried out in a magnetically stirred glass reactor (50 mL) fitted with a reflux condenser and an arrangement for temperature controller. In a typical hydroxyalkylation experiment, phenol (12.5 mmol), formaldehyde (2.5 mmol), and toluene (55 mmol) were taken and the catalyst ( $0.04 \text{ g/cm}^3$ ) without any pretreatment was added to the reaction mixture. The reaction mixture was then heated to a desired temperature for 40 min.

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.

### 2.5. Analysis

Phenol conversion and product selectivity were determined by HP6890 series GC System (Hewlett Packard) coupled with FID detector and capillary column (HP-1 capillary column, 30 m length  $\times$  0.32 mm i.d.). Products were identified by  $^1\text{H}$  NMR, GC-MS and by comparing retention time of samples with those of authentic samples.

## 3. Results and discussion

### 3.1. Catalyst characterization

X-ray diffraction patterns of mont K10, 10 and 20% DTP/Mont K10 are presented in Fig. 1. Mont K10 showed (Fig. 1a) sharp (001) and (003) reflections at  $2\theta = 9^\circ$  and  $18^\circ$ . The sharp reflection at  $2\theta = 27^\circ$  was assigned to  $\alpha$ -quartz (Yadav and Kirthivasan, 1997). 5% DTP/Mont K10 showed XRD pattern similar to that of mont K10. However, the intensity of reflections decreased significantly, particularly the reflection at  $2\theta = 18^\circ$  almost disappeared after impregnation of 10 and 20% DTP on mont K10 due to the excellent dispersion of DTP on mont K10 as well as that of K10 itself.

The specific BET surface areas of various solid acid catalysts are presented in Table 1. Among various solid acids, mont K10 showed the highest ( $230 \text{ m}^2/\text{g}$ ) specific BET surface area while DTP showed lowest ( $8 \text{ m}^2/\text{g}$ ) BET surface area. The specific BET surface areas of various catalysts showed the following order: mont K10 > 5% DTP/Mont K10 > 10% DTP/Mont K10 > 20% DTP/Mont K10 > 40% DTP/Mont K10 > 60% DTP/Mont K10 > DTP. The decrease in surface area with increase in DTP loadings was due to the better dispersion of DTP on mont K10 which made some of pores of mont K10 inaccessible to  $\text{N}_2$ .

$\text{NH}_3$ -TPD profiles of mont K10, bulk DTP and 5–60% DTP on mont K10 catalysts are shown in Fig. 2 and the values of ammonia adsorbed and (%) distribution of acid sites based on ammonia desorption are presented in Table 1. The total concentration of acid sites per unit surface area of various catalysts decreased in the following order: DTP > 60% DTP/Mont K10 > 40% DTP/Mont K10 > 20% DTP/Mont K10 > 10% DTP/Mont K10 > 5% DTP/Mont K10 > Mont K10. Among various solid acid catalysts, bulk DTP showed the highest ( $0.164 \text{ mmol S}^{-1} \text{ NH}_3$ ) concentration of acid sites with sharp desorption peak of ammonia at  $650^\circ\text{C}$  (Kamiya et al., 2007). The desorption temperature which reflects the acid strength was also highest for bulk DTP. As compared to bulk DTP, mont K10 showed low concentration of acid sites ( $0.008 \text{ mmol S}^{-1} \text{ NH}_3$ ). The concentration of acid sites and (%) distribution of acid sites in high temperature region of mont K10 increased from 0.008 to  $0.065 \text{ mmol S}^{-1} \text{ NH}_3$  and from 49 to 62% respectively with the increase in DTP loading from 0 to 60%. The linear increase in concentration of acid sites with the increase in DTP loading shows homogeneous dispersion of DTP particles on mont K10. Interestingly, sharp desorption peak of bulk DTP at  $650^\circ\text{C}$  disappeared and new acid sites were observed for DTP loading up to 20% in a range of  $250$ – $450^\circ\text{C}$  while, 40 and 60% DTP/mont K10 catalysts showed more intense desorption peaks in higher temperature region having maxima at  $500$  and  $610^\circ\text{C}$  respectively. The concentration of acid sites of bulk DTP which reflect total acidity

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