



Montmorillonite for selective hydroxyalkylation of *p*-cresol

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ABSTRACT

Performances of montmorillonite titanium silicate (TS-1) and dodecatungstophosphoric acid (DTP) were compared for the hydroxyalkylation of *p*-cresol into dihydroxydiarylmethane (DAM). Ammonia TPD studies of various catalysts showed that an appropriate combination of both strong and weak acid sites of montmorillonite was mainly responsible rather than only the stronger acidity of bulk DTP for its highest catalytic activity for selective hydroxyalkylation of *p*-cresol to DAM. The selectivity to DAM could be enhanced by adjusting reaction conditions like mole ratio of *p*-cresol to formaldehyde, reaction temperature, catalyst concentration, solvent and reaction time.

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1. Introduction

With increasing concern of the environmental problems in fine chemical industry, attempts are being made by the researchers to replace the conventional acid reagents by solid acid catalysts in various organic transformations (Corma, 1995; Singh et al., 2007). One such important reaction is the condensation of aldehyde or ketone with aromatic compounds commonly known as hydroxyalkylation for the synthesis of dihydroxydiarylmethane products, widely used in the chemical industry (Barthel et al., 2000; Angelis et al., 2004). Industrially hydroxyalkylation processes are carried out using strong mineral acids such as HCl, H₂SO₄ and H₃PO₄ (Okihama, 1996, 1997). Although, these reagents give acceptable yields of the desired product, these processes have some major drawbacks like difficulties in the separation and recovery of pure product from the reaction medium, handling of the reagents, problems due to corrosive nature of reagents and formation of inorganic wastes due to use of reagents in the stoichiometric quantities (Okihama, 1996). In order to overcome these drawbacks several solid catalysts such as zeolites, heteropolyacids, clay minerals, ion exchange resins and amorphous aluminosilicates have been proposed in the literature (Yadav and Kirthivasan, 1997; Alvaro et al., 1998, 2003; Jana et al., 2004, 2005; Udayakumar et al., 2006). Although, zeolites and sulphonic resins have been preferred as commercial solid acid catalysts, clay minerals and heteropolyacids are also an interesting class of solid acid catalysts having both Lewis and Brønsted acidity and therefore can be further explored for hydroxyalkylation reaction (Farhad, 1988; Perego et al., 2000; Bhure et al., 2007, 2008). In this paper, we report a com-

parative study of activity and selectivity of montmorillonite clay, titanium silicate (TS-1) and bulk dodecatungstophosphoric acid (DTP) as solid acid catalysts for the hydroxyalkylation reaction of *p*-cresol to 2, 2'-methylenebis (4-methylphenol), DAM (Scheme 1) which is used as an antioxidant in plastic and rubber industries (Huglin et al., 1972). Among these solid acids, montmorillonite clay was found to be the most active catalyst for selective hydroxyalkylation of *p*-cresol to DAM. Ammonia TPD studies of various catalysts showed that an appropriate combination of both strong and weak acid sites of montmorillonite was mainly responsible rather than only the stronger acidity of bulk DTP for its highest catalytic activity for selective hydroxyalkylation of *p*-cresol to DAM. Effects of various reaction parameters like mole ratio of *p*-cresol to formaldehyde, reaction temperature, catalyst concentration, solvent and reaction time on *p*-cresol conversion and DAM selectivity have also been investigated.

2. Experimental

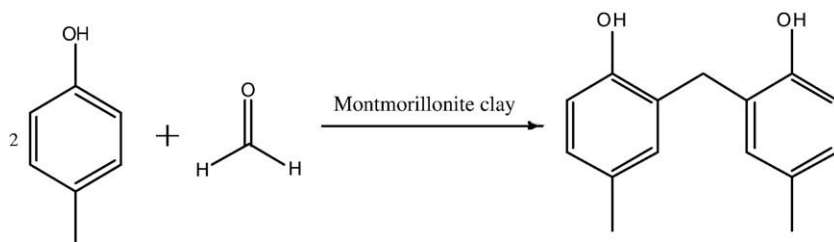
2.1. Materials

Montmorillonite was purchased from Sigma-Aldrich, Bangalore, India. TS-1 was prepared in NCL, Pune, India. *p*-Cresol, formaldehyde, toluene, isopropyl alcohol and DTP were purchased from Loba chemie, Mumbai, India. *n*-Decane was purchased from Sd fine chemicals, India and all solvents were used without further purification.

2.2. Physico-chemical characterization

BET surface area measurements were carried out by N₂ adsorption at 77 K (Quantachrome CHEMBET 3000). Ammonia temperature programmed desorption (TPD) was also done on Quantachrome CHEMBET

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Scheme 1. Hydroxyalkylation of *p*-cresol to DAM.

3000 by: (i) pre-treating the samples from room temperature to 200 °C in a flow of nitrogen (ii) adsorption of ammonia at room temperature (iii) desorption of adsorbed ammonia with a heating rate 10 °C min⁻¹ starting from the adsorption temperature to 725 °C.

2.3. Catalytic activity tests

The hydroxyalkylation of *p*-cresol 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, *p*-cresol (1 g), formaldehyde (0.15 g), toluene (2.5 ml) were taken and catalyst (0.15 g) without any pre-treatment was added to the reaction mixture. The reaction mixture was then heated to a desired temperature and the reaction was continued for 2 h. *p*-cresol 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 X 0.32 mm i.d.). The products were identified by ¹H NMR, ¹³CMR and by GC-MS. Recycling experiments were carried out at 353 K using *p*-cresol/ formaldehyde mole ratio 3:1 for 2 h with catalyst concentration (montmorillonite) 0.042 g/cm³ as follows. After the first hydroxyalkylation run, the used catalyst was filtered and washed with methanol followed by several times with deionized water. Then the catalyst was dried in an oven at 393 K for 8 h and reused for the subsequent run. The procedure was followed for two subsequent hydroxyalkylation experiments.

3. Results and discussion

3.1. Catalyst characterization

Table 1 presents the specific BET surface area and NH₃-TPD results of montmorillonite TS-1 and DTP. The surface areas of various catalysts were in the following order: TS-1 > montmorillonite clay > DTP.

NH₃-TPD profiles of montmorillonite clay, TS-1 and DTP are shown in Fig. 1 and the values of ammonia adsorbed are presented in Table 1. DTP showed two desorption peaks, one for the strongly chemisorbed ammonia at 650 °C (curve b, in Fig. 1) and another at 200 °C. The amount of desorbed ammonia for these two different acid sites was 0.70 and 0.66 mmol/g indicating almost same concentration of both the acid sites in case of DTP. Montmorillonite sample also exhibited two desorption peaks, one for the strongly chemisorbed ammonia in the range of 600–650 °C (curve a in Fig. 1) and another at 200 °C. However, the amount of ammonia desorbed at low temperature was more than 1.5 times than that at higher temperature. Interestingly, TS-1 showed only one peak in the low temperature region at 100–200 °C

Table 1
Textural properties of the catalysts

Sr. No.	Catalysts	S _{BET} (m ² /g)	TPD of NH ₃		
			Region I (LT-Peak)	Region II (HT-Peak)	Total acid site density (mmol/g)
1	Montmorillonite clay	59.2	1.48	0.91	2.39
2	TS-1	410.6	1.18	–	1.18
3	DTP	8.3	0.66	0.70	1.36

(curve c in Fig. 1). Among all these catalysts, montmorillonite sample has the highest total acid concentration.

3.2. Catalyst screening

Comparison of activities of montmorillonite clay with those of TS-1 and DTP for hydroxyalkylation of *p*-cresol are presented in Fig. 2. Montmorillonite clay and DTP showed almost similar conversion (32%) of *p*-cresol, while TS-1 showed the lowest activity (<4% conversion of *p*-cresol) in spite of its very high surface area (410 m²/g). Selectivity to DAM was maximum (>90%) for montmorillonite while it was much lower for both DTP and TS-1 (73% and 68% respectively). This indicates the nature and strength of acid sites play a dominant role in hydroxyalkylation of *p*-cresol with formaldehyde. The lowest activity (<4% conversion) of TS-1 could be attributed to its lowest acid strength as well as the presence of only Lewis acidic sites in the low temperature region at 100–200 °C (Mariscal et al., 2000; Capel-Sanchez et al., 2003). Montmorillonite showed marginally higher activity than that for DTP although its total acid strength was 1.75 times more than that of DTP, indicating that beyond a certain value, total acid strength does not affect the activity of the catalyst. However, selectivity to the desired DAM was maximum (>90%) in case of montmorillonite which can be due to the fact that density of low temperature acid sites was much higher (by about 50%) than that of high temperature acid sites. In case of DTP, both the acid sites were almost equal in concentration but the selectivity to DAM was lower (73%) while for TS-1, only low temperature acid sites were present which resulted in lowest selectivity to DAM. The decrease in selectivity of DAM for TS-1 was mainly because of predominant formation of carbinol. This clearly indicates that the presence of both types of acid sites as well as the total acid strength is crucial in determining the activity and selectivity performance for hydroxyalkylation of *p*-cresol. Since, montmorillonite clay was found to be the best catalyst because of its mixed acidic sites (Stackhouse et al., 2001) for hydroxyalkylation of *p*-cresol, further study on the effect of

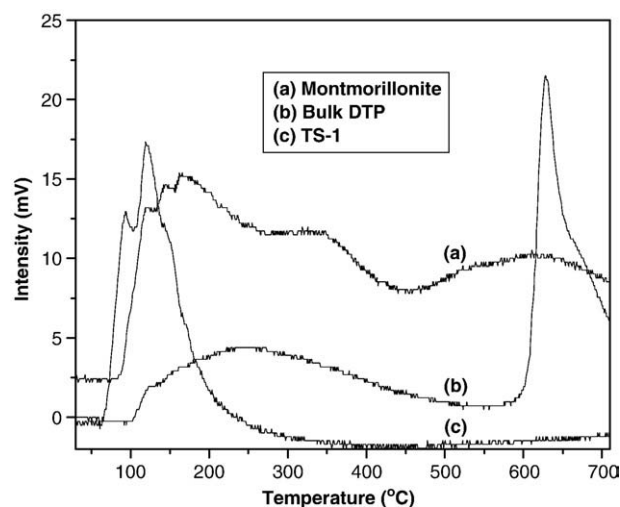


Fig. 1. Ammonia TPD profile over montmorillonite clay, DTP and TS-1.

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