Research paper

12-Phosphotungstic acid immobilized on activated-bentonite as an efficient heterogeneous catalyst for the hydroxyalkylation of phenol

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ARTICLE INFO

ABSTRACT

12-Phosphotungstic acid (PTA) supported on commercially activated-bentonite (BNT) was demonstrated to be efficient in the synthesis of bisphenol F (BPF) by hydroxyalkylation of phenol. In the series of PTA (10–40 wt.%) impregnated-BNT catalysts prepared, 20% PTA/BNT showed the highest product yield (93%) and selectivity (97%), which was higher than that of parent PTA and BNT individually, due to the excellent dispersion of PTA on BNT leading to the redistribution of Brönsted and Lewis acid sites on BNT. NH_3-TPD studies of various catalysts revealed that an appropriate combination of both strong and weak acid sites could contribute to a higher yield of BPF compared to the catalyst Al-MCM-41, and the Brönsted acid sites were more crucial in achieving a higher selectivity to 4,4′-isomer than Lewis acid sites.

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1. Introduction

The lower dynamic viscosity of BPF epoxy resin has made it of moderate importance as a precursor of liquid BPF resins which are used in plastic and rubber industries (De Angelis et al., 2004; Jana et al., 2005). In conventional methods, hydroxyalkylation processes like bisphenols are produced in catalysis of liquid protonic acid (HCl, H_2SO_4 and H_3PO_4 or other inorganic bases) which is corrosive, toxic, disposal, and difficult in separation, purification and recovery (Commarieu et al., 2002; Perego et al., 2006; Chen et al., 2008). Due to the increasing concern for developing environment-friendly chemical processes, several attempts have been reported to replace the conventional processes based on stoichiometric use of reagents by solid catalysts for the synthesis of bisphenols (Yadav and Kirthivasan, 1997; Nowiñska and Kaleta, 2000; Das et al., 2004; Shimizu et al., 2010). Among various solid acid catalysts, zeolites show better activity for bisphenol synthesis, but a major problem associated with these catalysts is the deactivation of the catalysts due to the deposition of bulky and higher molecular weight condensation products formed during the progress of the reaction (Corma et al., 2001; Jana et al., 2005).

Heteropolyacids, which were found to be eco-friendly, are in widespread use for its strong Brönsted acidity and chemical stability (Gurav et al., 2014; Nandiwale and Bokade, 2014). While the low surface area and high solubility in polar solvents limit heteropolyacids' industrial application (Newman et al., 2006). Hence, it is imperative to employ an appropriate support to distribute the heteropolyacid. Bentonite, a clay mineral which is abundant on the earth, consists of layers of two tetrahedral silica sheets sandwiching one octahedral alumina sheet. Both the modified-bentonite and bentonite are promising supports due to their common fascinating features, such as their inherent acidity, excellent thermal stability, and easily controlled structure and morphology (Rožić et al., 2011). Therefore, the modified-bentonite with larger specific surface area is widely used as a very good catalyst carrier (Segarra et al., 2003; Tomul and Balci, 2009; Borsacchi et al., 2013; Ma et al., 2013; Malamis and Katsou, 2013). Actually, heteropolyacid-impregnated solid acids have caused great interests in many fields (Haber et al., 2003; Liu et al., 2004; Kamalakar et al., 2006; Jin et al., 2009; Brahmkhatri and Patel, 2011).

Here we report highly dispersed PTA on BNT as a highly active, selective and reusable catalyst for BPF synthesis. Systematic researches about effects of different parameters, namely, PTA loading, phenol/ formaldehyde mole ratio, reaction time, temperature, and catalyst concentration on yield and selectivity of products were studied. The recycle of catalyst was also investigated by reutilization tests.

2. Experimental

2.1. Chemicals and materials

Commercially activated-bentonite, 12-phosphotungstic acid, phenol, formaldehyde (37–40%) and methanol are purchased from

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Sinopharm Chemical Reagent Co., Ltd, China. All the reagents were used without further purification. Al-MCM-41 was synthesized in our laboratory, and the detailed information is provided in supplementary information.

2.2. Catalyst preparation

PTA impregnated-BNT catalysts were prepared according to literature procedures with small modifications (Yadav et al., 2003a). In a typical synthesis of 10% PTA/BNT, 0.25 g of PTA dissolved in methanol was added into the flask containing 2.25 g of BNT and stirred for 3 h at room temperature. The resulting mixture was dried in an oven at 573 K for 5 h. A series of PTA/BNT (10–40 wt.%) were prepared in the same method.

In the assembly process of PTA/BNT in methanol, electrostatic interaction is the driving force owing to the negatively charged PTA Keggin unit and the positively charged surface of BNT. When numbers of PTA molecules/clusters are deposited on the surface of BNT, the anchored PTA/BNT is constructed (Patel and Singh, 2014). In such a structure, the PTA molecules/clusters exist on the whole surface of BNT. This design aims to increase and redistribute the amounts of active acid sites, thus realizing an efficient hydroxyalkylation of phenol to BPF.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were collected on a D8-Advance with a Bruker diffractometer using Cu Ka radiation ($\lambda =$ 1.54056 Å) at 40 kV and 40 mA. Diffraction data were recorded with a scanning speed of 0.5° of 2θ/s and 2θ = 0.02°. Nitrogen gas adsorption–desorption isotherms were performed at 77 K using a Micromeritics ASAP 2020 Sorptometer. Before adsorption, the catalysts were vacuum-dried at 573 K for 10 h. The Brunauer–Emmett–Teller (BET) specific surface area was calculated using adsorption data in the relative pressure range of 0.04–0.3 P/P_0. Ammonia temperature programmed desorption of NH_3 (NH_3-TPD) measurements were performed utilizing a Micromeritics 2920 apparatus using a thermal conductivity detector (TCD) under a flow of 5% NH_3/He gas mixture with a rate of 50 mL min^{-1} and a heating rate of 10 K min^{-1} from room temperature to 1023 K. Before the NH_3-TPD analysis, the catalysts (130 mg) were first heated by a rate of 10 K min^{-1} from room temperature to 473 K and pretreated for 30 min under highly purified argon atmosphere. Infrared spectra were collected on Bruker vector 22 FT-IR spectrophotometer in the range of 4000–400 cm^{-1} by using KBr pellet technique. The data were recorded at a resolution of 2 cm^{-1}. ^{31}P MAS NMR spectra were measured at 9.4 T on a Varian Infinity plus-400 spectrometer equipped with a Chemagnetic double-resonance 4-mm probe. The resonance frequency was 161.9 MHz. Chemical shifts were referred to external H_3PO_4 (85 wt.%).

2.4. Catalyst testing

The selective hydroxyalkylation of phenol with formaldehyde to BPF was carried out in a magnetically stirred glass reactor fitted with a reflux condenser and an arrangement for temperature control. In a typical experiment, phenol (1.800 mol), formaldehyde (0.120 mol) and 20% PTA/BNT (0.015 g/g) were added to the reactor and reacted for 4 h at 383 K. The products were determined by a Shimadzu LC-20AT system equipped with a SPD-20A UV/Vis detector and a Phenomenex Luna C18 column (250 × 4.6 mm, 5 μm) with a flow rate of 0.8 mL/min and detection wavelength of UV 275 nm.

3. Results and discussion

3.1. Catalyst characterization

The results of chemical compositions, specific surface area, and acid sites distribution of the catalysts are presented in Table 1. Obviously, the surface area of plain BNT is up to 264 $m^2 g^{-1}$, and decreased notably as the PTA loading increased from 10% to 40%, which seems logical for the deposition of PTA on the support surface (Lu et al., 2011). In addition, the chemical compositions analysis results confirmed that PTA has been anchored on BNT successfully.

In Fig. 1, the sharp desorption peaks exhibiting around 853 K and 543 K are ascribed to Brönsted and Lewis acid sites respectively (Su et al., 2009). Fig. S1 shows the NH_3-TPD profiles of bulk PTA and Al-MCM-41. The quantity of strong acid sites increased rapidly from 1.57 mmol g^{-1} to 1.93 mmol g^{-1} with the increase of PTA loading amount from 10% to 40%, meanwhile, the weak acid sites quantity decreased from 0.51 mmol g^{-1} to 0.39 mmol g^{-1} (Table 1).

Wide-angle XRD (WXRD) patterns of bulk PTA, plain BNT and PTA/BNT composites (with PTA loading from 10% to 40%) in 5° < 2θ < 80° are presented in Fig. 2. The four reflections between 25° and 60° are associated with Keggin structure unit possessed by bulk PTA (Nandiwale and Bokade, 2014). Sharp reflections exhibited at 2θ = 9° and 18° are characteristic of amorphous material plain BNT, and the one at 2θ = 27° is corresponding to α-quartz (Rožić et al., 2011). It's clear that XRD patterns of 10, 20, 30 and 40% PTA/BNT are similar to that of parent BNT, which means that the impregnation of PTA only caused a slight decrease in reflection intensity. Besides, no separate crystal phase was detected due to the large surface area of BNT, indicating that PTA was well dispersed on the surface of BNT, which is consistent with the previous chemical composition analysis results (Yadav et al., 2003b).

The primary structure of PTA/BNT composites was studied by comparing their FT-IR absorbance (Fig. 3). For bulk PTA, characteristic bands exhibiting at 1080 ($P-O_a$ in central tetrahedral), 982 (terminal $W=O_d$), 894 ($W-O_b-W$), and 804 cm^{-1} ($W-O_c-W$) are coincided with asymmetric vibrations in Keggin unit (Kreuer, 1996). These bands were also detected in PTA/BNT composites with different PTA contents, which indicated the successful assembly of PTA onto BNT after impregnation treatment. Small shifts in frequency that appeared in IR spectra may be caused by the electrostatic interactions between PTA Keggin unit and parent BNT (Lu et al., 2010). In addition, the band between 1631 and 1642 cm^{-1} is attributed to the $-OH$ bending frequency of water molecules absorbed by catalysts.

Table 1
Textural properties of various catalysts.

Catalysts	Compositions (wt.%)				Specific surface area ($m^2 g^{-1}$)	NH_3 adsorbed (mmol g^{-1})	
	SiO_2	Al_2O_3	WO_3	P_2O_5		Weak acid sites (LT-peaks)	Strong acid sites (HT-peaks)
Plain BNT	64.5	12.9	–	–	264	0.22	1.90
10% PTA/BNT	58.8	11.5	5.9	0.12	176	0.51	1.57
20% PTA/BNT	53.6	10.6	12.6	0.20	142	0.51	1.68
30% PTA/BNT	48.4	9.7	20.8	0.26	134	0.49	1.74
40% PTA/BNT	43.3	8.5	27.3	0.33	121	0.39	1.93
Bulk PTA	–	–	0.95	0.05	6	0.12	1.97
Al-MCM-41	94.7	5.3	–	–	962	0.24	0