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Phosphoric acid modified SBA-15 as a highly efficient heterogeneous catalyst for the synthesis of 4,4'-diamino-3,3'-dibutyl-diphenyl methane

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1. Introduction

Aromatic polyimides [1] have received much attention for its excellent thermal stability, chemical resistance, outstanding mechanical and electronic properties, and been employed broadly in many high technique areas, such as electronics [2], membranes [3–5], coatings [6,7], and composite materials [8]. However, the commercial use of these materials is limited because of their poor solubility and high softening or melting temperatures. To resolve these problems, researchers focused on synthesis of soluble and processable aromatic polyimides in a fully imidized form without sacrificing their excellent properties. Introducing tert-butyl-substituted monomer, 4,4'-diamino-3,3'-dibutyl-diphenyl methane (MBTBA), into the backbone of aromatic polymers displayed great improvement of the solubility and processability without causing the unacceptable loss of thermal properties of the polymer [9,10].

MBTBA can be used not only as monomer in the preparation of advanced polyimide, but also as chain extender of polyurethane and curing agent of epoxy resin [11]. Therefore, it is attractive to explore the synthetic method of MBTBA. Traditionally, *o*-tertbutylaniline is condensed with formaldehyde to give MBTBA in the presence of HCl. This method suffers from the difficulty in separation and the environmental pollution. Heterogeneous catalysis has received more and more attention, which gives an easier separation and offers the opportunity to reduce the impact on the

ABSTRACT

Phosphoric acid modified SBA-15 (P/SBA-15) was employed as catalyst in the synthesis of 4,4'-diamino-3,3'-dibutyl-diphenyl methane (MBTBA) *via* condensation of *o*-tert-butylaniline with paraformaldehyde. It performed more efficiently than HY, kaolinite, γ -Al₂O₃ in heterogeneous reaction and HCl in homogeneous catalysis did. The catalyst preparation and reaction conditions were investigated and the yield reached 50% under the optimized term. The BET and Py-FTIR results suggested that the excellent performance of P/SBA-15 in the synthesis of MBTBA should be attributed to the weak acidity of the material and its large pore size that facilitated the diffusion of substrate and product.

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environment and increase the profit [12]. Recently, it is reported that heterogeneous catalysis has been applied in similar reactions. Corma et al. [13] employed delaminated zeolite instead of HCl in the production of 4,4'-diaminodiphenylmethanes, which gave high conversion and selectivity. Bahulayan et al. [14] developed an efficient method of synthesis of 4,4'-diaminodiphenylmethanes catalyzed by an eco-friendly catalyst, kaolinitic clay. However, there was no description of the synthesis of MBTBA under heterogeneous catalysis, which might be the consequence of large molecule size of the substrate and the product (ca. 1.1 nm and 1.5 nm, respectively, measured by Gaussview 3.0).

Mesoporous materials have received much attention because of their unique properties with well-controlled pore structure, high surface area, large and tunable pore size which facilitate the diffusion of reactant and product inside the pore [15-19]. However, purely mesoporous materials show limited application for catalysis because of the lack of acidity and capacity for ion-exchange. Previous research in our group [20,21] and other groups [22,23] revealed that phosphoric acid modified mesoporous materials could exhibit Brønsted acidity and large pore size. And, Mauder et al. [24] presented their detailed study on the hydrogen bond interaction of pyridine with phosphonic acid moieties at the surface of SBA-15 mesoporous silica by a combination of solid-state NMR techniques. Moreover, Paul et al. [25] synthesized mesoporous titanium-phosphorus mixed oxides that showed excellent catalytic activity in acid catalyzed Friedel-Crafts benzylation of bulky aromatics and partial oxidation of styrene to benzaldehyde with dilute H₂O₂ oxidant. Panneerselvam et al. [26] reported that phosphoric acid modified β-zeolite was an efficient sorbent media for the removal of copper ions from aqueous solution and wastewater.





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Due to the need of acidic heterogeneous catalyst, phosphoric acid modified materials highlight an opportunity in the development of novel efficient catalysts for the synthesis of MBTBA. Here, we present a novel synthetic method of MBTBA *via* condensation of *o*-tert-butylaniline with paraformaldehyde, in which phosphoric acid modified SBA-15 (P/SBA-15) is employed as catalyst.

2. Experimental

2.1. Catalyst preparation

Concentrated HCl, paraformaldehyde, natural kaolinite, HY and γ -Al₂O₃ catalysts were purchased from Sinopharm. *o*-Tert-butylaniline (Aldrich) and butyl acetate (Qiangsheng Chemical) were used as commercial products without further treatment.

Mesoporous SBA-15 was synthesized *via* a surfactant-templating method in acid condition, according to [27]. The synthesized product was then calcined at 550 °C in air for 4 h. P/SBA-15 was prepared by incipient impregnation method. A certain amount of phosphoric acid and 1 g SBA-15 were stirred with 4 ml absolute ethanol solution at room temperature for 6 h. Then, solvent was evaporated and the solid was dried at 110 °C for 6 h and calcined at 400 °C for 4 h in air. The catalysts are denoted as *x*P/SBA-15, where *x* represents phosphoric acid concentration.

2.2. Catalyst characterization

The X-ray diffraction (XRD) measurements were taken on a RINT2000 vertical goniometer using Cu K α radiation (40 kV, 200 mA, 0.5°–8°).

 $\rm N_2$ adsorption-desorption isotherm was measured at 196 °C with Quantachrome NOVA instrument. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms.

FTIR spectra of adsorbed pyridine were collected on a Nicolet Magna 550 Fourier transform infrared spectrometer at 4 cm^{-1} resolution. The sample was finely grounded and pressed into a self-supporting wafer, and then placed into the measurement cell with CaF₂ windows. The evacuation at 300 °C for 2 h was carried out prior to adsorption of pyridine at room temperature. IR spectra were recorded after subsequent evacuation at increasing temperatures from 50 to 300 °C.

2.3. Catalyst activity measurement

A mixture of o-tert-butylaniline (4 mmol), paraformaldehyde (1 mmol), catalyst (0.18 g) butyl acetate (3 ml) was stirred at 130 °C for 4 h under N₂ atmosphere. After cooling to room temperature, the catalyst was filtered off and the organic layer was evaporated. The crude product was subjected to column chromatography on silica gel with petroleum ether/EtOAc as eluent. Isolated products were determined by ¹H NMR and ¹³C NMR spectroscopes. Yield of MBTBA was calculated based on the input of paraformaldehyde.

3. Results and discussion

In literature, zeolite and kaolinitic clay [13,14] behaved as efficient catalysts in the synthesis of 4,4'-diaminodiphenylmethanes. However, both of them showed very low activities in the reaction of condensation of *o*-tert-butylaniline and paraformaldehyde, as shown in Table 1. Since the molecular sizes of *o*-butylaniline and MBTBA reach ca. 1.1 nm and 1.5 nm, while the layer

Table 1

Screening catalysts for the synthesis of MBTBA.^a



Entry	Catalysts	Yield (%) ^b
1	HCl	44
2	Natural kaolinite	1
3	HY zeolite	13
4	γ-Al ₂ O3	2
5	30P/SBA-15	50

^a Reaction conditions: *o*-tert-butylaniline (4 mmol), paraformaldehyde (1 mmol), catalyst (0.18 g), in butyl acetate (3 ml) at 130 °C under N_2 for 4 h.

^o Isolated yields.

distance of natural kaolinite and the pore diameter of HY are smaller than 1 nm, the steric effect of *t*-butyl group on benzene ring should be responsible for the inferior performance of kaolinite and HY in the synthesis of MBTBA. γ -Al₂O₃ and P/SBA-15 were also tested for the condensation of *o*-tert-butylaniline and paraformal-dehyde and the results are presented in Table 1. γ -Al₂O₃ was generally regarded as a heterogeneous Lewis acid catalyst. The yield of the desired product was only 2%, which indicated that the reaction was not catalyzed by Lewis acidic centers. Comparing with the above catalysts, P/SBA-15 catalyst exhibited high activity in the MBTBA synthesis. The yield was even higher than that of reaction catalyzed by HCl.

The catalytic performance for P/SBA-15 catalysts under different preparation conditions was tested and the results are listed in Table 2. As can be seen, the yield of MBTBA increased moderately with the increase of the concentration of phosphoric acid on SBA-15 and the highest yield of 50% was achieved at 30 wt.% phosphoric acid concentration. The increase of acid sites on the catalysts should be the reason for the improvement of the catalytic activity. The further increase of phosphoric acid loading to 40 wt.% led to the distinct drop in MBTBA yield. This decrease might be due to the blockage of pores and the collapse of structure of SBA-15 which was caused by the overweight of phosphoric acid. In addition, the calcination temperature of 30P/SBA-15 should be adjusted to obtain the best catalytic performance. At the low temperature (300 °C), the drop of MBTBA yield (19%) might be caused by the weak interaction between phosphoric acid and SBA-15 which resulted in the leakage of surface acidity of the catalyst. At the high temperature (500 °C), low yield was obtained (29%), which should account for the decomposition of phosphoric acid and the following decrease of surface acidity.

The effect of different reaction conditions for the condensation reaction of *o*-tert-butylaniline and paraformaldehyde is given in Table 3. Butyl acetate was the most effective solvent, whereas

Table 2Optimization of catalyst for synthesis of MBTBA.^a

Entry	P concentration (wt.%)	Calcination temperature (°C)	Yield (%) ^b
1	10	400	42
2	20	400	48
3	30	400	50
4	40	400	35
5	30	300	19
6	30	500	29

 a Reaction conditions: o-tert-butylaniline (4 mmol), paraformaldehyde (1 mmol), catalyst (0.18 g), in butyl acetate (3 ml) at 130 °C under N_2 for 4 h.

' Isolated yields.

Table	3
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Effect of reaction	conditions or	n synthesis	of MBTBA	over 30P	/SBA-15

Entry	Solvent	Mole ratio of <i>o</i> - butylaniline to paraformaldehyde	Reaction temperature (°C)	Catalyst loading (g)	Yield (%) ^a
1	1,4- dioxane	4:1	130	0.18	35
2	Acetonitrile	4:1	130	0.18	45
3	Butyl acetate	5:1	130	0.18	40
4	Butyl	4:1	130	0.18	50
	acetate				
5	Butyl	3:1	130	0.18	47
C	acetate	0.1	120	0.10	25
0	acetate	2.1	150	0.18	55
7	Butyl	4:1	90	0.18	26
	acetate				
8	Butyl	4:1	110	0.18	32
	acetate				
9	Butyl	4:1	140	0.18	45
10	Butyl	1.1	130	0.00	35
10	acetate	4.1	150	0.05	55
11	Butyl	4:1	130	0.12	45
	acetate				
12	Butyl	4:1	130	0.24	19
	acetate				

^a Isolated yields.

1,4-dioxane and acetonitrile gave lower yield of MBTBA. When the mole ratio of *o*-tert-butylaniline to paraformaldehyde increased from 2:1 to 4:1, the yield of MBTBA increased from 35 to 50%, which might be due to the reduction of the possibility of the reaction of paraformaldehyde with product. Further increase of this ratio decreased the product yield, which should be the result of small amount of paraformaldehyde in reaction, similar to the results observed by Ajaikumar [28]. With regard to reaction temperature, the highest yield was achieved at 130 °C, since paraformaldehyde cannot decompose completely at lower temperature [29]. The optimized catalyst loading was 0.18 g, because the catalytic centers were not enough and the reaction proceeded slowly at lower catalyst loading, while a large quantity of by-products formed with excessive P/SBA-15.

Fig. 1 shows the X-ray diffraction patterns of P/SBA-15 catalysts. Representative small-angle XRD patterns of the two-dimensional (2-D) hexagonal mesostructure, namely, one strong (1 0 0) diffraction at $2\theta = 0.5$ – 1.5° and two weak peaks ((1 1 0) and (2 0 0)) at



higher angles, were exhibited when the phosphoric acid loading didn't exceed 30 wt.%. It clearly indicated that the mesoporous SBA-15 was stable and the highly ordered mesostructure was retained after the appropriate impregnation of phosphoric acid. However, 40 wt.% of phosphoric acid loading on the catalyst led to the disappearance of all the diffraction peaks, which suggested the damage of the mesostructure and comfirmed that a high amount of phosphoric acid led to a decrease of activity due to structure damage.

Fig. 2 shows the result of N₂ adsorption-desorption isotherms and pore size distribution of 30P/SBA-15. The type IV isotherm has the pore filling (by capillary condensation) restricted to a narrow range of the relative pressures of 0.5–0.9, which is a typical feature of SBA-15. Both XRD and N₂ adsorption results showed that the uniform framework and pore structure of SBA-15 could still be well maintained after the external introduction of phosphorus species onto its pore surface. As shown in Fig. 2, the pore size distribution of SBA-15 is very sharp, indicative of uniform mesopore with the size of 6.5 nm which is similar to that of SBA-15 before phosphoric acid modification. The pore diameter of 30P/SBA-15 is much larger than the sizes of substrate and product, which allows the adequate access and rapid diffusion of these molecules to the catalytic centers. On the contrary, the layer distance of natural kaolinite and the pore diameter of HY are smaller than 1 nm. Therefore, the steric effect of t-butyl group on benzene ring should be responsible for the inferior performance of kaolinite and HY in the synthesis of MBTBA. And the ordered mesoporous structure of 30P/SBA-15 should be one of the reasons that this material exhibits the higher activity than HY and kaolinite.

Py-FTIR analysis was used to discriminate acid type and strength on the surface of 30P/SBA-15. Fig. 3 shows the evolution of the IR spectra of 30P/SBA-15 with temperature during the evacuation after adsorption of pyridine of the catalyst. As revealed, the bands at 1450, 1545 and 1490 cm⁻¹ (representing Lewis acid, Brønsted acid and both, respectively [30]) were observed for the catalyst at desorption temperature of pyridine of 50 °C, which suggested that both Brønsted and Lewis acid sites existed on the phosphoric acid modified SBA-15 catalyst. However, all these bands decreased sharply when the evacuation temperature rose to 100 °C and almost disappeared after the evacuation at 200 °C, which indicated that the strength of the acid sites were weak on the surface of 30P/SBA-15. As a consequence, the acid sites with weak strength were supposed to be the catalytic centers for the condensation reaction of o-tert-butylaniline and paraformaldehyde.



Fig. 2. Nitrogen adsorption–desorption isotherms and pore size distribution of 30 $\ensuremath{\mathsf{P}/\mathsf{SBA-15}}$.



Fig. 3. Evolution with temperature of the IR spectra of 30P/SBA-15 during the evacuation after adsorption of pyridine. (a) 50 °C, (b) 100 °C and (c) 200 °C.

The above results confirmed the excellent performance of 30P/ SBA-15 in the synthesis of MBTBA should be attributed to the weak acidity of the material and its large pore size that facilitated the diffusion of substrate and product.

4. Conclusions

In summary, P/SBA-15 was found to be a highly active heterogeneous catalyst for *o*-tert-butylaniline condensation with paraformaldehyde. The optimized conditions for the catalyst preparation were phosphoric acid concentration of 30 wt.% and calcination temperature of 400 °C. Butyl acetate was found to be the best solvent and the mole ratio of *o*-tert-butylaniline to paraformaldehyde should be 4:1. Under the reaction temperature of 130 °C and the catalyst weight of 0.18 g, the yield of MBTBA reached 50%, which was even higher than that in homogeneous reaction in presence of HCl, and the further improvement of the efficiency of this method is under the way. The sorption isotherm of P/SBA-15 indicated the uniform mesopore with the size of 6.5 nm and Py-FTIR analysis suggested that the acid centers were weak on the surface of P/SBA- 15. Therefore, the excellent performance of P/SBA-15 in the synthesis of MBTBA should be attributed to the weak acidity of the material and its large pore size.

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