



Confinement effect as a tool for selectivity orientation in heterogeneous synthesis of 4,4'-diamino-3,3'-dibutyl-diphenyl methane over montmorillonite catalysts

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ABSTRACT

Montmorillonite was employed as a heterogeneous catalyst in the condensation of *o*-tert-butylaniline with paraformaldehyde for its significant confinement effect on the selective synthesis of 4,4'-diamino-3,3'-dibutyl-diphenyl methane (4,4'-MBTBA). Due to the appropriate *d*-spacing which is larger than the molecular size of 4,4'-MBTBA but smaller than that of 4,4'-(4-amino-5-tert-butyl-1,3-phenylene)bis(methylene)bis(2-tert-butylaniline) (PBMBA), montmorillonite favored the production of 4,4'-MBTBA, comparing with HY, P/SBA-15 and PW/C catalysts. In addition, with the decrease of the *d*-spacing of montmorillonite, the formation of PBMBA was inhibited and the selectivity of 4,4'-MBTBA became more and more remarkable, which verified the confinement effect as a tool for selectivity orientation on the heterogeneous synthesis of 4,4'-MBTBA over montmorillonite catalysts. When paraformaldehyde was used as starting material and the ratio of *o*-tert-butylaniline to paraformaldehyde was as low as 4:1, the yield of 4,4'-MBTBA reached 83.9% with butyl acetate as solvent, reaction temperature of 130 °C and catalyst loading of 0.18 g.

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1. Introduction

Aromatic polyimides, owing to the excellent properties of thermal stability, chemical resistance, mechanical and electronic properties, are widely applied in many high technology areas, such as separation membranes [1–3], coatings [4–6], composite materials [7], plastic film [8] and electronics [9,10]. However, the commercial use of aromatic polyimide 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 the other properties.

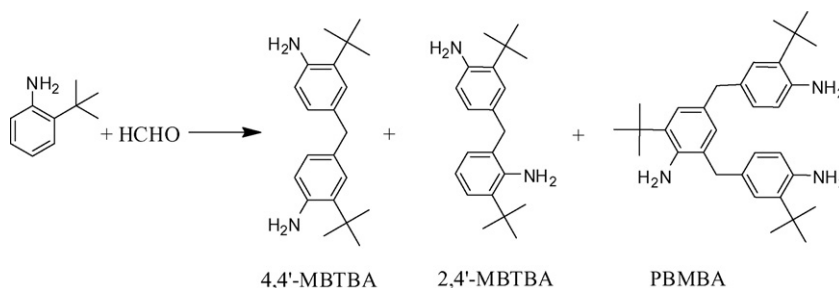
Introducing tert-butyl-substituted monomer, 4,4'-diamino-3,3'-dibutyl-diphenyl methane (4,4'-MBTBA), into the backbone of aromatic polymers displays great improvement of the solubility and processability without causing the unacceptable loss of thermal properties of aromatic polyimide [11]. Traditionally, *o*-tert-butylaniline is condensed with formaldehyde to give 4,4'-MBTBA in the presence of HCl. This method suffers from the difficulty in environment and separation problems. Compared with homogeneous catalysis, heterogeneous catalysis has many advantages, such as facile recovery of the solid catalyst from the reaction mixture for recycling without tedious workup [12,13]. Therefore, our research group pioneered new synthetic route for the syn-

thesis of 4,4'-MBTBA under heterogeneous catalysis and found that the condensation of *o*-tert-butylaniline with paraformaldehyde catalyzed by P/SBA-15 could provide a considerable yield of 4,4'-MBTBA [14].

However, the drawback of the new route is its low selectivity. With the continuous exploration of this reaction, we find that the major by-products in this reaction are 2,4'-diamino-3,3'-dibutyl-diphenyl methane (2,4'-MBTBA) and 4,4'-(4-amino-5-tert-butyl-1,3-phenylene)bis(methylene)bis(2-tert-butylaniline) (PBMBA) (see Scheme 1). The former is not thermodynamically favorable and its formation could be controlled by adjusting the catalyst properties and reaction conditions [15,16]. However, the latter is hardly suppressed since it forms by the condensation of 4,4'-MBTBA and formaldehyde at the similar catalytic sites under the similar conditions to that of 4,4'-MBTBA. Fortunately, there exists a significant difference in molecular size between 4,4'-MBTBA and PBMBA (1.5 and 1.9 nm, respectively, estimated by Gaussview 3.0). Therefore, confinement effect of shape-selective catalysts is proposed to increase the selectivity of 4,4'-MBTBA.

Montmorillonite, with both Brønsted and Lewis acidic sites available, is a kind of solid acid catalyst widely used in various alkylation reactions. And what is more, montmorillonite possesses definite layered structure, which makes it an excellent shape-selective catalyst. Suzuki and co-worker [17] found metal-pillared montmorillonite could provide a significant shape-selective effect for various reactions. Choudary and Valli [18] employed vanadium-pillared montmorillonite for isomerization

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Scheme 1. Condensation of *o*-tert-butylaniline with formaldehyde in presence of acidic catalysts.

of α -acetylenic alcohols, which could selectively generate α,β -ethylenic carbonyl compounds. Da and Enze [19] mentioned that platinum-pillared montmorillonite exhibited a clear shape-selective effect for isomerization of *n*-paraffins. Knifton et al. [20,21] reported the selective synthesis of linear alkylbenzenes by restrictions of montmorillonite *d*-spacing. Garade et al. [22,23] research group had successively researched alkylation reaction of phenol, *p*-cresol with formaldehyde, and found that montmorillonite gave a higher conversion and selectivity owing to its unique layered structure. Binitha and Sugunan [24,25] reported alkylation reaction of benzene and toluene catalyzed by an eco-friendly catalyst, titania-pillared montmorillonite and chromia-pillared montmorillonites. The alkylation of benzene with ethanol produced ethylbenzene as the only product by restrictions of titania-pillared montmorillonite layered structure.

The *d*-spacing of montmorillonite locates in the range of 1–2 nm, which is similar to the molecular sizes of 4,4'-MBTBA and PB MBA. In this work, we employed montmorillonite as a heterogeneous catalyst for the condensation of *o*-tert-butylaniline with paraformaldehyde. The confinement effect of montmorillonite on the selectivity of 4,4'-MBTBA and PB MBA was investigated via the subtle adjustment of the *d*-spacing. Besides, reaction conditions were screened for the optimization of the yield of 4,4'-MBTBA.

2. Experimental

2.1. Catalyst preparation

Concentrated HCl, paraformaldehyde, phosphotungstic acid (PW), HY zeolite and active carbon (C) were purchased from Sinopharm. *o*-tert-Butylaniline (Aldrich) and butyl acetate (Qiangsheng Chemical) were used as commercial products without further treatment. Montmorillonite was purchased from Zhejiang Feng Hong Clay Chemical Co., Ltd. and designated as Na-Mont.

Acidified montmorillonite was prepared according to [26]: montmorillonite (10.0 g) and 100 g of aqueous HNO₃ (0.5 wt.%) was stirred at 80 °C for 24 h. The slurry obtained was filtered, washed with distilled water and calcined in air at a certain temperature for 4 h. Depending on different calcination temperatures of 200, 300 and 400 °C, acidified montmorillonites were designated as H-Mont-200, H-Mont-300 and H-Mont-400, respectively.

The preparation of PG-H-Mont and CTAB-H-Mont was as follows: H-Mont-200 (10.0 g) was mixed with polyethyleneglycol (4.0 g) or cetyltrimethylammonium bromide (4.0 g) in 100 ml water and then stirred at 80 °C for 24 h. The slurry obtained was filtered and washed with distilled water, dried in air at 80 °C for 10 h and then at 120 °C for 4 h.

The preparation of B-A-Mont was as follows: montmorillonite (1.0 g) in 50 ml aqueous NaOH (0.1 mol/L) was stirred at 80 °C for 24 h. The slurry obtained was filtered, washed with distilled water and dried in air at 80 °C for 10 h. Then, the obtained powder was mixed with 50 ml aqueous HNO₃ (0.2 mol/L), stirred at 80 °C for 24 h

and followed by filtration and wash with distilled water. Finally, the sample was dried in air at 80 °C for 10 h and then at 120 °C for 4 h.

Phosphoric acid modified SBA-15 (P/SBA-15) was synthesized according to [14]. PW/C and PW/H-Mont were prepared via wet impregnation method: 0.3 g PW and 1 g active carbon or H-Mont-200 was stirred with 4 ml absolute ethanol solution at room temperature for 6 h. Then, the solvent was evaporated and the solid was dried at 110 °C for 6 h and calcined at 285 °C for 3 h in air.

All the catalysts were activated at 120 °C before use [27].

2.2. Characterization

X-ray diffraction (XRD) measurements were taken on a RINT2000 vertical goniometer using Cu K α radiation (40 kV, 200 mA, 1.2–10°).

Nitrogen adsorption/desorption: The nitrogen adsorption and desorption isotherms were measured at –196 °C on an ASAP 2400 system in static measurement mode. The samples were outgassed at 160 °C for 4 h before the measurement. The specific surface area was calculated using the BET model.

2.3. Catalytic activity measurement

A mixture of *o*-tert-butylaniline (4 mmol), paraformaldehyde (1 mmol), catalyst (0.18 g) and 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 (6:1) as effluent. Isolated products were determined by ¹H NMR and ¹³C NMR. Yields of products were calculated based on the input of paraformaldehyde.

3. Results and discussion

Traditionally, 4,4'-MBTBA was synthesized in homogeneous condition in presence of HCl. However, the difficulty in separation and the pollution made this route unfavorable for the environment. Our research group discovered a new synthetic route under the heterogeneous catalysis by P/SBA-15 [14], with unsatisfactory selectivity. To improve the selectivity of 4,4'-MBTBA, several catalysts were tested on the condensation of *o*-tert-butylaniline with paraformaldehyde and their catalytic performances are presented in Fig. 1. Obviously, HY zeolite showed the worst catalytic performance with only 12.9% for the yield of 4,4'-MBTBA. The result could be explained by the narrow pore size of 0.75 nm of HY zeolite, which led to the impossibility of the accessibility of *o*-tert-butylaniline (ca. 1.1 nm) to the acidic sites in the pores. When P/SBA-15 and PW/C were used as catalysts for the condensation, the products' distribution was similar to that in homogeneous condition: about 50% yield of 4,4'-MBTBA, 20% of PB MBA and 8% of 2,4'-MBTBA. This phenomenon was assumed to be brought about by the reac-

Table 1
Confinement effect on the synthesis of 4,4'-MBTBA over heterogeneous catalysts.

Entry	Catalyst	Yield (%) ^a			4,4'-MBTBA/ PBMBBA	<i>d</i> -Spacing ^b	BET surface area (m ² g ⁻¹)
		2,4'-MBTBA	PBMBBA	4,4'-MBTBA			
1	B-A-Mont	4.3	2.3	49.5	21.5	1.33	129.1
2	Na-Mont	6.4	5.4	75.1	13.9	1.46	3.6
3	H-Mont-200	8.6	6.4	83.9	13.1	1.53	89.8
4	PG-H-Mont	6.4	6.4	62.6	9.8	1.58	57.2
5	H-Mont-300	10.7	8.6	73.1	8.5	1.59	75.1
6	CTAB-H-Mont	6.4	12.9	32.3	2.5	1.83	45.4
7	H-Mont-400	8.6	10.7	64.5	6.0	–	–
8	PW-H-Mont	8.6	10.7	75.2	7.0	–	55.6

The bold indicates the best catalyst and the highest yield in the reaction.

^a Isolated yield.

^b Calculated by XRD.

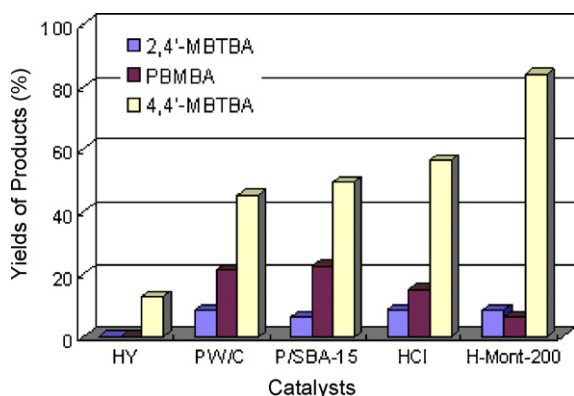


Fig. 1. Optimization of catalysts for synthesis of 4,4'-MBTBA.

tions occurred without spatial limitation, since the pore diameter of P/SBA-15 of 6 nm is much larger than the molecular sizes of all the products, while the reactions took place only on the outside surface of active carbon. However, when montmorillonite was employed, a significant difference appeared. The yield of 4,4'-MBTBA increased to 83.9%, while that of PBMBBA decreased sharply to 6.4%. As revealed by XRD (see Fig. 2 and Table 1), the *d*-spacing of acidified montmorillonite is 1.53 nm, which could accommodate 4,4'-MBTBA molecule (1.5 nm), so that MBTBA's formation proceeded successfully on it. But for PBMBBA (1.9 nm), the *d*-spacing is so small that the formation was confined and the yield dropped accordingly.

For further clarification of the confinement effect on the selectivity of the condensation of *o*-tert-butylaniline with paraformal-

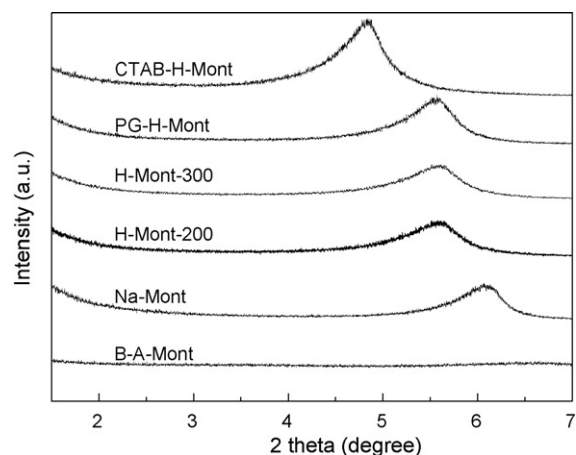


Fig. 2. XRD patterns of montmorillonites with different treatments.

hyde, the *d*-spacing of montmorillonite was adjusted and the catalytic performances were tested (see Table 1). Fig. 2 shows the XRD patterns of montmorillonites with various modification methods and the corresponding values are listed in Table 1. As can be seen, the *d*-spacing of CTAB-H-Mont reached 1.83 nm. And the ratio of 4,4'-MBTBA/PBMBBA produced on this catalyst was 2.5, which was similar to the result obtained in the homogeneous condition. As mentioned above, the molecular sizes of *o*-tert-butylaniline, 4,4'-MBTBA and PBMBBA equal to 1.1, 1.5 and 1.9 nm, respectively. Therefore, when the *d*-spacing of catalyst equals to or is larger than the size of all products, the reactant could access to the acidic sites inside the layers of CTAB-H-Mont and the condensation reaction should occur. As a result, confinement effect could not put any influence on the selectivity of products and the products' distribution kept unchanged.

However, when the *d*-spacing of catalyst became smaller than the size of products, confinement effect was exhibited in the change of the products' distribution. H-Mont-300 showed a smaller *d*-spacing of 1.59 nm and apparently, the formation of PBMBBA was limited by the shrink of layer distance. The selectivity of PBMBBA dropped and the ratio of 4,4'-MBTBA/PBMBBA increased to 8.5. With the further decrease of the *d*-spacing of montmorillonite, the confinement effect became more and more clear. For PG-H-Mont, H-Mont-200 and Na-Mont, the *d*-spacing reduced from 1.58 to 1.46 and the 4,4'-MBTBA/PBMBBA ratio increased from 9.8 to 13.9. When B-A-Mont was used as catalyst, it presented the highest diffraction angle of ca. 6.5°, which corresponds to the *d*-spacing of 1.33 nm. The yield of PBMBBA on this catalyst dropped so much that the ratio of 4,4'-MBTBA/PBMBBA reached as high as 21.5, while the conversion of *o*-tert-butylaniline decreases significantly, which may be due to diffusional resistance in catalyst pores and interlayer [28]. For H-Mont-400 and PW-H-Mont, although the diffraction peaks almost disappeared, the layered structures should not be destroyed completely but became irregular. Thereafter, the catalytic performances of these catalysts on selectivity were still higher than that of CTAB-H-Mont because of the limitation of the layered structures of montmorillonites.

Anyway, with the decrease of the *d*-spacing of the montmorillonites, the formation of PBMBBA was inhibited and the selectivity of 4,4'-MBTBA become more and more remarkable. Although the other elements such as acid properties could not be ruled out for the change of the activity and selectivity, the certainty is that, in heterogeneous synthesis of 4,4'-MBTBA over montmorillonite catalysts, confinement effect was employed successfully as a tool for selectivity orientation.

The results of BET surface areas of various catalysts are presented in Table 1. Among them, Na-Mont showed the lowest surface area of 3.6 m² g⁻¹. After acid treatment, the surface area of H-Mont-200 reached 89.8 m² g⁻¹ and B-A-Mont presented the highest one of 129.1 m² g⁻¹. However, the same amount of catalysts did not ren-

Table 2
Effect of reaction conditions on the synthesis of 4,4'-MBTBA over H-Mont-200 catalyst.

Entry	Solvent	Reaction temperature (°C)	Reaction time (h)	Catalyst loading (g)	Yield (%) ^a
1	Toluene	130	4	0.18	58.1
2	Acetonitrile	130	4	0.18	73.1
3	Butyl acetate	130	4	0.18	83.9
4	Butyl acetate	110	4	0.18	70.9
5	Butyl acetate	130	2	0.18	79.6
6	Butyl acetate	130	24	0.18	84.5
7	Butyl acetate	130	4	0.12	73.1
8	Butyl acetate	130	4	0.24	84.2

The bold indicates the best catalyst and the highest yield in the reaction.

^a Isolated yields.

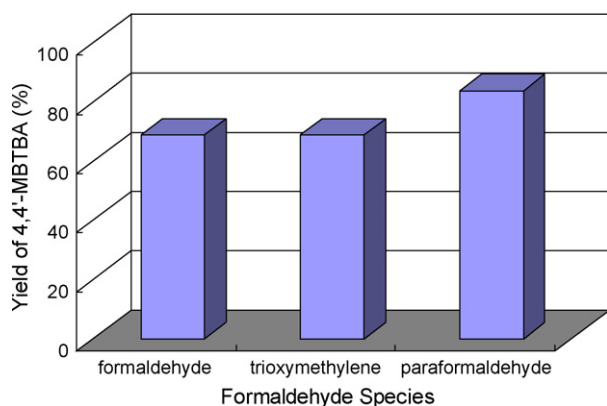


Fig. 3. Effect of formaldehyde species on synthesis of 4,4'-MBTBA over H-Mont-200 catalyst.

der the significant discrepancy in their reactivity. Therefore, the BET area should not be a decisive factor in terms of activity of catalysts.

Since H-Mont-200 gave the best yield of 4,4'-MBTBA and satisfactory ratio of 4,4'-MBTBA/PBMBA, the catalytic performance on H-Mont-200 under different reaction conditions was evaluated for condensation reaction of *o*-tert-butylaniline and paraformaldehyde. Fig. 3 exhibits the effect of formaldehyde species on the reaction. As can be seen, the use of formaldehyde and trioxymethylene gave lower yield of 4,4'-MBTBA than paraformaldehyde did. When paraformaldehyde was employed, considering its slow decomposition, the released formaldehyde consumed quickly to form 4,4'-MBTBA, which led to the very low concentration of formaldehyde species in the reaction system. As a result, the formation of PBMBA was inhibited and the selectivity of 4,4'-MBTBA increased.

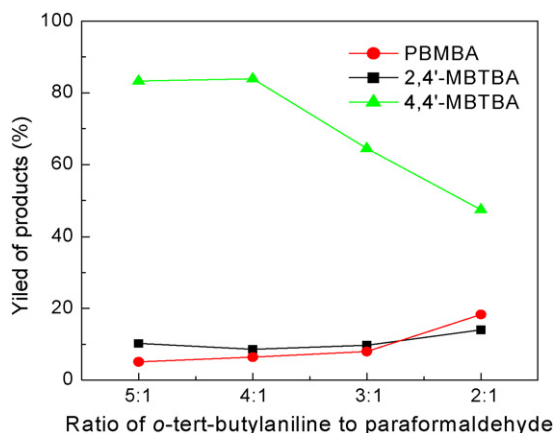


Fig. 4. Effect of mole ratio of *o*-tert-butylaniline to paraformaldehyde on synthesis of 4,4'-MBTBA over H-Mont-200 catalyst.

Fig. 4 gives the influence of the ratio of *o*-tert-butylaniline to paraformaldehyde on the reaction. When the ratio changed from 5:1 to 4:1, the products' distribution did not change much, which was similar to the result reported by Ajaikumar and Pandurangan [16]. The further increase of the proportion of paraformaldehyde led to the decrease of the selectivity of 4,4'-MBTBA and the opposite trend of PBMBA, which was also caused by the increased concentration of the released formaldehyde species and the resulting reaction between 4,4'-MBTBA and formaldehyde.

Table 2 presents the effect of the other reaction conditions on the condensation reaction of *o*-tert-butylaniline and paraformaldehyde. It is indicated that butyl acetate was the most effective solvent, whereas toluene and acetonitrile gave lower yield of 4,4'-MBTBA of 58.1% and 73.1%, respectively, which was in accordance with the report by Lipshutz et al. [29]. The poor performance in toluene might be due to its weak polarity which led to the difficulty of the solubility of substrates and products. On the other hand, acetonitrile presented too strong polarity to bring about the problem of the competitive adsorption between the solvent and substrates. Therefore, the medium polarity of solvent, like butyl acetate, should be advantageous in this reaction.

With regard to reaction temperature, the highest yield was achieved at 130 °C. Lowering the temperature caused the decrease of the yield of 4,4'-MBTBA (see Table 2, entry 4). Two reasons should be responsible: (1) paraformaldehyde cannot decompose completely at lower temperature [30]; (2) 4,4'-MBTBA is thermodynamic stable and higher temperature favors its formation. As to the reaction time, the yield reached 79.6% at 2 h and did not show significant increase after 4 h (see Table 2, entry 6), which was similar to the result reported by Siddhartha [27]. The optimized catalyst loading was 0.18 g. The less catalysts loading of 0.12 g gave lower yield of 73.1%. But higher loading could not improve that (see Table 2, entry 8), which might be due to the diffusional resistance in catalyst interlayers [31,32].

4. Conclusions

Since the *d*-spacing of montmorillonite is wide enough to accommodate 4,4'-MBTBA molecule, but too narrow to hold PBMBA, montmorillonite showed excellent catalytic activity in the synthesis of 4,4'-MBTBA, comparing with HY zeolite, P/SBA-15 and PW/C catalysts. With the decrease of the *d*-spacing of montmorillonite, the formation of PBMBA was inhibited and the selectivity of 4,4'-MBTBA became more and more remarkable. Therefore, the confinement effect on the selectivity of the condensation of *o*-tert-butylaniline with paraformaldehyde was verified to be successful as a tool for selectivity orientation in heterogeneous synthesis of 4,4'-MBTBA over montmorillonite catalysts.

Different reaction conditions were evaluated for condensation reaction of *o*-tert-butylaniline and paraformaldehyde. Due to the low concentration of formaldehyde species released in the reaction

system, the formation of PBMBA was inhibited and the selectivity of 4,4'-MBTBA increased when paraformaldehyde was employed and the ratio of *o*-tert-butylaniline to paraformaldehyde was lower than 4:1. Butyl acetate was the most effective solvent, due to its medium polarity. The optimized reaction temperature and catalyst loading were 130 °C and 0.18 g.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.03.032.

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