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Short Communication

Synthesis of 3,3'-dimethyl-4,4'-diaminodiphenylmethane catalyzed by zeolites replacing mineral acids



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ABSTRACT

Synthesis of 3,3'-dimethyl-4,4'-diaminodiphenylmethane (MDT) from o-tolylamine and formaldehyde over zeolites was investigated. Among the three tested zeolites, $H\beta$ showed higher catalytic activity than HY and HZSM-5 for MDT synthesis. In the case of $H\beta$ as a catalyst, the effects of feed composition, reaction time and temperature on the yield and selectivity of product MDT were further examined to optimize process conditions. In an o-tolylamine:formaldehyde = 8:1 molar ratio, the two-step reaction running at 413 K for 0.5 h and then 433 K for 0.5 h gave the MDT yield of 87.5%.

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1. Introduction

3,3'-Dimethyl-4,4'-diaminodiphenylmethane (MDT) is an important curing agent and polymer additive with a variety of industrial applications [1–3]. For examples, MDT has been used in preparing electric cables, wires and electromagnetic strings with good heat-resisting, chemical-resisting and electric-insulating property [4]. Isocyanate prepared from MDT can be used as room temperature curing agent with good adhesion property [5].

MDT is traditionally synthesized by condensation of *o*-tolylamine with formaldehyde catalyzed by mineral acids such as HCl [6]. The synthetic process went through salinization, condensation, transposition rearrangement and neutralization. A large amount of waste acids needed to be neutralized, and substantial aqueous salt waste could cause environmental contamination seriously.

As environmental awareness increasingly expanded, developing new non-toxic and highly-effective catalysts is becoming a hot research topic in the area of green catalysis [7,8]. While a green technology for MDT synthesis waited to be developed, the replacement of homogeneous catalysts with heterogeneous catalysts might provide a solution to the problems of waste pollution. Using a heterogeneous catalyst allowed easy separation of catalyst from product without needing neutralization, so that the aqueous waste stream could be eliminated, and the catalyst could be recovered and reused. For synthesis of 4,4'- diaminodiphenylmethane (MDA) by condensation of anilines and formaldehyde, solid acids were suggested by several researchers to replace mineral acids as catalysts. The selected solid acids included ion-exchanged resins [9], metallic compounds [10–12], organosilanesulfonic acid-functionalized Zr-TMS [13], clays [14,15], zeolites and modified zeolites [16–19].

In this work, synthesis of 3,3'-dimethyl-4,4'-diaminodiphenylmethane by condensation of *o*-tolylamine and formaldehyde over zeolite catalysts was conducted. The catalytic activity of H β , HY and HZSM-5 was first scanned, and then, the catalytic performance of H β zeolite for this synthetic reaction was further investigated. The out-coming results would establish the foundation of a green and environment-friendly technology for the synthesis of MDT and analog compounds.

2. Experimental

2.1. Materials

Chemicals *o*-tolylamine, formaldehyde (37 wt.% aqueous solution), anhydrous ethanol, dimethyl-formamide (DMF) and potassium dihydrogen phosphate were purchased from Sinopharm Chemical Reagent Corporation Ltd., China. Methanol and methyl cyanide were purchased from Tedia Corporation Ltd, United States. Zeolites H β was supported by Tianjin NCIC catalyst Corporation Ltd., HY and HZSM-5 were supported by Shandong Qilu Huaxin Gaoke Corporation Ltd., China.

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 Table 1

 HCHO conversion and MDT selectivity in condensation of *o*-tolylamine and formaldehyde over various zeolites.

Catalysts	HCHO conversion (%)	MDT	
		Yield (wt.%)	Selectivity (wt.%)
Нβ	80.6	52.5	65.1
HY	75.2	42.9	57.0
HZSM-5	73.6	30.7	41.7

Reaction conditions: n(o-tolylamine):n(HCHO) = 3:1 (molar ratio), w(HCHO): w(catalyst) = 1:1 (weight ratio), 1 h, 433 K.

2.2. Procedures

In a typical run, zeolite (9.0 g), formaldehyde (0.3 mol), and *o*-tolylamine (0.6–3 mol) were added into a 500 mL autoclave made in Weihai Zhengwei Machinery Equipment Corporation Ltd, China. The sealed reactor was purged with nitrogen and then heated up to the designed temperature with stirring. After the reaction went through the scheduled times, the product mixture was sampled for HPLC analysis.

2.3. Analysis

Product samples were analyzed by EX1600SM High Pressure Liquid Chromatography with conditions: detection wavelength of UV 254 nm, C18 column, room temperature, methanol solvent, mobile phase of acetonitrile/water (1:1 volume ratio) at flow rate of 1.00 mL min⁻¹.

The textural properties of zeolites were characterized by BET method using a ASAP 2020 V3.01 H analyzer, and the acid properties were measured by NH_3 temperature programmed desorption (TPD) analysis. The TPD experiments were carried out in a flow apparatus with helium as carrier gas, and for evolved gas detection, a thermal conductivity detector (TCD) was used. A small amount of the granulated zeolite (100 mg) was heated at 823 K in a He flow (30 mL min⁻¹) for 1 h, and then cooled to 373 K. The activated sample was saturated with ammonia at 373 K for 1 h and, after being purged with pure He for 1.5 h at the same temperature, was heated at 10 K min⁻¹ to 973 K under helium flow (20 mL min⁻¹).

3. Results and discussion

3.1. Catalytic activity of zeolites

Catalytic activities of H β , HY and HZSM-5 zeolites for MDT synthesis were tested at 413 K. As summarized in Table 1, HCHO conversion changed from 80.6 to 75.2 to 73.6%, MDT yield from 52.5 to 42.9 to



Fig. 1. $\text{NH}_3\text{-}\text{TPD}$ curves of HY, HZSM-5 and H β zeolites.

Surface area, pore diameter, pore volume and acidity of H $\!\beta,$ HY and HZSM-5 zeolites.

Zeolites	Surface area (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)	Acidity (µmol/g)
Нβ	461.3	0.66	0.28	517
HY	684.0	0.74	0.36	381
HZSM-5	352.7	0.56	0.19	643

30.7%, and MDT selectivity from 61.5 to 57.0 to 41.7% with shifting catalyst from H β to HY to HZSM-5. By comparison, H β exhibited the best performance, while HZSM-5 gave the poor performance to this reaction system.

Catalytic activity of a zeolite depended on its properties of acid, surface and structure. As illustrated in Fig. 1, NH₃ temperatureprogrammed desorption (NH₃-TPD) showed the difference of acid site density and acid strength distribution among the three zeolites. One NH₃ desorption peak was detected in 450–500 K for each zeolite, and second peak detected in 730-770 K for HZSM-5 and HB, indicating existence of stronger acid sites. Theoretically, the catalytic activity should be in the order of HZSM-5 > H β > HY if the acid strengths would have played a dominant role, and also the HZSM-5 should give the better performance than HB if the acid amounts have played a critical role in MDT synthesis. The data in Table 1, however, declared that $H\beta$ gave the best catalytic performance, indicating that the structure and surface of zeolites might have determinant effects on this synthetic reaction. Based on the data in Table 2, HZSM-5 with smaller pore opening (0.56 nm) and volume (0.19 cm³/g) is poorly active because diffusion of product MDT and rearrangement of reaction intermediate were strongly hindered, while HY with pore diameter (0.74 nm) and volume $(0.36 \text{ cm}^3/\text{g})$ was less active due to low acid density and weaker acid strength. In addition, the effect of acid density (amount) on the activity might be insignificant at a high ratio of catalyst to HCHO (1:1), and therefore, the H β with moderate pore size (0.66 nm), pore volume $(0.28 \text{ cm}^3/\text{g})$ and surface area $(461.3 \text{ m}^2/\text{g})$ exhibited the best overall performance for catalytic synthesis of MDT.

3.2. MDT synthesis over $H\beta$ zeolite

3.2.1. Effect of reactant composition

The effect of *o*-tolylamine/formaldehyde molar ratio on yield and selectivity of MDT in the catalytic reaction over H β at 433 K for 1 h was shown in Fig. 2. As the ratio increased from 2 to 10, MDT yield increased from 39.8 to 74.6%, and selectivity increased from 58.3 to 88.7%, respectively. The significant effect of reactant composition on MDT yield and selectivity indicated that the excess of *o*-tolylamine favored the formation of product MDT. However, a high ratio of



Fig. 2. Effect of *o*-tolylamine/formaldehyde ratio on yield and selectivity of MDT. Reaction conditions: $w(H\beta)$:w(HCHO) = 1:1; 433 K; 1 h.



Fig. 3. Effect of reaction temperature on yield and selectivity of MDT. Reaction conditions: $n(o-tolylamine):n(HCHO) = 3:1, w(H\beta):w(HCHO) = 1:1, 1$ h.

o-tolylamine/formaldehyde implied that a large amount of unreacted *o*-tolylamine required to be recycled, and thus an optimal ratio of *o*-tolylamine/formaldehyde should be selected for industrial production of MDT.

3.2.2. Effect of temperature

As shown in Fig. 3, HCHO conversion generally increased from 42.4 to 80.7% with increasing temperature from 393 to 433 K, and then stabilized in 433–473 K. At the same time, both yield and selectivity of MDT increased gently from 393 to 413 K, and then rapidly from 413 to 433 K. As temperature continually increased from 433 to 473 K, MDT yield almost remained without significant variation, but MDT selectivity slightly decreased, probably due to the generation of more by-reactions in higher temperature. Overall, the optimal temperature to this reaction system was about 433 K.

It was interesting to see the rapid increase of MDT yield and selectivity from 393 to 433 K (Fig. 3). HPLC chromatograms of the product samples from the synthetic reactions at 393, 413, 423, 433, 453 and 473 K were presented in Fig. 4. One can see that a large peak of the intermediate aminal (*N*, *N'*-di-*o*-tolyl-methanediamine) appears at a retention time of 9.2 min in the chromatograms of samples from the reaction at 393 and 413 K, becomes much smaller for the sample at 423 K, and almost disappears for the sample at 433 K. At the same time, the peak area of reactant *o*-tolylamine decreases and the peak area of product MDT increases significantly with raising temperature from 413 to 423 to 433 K. Therefore, we deduce that synthesis of MDT from *o*-tolylamine and formaldehyde over H β involves the formation of *N*, *N'*-di-*o*-tolyl-methanediamine which is quite stable at temperature below 413 K, and goes on rearrangement to form MDT over 413 K.



Fig. 4. HPLC chromatograms of product samples from reaction at various temperatures. Reaction conditions: n(o-tolylamine):n(HCHO) = 3:1, w(H\beta):w(HCHO) = 1:1, 1 h.

Table 3

Effect of two-step heating and one-step heating on H_β catalytic performance.

	Two-step reaction		One-step reaction
	413 K for 0.5 h	433 K for 0.5 h	433 K for 1 h
MDT (%)	21.3	87.5	71.6
Reaction condit	tions: n(o-tolylamine):n($(HCHO) = 8:1, w(H\beta):w$	v(HCHO) = 1:1

3.2.3. Combinatorial effect of temperature and time

To optimize the synthetic conditions, a two-step heating method was tested. The reaction was first carried out at 413 K for 0.5 h, and then went through another 0.5 h at 433 K. As presented in Table 3, a high MDT yield of 87.5% was obtained from the two-step heating reaction, in comparison with the MDT yield of 71.6% obtained from the one-step reaction at 433 K for 1 h. The significant difference was an inevitable result from the reaction mechanism which was still waiting to be verified. Further improvement of process performance could be expected by combinatorial optimization of reaction time, temperature and other conditions.

3.3. Overview of reaction mechanism

The mechanism of MDT synthesis from *o*-tolylamine and formaldehyde over solid acids has, to the best of our knowledge, not been interpreted so far. As well known, there were both Bronsted acid and Lewis acid sites on H β zeolite. In general, the synthesis of MDT might be catalyzed by Bronsted acid or Lewis acid, or both simultaneously. There were no enough evidences to confirm the role of different acids at moment. Nevertheless, an overview of reaction sequence for the synthesis of MDT from *o*-tolylamine and formaldehyde was suggested in Fig. 5.

The suggested sequence involves the formation and reactions of four intermediates:

- (1) direct reaction of an *o*-tolylamine with a formaldehyde to form an *o*-tolylamino-methanol;
- (2) conversion of the *o*-tolylamino-methanol into a methylene-*o*-tolyl-amine by loss of a water;
- (3) reaction of methylene-*o*-tolyl-amine with *o*-tolylamine to form *N*, *N*'-di-*o*-tolyl-methanediamine;
- (4) rearrangement of *N*, *N'*-di-*o*-tolyl-methanediamine to 2-methyl-4-(*o*-tolylamino-methyl)-phenylamine;
- (5) rearrangement of 2-methyl-4-(*o*-tolylamino-methyl)-phenylamine to final product MDT.

The above description on the reaction sequence of MDT synthesis from *o*-tolylamine and formaldehyde was preliminary rather than profound. We will present a thorough discussion on the details of reaction mechanism elsewhere in the future.

4. Conclusions

Zeolites H β , HY and HZSM-5 are found to be active for synthesis of MDT by condensation of *o*-tolylamine and formaldehyde, and the catalytic activity increases in the order of H β > HY > HZSM-5. Microporous H β is capable to replace mineral acids for the acid-catalyzed synthesis of MDT. The synthetic methodology is novel in its simple operation procedure, shorter reaction time, easy catalyst recovery, and eco-friendly nature.



Fig. 5. Overview of reaction sequence for MDT synthesis over H β zeolite.

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