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### Overview of reaction sequence for MDT synthesis over Hß zeolite

### Highlights

- > A novel method for synthesis of MDT catalyzed by acidic zeolites replacing mineral acids
- $\succ$  H $\beta$  with strong Bronsted acidity and proper textural property showed good catalytic performance
- > Synthetic process went through multiple steps involving several reaction intermediates
- > The detailed interpretation to the mechanism of various intermediates reaction was presented.

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# Insight into the mechanism of 3,3'-dimethyl-4,4'-diaminodiphenylmethane synthesis over Hβ zeolite

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### ABSTRACT

Heterogeneous synthesis of 3,3'-dimethyl-4,4'-diaminodiphenylmethane (MDT) from *o*-tolylamine and formaldehyde on acidic zeolites HY, HZSM-5, H $\beta$  and TS-1 was investigated. H $\beta$  zeolite with strong Bronsted acidity and proper textural property demonstrated better catalytic performance than other three zeolites for this synthetic reaction. Yield and selectivity of product MDT from the catalytic reaction over H $\beta$  strongly depended on temperature, and optimal reaction temperature appeared to be about 433 K. Based on analyses of LC/MS and <sup>1</sup>H NMR for reaction intermediates, it was suggested that the synthetic process went through multiple steps involving intermediates *o*-tolylamino-methanol, methylene-*o*-tolylamine, *N*,*N*'-di-o-tolyl-methanediamine and 2-methyl-4-(*o*-tolylamino-methyl)-phenylamine. Interpretation to the mechanism of various intermediates formation and conversion was presented.

Keywords: MDT; Catalytic synthesis; H<sub>β</sub>-zeolite; Intermediates; Mechanism

### 1. Introduction

The condensation reaction of aromatic amines with aldehydes is a useful vehicle for production of diaminodiphenylmethanes and derivatives, which find a variety of applications in plastic and paint industry. As well known, 4,4'-diaminodiphenyl methane (MDA) is an important starting materials for production of polyurethanes and thermoplastics [1,2], 3,3'-dichloro-4,4'-diaminophenyl methane (MOCA) is used as curing agent of polyurethane rubber and solidifying agent of epoxide resin [3], and 3,3'-dimethyl-4,4'-diaminodiphenylmethane (MDT) is an important curing agent and polymer additives [4-6] in the preparation of electric cables, wires and electromagnetic strings with good heat-resisting, chemical-resisting and electric-insulating property [7,8]. For example, isocyanate prepared from MDT can be used as room temperature curing agent with good adhesion property [9].

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Traditionally, MDT has been prepared by the condensation reaction of *o*-tolylamine with formaldehyde in the presence of a liquid protonic acid such as HCl. The synthetic process goes through a complex mechanism involving salinization, condensation, transposition rearrangement and neutralization as showed in **Scheme 1** [10]. Since MDT is yielded in the hydrochloride form, it has to be neutralized with NaOH to obtain the final product. Obviously, the use of HCl and NaOH poses several problems such as corrosion, high toxicity and the disposal of a large amount of aqueous waste containing NaCl contaminated with traces of aromatic amines, which have to be removed before discharging to pollute the residual water. Although a completely green solution to the existing problems might involve the replacement of this chemistry with an inherently less toxic combination of reagents, the replacement of current homogeneous catalysts with heterogeneous catalysts might eliminate the pollution of a waste aqueous phase [11].

Therefore, there is great academic interest and practical importance to develop easily separable, highly active and reusable solid acids to replace mineral acids for the synthetic process of diaminodiphenylmethanes [1,12]. When the uses of heterogeneous catalysts for MDT synthesis is scarcely disclosed in the literature, several solid acids including ion-exchanged resins [13], metallic compounds [14-17], clays [11,18], and zeolites [1,19-22] have been tested for the synthesis of 4,4'-diaminodiphenylmethane (MDA) by condensation of anilines and formaldehyde. According to the research results published in literature so far, zeolites are among the most promising candidates for choice of such solid catalysts due to their strong Brönsted acidity, high hydrothermal stability, tailorable acid site density and porosity.

In our recent studies, the catalytic activities of several zeolites in the synthesis of 3,3'-dimethyl-4,4'-diaminodiphenylmethane (MDT) from *o*-tolylamine and formaldehyde have been scanned, and H $\beta$  zeolite exhibited good performance to catalyze this synthetic reaction [23]. Therefore, there are further interests to determine the mechanism of MDT synthesis over H $\beta$  zeolite and optimize reaction conditions. In this paper, the effects of catalyst property and reaction conditions on MDT synthesis over H $\beta$  zeolite are deeply discussed, and the detailed interpretation to reaction mechanism of various intermediates are presented, which will establish the foundation of developing and applying a green

technology for the synthesis of MDT and similar compounds.

### 2. Experimental

### 2.1. Materials

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

#### 2.2. Reaction procedures

In a typical run, a certain amount of formaldehyde, *o*-tolylamine purified by distillation, and zeolite catalyst activated at 823 K for 3 h 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 vigorous stirring. After the reaction went through the scheduled times, the product mixture was collected and sampled for HPLC analysis.

#### 2.3. Sample analysis

The textural properties of zeolites were characterized by BET method using an ASAP2020M analyzer of Micromeritics Co., USA, and the acidic properties was measured by NH<sub>3</sub> temperature programmed desorption(TPD) analysis. The NH<sub>3</sub>-TPD experiments were conducted in a flow apparatus (PX200 analyzer of Tianjin Golden Eagle Technology Lit. Co., China) with helium as carrier gas, and a thermal conductivity detector (TCD) was used for evolved gas detection. A small amount of the granulated zeolite (100 mg) was heated at 823 K in an He flow (30 mL min<sup>-1</sup>) for 1h, 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 the rate of 10 K min<sup>-1</sup> up to 973 K under helium flow (20 mL min<sup>-1</sup>).

The samples of reactants and products were analyzed by EX1600SM High Pressure Liquid Chromatography (HPLC) with the conditions: detection wavelength of UV254 nm, C18 column, room temperature, methanol solvent, mobile phase of acetonitrile / water (1:1 volume ratio) and potassium dihydrogen phosphate (0.5%) at flow rate of 1.00 mL min<sup>-1</sup>. The content of each component was

determined by corresponding calibration factor.

Reaction intermediates were identified by Agilent 6520 Q-TOF LC/MS, and <sup>1</sup>H NMR spectra were generated from Brucker Avance 400 NMR using DMSO-d<sub>6</sub> as solvent and TMS as internal standard.

### 3. Results and discussion

#### 3.1. Effects of zeolite acidity and textural properties on MDT synthesis

For a heterogeneous reaction over molecular sieve catalysts, the reaction activity and selectivity depended on the acidity and textural property of zeolites. In general, the acidity of zeolite refers to acidic type, strength and density. For the synthesis of MDT from o-tolylamine and formaldehyde in the presence of zeolites, there was the prime interest to find out if either Brönsted acid or Lewis acid or both would be active in reaction. For this purpose, three comparable runs of MDT synthesis were first carried out in the absence of a catalyst and in the presence of TS-1 or H $\beta$  zeolite at 413 K, respectively, and the HPLC chromatograms of product samples were presented in Fig. 1. One can see that besides the large peak of reactant o-tolylamine, no peak of final product MDT and a very small peak appeared at retention time of 10.5 min in the absence of catalyst, and a negligible peak of MDT and a visible overlapping peak at 10 min appeared in the presence of TS-1 zeolite. Meanwhile, the HPLC picture of the sample from the reaction in the presence of H $\beta$  zeolite showed a large peak of product MDT, two small peaks of intermediates M1 and M2 at 6 and 7 min, and a very large peak of intermediate M3 at 9 min as well as a very small peak of by-product P at 12.3 min. As well known, HB as a aluminum-silicon zeolite contains both Brönsted acid sites (proton-donors) and Lewis acid sites (electron-acceptors), while TS-1 as a titanium-silicon zeolite contains Lewis acid sites alone [24,25]. Therefore, we conclude that Brönsted acid sites may play the principal role in catalyzing formation of the intermediates and consequent product MDT.

There were more interests to investigate how the acid strength and density of zeolite affect the MDT synthesis. Therefore, three kinds of aluminum-silicon zeolites H $\beta$ , HY and HZSM-5 as well as a titanium-silicon zeolite TS-1 were comparatively tested for MDT synthesis from *o*-tolylamine and formaldehyde at 433K. As showed in **Fig. 2**, TS-1 has very poor catalytic performance regarding HCHO

conversion and MDT production. For the three aluminum-silicon zeolite catalysts, HCHO conversion decreased from 80.7 to 75.2 to 73.6%, MDT yield from 53.3 to 42.9 to 30.7%, and MDT selectivity from 66.1 to 57.0 to 41.7% with shifting catalyst from H $\beta$  to HY to HZSM-5. By comparison, H $\beta$  demonstrated the best performance, while HZSM-5 gave the disappointing performance to this reaction system.

On the other hand, the NH<sub>3</sub> temperature programmed desorption (TPD) analysis showed the difference of acid site density and strength distribution among the four zeolites. As illustrated in **Fig. 3**, one peak of NH<sub>3</sub> desorption was detected in 375-550 K for each zeolite, and second peak detected in 700-850 K for HZSM-5 and H $\beta$  which indicated the existence of stronger acid sites. As presented in **Table 1**, the amount of NH<sub>3</sub> absorbed on HZSM-5, H $\beta$ , HY and TS-1 decreased from 643 to 517 to 381 to 233µmol/g, indicating HZSM-5 possessed the highest acid density while TS-1 possessed the lowest acid density. Imaginably, the catalytic activity of zeolites should follow the order of HZSM-5 > H $\beta$  > HY if the acid strength would have played a dominant role, and also the HZSM-5 should give the better performance than H $\beta$  if the amount of acid site would have played a critical role in MDT synthesis. The data in **Fig. 2**, however, declared the best catalytic performance for H $\beta$  and the better performance of HY than HZSM-5, suggesting that the pore structure and surface area of zeolites might have significant effects on this reaction.

As well known, H $\beta$ , HY and HZSM-5 are the protonated (H<sup>+</sup>)form of parent zeolites  $\beta$ , ZSM-5 and Y respectively. The high-silica zeolite  $\beta$  has an unique crystal structure with 12-membered ring channels (6.6 × 6.7 Å)crossed by a second type of 12-membered ring channels (5.6 × 5.6 Å) [26], and such interconnected pore (channel) system can promote reactants to easily pass from one pore to another. As one of the high-silica zeolites with MFI-type structure, ZSM-5 has also a two-dimensional pore structure with straight 10-membered ring channels (5.1 × 5.5 Å) intersected by a second type of 10-membered ring channels (5.3 × 5.6 Å) [27]. The low-silica zeolite Y is a member of the structural group named after the mineral Faujasite [28], which has a framework structure with the 12-membered ring pores to be arranged perpendicular to each other. Based on the data in **Table 1**, HZSM-5 with smaller pore opening (0.56 nm) and volume (0.19 cm<sup>3</sup>/g) might significantly hinder the diffusion of product MDT and rearrangement of reaction intermediates, while HY with larger pore diameter (0.74 nm) and volume (0.36 cm<sup>3</sup>/g) was less active due to low acid density and weaker acid strength. By comparison, the H $\beta$  with enough strong acidity,

moderate pore size (0.66 nm), pore volume (0.28 cm<sup>3</sup>/g) and surface area (461.3 m<sup>2</sup>/g) exhibited the best overall performance to catalytic synthesis of MDT.

Surface area, j Zeolites	si/Al	Surface area (m <sup>2</sup> /g)	ty of Hβ, HY, HZSM-5 Pore diameter (nm)	and TS-1 zeolites Pore volume (cm <sup>3</sup> /g)	Acidity ( µmol/g)
Нβ	40	461.3	0.66	0.28	517
HY	4.8	684.0	0.74	0.36	381
HZSM5	45	352.7	0.56	0.19	643
TS-1	_	359.6	0.54	0.16	233

### Table 1

### 3.2. Identification of key reaction intermediates

There might be several active intermediates in MDT synthesis by condensation of o-tolylamine and formaldehyde over H $\beta$  zeolite. The identification of these intermediates is useful for us to understand the reaction mechanism and optimize the reaction conditions. Some efforts have been spent for determination of the three intermediates M1, M2, and M3 in Fig. 1(c). LC-MS analysis of the product sample was first conducted and indicated that the three intermediates had the same molecular weight as final product MDT (226g/mol). In other words, these intermediates and MDT were isomers with chemical formula  $C_{15}H_{18}N_2$ . Unfortunately, the chemical structures of three isomeric intermediates could not be convincingly determined by LC-MS alone, due to lack of the information of standard reference compounds. Considering that there might be some differences of H position and vibration among the isomers, the three intermediates M1, M2 and M3 were carefully isolated each other by preparative chromatography, purified and then analyzed by <sup>1</sup>H nuclear magnetic resonance (NMR). Figure 4 illustrated the <sup>1</sup>H NMR spectra of the final product MDT (purity > 98%) and intermediates (purity > 95%) with the indication of H number and vibration frequency. The patterns of H in Fig. 4(a) well match the structural features of H in MDT molecule. By carefully interpreting the patterns of H in **Fig. 4**(b), we could confidently assign this <sup>1</sup>H NMR spectrum of the intermediate M3 to N,N'-di-o-tolyl-methanediamine. Based on the theoretical analysis of H shift and the follow-up discussion for temperature effects on the reaction mechanism, we have also deduced that the <sup>1</sup>H NMR spectra of intermediates M1 and M2 in Fig. 4(c) and (d) belonged to

2-methyl-6-(o-tolylamino-methyl)-phenylamine and 2-methyl-4-(o-tolylamino-methyl)-phenylamine respectively, although it was not entirely sure whether there was any interference of isomers 2methyl-5-(o-tolylamino-methyl)-phenylamine and 2methyl-3-(o-tolylamino-methyl)-phenylamine. Nevertheless, these <sup>1</sup>H NMR spectra gave us great help to understand the mechanism of MDT synthesis.

#### 3.3. Influence of reaction temperature and time

In general, reaction temperature has some significant effects on kinetics, selectivity and mechanism of a heterogeneous catalytic reaction. Under the conditions of n(o-tolylamine):n(HCHO)=3/1,  $w(H\beta):w(HCHO)=1:1$  and 1h, the synthesis of MDT from o-tolylamine and formaldehyde over H $\beta$  was investigated in temperature range of 373 to 473 K. As shown in Fig. 5, HCHO conversion significantly increased from 21.4 to 80.7% with increasing temperature from 393 to 433 K, and then stabilized in 433 -473 K. The selectivity of final product MDT gently increased from 4.5 to 28.7 % as temperature increased 373 to 413 K, rapidly rose up to 66.1% from 413 to 433 K, and then slightly decreased as temperature continually increased from 443 to 473 K, probably due to the generation of polymeric by-products in higher contrary, M3 temperature. On the the selectivity of key intermediate (N,N)-di-o-tolyl-methanediamine) significantly declined from 86.1 to 16.9 % with increasing temperature from 373 to 433 K, and then continually decreased to 2.4 % at 473 K. Clearly, there was a strong relationship between MDT production and  $N, N^{2}$ -di-o-tolyl-methanediamine consumption indicating that the synthetic mechanism of MDT must involve formation and conversion of this intermediate. Also as temperature increased, selectivity of intermediate M2 (2-methyl-4-(o-tolylamino-methyl)-phenylamine) gradually increased to a maximum of 9.4 % at 393 K, and then decreased to 2.4 % over 453 K, while the selectivity of intermediate M1 (2-methyl-6-(o-tolylamino-methyl)-phenylamine) slightly reached a small maximum of 3.5% and then decreased to 2.9% over 443 K. Besides, the selectivity of other by-products such as P in Fig. 1(c) significantly increased from 9.9 to 26.3% with increasing temperature from 433 to 473 K. In view of both higner HCHO conversion and higher MDT selectivity required by practical application, the optimal reaction temperature was about 433 K.

On the other hand, the effect of reaction time on the yield and selectivity of MDT in the condensation reaction of *o*-tolylamine and formaldehyde over H $\beta$  at 433 K was illustrated in **Fig. 6**. The yield of MDT slightly increased from 48.5 to 51.5 % with increasing reaction time from 0.5 to 1h, almost remained the same level up to 4 h, and then decreased to 45.1% after 8 h, while the selectivity of MDT slightly increased from 64.6 to 66.1 % with increasing time from 0.5 to 1 h, and gradually decreased to 62.4 % after 8 h. In comparison with reaction temperature, the effect of reaction time during 0.5 to 8 h on this reaction system was less significant.

### 3.4. Insight into the mechanism of MDT synthesis over $H\beta$ zeolite

#### 3.4.1. Overview of synthetic sequence

The reaction network and mechanism of MDT synthesis from *o*-tolylamine and formaldehyde over solid acid catalysts have, to the best of our knowledge, not been fully interpreted so far. According to the basic chemistry of amine-aldehyde condensation reaction and the implication of experimental data in above, an overview of sequence for this synthetic reaction was suggested in **Scheme 2**. This overall reaction sequence involves the formation and conversion of four major intermediates, including

- an *o*-tolylamine molecule reacted directly with a formaldehyde molecule to form an intermediate *o*-tolylamino-methanol;
- (2) the *o*-tolylamino-methanol was converted into a methylene-*o*-tolyl-amine (Schiff base ) by loss of a water;
- (3) the Schiff base reacted with an *o*-tolylamine to form a *N*, *N*'-di-*o*-tolyl-methanediamine;
- (4) N, N'-di-o-tolyl-methanediamine was rearranged to 2-methyl-4-(o-tolylamino-methyl)-phenylamine or isomers;
- (5) 2-methyl-4-(o-tolylamino-methyl)-phenylamine went through rearrangement to form final product MDT.

The detailed interpretation of the suggested mechanism and the idiographic description to reactions of various intermediate were presented below.

#### 3.4.2 The reactions of various intermediates

Great efforts have been made to sketch and describe the reaction mechanism of each individual intermediate in the synthetic process of MDT from *o*-tolylamine and formaldehyde catalyzed by  $H\beta$  zeolite.

#### o-Tolylamino-methanol formation

It is commonly accepted that the nucleophilic addition reaction of a carbonyl by an amine may take place easily to form an unstable carbinolamine, and thus an acidic catalyst could be, but not necessary to involve in this reaction step. As showed in **Scheme 3**, the direct attack of *o*-tolylamine to formaldehyde in the absence of catalyst went through the transitional state to form the *o*-tolylamino-methanol.

#### Methylene-o-tolylamine formation

Stoichiometrically, an *o*-tolylamino-methanol could convert to a methylene-*o*-tolylamine (Schiff base) by loss of a water. In fact, this process might be difficult to take place without the involvement of an acidic catalyst. Over H $\beta$  zeolite, this reaction was catalyzed by either a Brönsted acid or a Lewis acid site as showed in **Scheme 4**(a) or **Scheme 4**(b). However, Brönsted acid appeared more active to this reaction than Lewis acid, partly because the desorption of water from Lewis acid sites could be more difficult.

### N,N'-Di-o-tolyl-methanediamine formation

An extra *o*-tolylamine reacted with a methylene-*o*-tolylamine absorbed on a Brönsted acid or a Lewis acid site of H $\beta$  to form the key intermediate *N*,*N*'-di-o-tolyl-methanediamine, as showed in **Scheme 5**(a) and **Scheme 5** (b). The data in **Fig. 1** declared that this reaction was more favorable to be catalyzed by Brönsted acid instead of Lewis acid. In the absence of an acid catalyst, the formation of *N*,*N*'-di-*o*-tolyl

-methanediamine by the process as showed in Scheme 5 (c) was almost impossible.

#### 2-Methyl-4-(o-tolylamino-methyl)-phenylamine formation

The rearrangement reaction of *N*,*N*'-di-*o*-tolyl-methanediamine almost certainly required Brönsted acid sites on zeolite. As showed in **Scheme 6**, the amino group of *N*,*N*'-Di-*o*-tolyl-methanediamine was first protonated by a Brönsted acid, nearly causing the dissociation of the aminal into a molecule of *o*-tolylamine and a carbocation, which could interact by an electrophilic substitution with *para*-position and *ortho*-position on the aromatic ring of *o*-toluidine to 2-methyl-4-(o-tolylamino-methyl)-phenylamine and 2-methyl-6-(o-tolylamino-methyl)-phenylamine respectively, while the electrophilic attack of a carbocation on the *meta*-position or  $\delta$ -position on the ring of *o*-toluidine to form 2-methyl-5- or 2-methyl-3-(o-tolylamino-methyl)-phenylamine was almost impossible. Also, we assumed that the formation of 2-methyl-4-(o-tolylamino-methyl)-phenylamine was favored due to the lowest steric hindrance of the *para*-position compared to the *ortho*-position.

#### MDT formation

When the intermediate 2-methyl-4-(o-tolylamino-methyl)-phenylamine was adsorbed onto a Brönsted acid site of the catalyst, the C-N bond would be weakened by the additional charge. The resulting positive partial charge on the C-atom made it susceptible to a nucleophilic attack by the free electron pair of the amino function or the phenyl ring of the substrate itself (intramolecular rearrangement), or one of the other intermediates (intermolecular rearrangement). Considering the steric hindrance of intramolecular rearrangement as shown in **Scheme 7**(a), we suggested that the substrate most likely underwent the intermolecular rearrangement, i.e. an  $S_N^2$ -type nucleophilic substitution reaction to form the final product MDT as illustrated in **Scheme 7**(b). Obviously, the intermolecular rearrangement was favorable to a higher concentration of intermediate 2-methyl-4-(o-tolylamino-methyl)-phenylamine.

#### 3.4.3. The formation of by-products

Besides the main stream reactions in the above sequence, there were some side-reactions to produce by-products as indicated in **Fig. 1**. The data in **Fig. 5** have confirmed that the formation of these by-products could become very significant at higher temperature. These byproducts might mainly consist of trimeric or polymeric compounds, and the proposed mechanism of trimeric by-products from dimeric intermediates was presented in **Scheme 8**. It was believed that the formation and spread of such by-products could gradually plug the pore channels of catalyst and further cause catalyst deactivation. More experimental and theoretical studies for intermediates isomerisation, byproducts reaction and catalyst deactivation are underway. We will present a thorough discussion on the details of by-product reaction and catalyst deactivation mechanism elsewhere in near future.

#### 4. Conclusions

For the acid-catalyzed heterogeneous synthesis of MDT from *o*-tolylamine and formaldehyde, an effective solid acid catalyst should have strong Bronsted acidity and proper textural property. H $\beta$  zeolite demonstrated to be an good catalyst for this synthesis reaction. Reaction temperature significantly affected the activity and selectivity of H $\beta$  zeolite. The identification of key reaction intermediates and interpretation to various intermediates formation and conversion have provided us with an insight into the details of reaction mechanism.

- (1) The whole synthetic chain might start from the formation of an unstable intermediate *o*-tolylamino-methanol by the direct nucleophilic attack of *o*-tolylamine to formaldehyde either in the presence of catalyst or in the absence of catalyst.
- (2) The intermediate methylene-*o*-tolylamine (Schiff base) was produced from *o*-tolylamino-methanol by loss of a water in the presence of Hβ zeolite.
- (3) Key intermediate *N*,*N*'-di-*o*-tolyl-methanediamine was mainly formed by the reaction of *o*-tolylamine with a methylene-*o*-tolylamine absorbed on Brönsted acid rather than Lewis acid sites.
- (4) Rearrangement of *N*,*N*'-di-*o*-tolyl-methanediamine on Brönsted acid sites of Hβ generated
  2-methyl-4-(*o*-tolylamino-methyl)-phenylamine or 2-methyl-6-(*o*-tolylamino-methyl)-phenylamine.
  Of the two isomers, the former was more favorably produced than the latter.
- (5) Formation of final product MDT was accomplished by intramolecular or intermolecular

rearrangement of 2-methyl-4-(*o*-tolylamino-methyl)-phenylamine on H $\beta$ . The intermolecular rearrangement similar to an  $S_N^2$ -type nucleophilic substitution reaction was more favorable.

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**Fig. 1.** HPLC chromatograms of product samples from reaction of *o*-tolylamine and formaldehyde at 413 K. Reaction

conditions: n(o-tolylamine):n (HCHO)=3:1, 1 h. (a) no catalyst, (b) w(TS): w(HCHO)=1:1, (c) w(H $\beta$ ): w(HCHO)=1:1

**Fig. 2.** HCHO conversion, yield and selectivity of MDT in condensation of *o*-tolylamine and formaldehyde over various zeolites. Reaction conditions : n(o-tolylamine): n (HCHO)=3:1,  $w(H\beta)$ : w(HCHO)=1:1, 433K, 1 h. Color annotation: red

(HCHO conversion); blue (MDT yield); green (MDT selectivity)

**Fig. 3.** NH<sub>3</sub>-TPD curves of HY, HZSM-5, H $\beta$  and TS-1 zeolites

**Fig. 4** (a). <sup>1</sup>H NMR spectrum of product MDT

**Fig. 4** (b). <sup>1</sup>H NMR spectrum of intermediate M3

**Fig. 4** (c). <sup>1</sup>H NMR spectrum of intermediate M1

**Fig. 4** (d). <sup>1</sup>H NMR spectrum of intermediate M2

**Fig. 5.** Effect of reaction temperature on HCHO conversion and MDT selectivity. Reaction conditions : n(o-tolylamine): n (HCHO)=3:1,  $w(H\beta)$  : w(HCHO)=1:1, 1 h. M3: N, N'-di-o-tolyl-methanediamine; M2: 2-methyl-4-(o-tolylamino-methyl)-phenylamine; M1: 2-methyl-6-(o-tolylamino-methyl)-phenylamine; P: other byproducts

**Fig. 6.** Effect of reaction time on the yield and selectivity of MDT. Reaction conditions: n (*o*-tolylamine) : n (HCHO)=3:1, w(HGB) : w(HCHO)=1:1; 433 K.

Scheme 2. Overview of reaction sequence for MDT synthesis over Hβ zeolite

Scheme 3. Formation of o-tolylamino-methanol by the direct reaction of o-tolylamine with formaldehyde

Scheme 4(a). Formation of methylene-o-tolylamine from o-tolylamino-methanol catalyzed by Brönsted acid site on H $\beta$ 

Scheme 4(b). Formation of methylene-o-tolylamine from o-tolylamino-methanol catalyzed by Lewis acid site on Hβ

**Scheme 5**(a). Formation of *N*,*N*'-di-*o*-tolyl-methanediamine by reaction of *o*-tolylamine with *o*-tolylamino-methanol absorbed on Brönsted acid site

**Scheme 5**(b). Formation of *N*,*N*'-di-*o*-tolyl-methanediamine by the reaction of *o*-tolylamine with *o*-tolylamino-methanol absorbed on Lewis acid site

Scheme 5(c). Hypothetical process for the formation of N,N'-di-o-tolyl-methanediamine by reaction of o-tolylamine with o-tolylamino-methanol in the absence of catalyst

Scheme 6. Rearrangement of N,N'-di-o-tolyl-methanediamine over a Brönsted acid site on Hβ

Scheme 7(a). Formation of MDT by intra-rearrangement of 2-methyl-4-(o-tolylamine-methyl)-phenylamine adsorbed on a Brönsted acid site

Scheme 7(b). Formation of MDT by inter-rearrangement of 2-methyl-4-(*o*-tolylamine-methyl) -phenylamine adsorbed on a Brönsted acid site

Scheme 8. Possible pathways of trimeric by-product formation from dimeric intermediates





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2-Methyl-4-(o-tolylamino-methyl)-phenylamine

2-Methyl-6-(o-tolylamino-methyl)-phenylamine





