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Catalytic activity of zeolites for synthesis reaction of methylenedianiline from aniline and formaldehyde

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Abstract

The catalytic activities of Y-, β-, and ZSM-5-zeolites for methylenedianiline (MDA) synthesis from the condensation reaction of aniline and formaldehyde have been investigated. Among β-zeolites with various Al concentrations (Si/Al ratios from 10 to 120 mol mol^{-1}), β-zeolite with Si/Al ratio of 13.6 mol mol^{-1} shows the best catalytic performance in MDA synthesis. Y-zeolite exhibited lower catalytic activity than β-zeolites under the identical reaction conditions, however, exhibited the higher selectivity to 4,4′-MDA. Furthermore, it revealed that aniline/formaldehyde and catalyst/formaldehyde ratio, and reaction temperature also influenced on the MDA yield and isomers distribution.

Keywords: Y-zeolite; β-zeolite; Methylenedianiline; Aniline; Formaldehyde

1. Introduction

The condensation reaction of aromatic compounds with aldehydes is useful tool for the industrial production of important raw materials such as bisphenol-A and -F, methylenedianiline and other fine chemicals. The manufactural condensation process has been used mineral acid as catalyst. However, use of mineral acid is laden with several problems like, high toxicity, corrosion, difficulty in separation and recovery of products, etc. To avoid those problems, many efforts have been directed at the search for solid acid catalysts, which should be more safe and more environmentally friendly than mineral acids [1,2]. We have previously investigated the catalytic activities of the Al-incorporated MCM-41 [3,4] and β-zeolite [5] for bisphenol-F synthesis by the condensation reaction of phenol and formaldehyde, and revealed that the catalytic activity was strongly influenced by the hydrophobicity and the acidity on the surface of solid acid.

Methylenedianiline (MDA, diaminodiphenyl methane), which is important chemicals for the production of the corresponding diisocyanate which reacts with polyols to produce polyurethane. The industrial production of MDA is performed by adding for formaldehyde to stoichiometric amounts of hydrochloric acid and aniline. Hence, the several patents concerning MDA production over solid acid catalysts, such as ion-exchanged resins [6], clays [7], and zeolite [8], with hydrochloric acid, have been disclosed. In this study, we investigated the catalytic performances of Y-, β-, and ZSM-5-zeolite as solid acid catalyst for the synthesis reaction of MDA. The influences of Al concentration in zeolite, aniline/formaldehyde and catalyst/formaldehyde ratio and reaction temperature on the condensation reaction of aniline and formaldehyde were also investigated.

2. Experimental

Aniline and ca. 37% formaldehyde aqueous solution was obtained from Kanto Chemical Co. Aniline is purified by the distillation over sodium hydroxide. 37% formaldehyde aqueous solution is used without purification. β-zeolite with Si/Al molar ratio of 10 was obtained from Zeolyst International and Y-zeolite with Si/Al molar ratio of 10 was obtained from N. E. CHEMCAT.

β-Zeolites with various Al concentration were prepared by the dealumination [9] of that with Si/Al = Y-zeolite; β-zeolite; methylenedianiline; aniline; formaldehyde10. The dealumination was carried out by the following procedure. Typically, 10 g

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H type β-zeolite was added to 100 ml adequate concentration (0.1–1 mol dm^{-3}) of hydrochloric acid solution. The suspension was stirred at room temperature for 1 min ∼6 h. The solid phase was separated by the filtration, washed with pure water several times, dried at 100 °C for 3 h, and calcined at 400 °C for 12 h. The Al concentration in the dealiminaized zeolites was determined by the measurement of the X-ray fluorescence spectroscopy (JEOL, JSX-3201). The crystal structure and crystallinity for each dealuminated β-zeolite was confirmed by XRD measurement (JEOL JDX-8030).

Liquid-phase condensation reaction of aniline and formaldehyde over zeolite catalysts was carried out in a 50 ml round-bottomed flask equipped with a magnetic stir bar and a reflux condenser. The flask charged 0.05 or 0.15 g of catalyst and 2.0 or 12 g of aniline was heated by a digital temperature controller at 120 °C or an adequate temperature. After attaining the temperature, the reaction was started by adding 0.35 g of aqueous formaldehyde solution (1.6 mmol as formaldehyde) and stirred. At the end of the reaction, the reaction mixture was extracted by the mixture of 20 ml of diethyl ether and 20 ml of 10% sodium hydroxide solution. The organic layer was analyzed by GLC (SHIMADZU, GC-17A) for the quantitative analysis.

The qualitative analysis for the MDA isomers and aminal was performed by ^{1}H or ^{13}C NMR (JEOL alpha 500) after the isolation of each product by the column chromatograph by using of the silica gel and hexane as elute solution.

3. Results and discussion

The catalytic activities of Y-, β-, and ZSM-5 zeolites have been investigated for acid-catalyzed methylenedianiline (MDA) synthesis process. Table 1 is summarized the catalytic performance of these zeolites for the condensation reaction of aniline and formaldehyde at 120 °C for 3 h. As shown in Scheme 1, Y-, β-, and ZSM-5-zeolite used here exhibited the catalytic activities to obtain 4,4′-, 2,4′-, and 2,2′-MDA and aminal (*N*,*N*′-diphenylmethylenediamine), whereas a small amount of aminal was only obtained in the reaction without catalyst. The catalytic activity of ZSM-5 (Si/Al = 45) for the present reaction is much lower than that of β-zeolite (Si/Al = 40) and isomer distribution of 4,4′-MDA was also lower. Reaction catalyzed by β-zeolite exhibited the highest yield of total MDA. The catalytic activity of Y-zeolite (Si/Al = 10) was not so high, however, the highest fraction of 4,4′-MDA isomer in three isomers, 71.9%, was exhibited.

Table 1
Catalytic performance of zeolites for the MDA synthesis

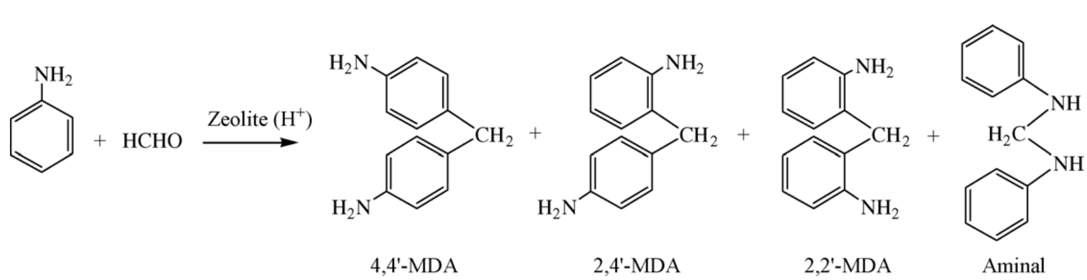
Catalyst		Yields (%)[a]		Isomers distribution of MDA (%)		
Zeolite	Si/Al	Aminal	MDA	4,4′-MDA	2,4′-MDA	2,2′-MDA
Non	–	3.1	–	–	–	–
ZSM-5	45	25.6	6.3	19.5	7.9	72.6
β-zeolite	40	9.6	49.1	47.8	39.9	12.3
β-zeolite	10	9.5	47.6	54.1	28.9	17.0
Y-zeolite	10	9.4	26.6	71.9	8.9	19.2

[a] Based upon the amount of formaldehyde reaction conditions; aniline/formaldehyde = 5 mol mol^{-1}, catalyst/formaldehyde = 0.4 mass ratio, 120 °C, and 3 h.

The order of the catalytic activities of three kinds of zeolite for the formation of MDA is β > Y > ZSM-5. The ZSM-5-zeolite exhibited very low activity, because the molecular dimension of MDA isomers is larger than the pore dimension of ZSM-5-zeolite and therefore the reaction takes place solely on the external surfaces of ZSM-5 crystallites. The β-zeolite exhibited a higher activity than the Y-zeolite, probably because of stronger acid sites on the β-zeolite [10].

The order of the selectivities to 4,4′-MDA for three kinds of zeolite is Y > β > ZSM-5. The β-zeolite with a Si/Al ratio of 10 exhibited little activity for the isomerization of 4,4′-MDA under similar reaction conditions for the condensation of aniline and formaldehyde. Al-loaded MCM-41 exhibited a higher selectivity to 4,4′-MDA isomer than Y-zeolite [11]. It is reported that the order of acid strength for zeolites is ZSM-5 > β > Y [10] and the acid strength of Al-MCM-41 is weaker than that of Y-zeolite [12]. From these facts it is apparent that the selectivity to 4,4′-isomer whose molecular dimension is the smallest among MDA isomers is not governed by so-called shape selectivity. It is suggested that the weaker acid sites may provide the higher selectivity to 4,4′-MDA. However the reason why catalysts with weaker acid sites exhibit higher selectivity is not clarified at the present time.

The influence of the Al concentration in β-zeolite on the catalytic activity for the MDA synthesis reaction at 120 °C for 3 h was also investigated. Fig. 1 shows the yields of all MDA isomers and aminal in the reactions over β-zeolite with various Si/Al molar ratio of between 10 and 120 mol mol^{-1} which range are corresponding to between 0.0083 and 0.091 mol mol^{-1} as Al concentration, Al/(Al + Si). These results indicate that the catalytic activity of β-zeolites for the synthesis reaction of MDA gradually increases with increase in



Scheme 1.

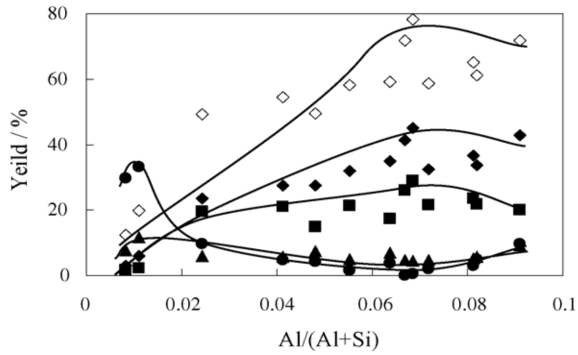


Fig. 1. The products yield: total MDA (◇), 4,4′-MDA (◆), 2,4′-MDA (■), 2,2′-MDA (▲) and aminal (●), vs. the Al concentration in β-zeolite for the condense reaction of aniline and formaldehyde at 120 °C under the reaction conditions of aniline/formaldehyde = 5 mol mol^{-1} and catalyst/formaldehyde = 0.4 mass ratio.

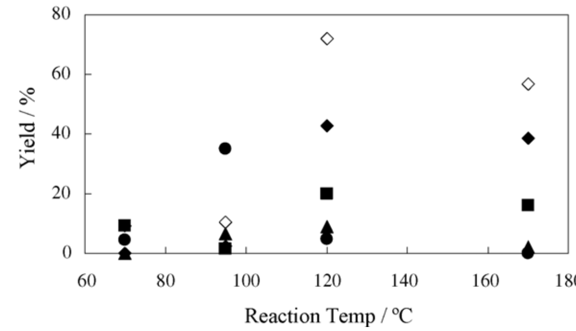


Fig. 2. The products yield: total MDA (◇), 4,4′-MDA (◆), 2,4′-MDA (■), 2,2′-MDA (▲) and aminal (●), for the condense reaction of aniline and formaldehyde over β-zeolite (Si/Al = 10.0) at 70, 95, 120, and 170 °C under the reaction conditions of aniline/formaldehyde = 5 mol mol^{-1} and catalyst/formaldehyde = 0.4 mass ratio.

the Al concentration from 0.0083 to 0.068 mol mol^{-1} (i.e. with decrease in the Si/Al ratio from 120 to 13.6 mol mol^{-1}), however, further increase in the Al concentration up to 0.091 mol mol^{-1} (i.e. decrease in the Si/Al ratio to 10 mol mol^{-1}) results in a gradual decrease in the product yield. Thus the Al concentration of 0.068 mol mol^{-1} in β-zeolite catalyst seems to be the optimum one for showing its highest aniline and formaldehyde condensation activity under the present reaction conditions. The gradual increase in the catalytic activity of β-zeolites with increase in the Al concentration from 0.0083 to 0.068 mol mol^{-1} is expected because β-zeolites with higher Al concentration has much acid sites [5] and hence, this is a better catalyst for the acid-catalyzed MDA synthesis process. The decrease in catalytic activity with increase in Al concentration (i.e. with increase in acid sites) above 0.068 mol mol^{-1} can be due to its decrease in hydrophobicity. An increase in hydrophobicity with increase in Si/Al ratio, the important property for the effective functioning of a solid acid in aqueous solution, seems to be partially responsible for this adverse behavior [13]. There is no significant effect of Al concentration in β-zeolite on the MDA isomers distributions.

The yield of aminal was higher, 33%, in the present reaction over the β-zeolite with lower Al concentration (Si/Al = 80). Since a little amount of aminal, 3.1%, was obtained by the reaction of aniline with formaldehyde without catalyst (Table 1), it is suggested that aminal synthesis reaction can be also catalyzed by zeolite. It was previously reported that the isomerization of aminal to MDA was catalyzed by solid acids [7]. The result indicates that the isomerization rate of aminal to MDA over β-zeolite with low Al concentration is so slow under the present reaction conditions.

The effect of reaction temperature, 70–120 °C, on MDA synthesis over β-zeolite (Si/Al = 10 mol mol^{-1}) is shown in Fig. 2. Results reveal that the total MDA yield drastically increases with increase in the reaction temperature from 95 to 120 °C, however it decreases with further increase in the reaction temperature to 170 °C. This result indicates the formation of trimer or oligomer at higher temperature. Aminal was obtained as main product at 95 °C, and this result can be due to the lowering the catalytic activity for the isomerization of aminal at low temperature. There is no significant difference on the MDA isomers distributions at the reaction temperature of between at 120 and 170 °C.

Fig. 3 shows the time profile of the each product yield for the reaction of formaldehyde with aniline at 120 °C over β-zeolite with Si/Al of 13.6 mol mol^{-1} which exhibited the highest total MDA yield among the β-zeolite with various Si/Al. It shows that the total MDA yield increases to 78.3% within the initial 3 h reaction period, and it decreases with increase in the reaction time. It indicates that MDA reacts with additional formaldehyde to produce the trimer or oligomer, which cannot be detected by GLC. The yield of each MDA isomer, 4,4′- 2,4′-, 2,2′-MDA, showed the similar time profiles having a maxima at 3 h. It supports the result that the isomerization of the produced MDA does not occur or is negligible over the β-zeolite. 4,4′-MDA is produced as the highest yield among the MDA isomers, and its yield reach to 42.4% at 3 h. The yield of aminal exponentially increase in a short initial reaction period, and decrease to almost zero after 3 h. It indicates that aminal is an

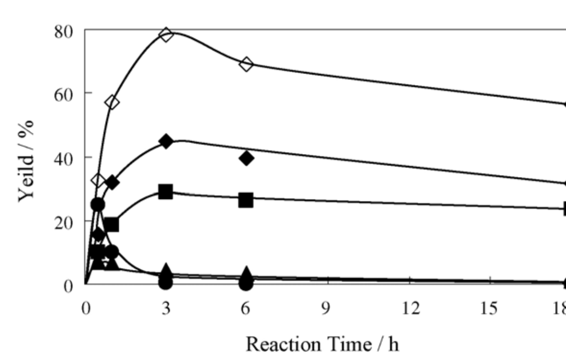


Fig. 3. Time profiles of products yield: total MDA (◇), 4,4′-MDA (◆), 2,4′-MDA (■), 2,2′-MDA (▲) and aminal (●), for the condense reaction of aniline and formaldehyde over β-zeolite (Si/Al = 13.6) at 120 °C under the reaction conditions of aniline/formaldehyde = 5 mol mol^{-1} and catalyst/formaldehyde = 0.4 mass ratio.

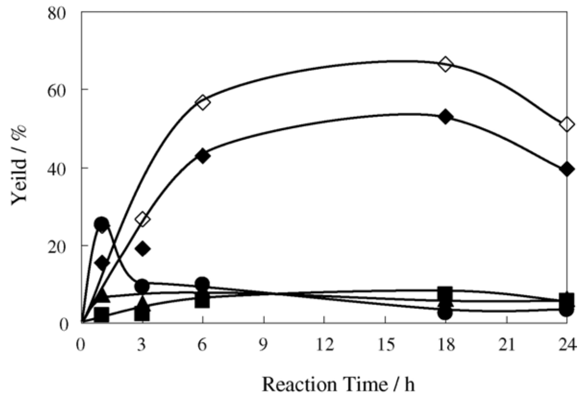


Fig. 4. Time profiles of products yield: total MDA (◇), 4,4′-MDA (◆), 2,4′-MDA (■) 2,2′-MDA; (▲) and aminal (●), for the condense reaction of aniline and formaldehyde over Y-zeolite (Si/Al = 10) at 120 °C under the reaction conditions of aniline/formaldehyde = 5 mol mol^{-1} and catalyst/formaldehyde = 0.4 mass ratio.

0.4 to 1.2) on the total MDA yield in the reaction over β-zeolite (Si/Al = 13.6). On the reaction catalyzed by Y-zeolite (Si/Al = 10), in contrast, the yield of total MDA is drastically increased to 59.2 from 26.6% with increase in Y-zeolite/formaldehyde to 1.2 from 0.4 mass ratio and increase up to 84.6% with increase in aniline/formaldehyde 30 from 5 mol mol^{-1}. These results indicate that the amount of effective catalytic site of Y-zeolite is fewer than that of β-zeolite, i.e., the increasing of the amount of the catalyst improves the catalytic performance and the increasing the aniline/formaldehyde ratio inhibits the formation of trimer or oligomer compounds. The highest MDA yield and 4,4′-isomer distribution herein was obtained as 96.1% and 81.3%, respectively, by the reaction under the conditions such as aniline/formaldehyde of 30 mol mol^{-1}, Y-zeolite/formaldehyde of 1.2 mass ratio, reaction temperature of 120 °C and reaction time of 3 h.

Table 2
Influence of catalyst/formaldehyde and aniline/formaldehyde ratio on the catalytic performance of zeolites

Catalyst	C/F[a]	A/F (mol mol^{-1} [b])	Products yield (%)[c]				
			Aminal	4,4′-MDA	2,4′-MDA	2,2′-MDA	MDA Total
β-zeolite Si/Al = 13.6	0.4	5/1	Trace	45.0	29.0	4.4	78.3
	0.4	30/1	17.1	32.8	40.5	0.3	79.7
	1.2	5/1	Trace	43.9	37.3	2.0	83.2
Y-zeolite Si/Al = 10	0.4	5/1	9.4	19.1	2.4	5.1	26.6
	0.4	30/1	Trace	70.5	7.6	6.5	84.6
	1.2	5/1	Trace	48.8	6.7	3.7	59.2
	1.2	30/1	–	81.3	12.4	2.4	96.1

[a] Mass ratio of catalyst to formaldehyde.
[b] Molar ratio of aniline to formaldehyde.
[c] Based upon the amount of formaldehyde reaction conditions; 120 °C, 3 h.

intermediate to form MDA. However, it was previously reported that methylol cation, $^{+}CH_2OH$, generated from formaldehyde on the zeolite acid sites, directly attacked the phenyl ring in phenol to produce bisphenol-F [5]. Therefore, the direct MDA synthesis route via an electrophilic aromatic substitution of methylol cation with aniline cannot be denied absolutely.

Fig. 4 also shows the time profiles of the yields of MDA isomers and aminal on the reaction of aniline with formaldehyde over Y-zeolite (Si/Al = 10) at 120 °C. Although the reaction rate over the Y-zeolite is much slower than that over the β-zeolite, the yield of total MDA is reached up to 67% at 18 h. It indicates that the amounts of the effective catalytic site on Y-zeolite are fewer than those on β-zeolite. Whereas the isomer distribution of 4,4′-MDA was kept high, 79.7%, after 18h. However, aminal was still remained after 24 h.

Table 2 is summarized the effects of aniline/formaldehyde and catalyst/formaldehyde ratio on the products yields for the present reaction over β-zeolite and Y-zeolite. There is no significant effect of the aniline/formaldehyde ratio (from 5 to 30 mol mol^{-1}) and the catalyst/formaldehyde mass ratio (from

4. Conclusions

The catalytic performance of Y-, β-, and ZSM-5-zeolite on the MDA synthesis from the condense reaction of aniline and formaldehyde was investigated. The trend of the catalytic activity of these zeolites was β > Y > ZSM-5, and that of the selectivity to 4,4′-MDA isomer was Y > β > ZSM-5 at 120 °C. It revealed that Si/Al in zeolite, aniline/formaldehyde, and catalyst/formaldehyde influenced on the products yields and MDA isomers distributions. The yield of 4,4′-MDA was reached up to 81.3% on the reaction over Y-zeolite (Si/Al = 10) which aniline/formaldehyde and catalyst/formaldehyde ratio was 30 mol mol^{-1} and 1.2 mass ratio, respectively.

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