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SYNTHESES OF METHYLENEDIANILINES OVER THE ZEOLITE CATALYSTS

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Abstract

Syntheses of methylenedianilines over zeolites with various structures were studied. It was found out that the most selective catalyst for the synthesis of 4,4´-methylenedianiline isomer was zeolite Y. Further, the kinetic data showed that initial N,N´-diphenylmethylenediamine reacted over zeolite catalysts by even one order of magnitude faster that the intermediate product 4-amino-N-benzylaniline. The most suitable temperature range for the synthesis of 4,4´-methylenedianiline isomer was further identified as a range of 100 to 120°C.

Keywords: zeolite; methylenedianiline; kinetic; aniline; formaldehyde.

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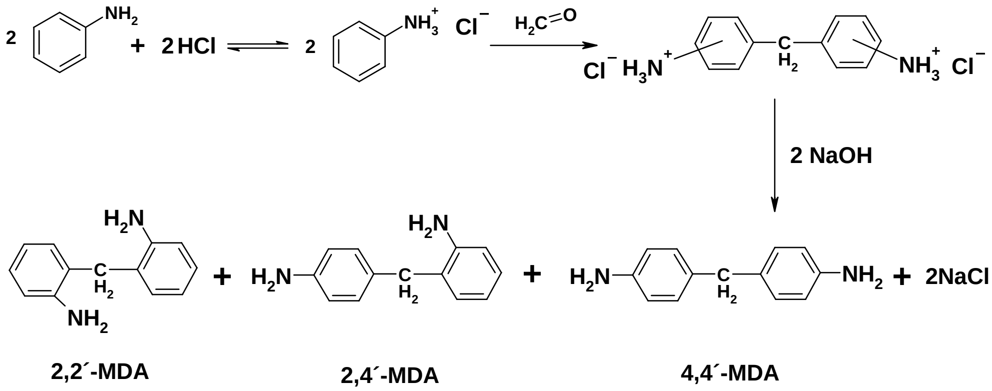
1. Introduction

Methylenedianilines (MDA) is formed by aniline condensation in the presence of an acid catalyst [1]. During the synthesis, isomers 2,2´-MDA (0,3 %) and 2,4´-MDA (4 %) also form apart from the required 4,4´-MDA isomer. Trimers and other heavier polymers of aniline and formaldehyde are formed during the synthesis apart from dimers (70 %) in the reaction mixture. MDA production belongs to high-capacity processes, and it constitutes a preliminary step for production of diisocyanate MDI, which is a basic component for production of polyurethane materials. This use comprises of over 90 % of MDA consumption. The rest, less than 10 %, is used for production of epoxy resins, anti-corrosion materials, dyes and other special products [2].

The oldest but still nowadays the most used catalyst for MDA synthesis is hydrochloric acid. The amount of the acid used for the synthesis is in effect stoichiometric with respect to aniline, which is used in excess with respect to formaldehyde, when the formaldehyde conversion is total. The reaction mixture is neutralized by a base, mostly NaOH (Scheme 1). A great advantage of the given procedure is that hydrochloric acid is a relatively cheap chemical substance, and a total conversion and a high yield of 4,4´-MDA isomer is reached. On the other hand, hydrochloric acid causes corrosion of the equipment and neutralization of waste salts.



Scheme 1. The traditional procedure of MDA production with the use of HCl as an acid catalyst

An alternative procedure of 4,4´-MDA production is catalysis by an acid heterogeneous catalyst. Over the years, a wide range of various catalyst was studied, such as various types of diatomaceous earth [3,4], amorphous aluminosilicates [5], barium nitrides [6], hydroxy ethane sulfonic acid [7] and silver tungstate [8].

Zeolites appear to be the most suitable for MDA syntheses in recent years. Zeolites are crystalline aluminosilicates with an exactly defined structure. An advantage of these materials is their high thermal stability, and also high activity due to the crystalline structure. A negative charge of aluminium in the zeolite structure is compensated by cations, which is H^+cation in case of an acid catalysis.

Clerici et al. [9] indicated the use of ZSM-5 and Y zeolites, whereas the zeolite structure could contain boron and titanium. Low aniline conversions up to 30 % and selectivity to 4,4-MDA to 70 % were reached. Kiso et al. [10] gave zeolite Y as a suitable catalyst. Selectivity to 4,4-MDA of 82 % was reached on an untreated catalyst, if the catalyst was modified by fluorine or ion exchange by various metals, selectivity of even 92 % could be reached. Perego et al. [11] proposed the use of zeolite Beta, whereas selectivity to 4,4-MDA of 50 to 60 % was reached for the total conversion. Similar results were reached in a batch arrangement even in a trickle bed reactor. The same team of authors in another paper [12] recommended modification of zeolite Beta by phosphorus or boron for increasing the selectivity to 4,4-MDA isomer. Corma et al. [13] recommended the use of zeolites like ITQ-2, ITQ-6 and ITQ-18. The authors presented that these zeolites had lower formation of side substances like quinazolines, and these zeolites were also more resistant to deactivation. Kugita et al. [14] found out, that the activity of zeolites to reaction of aniline with formaldehyde decreased in a succession of Beta > Y > ZSM-5, whereas the highest yield of 4,4-MDA was reached over zeolite Y.

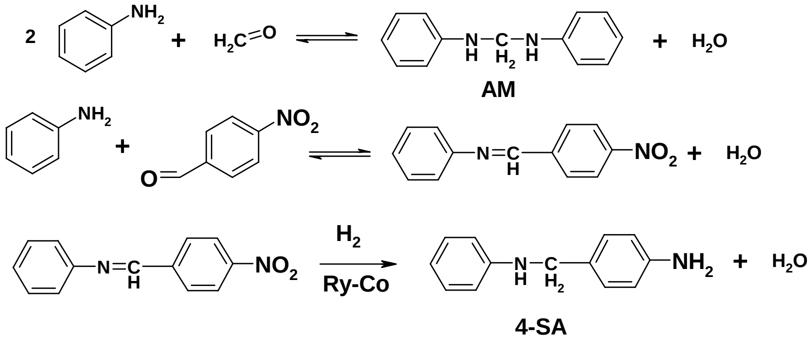
The objective of this work was to test zeolite catalysts of various structures for MDA synthesis. N,N´-diphenylmethylenediamine aminal (AM, the product of condensation of two molecules of aniline and one molecule of formaldehyde) was used as the starting substance, and secondary amine 4-amino-N-benzylaniline (4-SA) was also used. The formation of 4-SA amine is a necessary intermediate step during synthesis of 4,4-MDA isomer from the aminal. This way, it was possible to differentiate between the effect of catalysts on the initial aminal and 4-SA intermediate product, which has not been described in literature yet. The pure compounds were used to avoid effect of water and formaldehyde polymers which are present if the water solution of formaldehyde and aniline are used as a starting material.

2. Experimental

2.1 Chemicals

Catalysts by Zeolyst company supplied in H form were used for the experiments. Aniline (Aldrich 99 %) was distilled in an efficient column with 80 TP. Formaldehyde (operational sample BC-MCHZ) 37 % with a content of 11 % methanol was used without any modification.

Aminal was prepared by mixing formaldehyde and aniline in a molar ratio 1:2, the product should be extracted to ether and several times recrystallized. 4-amino-N-benzylaniline was prepared by hydrogenation of 4-nitro-benzylidenaniline over a cobalt catalyst (Grace) at a temperature of 70 °C and a hydrogen pressure of 5 MPa. 4-nitro-benzylidenaniline was prepared by condensation of 4-nitrobenzaldehyde (Aldrich 99 %) with aniline in methanol environment, whereas the product was obtained as a yellow crystalline substance (Scheme 2).



Scheme 2. Synthesis of initial substances, aminal and 4-amino-N-benzylaniline

2.2 Analytical methods

Quantitative analysis of reaction mixtures was carried out by means of SHIMADZU-GC9 gas chromatograph with a Flame Ionization Detector (FID). HP-PONA capillary column (50 m x 0.2 mm, film 1 μm) was used. Helium was the carrier gas. Qualitative analysis of the reaction mixtures was carried out by means of GC MS-QP 2010 SHIMADZU gas chromatograph equipped with a Mass Spectroscopy (MS) detector. DB-5 capillary column (60 m x 0.32 mm, film 1 μm) and helium as the carrier gas were employed. The samples were homogenized by methanol and they were analyzed using a method of an internal standard. The correction factors were determined using pure substances as standards. Catalysts were characterized by means of temperature programmed desorption (TPD) with the use of pyridine. From the known unit cell size (CBV600 24.33 A, CBV780 24.25 A) and with using Fichtner-Schmittler equation [15] the content of extraframework Al for the Y zeolites was calculated. Used catalysts are summarized in Table 1.

Table 1. Overview of used catalysts and their properties (pulse saturation with pyridine at a temperature of 200 °C, the increase of temperature during the desorption 10 °C/min to 850 °C)

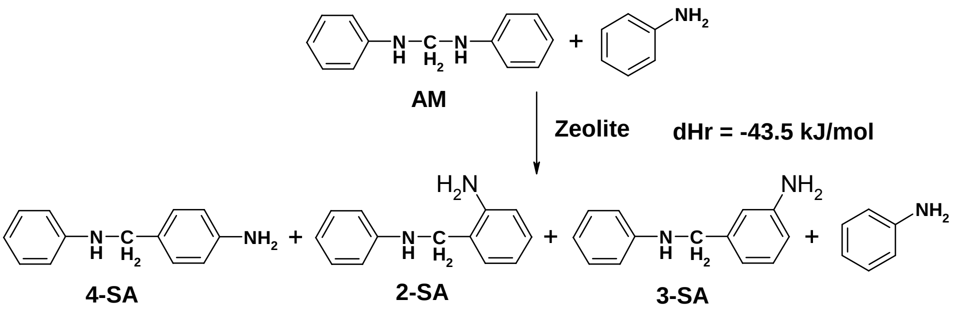
Zeolite	Si/Al	TPD Pyridine ($\mu mol/g_{cat}$)	Al ($\mu mol/g_{cat}$)	Ss (m^2/g_{cat})	Al_{ext} (%)
Y (CBV600)	2.6	280	4330	660	77.6
Y (CBV780)	40	137	407	720	50
ZSM-5 (CBV8014)	40	370	407	425	-
Beta (CP811E-75)	37.5	277	434	450	-
Mordenite (CBV90A)	45	257	363	500	-

2.3 Catalytic test

A molar ratio of aniline:aminal or aniline:4-SA = 20:1 was in the reaction mixture at the beginning. The total amount of the reaction mixture was about 50 g. This mixture was heated to the required temperature in an oil bath, and then a catalyst freshly calcinated to 550 °C was added. The zeolite was in a form of powder in all cases. The reaction was carried out with stirring at atmospheric pressure, and samples were taken out continuously.

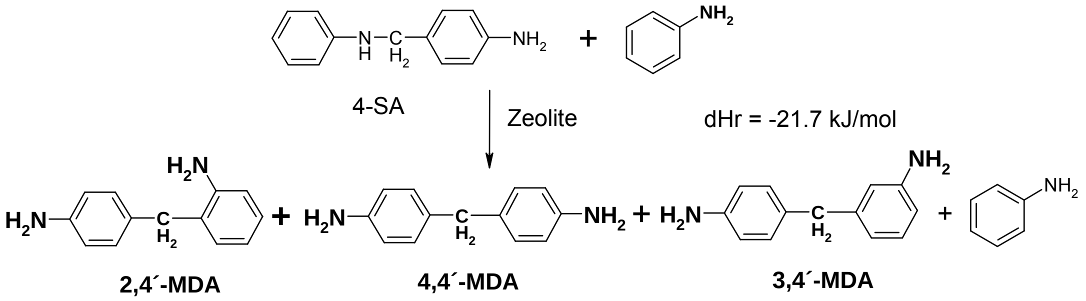
3. Discussion

If aminal and aniline were the starting substances and zeolite was the catalyst, at first secondary amines would form in the first step (Scheme 3). It is further obvious from the chemism that secondary amines did not form by an intramolecular rearrangement of aminal, but by a gradual substitution reaction, where the presence of the amine was necessary. Generally, substitution to 2, 3 and 4 positions was possible, whereas 2 and 4 positions were preferred with respect to the character of the reaction (electrophilic substitution, NH- group is a substituent of the first group). 2-SA and 4-SA isomers were found and observed over all zeolites, 3-SA isomer was not detected at all.



Scheme 3. Synthesis of secondary amines from aminal

The secondary amines reacted in the second step to final MDA isomers. Scheme 4 shows an example for 4-SA isomer. Substitution to 2, 3 and 4 positions was possible again, and the presence of aniline was also necessary.



Scheme 4. Synthesis of MDA isomers from 4-amino-N-benzylaniline

When 4-SA isomer was used as the starting substance, even substitution to 3 position was observed, though 3,4´-MDA isomer formed only in a small quantity (Figure 1). Formation of this isomer can be explained by the ability of the catalyst to protonate NH_2 group (NH_3^+ group is a substituent of the second group) possibly by steric selectivity of the catalyst. 3,4´-MDA isomer formed most over zeolite Beta (3.2 % of the total MDA isomers at the total conversion of 4-SA) the least then over zeolite Y with a low ratio of Si/Al (0.4 % of the total MDA isomers at the total conversion of 4-SA).

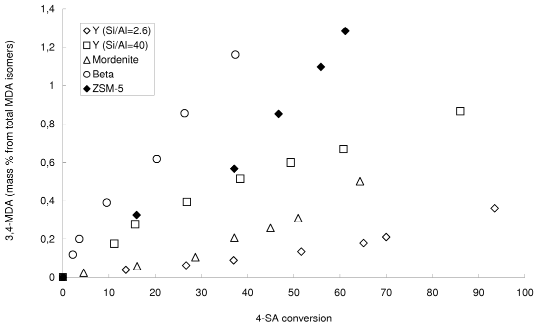


Fig. 1. Formation of 3,4´-MDA isomer from 4-amino-N-benzylaniline over zeolite catalysts (150°C, 50 g mixture with the molar ratio aniline/4-SA = 21.5, 0.3 g zeolite)

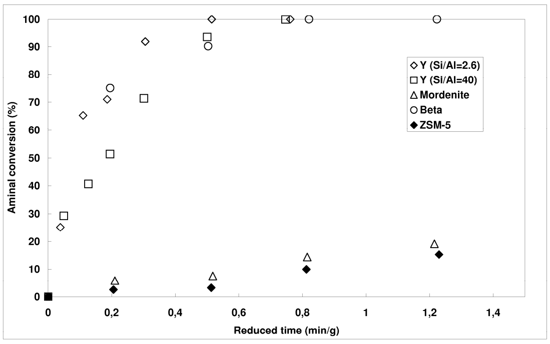


Fig. 2. Aminal conversion versus time relative to one gram of the catalyst (150°C, 50 g mixture with the molar ratio aniline/aminal = 21.5)

It was found out that zeolites of the structure Y and Beta were the most active catalysts for the aminal reaction. On the contrary, Mordenite and ZSM-5 showed very low activity (Figure 2). In each experiment the same amount of the reaction mixture was used but different amount of catalyst. Thus for the correct comparison of the catalysts activity reduced time was used (time which corresponds to using 1 g of catalyst). This was probably due to the crystalline structure of the zeolites, when zeolite Y had great inner cavities for the reaction, and zeolite Beta had relatively great channels. On the contrary, zeolite ZSM-5 and Mordenite had lower inner dimensions of the channels. When two zeolites of Y structure with different Si/Al ratios were compared, then it is obvious that the zeolite with Si/Al ratio = 2.6 was about twice active than the zeolite Y with Si/Al ratio = 40. This is in accord with a performed characterization by means of TPD technique, when about twice the amount of active centers able to adsorb pyridine was found for the zeolite Y with Si/Al = 2.6 (Table 1). Theoretically, each Al atom in the zeolite structure should represent one active center, though, as the characterization showed, not all the centers were available to molecules, which were more volume demanding, like pyridine. And these considerations also apply for sterically demanding molecule of aminal and its products. Also some affect of extraframework Al (77.6 % against to 50 %) may be responsible to higher activity of zeolite Y with Si/Al = 2.6.

Zeolites Y and Beta again suited the most with respect to the selectivity to the required product, 4-SA (Figure 3). Zeolites ZSM-5 and Mordenite showed a low yield of 4-SA isomer which could be related to their relatively lower channel structure in comparison with zeolites Y and Beta.

If 4-SA secondary amine synthetically prepared was used as the starting substance, it was observed that zeolites Y and Beta were again the most active (Figure 4) and zeolite Y was the most selective to the required isomer, 4,4´-MDA (Figure 5). The results indicate that the most suitable catalyst for selective preparation of 4,4´-MDA isomer from aminal was zeolite Y. On the contrary, if it was required to prepare a mixture of isomers with a high content of 2,4´-MDA isomer, then zeolite Mordenite was the most suitable. The results are in agreement with literature data [9-14] from the point of view the catalysts activity. It was found the second step (conversion of 4-SA) has affect on the overall low selectivity of formation 4,4-MDA over Beta zeolite as reported Perego et al. [11]

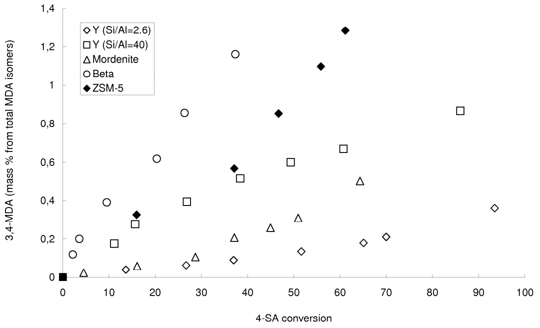


Fig.3. 4-SA isomer content versus aminal conversion (150°C, 50 g mixture with the molar ratio aniline/aminal = 21.5

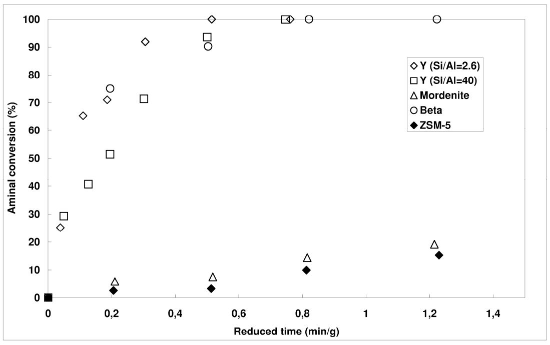


Fig.4. 4-SA conversion versus time related to one gram of the catalysts (150°C, 50 g mixture with the molar ratio aniline/4-SA = 21.5)

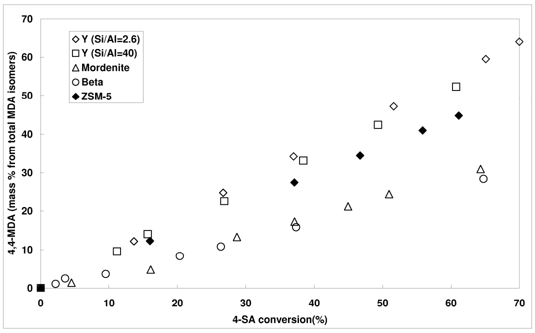


Fig. 5. 4,4´-MDA isomer content versus 4-SA conversion (150°C, 50 g mixture with the molar ratio aniline/4-SA = 21.5

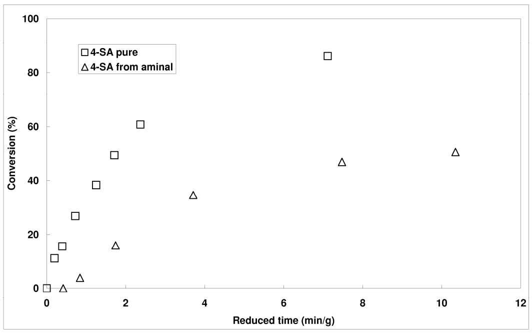


Fig. 6. 4-SA conversion on time related to one gram of the catalyst (150°C, 50 g mixture with the molar ratio aniline/4-SA = 21.5)

No catalyst deactivation was observed for the experiments with 4-SA. On the contrary, the deactivation was observed for the experiments with aminal, when after a fast reaction of aminal the conversion of secondary amines proceeded very slowly by one order of magnitude slower than for experiments with pure 4-SA isomer, and conversion of secondary amines did not occur at all (Figure 6). It can be deduced from these findings that the substance, which had an effect on catalyst deactivation was formaldehyde, which could be formed from aminal (decomposition to formaldehyde and aniline is the reverse reaction to aminal formation, and traces of water could be present in aniline or as humidity in the catalyst), and it could form carbon deposits in the catalyst. In terms of industrial implementation, it is necessary that water is completely removed from the starting mixture.

It is obvious from a comparison of the rates of both reaction steps that the same catalysts were by about one order of magnitude more active for aminal conversion than for 4-SA isomer conversion at all cases. This can be explained by an effect of thermodynamics, when aminal had energetically demanding arrangement (C-N-C-N-C bond), meanwhile 4-SA isomer was secondary amine (C-N-C-C bond), and thus it represented an arrangement less energetically demanding. Even the reaction enthalpies corresponded to this explanation [16], which was -43.5 kJ/mol for the aminal conversion to secondary amine, and it was only -21.7 kJ/mol for secondary amine conversion to MDA. Another possible explanation is that C-N-C-N-C arrangement in aminal was less hindered by aromatic rings, and thus it was better accessible for substitution on aniline.

With respect to the fact that zeolite Y with Si/Al ratio = 2.6 appeared to be the most selective to the formation of 4,4´-MDA isomer, it was further tested in detail. Kinetics of aminal conversion to secondary amines was measured, and then kinetics of 4-SA isomer to MDA isomers was measured separately. Following equations were proposed to describe the kinetics:

$$r_1 = k.m_{cat}.C_{Aminal}.C_{Anilin}$$

$$r_2 = k.m_{cat}.C_{4-SA}.C_{Anilin}$$

Only substitution to 4 and 2 positions was considered in the model. Experimental data were processed by means of ERA software [17]. The results of the kinetic measurements are summarized in Table 2., and Figure 7 and Figure 8 presents the agreement of the kinetics models with the experimental data.

Table 2. Rate constants and activation energies for reaction of aminal and 4-SA conversion

Reaction	Aniline/reactant (mol ratio)	Rate constant at 120 °C ($L.g_{cat}^{-1}.mol^{-1}.h^{-1}$)	Activation energy (kJ/mol)
AM >> 4-SA	13.5	0.198 ± 0.009	81.0 ± 2.5
AM >> 2-SA	13.5	0.0229 ± 0.0016	103.2 ± 2.0
AM >> 4-SA	21.5	0.185 ± 0,011	78.9 ± 2.3
AM >> 2-SA	21.5	0.0205 ± 0.0016	110.8 ± 1.6
4-SA >> 4,4´-MDA	21.5	0.0192 ± 0.0013	106.4 ± 2.1
4-SA>> 2,4´-MDA	21.5	0.00112 ± 0.000089	123.0 ± 2.1

Several conclusions can be drawn from the results. Aminal reacted at 120°C by one order of magnitude faster than 4-SA, and also substitution to position 2 was in case of aminal by one order of magnitude slower. Substitution to 2 position had greater activation energy (103.2 kJ/mol compared to 80 kJ/mol), and it proceeded faster at higher temperatures. Starting molar ratio did not have a great effect on the kinetics.

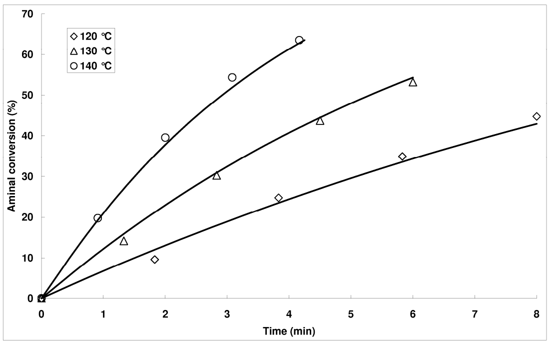


Fig. 7. Comparison of the kinetic model of aminal conversion with the experimental data (50 g mixture with the molar ratio aniline/aminal= 21.5, 0.1 g zeolite Y, Si/Al = 2.6)

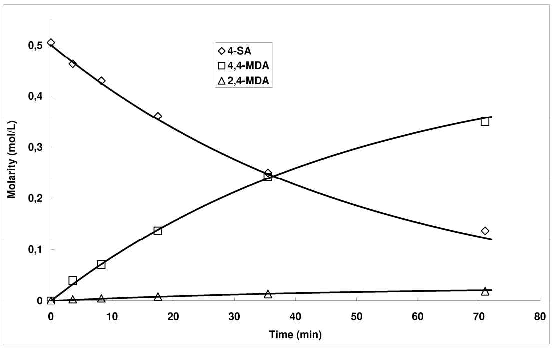


Fig. 8. Comparison of the kinetic model of 4-SA conversion with the experimental data (50 g mixture with the molar ratio aniline/4-SA= 21.5, 0.3 g zeolite Y, Si/Al = 2.6)

If 4-SA was the starting compound, substitution to position 4 was 17 times faster than substitution to 2 position at a temperature of 120°C. Substitution to 2 position had again higher activation energy (123 kJ/mol compared to 106.4 kJ/mol), and it proceeded faster at higher temperatures.

With respect to obtaining as high yield of 4,4´-MDA isomer from aminal as possible, it is purposeful to run the process at lower temperatures. However, this is limited by the presence of amines, which occupy all the active acid center irreversibly due to their basicity even at temperatures below 100°C, and the catalyst is not active for the conversion of aminal and secondary amines. From the process perspective also, primarily with the respect to the reaction rate and thus to the size of the reactor, it is suitable to carry out the reactions at temperatures 100 to 120°C.

4. Conclusions

Zeolite Y especially with low Si/Al ratio appeared to be the most selective catalyst for synthesis of 4,4´-MDA isomer among a large number of tested catalysts. The extent of substitutions to position 2 was low and also the substitution to position 3 was very limited for this zeolite at temperatures up to 120°C. The conversion of aminal over zeolite catalysts was by one order of magnitude faster that the conversion of secondary amines that are intermediate products for MDA isomer synthesis.

Acknowledgment

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Symbols used

MDA	Methylenedianilines
AM	N,N´-diphenylmethylenediamine
4-SA	4-amino-N-benzylaniline
3-SA	3-amino-N-benzylaniline
2-SA	2-amino-N-benzylaniline
4,4´-MDA	4,4´-Methylenedianiline
3,4´-MDA	3,4´-Methylenedianiline
2,4´-MDA	2,4´-Methylenedianiline
TPD	Temperature Programmed Desorption
Ss	Specific surface

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