



THE CONVERSION OF N – METHYLANILINE AND N –, 2 – DIMETHYLANILINE BY USING DIFFERENT CATALYSTS

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ABSTRACT

The catalytic conversion of N – methylaniline and N –, 2 – dimethylaniline in the presence of Pd – HSHM, $\text{CuFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ and vanadium – chromium – aluminium (VChA) oxide systems has been investigated. The comparative analysis of the results of the conversion of three different feedstocks with VChA catalyst shows that the xylidines, especially 2,6 – dimethylaniline is formed as a result of the methylation of aromatic amine because of the carbon in nucleus.

Indexing terms/Keywords

2 – methylaniline, methanol, N –, 2 – dimethylaniline, 2,6 – dimethylaniline, xylidines, catalyst, N – alkylation, C –alkylation

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

Chemical Technologies

TYPE (METHOD/APPROACH)

Experimental

INTRODUCTION

The researches of the previous years prove that alkylates which is formed as a result of the reaction of aniline and 2 – methylaniline with methanol contain alkylation products due to carbon and nitrogen. Their presence, concentrations and yields vary depending on the composition of catalyst and reaction medium. A group of researchers (1, 2) claim that the alkylation products due to nitrogen, as well as N – methyl amines act as intermediates in the synthesis of toluidine and xylidine. According to the opinion of the other researchers (3, 4), the alkylation of aniline and toluidine with methanol due to carbon dominates during the production of toluidines and xylidines..

EXPERIMENTALS

First, the catalytic properties of three catalysts in the alkylation reaction of aniline and 2 – methylaniline with methanol have been studied. These catalysts are Pd – HSHM, $\text{CuFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ and vanadium – chromium – aluminium (VChA) oxide systems.

The researches have been conducted in the continuous reactor and the volume of the immovable layer catalyst was 10cm^3 . The products were analyzed with chromatographic and spectral methods (5-7). The results of the conversions of N – methylaniline and N –, 2- dimethylaniline in the presence of these catalysts are given in table 1 and 2. Their evaluations show that all of these catalysts are able to convert N – methylaniline and N –, 2- dimethylaniline deeply. Pd – HSHM catalyst, which converts them 98-100%, produces complex mixture of toluidine and xylidine. More m- and p- isomers are formed as a result of the conversion of both N – methyl amine. 3- and 4- methylanilines are formed when N – methylaniline is used and 2,4- , 2,5- and 2,3- dimethylanilines are formed when N –, 2 – dimethylaniline is used. The total selectivity of these isomers of produced isomers is 44%, however the total selectivity of the mentioned isomer mixture of xylidines is 48%.

RESULTS AND DISCUSSIONS

Copper/iron catalyst shows high selectivity in o-isomer production. 2 – methyl aniline is formed with 52.5% selectivity from conversion of N – methylaniline whereas 2,6 – dimethylaniline is formed with 53.0% selectivity from conversion of N –, 2 – dimethylaniline. The rest of them is the other isomers of toluidine and xylydines, respectively. It should be mentioned that the conversion of N – methylamines is low (87.0 – 88.5%) in the presence of $\text{CuFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$.

Among the used catalysts, VChA oxide system has unique catalytic property. The mole ratio of orto isomers (2 – methylaniline and 2, 6 – dimethylaniline) which is formed as a result of the isomerization of N – methylaniline and N –, 2 – dimethylaniline in the presence of this catalyst, to the other isomers of toluidine and xylydine is 1:1.

The next stage of the research has been conducted in the presence of VChA catalyst.

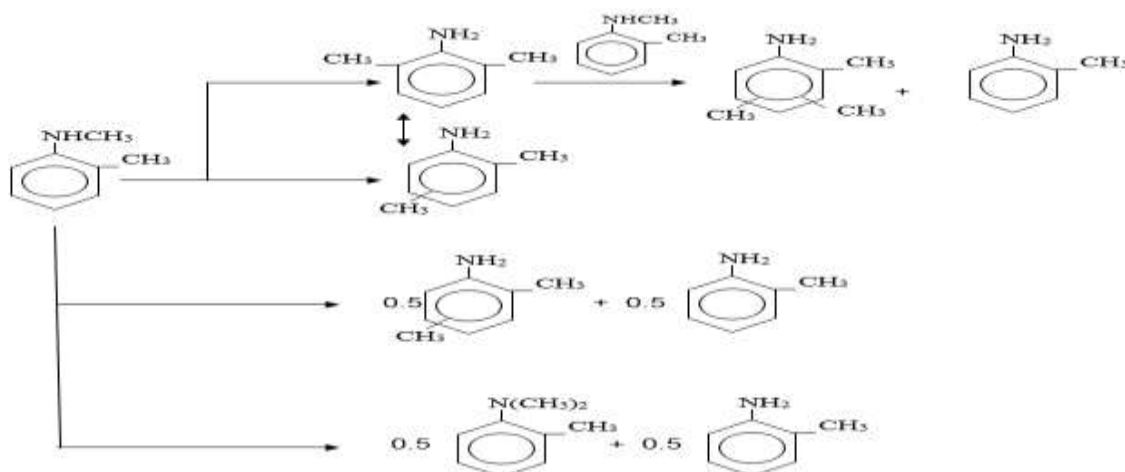
Table 1. The results of the conversion of N – methylaniline with different catalysts. Reaction conditions: $T=380^\circ\text{C}$, $\nu=1.0 \text{ hr}^{-1}$

Name	Content of catalyst		
	Pd,HSHM	$\text{CuFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$	$\text{V}_2\text{O}_5 \cdot \text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$
Conversion of N - methylaniline, %	98.5	87.0	91.5
Selectivity of products, %,			
2- methylaniline	40.0	52.5	45.5
3- and 4- methylanilines	44.0	39.5	46.0
Dimethylaniline	5.2	6.5	7.5

Table 2. The results of the conversion of N –,2 – dimethylaniline with different catalysts. Reaction conditions: $T=380^\circ\text{C}$, $\nu=1.0 \text{ hr}^{-1}$

Name	Content of catalyst		
	Pd,HSHM	$\text{CuFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$	$\text{V}_2\text{O}_5 \cdot \text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$
Conversion of N - methylaniline, %	100	88.5	94.0
Selectivity of products, %,			
2.6- dimethylaniline	38.0	53.0	48.0
3.4 -, 2.5- and 2.3- dimethylanilines	48.0	42.0	47.0
Trimethylanilines	3.5	4.5	4.0

Following researches have been conducted in order to determine the main and by conversions in the alkylation reaction of 2 – methylaniline with methanol in the presence of VChA catalyst. Firstly, the role of N –,2 – dimethylaniline in the alkylation reaction of 2 – methylaniline with methanol should be determined. That is why, the interaction of N –,2 – dimethylaniline with VChA catalyst in alkylation reaction has been studied. The results of the conversion of N –,2 – dimethylaniline with the influence of temperature are shown in Table 3.





As it is obvious from the results, a number of products are formed as a result of the catalytic conversion of N-,2-dimethylaniline. They are 2-methylaniline, N-, N-,2-trimethylaniline, 2,6-, 2,4-, 2,3- and 2,5-dimethylanilines and trimethylanilines. The formation of the mentioned products has been shown by the given reaction scheme.

As it is shown, the mixture of xylidines are formed as a result of the conversion of N-,2-dimethylaniline, however N-, N-,2-trimethylaniline is formed due to the same intermolecular conversion and trimethylanilines are formed due to the substitution in nucleus because of different intramolecular interactions during the catalytic cycle.

The rate of the reaction increases due to the increase in temperature. As a result of the analysis of the chemical content of the products, it is clear that the conversion of N-,2-dimethylaniline is 100% at 410°C by increasing temperature. In this case, the concentrations of 2-methylaniline and N-, N-,2-trimethylaniline increase, whereas the concentration of 2,6-isomer in xylidine mixture decreases a lot. This change is accompanied by the increase of the concentrations of the other isomers, as well as 2,4-, 2,3-, and 2,5-xylidines.

Table 3. The results of the conversion of N-,2-dimethylaniline with VChA catalyst. Reaction condition: T=380°C, v=1.0 hr⁻¹

Name	Temperature, °C			
	350	380	410	380*
% mass				
2- dimethylaniline	4.0	4.4	5.0	10.5
N-,2- dimethylaniline	14.0	2.4	-	11.5
N-,N-, 2- trimethylaniline	2.5	2.5	2.2	3.0
2.6- dimethylaniline	40.5	42.0	36.5	34.6
2.4- dimethylaniline	18.5	20.0	20.0	13.0
2.5- and 2.3- dimethylanilines	16.0	22.8	28.4	8.0
Trimethylanilines	2.5	2.9	3.3	1.5
Unidentified compounds	1.0	1.0	1.2	1.0
Water	-	-	-	7.0
Gas and loss	2.0	2.8	3.2	10.9
Total	100	100	100	100

*the reaction is conducted by using the feedstock which has 2-methylaniline:N-,2-dimethylaniline:methanol=1:1:2.mol/mol/mol ratio.

As a result of the comparison of the alkylate content which is formed as a result of the alkylation of 2-methylaniline with methanol at 380°C and the product which is formed from the catalytic conversion of N-,2-dimethylaniline, a significant difference is observed. Firstly, a huge difference in the content of the produced xylidine mixture draws the attention.

The mass proportion of 2,6-isomer in the dimethylamine mixture which is produced as a result of the reaction between 2-methylaniline and methanol is 0.87, however the same pointer for 2,6-dimethylaniline in the xylidine mixture which is formed from the conversion of N-,2-dimethylaniline is 0.50. On the other hand, unlike the alkylation reaction, trimethylaniline mixture is formed as a result of the conversion of N-,2-dimethylaniline and its concentration increases by increasing the temperature.

Figure 1 shows the comparative yields of the products which are formed as a result of thermocatalytic conversion of three different feedstocks by using VChA catalyst.

2-methylaniline-methanol, N-,2-dimethylaniline 2-methylaniline-N-,2-dimethylaniline methanol mixture have been taken as a feedstock and selectivity and yields of products according to 2,6-and other xylidines has been analysed as comparative criterion.

As it is obvious from the results, the yields of converted and calculated according to primary aromatic amine 2,6-dimethylaniline which is formed on the basis of 2-methylaniline and methanol are 81,4% and 77.3%, respectively. These pointers are 12.6 and 10.2% according to the other xylidine mixture respectively.

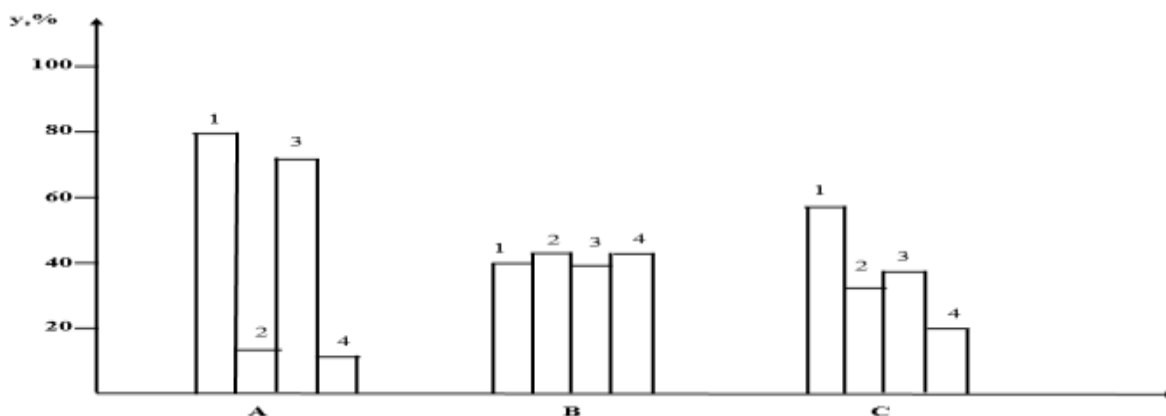


Figure 1: The selectivities and yields of xylidines according to 2,6 – dimethylaniline and other dimethyanilines (2,4-, 2,5-, 2,3 – isomers) that are formed from the catalytic conversions of different feedstocks (A,B,C). (3.4) Reaction condition: T= T=380°C, $\nu=1.0 \text{ hr}^{-1}$

The comparison of these data with 2,6 – and the other isomers of xylidine that are formed by the conversion of N – , 2 – dimethylaniline show a significant difference. The selectivity of 2,6 – isomer which is formed by the catalytic conversion of N – , 2 – dimethylaniline is 37.4% less, in another word, it is 43.0%, however the selectivity according to other xylidine mixture is 30.2% higher, in another word, it is 42.8%.

The yields of xylidines that are formed as a result of catalytic conversion of 2 – methylaniline, N – 2, - dimethylaniline and methanol mixture have a moderate place in comparison to mentioned feedstocks. The selectivity of the reaction according to 2,6 – xylidine is 56.7%, however the formation selectivity of the other xylidines was 34.2%. The yields of these products are 38.3% and 19.4%, respectively.

CONCLUSION

These results predict that the partial intermolecular isomerization of N – ,2 – dimethylaniline which is formed as a result of reaction of 2 – methylaniline with methanol to xylidines can also occur. However, these results show that the formation of xylidines, especially 2,6 – isomer because of the methylation of aromatic amine due to carbon in nucleus is more real.

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