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ORTHO-METHYLATION OF 2,3-XYLIDINE OVER SOLID CATALYSTS

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The methylation of 2,3-xylidine with methanol was carried out over various solid catalysts. Silver-alumina showed 70% selectivity in the methylation at the ortho-position. The activity and the selectivity of catalysts were briefly discussed in view of the acidic and basic properties of the catalysts.

The N-methylation of aromatic amines with methanol are now well known to proceed over a wide variety of catalysts.[1)] Under rather severe reaction conditions, the methylation yields also nuclear alkylated amines. However, the major products are para-isomers[2)] or a mixture of ortho- and para-isomers.[3)] Probably the only one example involving the selective methylation of aromatic amines at ortho-position is the methylation of aniline and toluidine using basic alumina or MgO-Al_2O_3 as a catalyst.[4)]

In the course of our study on the methylation of 2,3-xylidine to 2,3,6-trimethylaniline which is an useful synthetic intermediate[5)] for α-tocopherol, we have found that Ag-Al_2O_3 is an effective catalyst for the ortho-methylation of aromatic amines.

The reaction was carried out in a conventional flow type reactor under atmospheric pressure. The reactor was a quarz tube of 18 mm inside diameter packed with 8-12 mesh catalysts. Silver and other metal oxides catalysts supported on Al_2O_3 were prepared by impregnation with aqueous metal salt solutions, followed by calcination at 550°C under air. A mixture of 2,3-xylidine and methanol was fed to the reactor with hydrogen. The reaction product was collected in a trap cooled by ice-water, and then analyzed by GC. The structural analysis of the products was carried out by MS and NMR. The acidity of catalysts was determined by n-butylamine titration method.[6)] Before the determination, the powdered sample was dried in air at 300°C for 2 hr and cooled to room temperature under dry nitrogen atmosphere.

Table 1 shows the results over various solid acid and base catalysts. The acidity of the unused catalysts at various acid strengths is given in Table 2.

A low activity of MgO may be attributed to the basic character[7)] of the surface on which basic 2,3-xylidine is only weakly adsorbed. Al_2O_3 shows a moderate selectivity to the ortho-methylation. The addition of MgO or NaOH to Al_2O_3 decreases the nuclear methylation activity. It reduces the total acid amount of Al_2O_3, while the acid strength and the pattern of acidity distribution remain practically unchanged. Thus, in general the total acid amount of catalyst is considered to be an important factor in determining the selectivity.

Table 1. *Methylation of 2,3-xylidine*

Catalysts	Products (%)				
	2,3-Xylidine	N-Methyl-and N,N-Dimethyl-2,3-Xylidine	2,3,6-Trimethylaniline	2,3,4-Trimethyl- and 2,3,4,6-Tetramethylaniline	Others
MgO	86.5	3.2	0	0	10.3
$Al_2O_3{}^{a)}$	12.9	0.8	37.6	31.9	16.8
$MgO^{c)}-Al_2O_3$	7.8	55.8	13.3	4.6	18.5
$NaOH^{d)}-Al_2O_3$	16.7	20.7	21.4	21.0	20.2
$SiO_2-Al_2O_3{}^{b)}$	7.9	11.1	6.1	43.1	31.8
$H_3PO_4{}^{c)}-Al_2O_3$	9.6	2.4	30.4	47.0	10.6
$V_2O_5{}^{c)}-Al_2O_3$	32.5	0.1	41.4	13.0	13.0
$MoO_3{}^{c)}-Al_2O_3$	15.3	9.8	41.2	28.4	5.3
$Cr_2O_3{}^{c)}-Al_2O_3$	24.6	7.1	47.5	12.8	8.0
$Ag^{c)}-Al_2O_3$	17.4	1.0	58.0	23.0	0.6

Temperature: 450°C, LHSV: 1 hr^{-1}, Methanol/2,3-Xylidine/Hydrogen=2/1/1

a) γ-alumina from Nishio Ind. Co.

b) low alumina from Nikki Chem. Ind. Co.

c) 5 wt%

d) 0.5 wt%

Table 2. Acidity of catalysts[a)]

Catalysts	Acidity (m mol/g)			
	Ho $\leqq$ +3.3	Ho $\leqq$ +1.5	Ho $\leqq$ -3.0	Ho $\leqq$ -5.6
MgO	0	0	0	0
Al_2O_3	0.18	0.11	0.11	0
MgO-Al_2O_3	0.13	0.04	0.04	0
NaOH-Al_2O_3	0.11	0.05	0.04	0
SiO_2-Al_2O_3	0.35	0.35	0.24	0.24
H_3PO_4-Al_2O_3	0.18	0.18	0.18	0.02
MoO_3-Al_2O_3	0.23	0.18	0.13	0.05
Ag-Al_2O_3	0.29	0.29	0	0

a) Acidity of V_2O_5-Al_2O_3 and Cr_2O_3-Al_2O_3 could not be determined because they had colored surfaces.

H_3PO_4-Al_2O_3 and SiO_2-Al_2O_3 whose acid strengths are higher than that of Al_2O_3 are favorable for the formation of para-methylated derivatives. The infrared spectra[9)] of aniline adsorbed on Al_2O_3 showed that both the benzene ring and the amino group had some interactions with the catalyst surface. It was reported[10)] that SiO_2-Al_2O_3 adsorbed aromatic amines more strongly than Al_2O_3. These facts are thought to indicate that the para-position of the benzene ring of aromatic amines adsorbed on strongly acidic catalysts is located in the neighborhood of the surface active sites. A similar consideration was also reported by Tanabe et al.[8)] on the mechanism of the catalytic methylation of phenols with methanol. These arguments are consistent with the predominant para-methylation of 2,3-xylidine over strongly acidic catalysts, SiO_2-Al_2O_3 and H_3PO_4-Al_2O_3.

It was anticipated that a decrease in the acid strength of Al_2O_3 so as to diminish the interaction between the surface active sites and the benzene ring improved the selectivity of the ortho-methylation. This anticipation is supported by the observation that Ag-Al_2O_3, the most selective catalyst as shown in Table 1, has weaker acid sites than Al_2O_3. MoO_3-Al_2O_3 which has stronger acid sites than those of Al_2O_3, however, gives the ortho-methylation product more selectively than

Al_2O_3. This indicates that the difference in the ortho-methylation selectivity among these catalysts can not be accounted for only in terms of acidic and basic properties of the catalysts.

It can be postulated that the nuclear methylation at ortho-position proceeds not only through the rearrangement11) of methyl group from a nitrogen atom to a ring carbon but also through the direct nuclear methylation with methanol. Further study is required to clarify the reaction mechanism.

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