

Synthesis of *N*-Methylaniline and *N,N*-Dimethylaniline with Methanol over Alumina Catalyst

Hiromi MATSUHASHI* and Kazushi ARATA

Department of Science, Hokkaido University of Education, Hachiman-cho, Hakodate 040
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Synopsis. Alumina catalysts prepared by different methods were used for the synthesis of *N*-methylaniline and *N,N*-dimethylaniline from aniline and methanol. Al₂O₃ catalysts prepared from isopropoxide and nitrate showed high activity and JRC-ALO-1 and JRC-ALO-3 supplied by the Catalysis Society of Japan showed low activity. The highest selectivity for *N,N*-dimethylaniline was 82.8% with 90.1% aniline conversion. The catalytic activity of Al₂O₃ was not poisoned by pyridine and CO₂.

N-Alkylation of aniline with methanol was catalyzed by solid acid and base catalysts. Silica gel and ZSM-5 zeolites were applied for this reaction,^{1,2)} but catalytic activities of these catalysts were not high. In the case of acid catalysts, the activity for this reaction might be suppressed by the adsorption of aniline since aniline, itself, has a strong basic characteristic. It therefore seems that the use of a strong acid catalyst is not suitable for this reaction. Takemiya et al. reported aniline alkylation with methanol over solid base catalysts: MgO³⁾ and NaOH/Al₂O₃.⁴⁾ The products consisted exclusively of *N*-methylaniline. Alumina is one of the best catalysts for this reaction.⁵⁾ In this study, we report that Al₂O₃ catalysts prepared from isopropoxide and nitrate showed high activity for the *N*-methylation of aniline. We anticipate that Al₂O₃ has an acid-base bifunctional characteristic.

Four kinds of Al₂O₃ were used in this study.

Al₂O₃-1. Aluminum hydroxide was obtained by hydrolyzing Al[OCH(CH₃)₂]₃ (Wako Pure Chemicals, Guaranteed Reagent) dissolved in dried ethanol with distilled water. Water and ethanol were evaporated. Then, Al(OH)₃ was suspended in distilled water again and boiled for 1 h. Excess water was evaporated.

Al₂O₃-2. Aqueous ammonium was added to an aqueous solution of Al(NO₃)₃·9H₂O (Wako Pure Chemicals, Guaranteed Reagent) to precipitate

Al(OH)₃. The final pH of the suspension was 7—8. The precipitate was washed with distilled water, dried, and heated at 773 K in air.

Al₂O₃-3 and Al₂O₃-4 were JRC-ALO-1 and JRC-ALO-3, supplied by the Catalysis Society of Japan as reference catalysts. MgO was prepared by boiling commercial high-purity MgO (Merck) in water, followed by drying and a thermal treatment at 773 K in a He stream. ZrO₂ was obtained by hydrolyzing ZrO(NO₃)₂·8H₂O (Wako Pure Chemicals, Guaranteed Reagent) with aqueous ammonia, washing, drying, and a thermal treatment at 773 K in air. Li⁺/Al₂O₃ and Na⁺/Al₂O₃ were prepared by an impregnation method. Al₂O₃-1 was suspended in aqueous Li⁺ or Na⁺ carbonate; the water was evaporated to dryness over a hot plate. The content of alkali ions was 10 mol%.

All catalysts were heated in glass reaction tubes at 773 K for 3 h in a He stream before reaction. The catalytic reaction experiments were carried out with a conventional flow microreactor. After the catalyst (0.2 g) was heat-treated in a reactor in the He stream (20 cm³ min⁻¹), a vaporized mixture of methanol and aniline (mole ratio=5) was passed through the catalyst bed at a feed rate of 4.09 cm³ h⁻¹. The partial pressure of methanol and aniline was 5.15×10⁴ Pa and 1.03×10⁴ Pa respectively. The product stream was cooled and condensed at a reservoir attached under the reactor. The liquid product was sampled every 30 min and analyzed by using a G.L.C. column (2 m×3 mm o.d.), packed with SE-30. The products were identified by GC-MS. The conversion is explained as being proportions of *N*-methylaniline and *N,N*-dimethylaniline based on aniline.

The conversion and composition of the products between 60 and 90 min at 623 K are summarized in Table 1. In all cases, even though the catalytic activity

Table 1. *N*-Methylation of Aniline over Various Catalysts at 623 K

Catalyst	Conversion	Selectivity/%	
	%	<i>N</i> -Methylaniline	<i>N,N</i> -Dimethylaniline
Al ₂ O ₃ -1	32.1	78.2	21.8
Al ₂ O ₃ -1 ^{a)}	66.1	60.4	39.6
Al ₂ O ₃ -1 ^{a,b)}	81.2	39.0	61.0
Al ₂ O ₃ -1 ^{a,c)}	90.1	17.2	82.8
Al ₂ O ₃ -2	30.5	70.1	29.9
Al ₂ O ₃ -3	21.7	69.6	30.4
Al ₂ O ₃ -4	17.5	83.3	13.7
ZrO ₂	Trace	Trace	
Li ⁺ /Al ₂ O ₃	4.7	100	—
Na ⁺ /Al ₂ O ₃	0.8	100	—
MgO	Trace	Trace	

a) Reaction temperature: 673 K. b,c) Methanol/Aniline (mole ratio): b) 10, c) 15.

decreased rapidly during the initial period of the reactions, the catalysts showed almost constant activity after 60 min. Among the tested catalysts, the Al_2O_3 catalysts showed higher activity than did the other acid or base catalysts. In particular, Al_2O_3 -1 and Al_2O_3 -2 gave 32.1% and 30.5% methylated products, respectively. The selectivity for *N,N*-dimethylaniline was high when the flow rate of the He carrier was low. Table 1 also suggests that higher reaction temperatures and large ratios of methanol to aniline lead to a higher selectivity for *N,N*-dimethylaniline. In this study, the highest selectivity for *N,N*-dimethylaniline was 82.8%, with a 90.1% conversion. No liquid product was obtained when the reaction temperature was 723 K or higher. The activity of MgO, a typical solid base, was very low under the present conditions. ZrO_2 , which is known to hold basic sites together with acidic ones on the surface,^{6,7)} also showed low activity.

Pyridine, CO_2 , and H_2O were adsorbed on the Al_2O_3 surface for characterizing the active site. The supplement of the reactant mixture was stopped after a reaction for 120 min, and the adsorbant was introduced into the reaction system. The amount of pyridine or H_2O introduced was 0.5 cm^3 (as liquid); CO_2 was fed for 30 min. The results are shown in Table 2. The addition of pyridine and CO_2 had no (or less) effect on the catalytic activity, suggesting that the reaction did not occur at strong acid sites which were poisoned by pyridine. It was expected that the reaction proceeded on

Table 2. Effect of Adsorption of Pyridine, CO_2 , and H_2O

Addition	Conversion ratio (after/before)
Pyridine, 0.5 ml	1.0
CO_2 , 30 min	0.95
H_2O , 0.5 ml	0.48

Adsorbants were added after the reaction for 2 h.
Reaction condition, see Text.

the basic site of Al_2O_3 . Because the activity became slightly decreased by the adsorption of CO_2 , $\text{Li}^+/\text{Al}_2\text{O}_3$ and $\text{Na}^+/\text{Al}_2\text{O}_3$ were applied for the reaction. The basicity of Al_2O_3 -1 was enhanced⁴⁾ by doping of Li^+ and Na^+ . However, as is shown in Table 1, both of these catalysts showed much less activity. It was therefore clear that this reaction did not occur only at the basic sites.

As is shown in above, the catalytic activity was affected by the doping of Na^+ . Since Al_2O_3 -3 and -4 contain 0.03% and 0.3% Na_2O , respectively, the reason for the low activity of Al_2O_3 -3 and -4 was estimated to be that a small amount of Na^+ was contained as an impurity.

The effect of the addition of H_2O was, however, larger than that of pyridine or CO_2 , and the activity was decreased to half before the addition.

Since water molecules poison both acidic and basic sites and the activity of Al_2O_3 or *N*-methylation of aniline, acid-catalyzed dehydration was very high, and even though the catalyst did not have a strong acid character, it could be presumed that the Al_2O_3 catalyst might act as a bifunctional catalyst in this reaction.

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