Catalytic Alkylation of Aniline with Methanol

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Abstract—The alkylation of aniline with methanol on copper-containing catalysts was studied. The reaction conditions were optimized, and the mechanism of this reaction was refined. Based on the surface-modification principle, a new efficient catalyst for the synthesis of methylaniline was developed, which made possible the selective formation of *N*-methylaniline (up to 99%) in >97% yield with high productivity.

INTRODUCTION

It is well known that *N*-methylaniline (MA) exhibits good antioxidant and antidetonant properties [1, 2]. Small MA additives significantly improve the quality and performance of large-scale products such as gasoline, polymers, latexes, and rubbers. At present, the quality of gasoline can be improved by the use of antiknock additives based on aniline derivatives without significant investments in the reorganization of refineries and petrochemical plants [3].

N-Methylaniline is one of the most efficient antidetonant additives to gasoline [1]. The efficiency of MA, which is an ash-free additive, is second only to toxic tetraethyllead, the use of which is prohibited in developed countries. The use of pure MA minimizes the cost of increasing the octane number by 1 point. Moreover, the compatibility of MA with oxygen-containing additives like MTBE and lower alcohols makes possible an improvement in the composition of exhaust gases [3].

The vapor-phase catalytic alkylation of aniline with methanol is the main process for the current commercial production of MA [2–5]. It was proposed to alkylate aniline with alcohols in the presence of supported niobic acid [2]. The disadvantage of this process consists in a low selectivity for MA (usually, it is no higher than 85%). Moreover, the catalyst rapidly loses its activity and it should be regenerated after 24 h.

In the well-known processes of MA synthesis on Virgon and C-40 catalysts, containing active copper and manganese oxides on alumina [4], satisfactory yields of MA (up to 90%) were reached. However, up to 10% dimethylaniline (DMA) was formed as a by-product, and this is a serious disadvantage.

A supported copper-containing catalyst of complex composition (KA-94M) has been used in the industrial synthesis of MA [4]. In this process, the yield of the desired product and the selectivity for MA were as high as ~92 and 98%, respectively. However, the productivity (0.4 kg l^{-1} h^{-1}) and catalyst service life (100 h) do not meet current requirements. Therefore, the process productivity and selectivity in the synthesis of MA

should be improved and the catalyst service life should be prolonged.

The aim of this work was to improve the efficiency of a catalyst for MA synthesis and to refine the mechanism of this reaction.

EXPERIMENTAL

The synthesis of MA by the catalytic alkylation of aniline with methanol proceeds at a satisfactory rate at temperatures higher than 220°C. Under these conditions at atmospheric pressure, both of the reactants are in the vapor phase. The reaction was performed in a tubular fixed-bed flow reactor (12 mm in diameter) of quartz. In typical experiments, the catalyst volume was 5–10 ml. A heating zone whose surface area was sufficient for the complete evaporation of the reactants (~150–200 cm²) was above the catalyst bed. The bed temperature was maintained constant (±0.3°C) with the use of an electronic regulator.

Because the reactivity of methanol is higher than that of aniline, the initial reaction mixture contained a stoichiometric excess of methanol (~40–50%). This corresponded to a methanol concentration of 39–43 vol % in the mixture. The mixture of the reactants was supplied from a feed vessel to the reactor with a liquid pump. Nitrogen (special-purity grade) was simultaneously fed into the reactor for regulating the contact time of the reactants and protecting them from oxidation. The vapor mixture at the reactor outlet was condensed at 0°C.

The course of the reaction was monitored by analyzing samples of the liquid product. The quantitative analysis of the samples was performed by gas–liquid chromatography on a Chrom 5 instrument with a flame-ionization detector (a column 3000 mm in length and 3 mm in diameter with 10% Lukooil DF on Inerton Super). The relative error in the determination of component concentrations was no higher than 5%.

The following two types of catalysts were used in this study: commercial catalysts and catalysts prepared in the laboratory as described below. Calcined γ-Al₂O₃

Table 1. Characterization of commercial (c) and laboratory (l) copper-containing (~10%) oxide catalysts for the synthesis of N-methylaniline from a mixture of methanol and aniline (2 : 1) at 240°C

Specimen no.	Catalyst* (Al_2O_3 support)	Mixture VHSV V_0, h^{-1}	Yield, %		Aniline conversion, %
			MA	DMA	
1l	Cu**	0.3	57.0	1.0	58.0
2c	KA94-CuCrMnZnFeNi	0.4	92.0	1.0	93.0
		1.4	80.0	0.2	80.3
3c	NTK1-CuZnCrMnMg**	1.0	94.0	0.4	94.6
4c	NTK4-CuZnCr**	1.0	94.4	0.8	95.2
5c	GIPKh-CuCrBa**	1.0	91.8	0.8	93.4
6c	Virgon-CuMn	0.3	75.0	10	85.0
7l	Cu(SO$_4$)ZnNi	1.4	6.0	–	6.0
8l	Cu(Cl)NiMg	1.4	8.0	–	8.0
9l	Cu(NO$_3$)ZnNi	1.4	59.0	0.2	59.3
10l	Cu(MA)ZnNi	1.4	71.0	0.1	71.0
11c	NTK4m***	1.4	97.3	0.2	97.5

   * The metals and starting ligands (in parentheses) at the copper ion are specified.

  ** The CuO content was 20–30%.

*** The specimen was modified with Cu(MA) (m).

was impregnated with an ammonia complex of copper. Next, chromium oxide and zinc oxide were added, and the mixture was thoroughly stirred in a rotary evaporator at 70–80°C. The resulting powder was calcined at 350°C for 3 h and, after cooling, treated with a copper complex containing ammonia and MA molecules as ligands. All chemicals were reagent grade.

The catalyst was activated immediately before experiments by feeding methanol (0.2 l l^{-1} h^{-1}) into the reactor at 230–250°C for 2 h.

In order to maintain a constant activity in long-term tests, the catalysts were treated at regular intervals with a steam–air mixture at 400°C (for tar oxidation) after blowing the reactor with steam at 230°C for 30 min.

RESULTS AND DISCUSSION

Optimization of Catalyst Composition for the Synthesis of N-Methylaniline

It is well known [3–6] that the best commercial catalyst for MA synthesis, KA94M, contains a mixture of six supported oxides (Table 1). To optimize the composition and to improve the performance of the catalyst, it is necessary to determine the significance of its particular components. For this purpose, we tested a number of commercial catalysts and catalysts prepared in the laboratory. Table 1 summarizes these results.

As can be seen in Table 1, the copper catalyst without promoters exhibited an insufficient activity. Moreover, this catalyst rapidly lost its activity and was hard to regenerate. The addition of an acidic manganese

oxide (no. 6) resulted in a considerable increase in the yield of DMA as a by-product. The addition of magnesium oxide (~1%, no. 8) dramatically inhibited the alkylation reaction, whereas zinc oxide (up to 20%, nos. 3, 4, 9, and 10) had a promoting effect. The addition of copper as sulfate or chloride (nos. 7–9) adversely affected the catalyst activity. The absence of magnesium, iron, and nickel had almost no effect on the performance of the catalyst, whereas chromium was a necessary additive that improved the stability of the catalyst after oxidative regeneration and activation.

Thus, we can conclude that the CuZnCrO$_x$ oxide catalyst on alumina is the most promising alternative to the industrially used catalyst KA94M. Note that a similar catalyst (NTK4) is commercially available. Among the catalysts tested, this catalyst (no. 11) exhibited the highest activity, selectivity, and productivity after surface modification. In accordance with a surface-modification procedure [7, 8], the catalyst was treated with a copper complex containing ammonia and MA molecules as ligands. For comparison, the catalyst prepared was also treated with MA. Table 2 summarizes the results obtained with CuZnAl catalysts containing ~10% copper.

As can be seen in Table 2, the treatment of the catalyst with MA significantly decreased its activity. This was likely due to the blocking of the entire catalyst surface. However, after treatment with the copper complex with MA, the catalyst activity considerably increased.

Table 2. Effect of surface modification on the properties of catalysts for aniline alkylation

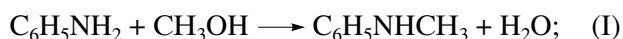| Oxide catalyst	Aniline conversion, %	Selectivity for MA, %
CuZn/Al$_2$O$_3$	46	99.6
CuZn/Al$_2$O$_3$, treated with MA	5	99.9
CuZn/Al$_2$O$_3$, treated with Cu(MA)	71	99.9

Note: $T = 240°C$; VHSV = 1.1 h^{-1}.

Table 3. Effect of water added to a reaction mixture for the synthesis of *N*-methylaniline on NTK4m at 240°C at a VHSV of 1.0 h^{-1} (39% methanol and 61% aniline)

Time, min	Water added, %	Yield of MA, %
20	–	94.1
40	20	78.5
60	20	80.8
90	–	95
120	–	95.6
140	10	89.8
180	10	89.5
200	–	95.4

Mechanism of Aniline Alkylation with Methanol

The analysis of the reaction mixture suggests that, under the reaction conditions, MA can undergo alkylation to form DMA, the amount of which increases with time. We found that the yield of MA on the NTK4 catalyst at 230–270°C reached a maximum (95%) at a contact time of 1.5–4 s. This corresponds to a feed rate of liquid reactants of 0.7–1.5 l/h per liter of a catalyst at a nitrogen flow rate of 3000–4000 l l^{-1} h^{-1}. Under these conditions, the yield of the DMA by-product was no higher than 0.6%. Consequently, the test process is a typical consecutive reaction, in which MA is an intermediate product:

$$C_6H_5NH_2 + CH_3OH \longrightarrow C_6H_5NHCH_3 + H_2O; \quad (I)$$

$$C_6H_5NHCH_3 + CH_3OH \longrightarrow C_6H_5N(CH_3)_2 + H_2O. \quad (II)$$

As found by Ivanova *et al.* [9] for zeolite HY, the adsorbed methoxy group is an active alkylating agent.

The above temperature range is an optimum range for the alkylation reaction because below 230°C the conversion of aniline considerably decreased (<80%). At the same time, above 270°C, the yield of MA decreased because most of the methanol decomposed without reacting with aniline.

A three-step dehydrocondensation mechanism was also proposed for the *N*-alkylation of aniline [5, 9–11]. At the first step, an alcohol is dehydrogenated to an aldehyde (ketone); at the second step, the aldehyde (ketone) is condensed with aniline to form a Schiff base (Ph–N=CHR). The final product is formed by the hydrogenation of this base. The participation of formate intermediates in the synthesis of MA on strongly basic zeolites CsOH/CsNaY was demonstrated by ^{13}C NMR spectroscopy [9]. The following facts provide support for the possibility of this mechanism of aniline alkylation with C$_2$–C$_6$ alcohols: (1) the above alcohols are readily converted into carbonyl compounds on copper-containing catalysts at 230–270°C and (2) the addition of a small amount of water (5–10%) inhibits the alkylation [10, 11]. Indeed, the Schiff base is readily hydrolyzed; that is, the reaction

$$C_6H_5NH_2 + RCHO \longleftrightarrow C_6H_5N = CHR + H_2O \quad (III)$$

is reversible, and its equilibrium constant is $K_3 \ll 1$.

To refine the mechanism of alkylation on copper-containing catalysts, we performed the synthesis of MA with the addition of 10 and 20% water to the starting mixture of the reactants. The results were compared with experimental data obtained without water additives (Table 3).

As can be seen in Table 3, the addition of 10 and 20% water insignificantly decreased the yield of MA, by 6.6 and 15 rel %, respectively. Note that this effect is reversible, and it is likely due to adsorption competition between water and the reactants at the active sites of the catalyst.

With consideration for the above experimental results, we can conclude that, in the alkylation of aniline with methanol on copper-containing catalysts, the contribution of the dehydrocondensation mechanism is insignificant. It is believed that the synthesis of MA involves an attack of the –OCH$_3$ group on chemisorbed aniline with the formation of the (aniline *OCH$_3$) complex followed by the elimination of a water molecule. The new information on the mechanism of MA synthesis can be used for further improvement of the catalyst. It is evident that the key function of the catalyst is the acid–base and coordination function rather than the hydrogenation–dehydrogenation activity.

At the final stage of the experiment, we compared changes in the activity and selectivity of the KA94M and NTK4m catalysts upon continuous operation ($V_0 = 1.5$ h^{-1}). A decrease in the activity was compensated by gradually increasing the temperature in the range 230–270°C. We found that, in the course of testing, the catalyst developed by us exhibited a higher activity (by ~10%) than that of KA94M with comparable selectivity (~98–99%). Moreover, the NTK4m catalyst exhibited a prolonged service life of 200 h against 120 h for KA94M (with a single regeneration).

Thus, we developed a highly efficient catalyst for the process of aniline alkylation with methanol by the modification of NTK4. The catalyst developed significantly improved the performance characteristics of the

process: the yield of MA was increased to 97%, the productivity was as high as 1.4 kg l^{-1} h^{-1}, and the service life was 200 h. The mechanism of aniline alkylation with methanol was refined, and the conditions for the synthesis of MA were optimized.

REFERENCES

1. *RF Specifications TU 38.401-58-61-93: Antiknock Additive Based on Aromatic Amines*, 1993.
2. German Patent 3 942 413, 1991.
3. Stytsenko, V.D. and Vinokurov, V.A., *Tezisy dokladov Nauchnoi konferentsii Rossiskogo Gosudarstvennogo Universiteta Nefti i Gaza po kataliticheskomu sintezu vysokooktanovykh komponentov i antioksidantov* (Scientific Conf. of the Russian State University of Oil and Gas on the Catalytic Synthesis of Blending Fuels and Antioxidants), Moscow, 1999, p. 151.
4. *Promyshlennye katalizatory SSSR* (USSR Industrial Catalysts), Novosibirsk: Inst. Kataliza, 1988, p. 232.
5. Batrin, Yu.D., Rudakova, T.V., Kozhevnikov, V.S., and Belousov, E.K., *Nefteperab. Neftekhim.*, 1999, no. 7, p. 27.
6. RF Patent 2 152 382, 2000.
7. Stytsenko, V.D., Kovalenko, O.V., and Rozovskii, A.Ya., *Kinet. Katal.*, 1991, vol. 32, p. 163.
8. Stytsenko, V.D., *Appl. Catal., A*, 1995, vol. 126, p. 1.
9. Ivanova, I.I., Pomakhina, E.B., Rebrov, A.I., Vang, V., Khunger, M., and Veitkamp, E., *Kinet. Katal.*, 2003, vol. 44, p. 764.
10. Belov, V.V., Stytsenko, V.D., Romanovskaya, L.G., Kopeikina, S.B., and Eigenson, I.A., *Neftekhimiya*, 1998, vol. 38, p. 143.
11. Belov, V.V., Stytsenko, V.D., Markov, V.I., and Sova, S.V., *Tezisy dokladov 2-oi mezhdunarodnoi konferentsii "Nauka i prosveshchenie. Issledovanie protsessa metilirovaniya anilina"* ("Studies in Aniline Methylation," 2nd Int. Science and Education Conf.), Dnepropetrovsk, 1998, vol. 12, p. 3.