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Amination of alcohols, using Cu/Ni-based colloidal catalyst, for consecutive reaction system

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Animation of dodecyl alcohol and monomethylamine (MMA, di-functional) using Cu/Ni-based colloidal catalyst stabilized by barium stearate, and its kinetic study were performed to effectively synthesize didodecylmethylamine (DDMA). For the initial 3–4 h when MMA/dodecyl alcohol mole ratio was less than 1, the amination reaction proceeded very fast (72 mole-alcohol h^{-1} mole-Cu at 200 °) by zero-order kinetics to directly produce DDMA (85%), with complete consumption of MMA, without liberation of the intermediate, momomethyldodecylamine (MMDA) at all. Then, immediately after the mole ratio exceeded 1, the amination proceeded very slowly (3.4 mole-alcohol h^{-1} mole-Cu) by consecutive mechanism (second order) with liberation of MMDA. Aldolization of dodecyl aldehyde, formed by dehydrogenation of dodecyl alcohol, was found to be catalyzed by methylamines. Maintaining the zero-order kinetics by continuous control of MMA/alcohol mole ratio at less than 1 through out the amination is essential to obtain a highest DDMA yield by preventing the unwanted aldolization and transalkylation of MMA leading to various byproducts. Catalytic activity of the colloidal catalyst was sevenfold active than that of corresponding solid ones. Amination of 1,6-hexanediol and dimethylamine, using the colloidal catalyst and liquid paraffin as a solvent, was proceeded by consecutive mechanism to form *N*,*N*,*N*′,*N*′-tetramethyl-l,6-hexamethylenediamine with an yield of 80%.

KEY WORDS: synergism, Cu/Ni/Ba, Cu/Ni/Ca/Ba, amination, metal colloid, nanoparticles.

1. Introduction

Cu/Ni-based colloidal catalyst stabilized by barium stearate (Cu/Ni/Ba) [1–5], used for one-step amination of fatty alcohols and dimethylamine (DMA) to *N*,*N*-dimethyl-long-alkyl tertiary amines (DMTA), was developed in 1977. In the amination reaction, active hydrogen, required for the hydrogenolysis of aldehyde-DMA adduct to DMTAs, was effectively supplied by dehydrogenation of a starting alcohol itself. Therefore, bulk hydrogen was not required basically in this catalytic system [1].

We named this interesting phenomenon, produced by the sole combination of copper and nickel especially in a colloidal state, as "self-supplying system for active hydrogen". A new process using the colloidal catalyst was commercialized in 1981 for the production of limited alkyl-range (C_{10}, C_{12}, C_{14}) of DMTAs until 1985 when the catalyst was substituted to corresponding solid one with improvement in hydrogenolysis activity by incorporation of a precious metal [2b]. These Cu/Ni based catalysts were also used for the amination of fatty alcohols and monomethylamine (MMA, di-functional), which constitutes consecutive reaction, to produce dialkylmethyl tertiary amines (DDMAs), intermediates for quarternary ammonium salts as softening agents [6]. These amination reaction were the first examples using Cu/Ni-based catalysts, and their catalytic activity was much higher than that of Cu-based catalyst such as copper-chromite [7]. From the end of 80s, Chinese groups started active research on Cu/Ni-based solid catalyst for the production of DMTAs [8a–e] and DDMAs [8f], and commercialized these catalytic amination. At present, Cu/Ni-based catalysts are used worldwide industrially for the amination of various alcohols. In this article, we described some of the topics, not presented so far, on catalytic activity of the active Cu/Ni/Ba colloidal catalyst, optimum amination conditions, especially MMA/dodecyl alcohol mole ratio and kinetic studies for the amination of dodecyl alcohol and MMA as consecutive reaction. Amination of 1,6-hexanediol and DMA and hydrogenation of fatty nitrils to secondary amines were also presented as another example of consecutive reaction.

2. Experimental

2.1. Materials

Dodecyl alcohol and dodecyl nitrile used were Kao's brand, K-20 (>99%) and Farnil20 (>98%), respectively. Dimethylamine (DMA) and monomethylamine (MMA) were purchased from Seitetsu Kagaku in Japan. Hydrogen was purchased from Kaito Sangyo in Japan. Guaranteed reagents of stearates of nickel and barium as catalyst components for Cu/Ni/Ba colloidal catalyst were purchased from Tokyo Kasei Kogyo in Japan and were used as obtained. Cupric acetate, stearic acid and

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ethyl alcohol used for the preparation of cupric stearate as the main catalyst component were purchased from Tokyo Kasei Kogyo in Japan, and were used without purification. Guaranteed dioxane used for recrystallization of prepared crude cupric stearate was purchased from Tokyo Kasei Kogyo in Japan, and were used without purification 1,6-hexanediol (HD) and liquid paraffin (LP) were purchased from Tokyo Kasei Kogyo in Japan and were used as obtained.

2.2. Preparation of cupric stearate as the main catalyst material

Cupric stearate as the main catalyst material was prepared by conventional precipitation method using cupric acetate and stearic acid in ethyl alcohol. 50 g (0.25 mole) of cupric aceteate monohydrate was dissolved in 300 mL of ethyl alcohol at 60 °C in a 1 L round bottom flask equipped with a stirrer, a condenser and a thermometer 142 g (0.5 mole) of stearic acid, dissolved in 200 mL of ethyl alcohol at 60 °C, was added drop wise in an hour into the cupric acetate solution under vigorous agitation. The obtained crude cupric stearate was recrystallized in dioxane twice and washed with ethyl alcohol twice, and was filtrated under reduced pressure followed by being dried under reduced pressure (20–30 mmHg) for two days.

2.3. Reaction set-up

A four-necked 1 L-round-bottom flask equipped with a stirrer, a thermometer, lines for charging and venting a reaction gas composed of MMA and hydrogen, and a phase separator with a condenser to separate formed water and an organic phase, was used Liquified MMA, stored in a 0.5 L-autoclave, was used to obtain MMA gas by warming the autoclave in hot water.

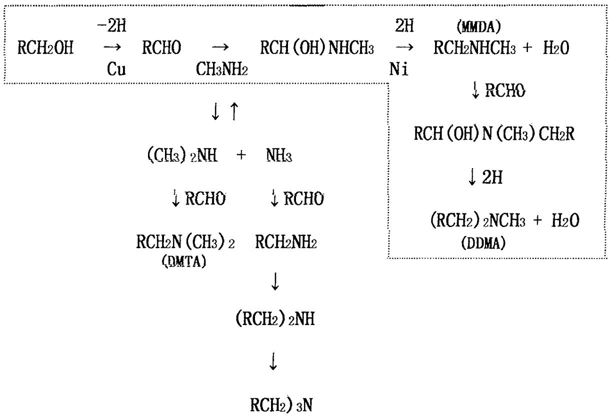
DMA gas used for amination of 1,6-hexanediol was generated in the same way. For hydrogenation of dodecyl nitrile using Cu/Ni/Ba colloidal catalyst, a 0.5 L autoclave was used.

2.4. Reaction method

For amination of dodecyl alcohol and MMA, 3 g of cupric stearate (4.779 mmole; Cu, 1000 ppm versus dodecyl alcohol), 0.6 g of nickel stearate (0.96 mmole), 0.6 g of barium stearate (0.84 mmole) (Cu:Ni:Ba = 5:1:1 mole ratio, an optimum composition) and 300 g (1613 mmole) of dodecyl alcohol were charged into the reactor, and catalyst activation was performed by charging normal pressure hydrogen at 60 nL/h at normal pressure. At about 160 °C, reduction of catalyst materials began to proceed with a typical color change, and dark red active Cu/Ni/Ba colloidal catalyst was produced [1–3,6]. After catalyst activation, hydrogen and MMA were charged at 30 and 4.2 nL/h, respectively, to start the amination at a normal pressure. The amination reaction was proceeded at 200° with liberation of water. The amination reaction also could be performed at a lower Cu concentration of only 333 ppm at 210°. Reaction mixture distilled out with water was returned to the reactor manually. For the initial for hours, MMA charged was completely consumed and the amination reaction proceeded by zero-order kinetics. Aliquot of a reaction mixture was taken out every 1 h for analyses by titration and gas liquid chromatography (OV-17 (3%)/chromosorb WAW DMCS).

For the amination of 1,6-hexanediol (HD) and DMA, liquid paraffin (LP) had to be used because activation of catalyst materials and the amination reaction could not be performed effectively due to coagulation of activated Cu/Ni/Ba collodial catalyst in polar substances such as water, methyl alcohol and HD. Regeneration of coagulated active catalyst was difficult. About 150 g of HD (1.27 moles), 75 g of LP, 3.0 g of cupric stearate, 0.6 g of nickel stearate and 0.6 g of barium stearate were charged into the reactor and catalyst activation was performed by charging hydrogen and DMA at 60 and 5 nL/h, respectively, and at 150–160°. Cu concentration of the Cu/Ni/Ba colloidal catalyst (Cu:Ni:Ba = 5:1:1) was 2000 ppm versus HD. After catalyst activation, a reaction mixture was composed of the upper phase of LP containing the activated colloidal catalyst (dark reddish) and the lower phase of HD (no color). At 190°, DMA and hydrogen were charged at 30 and 30 nL/h, respectively, to start the amination reaction at a normal pressure. For the initial 2–3 h, the amination reaction was proceeded in a heterogeneous state composed of the LP and HD phases, because solubility of HD in LP was only about 4% at 190°. The amination reaction was proceeded in a LP phase or at the inter phase of the two phases in this period. Then a reaction mixture gradually became homogeneous as polarity of HD phase was decreased by the formation of 6-*N*, *N*-dimethyl-hexanol-1 (DMHD) and *N*, *N*, *N*′, *N*′-tetramethylhexamethylenediamine (TMHD), and the colloidal catalyst was existed with stability in a homogeneous single phase reaction mixture. The amination reaction was completed in 6 h with a HD conversion of 100%. Sampling was performed for every 2 h or analyses. During the amination reaction TMHD was distilled out of the reactor with formed water because its boiling point was lowest. Therefore, TMHD distilled out was separated by salting out using sodium hydroxide, and it was added to TMHD obtained by fractional distillation of a reaction mixture in the reactor A TMHD yield as a whole was about 80% with a conversion of 100%. When the amination reaction was performed without using LP, stability of the colloidal catalyst was not obtained.

Hydrogenation of dodecylnitrile was performed by activation of a mixture of catalyst materials (1.5 g of cupric stearate, 0.3 g nickel stearate and 0.6 g barium stearate) in 300 g of dodecyl nitrile using normal



Scheme 1. Reaction scheme for the amination of dodecyl alcohol and MMA.

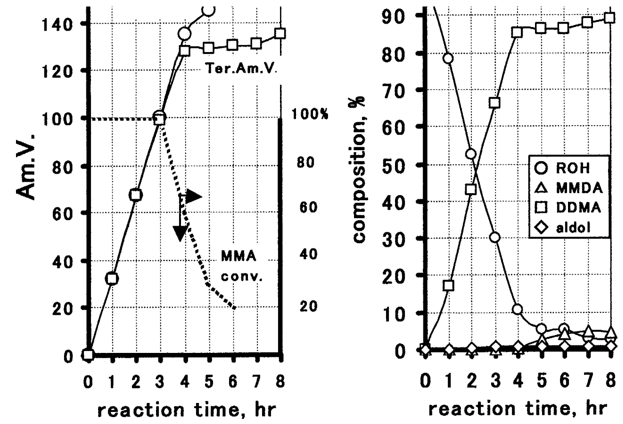


Figure 1. Amination of dodecyl alcohol and MMA at optimum conditions.

pressure hydrogen, followed by hydrogenation at 15–20 atoms and 210 °.

A reaction mixture was analyzed by titration method.

3. Results and discussion

3.1. Reaction scheme

Reaction scheme for the amination of dodecyl alcohol and MMA using Cu/Ni/Ba colloidal catalyst is shown in scheme 1. The main reaction starts with dehydrogenation of dodecyl alcohol, followed by the addition of MMA to dodecylaldehyde, to form a corresponding imine after dehydration or followed by hydrogenolysis of the adduct, to form momomethyldodecylamine (MMDA) as an intermediate.

Then the addition of MMDA to dodecyaldehyde is proceeded to form didodecylmethylamine (DDMA) by hydrogenolysis. Transalkylation of MMA to dimethylamine (DMA) and ammonia is one of the main side reaction, which can produce significant amount of dimethyldodecylamine (DMTA), didodecylamine and tridodecylamine as byproducts. Therefore, charging of MMA in excess has to be prevented, and MMA preferably has to be charged at a comparable feed rate to its consumed rate [6].

Aldolyzation of dodecylaldehyde, catalyzed by methylamines, is the other side reaction.

Prevention of these two side reaction as much as possible has been the major target for this consecutive amination reaction to obtain a maximum yield of dialkylmethyl tertiaryamines.

Amination of HD with DMA also proceeds by aldehyde mechanism, via formation of 6-*N*,*N*-dimethylaminohexanol-1 (DMHD), to form *N*, *N*, *N*′, *N*′-tetramethyl-hexamethylenediamine (TMHD). Hydrogenation of nitriles, using Cu/Ni/Ba colloidal catalyst, to form a corresponding secondary amine also constitutes consecutive reaction system.

3.2. Amination of dodecyl alcohol and MMA at optimum conditions

Amination of dodecyl alcohol and MMA was performed at optimum conditions, results are shown in figure 1.

The left figure shows a reaction profile expressed in amine values obtained by titration method and a profile for MMA conversion (right scale). Total amine value (To.Am.V.) is a measure of content of total amines (primary, secondary and tertiary amines) existed in a reaction mixture, and tertiary amine value (Ter.Am.V.) is a measure of a content of tertiary amines such as DDMA. Each amine value is expressed in mg-KOH/g-sample which is equivalent to hydrogen chloride required for neutralization of the amines. An amine value difference, ΔAm.V. - (To.Am.V.–Ter.Am.V.), shows a content of secondary amine such as MMDA. Therefore, for the DDMA synthesis, ΔAm.V. has to be lowered as much as possible to obtain a highest selectivity for DDMA.

The right figure shows a composition of the corresponding reaction mixture. It can be seen from the left figure that ΔAm.V. was zero and MMA conversion was 100% for the initial 3 h, and after that MMA conversion was decreased drastically, resulting in slight increase in ΔAm.V for 1 h, followed by significant increase in ΔAm.V. until 7 h. At 7 h, MMA supply was stopped for 1 h to promote the following amination reaction of remaining dodecyl alcohol and MMDA, while hydrogen was charged. It was named as “hydrogen treatment” [6].

$$RNHC_3 + ROH \rightarrow R_2NCH_3 + H_2O$$

It can be seen from the left figure (from 7 to 8 h) that the hydrogen treatment, Ter.Am.V was increased by 10 units resulting in decrease in ΔAm.V. by 10 units, which corresponds to an additional increase in DDMA yield by 3% and a decrease in MMDA by 1.5% in the right figure. It can be seen from the right figure that from four hour (alcohol conversion, 90%) reaction rate was significantly decreased and DDMA formation was almost stopped with a gradual increase in MMDA which was not observed for the initial 4 h. These observations in the right figure coincide with drastic decrease in MMA conversion and significant increase in ΔAm.V. after 4 h in the left figure, and these phenomena were synchronized each other. It should be noted that for the initial 4 h, DDMA formation proceeded by zero-order kinetics, and after that the amination reaction proceeded by a consecutive reaction mechanism with liberation of MMDA. At eight hour, an alcohol conversion was 97% with a DDMA selectivity and yield of 90.7% and 88.0%, respectively, and small amount (4%) of MMDA was left unreacted in this experiment. Content of aldol was only 0.8% at eight hour. It was concluded from these observations that maintaining a MMA conversion of 100% (zero order kinetics) is essential to obtain a highest selectivity for DDMA by preventing the liberation of MMDA as an intermediate, and that continuous monitoring of content of remaining dodecyl alcohol and MMDA and continuous control of MMA feed rate are essential to obtain a highest yield for DDMA.

3.3. Purity of DDMA prepared at optimum conditions

Distillation of a reaction mixture in the previous paragraph was performed to separate mono-alkyl, di-alkyl and di-alkyl components and to clearly understand the side reaction. The result is shown in table 1.

It can be seen from the table that the amount of the main distillate was 90.1 wt% with To.Am.V and Ter.Am.V., 150.1 and 149.4, respectively. ΔAm.V. value was 0.7, which corresponds to MMDA content of 0.25%. Purity of DDMA of the main distillate based on GLC analyses was 99.1% with small amount of byproducts such as aldol (0.5%) and waxes (0.2%) both of which are di-alkyl components. If amination of dodecyl alcohol and MMA is performed at an excess feed rate of performed at an excess feed rate of MMA, these unwanted byproducts will be formed in excess, and they cannot be effectively removed by distillation. Content of non-amine materials analyzed by extraction method was 1.7% (aldols, 0.46%; waxe, 0.64; others, 0.60%).

Table 1
Distillation of a reaction mixture prepared by amination of dodecyl alcohol and MMA

	Main distillate 90.1 wt%	First distillate 8.2%	Residue 1.7%
To.Am.V.	150.1	187.0	57.3
Ter.Am.V	149.4	38.6	41.8
ΔAm.V.	0.7	148.4	15.5
Composition, %			
ROH	–	12.0	
$RNHCH_3$(MMDA)	0.25	53.2	4.0
$RN(CH_3)_2$(DMTA)		7.1	
R_2NCH_3(DDMA)	99.1	13.6	
Aldol	0.5		
Wax	0.2		36.0
R_3N			41.7
Non-amine (versus distillate)	1.7[a]		24.6[b]

[a] Aldols 0.46%, waxes 0.64, others 0.60%.
[b] ROH, hydrocarbon, fatty acid methylester.

The first distillate was composed of MMDA (53.2%), DMTA (7.1%), DDMA (13.6%) and non-amine materials such as unreacted alcohol (12.0%) and hydrocarbons.

The residue was composed of lauryllaurate as a wax (36.0%) and tridodecylamine (41.7%) which was produced by stepwise amination of dodecyl alcohol and ammonia produced by transalkylation of MMA. DMTA is also another transalkylation product of MMA. It was demonstrayted from these observations that Cu/Ni/Ba colloidal catalyst, which was the first Cu/Ni-based catalyst used for the commercial production of DMTAs and has much higher catalytic activity over the corresponding solid catalysts, can also be used for the synthesis of DDMAs by controlling MMA feed rate.

3.4. Comparison of catalytic activity ofCu/Ni/Ba colloidal catalyst and solid ones

Amiantion of dodecyl alcohol and MMA was performed using $Cu/Ni/SiO_2$ catalyst (Cu/Ni = 4:1; SiO_2 content, 50 wt%) prepared by co-precipitation method, and the result is shown in figure 2.

It can be seen from the figure that similar reaction profiles as in figure 1 were obtained. Initial reaction rates for the zero order region (0–4 h) and the following consecutive reaction region (4–6 h) in the figure are compared with those of Cu/Ni/Ba colloidal catalyst in figure 1, and the results are shown in table 2.

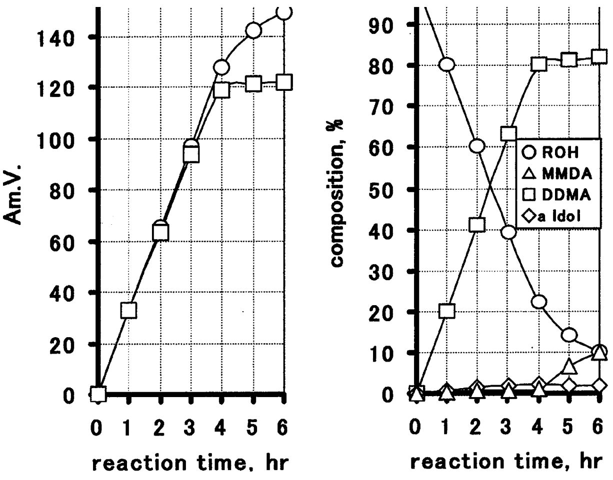


Figure 2. Amination of dodecyl alcohol and MMA using $Cu/Ni/SiO_2$ catalyst.

Table 2
Comparison of catalytic activity of Cu/Ni/Ba colloidal catalyst and Cu/Ni/SiO_2 solid catalyst for the amination of dodecyl alcohol and MMA

	(mol-ROH h^{-1} mol-Cu)	(mol-DDMA h^{-1} mol-Cu)
Zero-order region		
Cu/Ni/Ba	75.2	37.6
Cu/Ni/SiO_2	10.5	5.3
Second-order region		
Cu/Ni/Ba	6.8	1.7
Cu/Ni/SiO_2	3.3	0.26

It can be understood from the table that Cu/Ni/Ba colloidal catalyst showed seven times higher catalytic activity than that of Cu/Ni/SiO_2 solid catalyst in DDMA formation as well as alcohol consumption, and that the superiority of the colloidal catalyst was also true for the second order region. If Cu/Ni/Ca/Ba four component colloidal catalyst [3], which showed 10 times higher catalytic activity than that of Cu/Ni/Ba colloidal catalyst, is used, much higher performance will be achieved. It was concluded from these observations that Cu/Ni-based catalyst in a colloidal state is superior in catalytic activity than the corresponding solid one, and that these essential characteristics of the colloidal catalyst have to be used for the development of further advance catalytic systems.

3.5. *Simulation studies of amination of dodecyl alcohol and MMA*

A simulation study was performed for amination of dodecyl alcohol and MMA using the right figure of figure 1. DDMA formation by zero-order kinetics for the initial 4 h and the following consecutive mechanism were taken into considerations. For the equations (1) and (2), rate equations (3), (4) and (5) are shown.

$$RCH_2OH + MMA \rightarrow MMDA + H_2O \tag{1}$$

$$RCH_2OH + MMDA \rightarrow DDMA + H_2O \tag{2}$$

$$\begin{aligned} -d[ROH]/dt = k1 * [ROH] * [MMA] \\ + k2 * [ROH] * [MMDA] \end{aligned} \tag{3}$$

$$\begin{aligned} d[MMDA]/dt = kl * [ROH] * [MMA] \\ - k2 * [ROH] * [MMDA] \end{aligned} \tag{4}$$

$$d[DDMA]/dt = k2 * [ROH] * [MMDA] \tag{5}$$

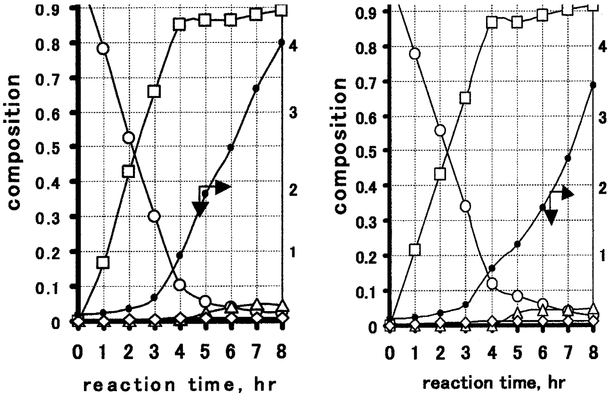


Figure 3. Simulation study for amination of dodecyl alcohol and MMA feed rate. ○; dodecyl alcohol; *angle*; MMDA; □; DDMA; right scale, MMA/dodecyl alcohol mole ratio.

In a preliminary study based on a simple consecutive reaction mechanism using the equations, (3), (4) and (5), simulation could not be achieved for any set of $k1$ and $k2$ values for the initial 4 h in which DDMA formation proceeds by zero-order kinetics without liberation of MMDA.

Therefore, equation, (6) had to be used for the initial zero-order period, and after that equations, (3)

$$d[DDMA]/dt = k3 \tag{6}$$

through (5) had to be used instead of equation (6). A simulation result is shown in figure 3.

The left figure shows the observed reaction profile (right figure of figure 1) with a profile for MMA/dodecyl alcohol mole ratio(right scale), and the right figure shows a simulation result using the zero-order and second order kinetics for the initial 4 h and the following 4 h, respectively. It can be seen from the figure that simulation was successfully performed by the combination of the two mechanism, and that MMA/dodecyl alcohol mole ratio is a key factor controlling the kinetics and it has to be less than 1 throughout the amination reaction to achieve a highest productivity for DDMA. Simulated apparent rate constants, $k1$, $k2$ and $k3$ were 3.0 L/mole/h, 6.0 L/mol/h and 0.217 mole/L/h, respectively. It was concluded from these observations and discussions that for the zero order region, one-step formation of DDMA by the reaction of two molecules dodecyl alcohol and MMA might be proceeded, and that MMA feed rate has to be decreased continuously or intermittently as alcohol conversion increases to keep the MMA/dodecyl alcohol mole ratio at less than 1.

3.6. *Aminationof dodecyl alcohol at an excess feed rate of MMA*

We investigate the effect of excess MMA on catalytic activity of Cu/Ni/Ba colloidal catalyst. Amination of

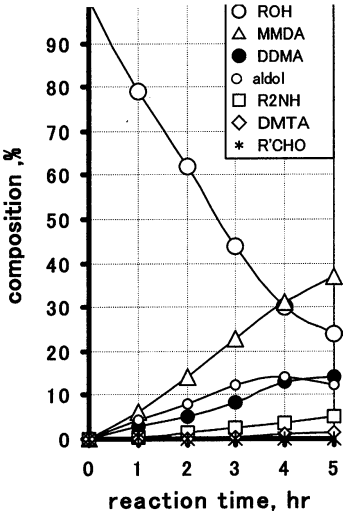


Figure 4. Amination of dodecyl alcohol and MMA charged in excess.

dodecyl alcohol and MMA was performed at MMA and hydrogen feed rates of 37 and 18 nL/h, respectively, at Cu concentration of 1000ppm and 200 °. Initial MMA/dodecyl alcohol mole ratio was 0.94, which was much higher than the optimum one (<0.1). The result is shown in figure 4.

It can be seen from the figure that an alcohol conversion was only 75% at five h with DDMA content of only 14% and its selectivity of 19%. On the other hand, MMDA content was 37% and its selectivity was 49%. Furthermore, the reaction mixture contained significant amount of byproducts such as aldol (12%), didodecylamine(R_2NH, 5%) and dimethyldodecyl tertiary amine (DMTA, 3.0%). Alcohol-based initial formation rates for DDMA, MMDA, aldol and didodecylamine were 11.0, 25.6, 13.7 and 1.4 mol-ROH h^{-1} mol-Cu, respectively. It can be understood from these observations that excess charging of MMA significantly decreased the formation of DDM as an objective product increasing the formation rates of aldols as well as MMDA.

3.7. Aldolization of dodecylaldehyde catalyzed by methylamines

Possibility for the aldolization of produced aldehydes, catalyzed by methylamines such as trimethylamine(TMA) which does not react with dodecyl alcohol, was investigated. After catalyst activation in a mixture of palmityl alcohol and stearyl alcohol, TMA was charged instead of DMA or MMA. The result is shown in figure 5.

TMA was continuously charged except the period indicated by bold lines (1.0–1.5 and 3.0–3.5 h) in the figure. It can be seen from the figure that aldolization was effectively proceeded during TMA charging, and that it was stopped while TMA supply was stopped. Aldolization rate was 11.2 mol-ROH h^{-1} mol-Cu. It was confirmed from these observations that aldolization was catalyzed by methylamines such as TMA. It was concluded from these observations that MMA functions as a base catalyst for aldolization, therefore, charging of excess MMA has to be prevented to prevent transalkylation of MMA as well as aldolization of *in situ* generated aldehydes.

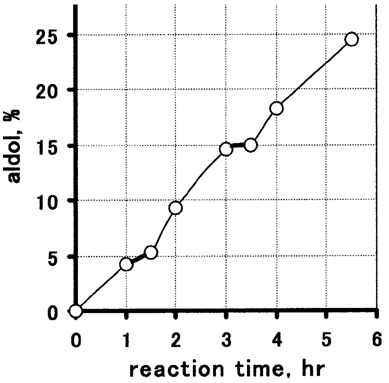


Figure 5. Aldolization, catalyzed by TMA, of aldehydes produced *in situ* by dehydrogenation of fatty alcohols in the presence of Cu/Ni/Ba. Palmityl alcohol, 180 g; stearyl alcohol, 120 g; Cu, 1000 ppm versus alcohols; reaction temp., 240 °C; TMA and hydrogen feed rates, 26 and 30 nL/h, respectively.

3.8. Catalytic activity of Raney nickel

Amination of dodecyl alcohol and MMA was performed using Raney-nickel. The result is shown in figure 6.

It can be seen from the figure that DDMA yield was only 52.6% (selectivity 53.0%) at an alcohol conversion of 99% at six h. It should be noted that significant amount of byproducts such as R_2NH (9.5%) and R_3N (30%) were formed.

They were amination products such as dodecyl alcohol and ammonia formed by transalkylation of MMA over the Ni catalyst. It was understood from these observations that nickel-based catalyst promotes transalkylation of MMA, resulting in significant formation of various unwanted amines as byproducts. It was concluded from these observations that Ni-based catalyst cannot be used for the synthesis of DDMA even if a MMA feed rate is controlled.

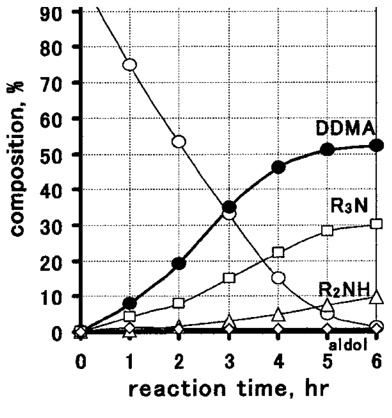


Figure 6. Amination of dodecyl alcohol and MMA over Raney-Nickel.

3.9. *Amination of diols*

Amination of polar 1,6-hexanediol (HD) and DMA was performed using Cu/Ni/Ba colloidal catalyst to synthesize *N,N,N′,N′*-tetramethyl-1,6-hexamethylenediamine (TMHD) used as catalyst for production of urethanes. The amination reaction was performed using liquid paraffin (LP) as solvent to stabilize the activated Cu/Ni/Ba colloidal catalyst which coagulates in polar solvents such as water, methyl alcohol and ethyl alcohol. HD has a comparable polarity to ethyl alcohol. The result is shown in figure 7.

It can be seen from the figure that the amination reaction was proceeded by consecutive reaction mechanism via the formation of 6-*N,N*-dimethylamino-hexanol-1 (DMHD) as an intermediate in the following scheme.

$$\begin{aligned} \mathrm{HO-(CH_2)_6-OH} &\rightarrow \mathrm{(CH_3)_2N-(CH_2)_6-OH} \\ &\rightarrow \mathrm{(CH_3)_2N-(CH_2)_6-N(CH_3)_2} \end{aligned}$$

A reaction mixture was composed of two phases, a lower HD phase and an upper LP phase containing Cu/Ni/Ba catalyst, for about three h until a HD conversion of more than 95%. Then a reaction mixture gradually form a homogeneous single phase.

TMHD yield was 80–85%, and content of dimeric compounds of HD and their derivatives were about 10%. It can be thought that application of Cu/Ni/Ca/Ba four component colloidal catalyst [3]; which showed higher stability to polar substances and six to sevenfold higher catalytic activity than Cu/Ni/Ba catalyst, might be effective for the amination of HD. It was concluded from these observations and discussions that Cu/Ni/Ba colloidal catalyst can be used for the amination of polar diols such as HD as long as LP is used.

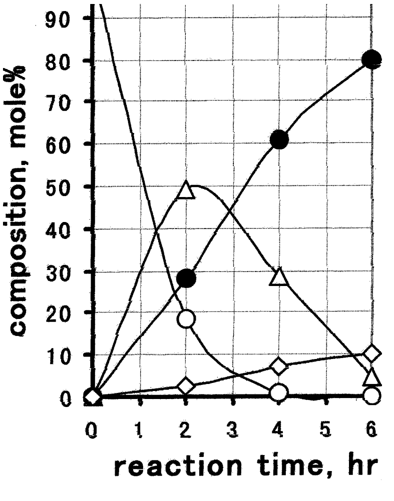


Figure 7. Amination of HD and DMA using Cu/Ni/Ba colloidal catalyst. ○, HD; △, DMHD; ●, TMHD; ◇, dimer of HD and their derivatives.

3.10. *Other consecutive reaction performed using Cu/Ni/Ba colloidal catalyst*

Hydrogenation of dodecylnitrile was performed by using Cu/Ni/Ba catalyst (Cu conc, 500 ppm versus nitrile) at 210° and at a hydrogen pressure of 15–20 atm. Didodecyl secondary amine was obtained with a yield of 82.4% for 5 h.

Amination of fatty alcohols and ammonia to synthesize tridodecylamine [1] also could be performed by using Cu/Ni/Ba colloidal catalyst. For this amination, excess charging of ammonia had to be prevented to prevent aldolization of *in situ* produced dodecylaldehyde.

Amination of fatty alcohols and fatty primary amines to produce corresponding secondary amines was also proceeded by using Cu/Ni/Ba catalyst [1]. These examples and amination with MMA was a basis for the amination reaction using Cu/Ni-based solid catalyst [9].

It was concluded from these observations that Cu/Ni/Ba colloidal catalyst has wide application in various types of amination.

4. Conclusions

Amination of dodecyl alcohol and MMA to DDMA using Cu/Ni/Ba colloidal catalyst proceeded by zero-order kinetics without liberation of the intermediate secondary amine, MMA while MMA/dodecyl alcohol mole ratio was less than 1. A lower mole ratio was also effective for the prevention aldolization catalyzed by MMA. Catalytic activity of the colloidal catalyst was seven times higher than that of Cu/Ni/Si0$_2$ solid catalyst. Amination reaction of a polar diol, HD and DMA required non-polar LP to stabilize the activated colloidal catalyst, and the reaction effectively proceeded in a LP phase or at interface of the two phases until most of the polar organic phase were consumed. Hydrogenation of fatty nitriles using Cu/Ni/Ba catalyst produced corresponding secondary amine with a yield of 80%. Cu/Ni-based colloidal catalyst such as Cu/Ni/Ba and Cu/Ni/Ca/Ba, which has tolerance to polar materials, can be used for various types of amination reaction.

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