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Basic function of Cu/Ni-based catalyst in a colloidal state for one-pot amination alcohols to N,N-dimethyl tertiary amines

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One-pot amination of fatty alcohols with dimethylamine at normal pressure, using Cu/Ni-based colloidal catalyst stabilized by barium sterate (Cu/Ni/Ba colloidal catalyst, Cu:Ni:B = 5:1:1). proceeded without charging bulk hydrogen with an amine yield of more than 90%. It demonstrated the effective use of active hydrogen, generated by the dehydrogenation of a starting alcohol over copper, for the following hydrogenolysis of an aldehyde-dimethylamine adduct to form the final product, *N*,*N*-dimethil-long alkyl-tertiary amines. The basic function generated by the combination of copper and nickel, especially in a colloidal state, was named as "Self-supplying System for Active Hydrogen". On the other hand, reductive amination of aldehydes with dimethylamine, in the presence of hydrogen flow at a normal pressure using the same colloidal catalyst, proceeded with an amine yield of 40–80%, and significant amount (12–26%) of aldols were formed. These observations demonstrated the essential difference between one-pot amination of alcohols containing active hydrogen and reductive amination of aldehydes in the presence of bulk hydrogen which has to be activated separately. This is the first description of basic function of Cu/Ni-based catalyst by the original inventors of the catalytic system. More than five-fold increase in catalytic activity by incorporation of calcium stearate with Cu/Ni was observed for one-pot amination of fatty alcohols. Comparison of catalytic activity of Cu/Ni-based catalyst in a colloidal state and in a solid state showed superiority of the former catalyst in catalytic activity, 40–50 times higher based on a unit amount of copper.

KEY WORDS: reductive amination; one-pot amination; synergism; Cu/Ni/Ba; calcium; amination; metal colloid; nanoparticles.

1. Introduction

N,*N*-dimethyl-long-alkyl-tertiary-amines (DMTAs), derived from fatty alcohols (alcohol-based process) or alpha-olefins (alpha-olefin-based process), are important intermediates for foam boosters in household detergents, softening agents for fabrics, dye adjuvants, fungicides and so on.

After restructuring of DMTA producers in the world during the last two decades, these two became the leading commercial processes, and; they are competing. The alcohol-based process has been used by KAO Corporation (Japan), Clariant (Germany), Feixiang Chem (China) and Lonza (USA). The alpha-olefin-based process has been used by P&G-Chemicals (the biggest producer for DMTAs), Albemarle and Huntsman. In alcohol-based process, DMTAs are produced in one-step directly from various fatty alcohols (natural-, Ziegler-, Guerbert- and oxo-) using copper-based catalysts such as copper-chromite (Cu-Cr-O) [1], or Cu/Ni-based multi-functional solid catalyst [2,3] developed with the basic concept of Cu/Ni/Ba colloidal catalyst by KAO Corporation [4,6]. The colloidal catalyst developed in 1977 after detailed screening and optimization and was patented in many countries [4,6]. The new process for DMTAs (4800 metric tons/year) using the colloidal catalyst was commercialized in 1981 to produce mainly C_{10}, C_{12} and CH_{14} alkyl range of DMTAs until 1985 when the catalyst was substituted to the corresponding solid one with increased hydrogenolysis activity by incorporation of a precious metal [3]. At present, most producers in the world use Cu/Ni-based solid catalyst. China Research Institute of Daily Chemical Industry reported several articles on Cu/Ni-based solid catalyst. and a review on recent trend in DMTAs [5].

However, so far, there has not been reported any articles concerning the following essential function typical of Cu/Ni-based catalyst for one-pot amination of alcohols. When we developed the Cu/Ni/Ba colloidal catalyst in 1977 to increase productivity of DMTAs as much as Possible, we found that one-pot amination of dodecyl alcohol with dimethylamine proceeded without charging bulk hydrogen, (sometimes, a reactor was broken by vigorous bumping of formed water), to produce the corresponding DMTA with an amine yield of more than 90% [4]. It demonstrated that one-pot amination of alcohols is completely different from conventional reductive amination of aldehydes, in which bulk hydrogen is required and has to be activated. We confirmed that the active hydrogen generated by the

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dehydrogenation of dodecyl alcohol was effectively consumed for the following hydrogenolysis of a dodecylaldehyde-dimethylamine adduct to form the corresponding DMTA. We named this exciting phenomenon as "Self-supplying system for active hydrogen" produced by the synergism of copper and nickel, a sole combination [10]. Besides this essential phenomenon, we also have following topics typical of the combination of copper and nickel.

(1) Stabilizers, key components for Cu/Ni-based colloidal catalyst [9].
(2) Carbon monoxide as catalyst poison and development of CO-resistive catalyst [10].
(3) How the Cu/Ni-based catalytic system was developed and optimized [4,10].
(4) Various amination reaction using Cu/Ni/Ba colloidal catalyst [11].

Later, Cu/Ni/Ba catalyst was briefly reported by later researchers [7] based on our original research [4,6,8], and present authors reported calcium-containing Cu/Ni-based colloidal catalyst for one-pot amination of low reactive oxo-alcohols [9]. However, essential function of Cu/Ni-based catalyst. such as "Self-supplying system for active hydrogen" and other interesting basic characteristics have not been reported so far since catalyst development. In this article, we, original inventors for the Cu/Ni based catalyst described several basic functions of the catalytic system developed prior to the later limited study [7] based on our original research [4,6,8–10].

2. Experimental

2.1. *Preparation of cupric stearate as a main catalyst material*

Cupric stearate as the main catalyst material was prepared by conventional precipitation method (1) in ethyl alcohol using cupric acetate and stearic acid, or by double-decomposition method (2) in water using cupric chloride and sodium stearate (or stearic acid and sodium hydroxide). For the method (2), addition of an surface active, agent such as monoglycerides was favored for efficient mixing of a heterogeneous reaction mixture. All the metal compounds were purchased from Tokyo Kasei Kogyou, in Japan.

Other stearates of VIII-group metals used for catalyst optimization were guaranteed reagents and were used as obtained. Several chelate-compounds such as acetylacetonates of various VIII-group metals were used as obyained. Reagents of stearates of alkali or alkali-earth metals as stabilizers for the Cu/Ni-based colloidal catalyst were used as obtained. Cupric stearate prepared by the method (1) or (2) had to be purified to obtain a maximum catalytic activity. It should be noted that acetic acid generated and smelled during preparation of Cupric stearate by the method (1), was catalyst poison. Therefore, it had to be removed as much as possible by recrystallization of crude cupric stearate in dioxane twice or three times, and then the purified cupric stearate had to be dried in vacuum to remove trace of liberated acetic acid over night.

Otherwise, serious sintering of reduced copper was proceeded and catalytic activity was significantly decreased. In method (2), purification could be performed by making a homogeneous solution of a catalyst material such as cupric stearate or mixed stearates of copper and nickel at an optimum composition in a starting fatty alcohol, followed by washing with hot water. It was patented as an industrial method for the production of the catalyst materials [6]. However, it should be noted that excess washing with hot water produce metal hydroxides, which somewhat decreased catalytic activity. In a previous article, [7] on Cu/Ni/Ba colloidal catalyst based on our original studies [4,6], this purification method was used, but in the present studies, method (1) as a standard method was used.

2.2. *Materials for one-pot amination of* N,N-*dimethyl-tertiaryamines (DMTAs)*

Commercially available various fatty alcohols, branched chain (oxo-) and straight chain alcohols such as KALCOL-20 (KAO's dodecyl alcohol, C_{12} 98% <), were used as starting materials for one-pot production of DMTAs. Some information on reactivity of various branched chain alcohols was reported elsewhere[9]. Hydrogen was purchased from Kaito-Sangyo, and liquefied dimethylamine (DMA) from Nitto-Kagaku were used as obtained. Carbon monoxide, for the experiment on catalyst poison, was purchased from Seitetsu-Kagaku Kogyo. Triphenylphosphine and triphenylphosphite (TTPO) used for preparation of CO-resistant catalyst were from Tokyo-Kasei and were used as obtained.

2.3. *Reaction set-up*

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

2.4. *Activation of catalyst materials*

Three grams (4.77 mmol) of cupric stearate, 0.6 g (0.96 mmol) of nickel stearate, 0.6 g (0.85 mmol) of barium stearate and 300 g (1613 mmol) of dodecyl alcohol were charged into the reactor. The reactor was heated under vigorous stirring and nitrogen flow in a mantle heater equipped with an automatic temperature controller. Then nitrogen feed was stopped and hydrogen was fed at 60 NL/h the catalyst materials charged were completely dissolved in dodecyl alcohol by 100 °C to form a homogeneous and transparent bluish green solution typical of divalent copper and nickel. At about 160 °C, reduction of cupric stearate started with a typical color change, bluish green → yellowish green → pale yellow → no color, which showed gradual proceeding of reduction of copper and nickel stearates. And then instantly changed to dark red which is a typical color of Cu/Ni/Ba colloidal catalyst. Reduction of copper and nickel was almost completed by 200 °C.

2.5. Reaction method for one-pot amination of dodecyl alcohol with dimethylamine (DMA)

Then temperature was gradually raised to 210 °C. a standard reaction temperature. and kept at that temperature during the amination reaction. At 210 °C. hydrogen and DMA-gas was charged at 18 and 35 NL/h, respectively. The total flow rate of a mixed gas composed of hydrogen and DMA was 53 NL/h. Standard reaction conditions are: charged materials, dodecyl alcohol (300 g), cupric stearate (3.0 g), nickel stearate (0.6 g), barium stearate (0.6 g); H2 feed rate, 18 NL/h; dimethylamine (DMA) feed rate. 35 NL/h; reaction temp., 210 °C; Cu concentration. 1000 ppm vs dodecyl alcohol; Cu:Ni:Ba = 5:1:1 mole ratio (or Cu:other second catalyst component:Ba = 5:1:1); reaction pressure, normal pressure. These standard conditions were used otherwise noted. Hydrogen flow rate could be reduced to 0 NL/h during the amination reaction. However, for catalyst activation, hydrogen flow rate of 60 NL/h was favored for effective removal of water formed in the activation of catalyst materials. Because water is a catalyst poison and it seriously deteriorated copper-based colloidal catalyst. Amination reaction proceeded shortly after charging of DMA (some induction period existed), and formed water was distilled out from the reactor with reaction mixture. Formed water was separated in a separator equipped with a condenser, and organic phase was returned to the reactor manually. The line between the reactor and the condenser had to be heated to more than 100 °C to achieve effective removal of formed water. In the initial stage of the amination reaction, DMA charged was completely consumed. Notice that lack of DMA will accelerates generation of carbon monoxide by the decarbonylation of formed aldehydes.

2.6. Method for one-pot amination of dodecyl alcohol with dimethylamine without charging hydrogen

For one-pot amination of dodecyl alcohol with dimethylamine performed without charging bulk hydrogen, catalyst materials were activated first as described above, and then amination reaction was performed by stopping hydrogen supply. Or nitrogen as an inactive gas can be used instead of stopping hydrogen supply, which is not economical industrially. Serious bumping due to formed water was observed in the reactor made of pyrex glass. Therefore, vigorous stirring at least at 1000 rpm was required.

2.7. Analyses of a reaction mixture and reaction gases

2.7.1. Estimation of amine yield of a reaction mixture by titration

Amine yield was estimated by using titration method [9], and composition of a reaction mixture was obtained by using gas-liquid chromatography. Selectivity for objective amines (DMTAs) were 97.0–98.5% in one-pot amination of alcohols with dimethylamine using Cu/Ni-based colloidal catalyst.

2.7.2. Gas-liquid chromatography (GLC)

A 5% solution of a reaction mixture in isopropyl alcohol was used for GLC analyses to obtain composition of a reaction mixture. Following analytical conditions were used; column: OV-17 (3%)/Chromosorb WAW DMCS; column temp.: 100 ~ 280 (8 °C/min); detector: 100 MΩ, 0.32 V; carrier gas: He 60 mL/min. For the GLC analyses of mainly mono-alkyl components such as DMTAs, monoalkylmonomethylamines, analytical conditions were used; column: aldehydes and hydrocarbons, following Carbowax: 20 M 3%/chromosorb WAW DMCS; column temp.: 160 °C; detector: 100 mA, 4 mV, carrier gas: He 60 mL/min. For the GLC analyses of a reaction gas containing DMA and its transalkylation products such as monomethylamine (MMA) and trimethylamine (TMA), following analytical conditions were used; column: triethanolamine 30%/chromosorb WAW; column temp.: 70 °C; range: 8; carrier gas: He 60 ml/min; sample: 2.5 ml. For the GLC analyses of carbon monoxide, CO generated by decarbonylation of aldehydes, and methane, following analytical conditions were used; column: molecular sieve 5A; column temp.: 70 °C; range: 1; carrier gas: He 60 ml/min; sample: 1.0 ml.

3. Result and discussion

3.1. Reaction mechanism for one-pot amination of fatty alcohols and dimethylamine

Before describing one-pot amination of fatty alcohols with dimethylamine performed without charging bulk hydrogen, general reaction mechanism for the amination using Cu-based or Cu/Ni-based catalyst under a hydrogen flow at normal pressure and a temperature range of 190–230 degree centigrade is shown below [7,13].

$$\mathrm{RCH_2OH \rightarrow RCHO + H_2} \tag{1}$$

$$\mathrm{RCHO + (CH_3)_2NH \rightarrow RCH(OH)N(CH_3)_2} \tag{2}$$

$$\mathrm{RCH(OH)N(CH_3)_2 + H_2 \rightarrow RCH_2N(CH_3)_2 + H_2O} \tag{3}$$

The first step is dehydrogenation of a starting alcohol over reduced copper to a corresponding aldehyde, and the second one is non-catalytic formation of a dimethylamine-aldehyde adduct. Other intermediates except dodecylaldehyde was not detected. The third one is hydrogenolysis, over reduced nickel, of the adduct to form the corresponding *N*,*N*-dimethyl-tertiary-amines (DMTAs) and water. However, in previous studies [7,13], there was almost no discussion on hydrogen produced by the dehydrogenation of a starting alcohol in the equation (1).

Therefore, it has been thought for a long time that charging of bulk hydrogen is required for the hydrogenolysis step, (3). On the other hand, in our original studies from 1976 for the development of Cu/Ni-based catalyst in a colloidal state stabilized by one of alkali or alkali-earth metal ions, we found that one-pot amination of fatty alcohols proceeded with out charging bulk hydrogen with an amine yield of more than 90% [4,10]. Although a reactor made of Pyrex-glass was sometimes broken due to serious bumping of formed water, we found the essential and basic function of Cu/Ni-based catalyst in one-pot amination of fatty alcohols, and it showed us that one-pot amination of alcohols is essentially different from conventional reductive amination of aldehydes in terms of an active hydrogen source needed for the hydrogenolysis of dimethylamine–aldehyde adducts. Here, we presented a new reaction mechanism which was observed in experiments to increase productivity of DMTAs as much as possible. If we did not performed the dangerous experiments and performed first the amination reaction using corresponding Cu/Ni-based solid catalyst, we did not notice the basic function of Cu/Ni-based catalyst.

3.2. *Effect of DMA concentration on catalytic activity of Cu/Ni/Ba catalyst*

To obtain a highest productivity for DMTA synthesis, effect of increasing a DMA concentration, from 66% to 100%, on catalytic activity of Cu/Ni/Ba catalyst was investigated. A feed rate of a mixed gas, composed of DMA and hydrogen with a DMA concentration ranged from 66% to 100%, was set to 51 ~ 53 NL/h for 300 g (1.613 mol) of charged dodecyl alcohol. The result is shown in figure 1 and table 1.

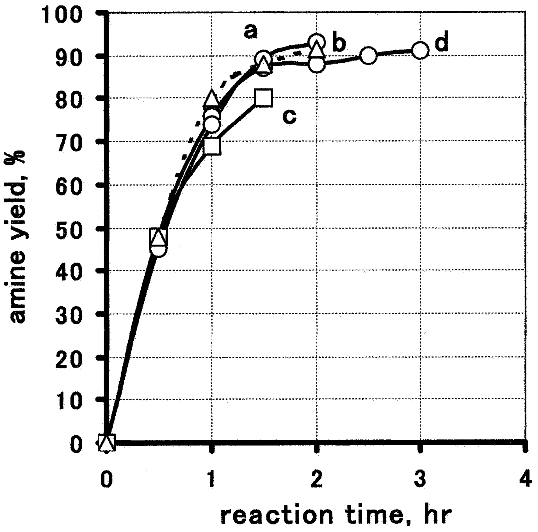


Figure 1. Effect of DMA concentration on catalytic activity of Cu/Ni/Ba catalyst in one-pot amination of dodecyl alcohol and DMA.

Table 1
Effect of DMA concentration on catalytic activity of Cu/Ni/Ba colloidal catalyst

	Feed rate (NL h^{-1}) DMA	H2	DMA vol% vs DMA + H2	conv. (%)	DMTA selectivity (%)	Initial reaction rate (mol/h/mole-Cu)
a	35	18	66	97.9	96.3	304
b	40	12	77	95.7	97.3	338
c	45	6	88	84.8	97.1	311
d	41	0	100	96.2	97.2	335

For the experiment, (d) bulk hydrogen was not charged at throughout the amination reaction.

For the experiment, a(○), b(△), c(□) and d(○), DMA concentration were set to 66%, 77%, 88% and 100%, respectively. Especially in the experiment, d, only DMA was fed at 41 NL/h without charging bulk hydrogen. Therefore, in this experiment, vigorous bumping was observed due to vaporization of formed water especially in the first part of the amination reaction, and sometimes a reactor made of Pyrex-glass was broken. It can be seen from the figure and table that initial reaction rate for d was comparable to those for a, b and c in all of which hydrogen was charged.

The most important point for the experiment, d, is that one-pot amination was effectively proceeded with a DMTA yield of more than 90% even in the absence of bulk hydrogen. This exciting and surprising phenomenon demonstrated that active hydrogen, required for the hydrogenolysis of a dodecylaldehyde–dimethylamine adduct to the final product, DMTA, was effectively supplied by the dehydrogenation of a starting dodecyl alcohol itself, and that the generated active hydrogen was effectively consumed for the hydrogenolysis step. We named the basic phenomenon, typically observed for Cu/Ni-based catalyst in a colloidal state stabilized by barium stearate, as "Self-supplying system for active hydrogen". In previous articles on one-pot amination of fatty alcohols with dimethylamine using Cu/Ni-based solid catalyst [5,7], this basic phenomenon typical of Cu/Ni-based catalyst was; not presented nor discussed.

3.3. *Demonstration of self-supplying system for active hydrogen in a commercial plant*

Existence of the self-supplying system for active hydrogen was also observed in a commercial plant operated using the Cu/Ni/Ba colloidal catalyst from 1981. Table 2 shows an example of amount of starting materials charged for commercial production of a DMTA.

The amination reaction was completed in 4 h. Total hydrogen, charged during one-pot amination of dodecyl alcohol with DMA using Cu/Ni/Ba colloidal catalyst in a commercial plant, was only 0.29 eq. Alcohol conversion and an amine yield were 99.5% and 90.0%, respectively. If the amination reaction was conventional reductive amination of dodecylaldehyde, at least one equivalence of hydrogen had to be required. Therefore, this commercial plant based experiment also showed that hydrogen generated by dehydrogenation of dodecyl alcohol was effectively consumed for the hydrogenolysis of a dodecylaldehyde–dimethylamine adduct. From these observations and those in 3.2, it was concluded that self-supplying system for active hydrogen based on dehydrogenation of a starting alcohol itself over over copper does exist. This essential phenomenon for one-pot amination of alcohols was clearly observed when using Cu/Ni-based catalyst in a colloidal state (highly dispersed nanoparticles), and this is one of basic differences from Cu/Ni-based solid catalyst in terms of catalytic activity It will be presented in 3.8 (figure 9).

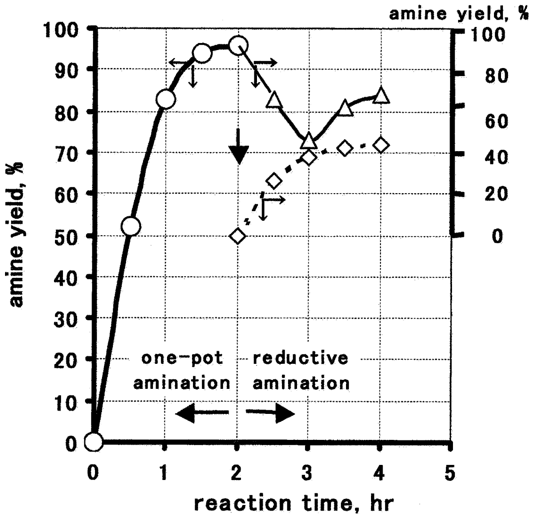


Figure 2. Reductive amination of dodecylaldehyde with dimethylamine.

Table 2
Demonstration of the existence of self-supplying system for active hydrogen by a commercial plant

Materials	Charged amount (kg-mole)	Equivalence
Dodecyl alcohol	5763 Kg (31.0)	1.00
Dimethyl amine	1903 Kg (42.3)	1.36
Hydrogen	222 Nm^3 (9.1)	0.29

Catalyst materials: strearates of copper, nickel and barium; Cu:Ni:Ba = 5:1:1; Cu conc., 1000 ppm vs dodecyl alcohol; reaction temp., 210 °C; reaction time, 4 h.

3.4. *Reductive amination of dodecylaldehyde with dimethylamine using Cu/Ni/Ba colloidal catalyst*

To further confirm the existence of self-supplying system for active hydrogen, conventional reductive amination of dodecylaldehyde, which carries no active hydrogen like dodecyl alcohol, was performed using Cu/Ni/Ba colloidal catalyst under the continuous charging of hydrogen and DMA at normal pressure, and it was compared with one-pot amination of dodecyl alcohol. A reaction mixture prepared by one-pot amination of dodecyl alcohol was used as a reaction solvent for reductive amination of dodecyl aldehyde, and dodecylaldehyde was charged at one time or continuously. The result is shown in figure 2 and table 3.

In the figure, one-pot amination of dodecyl alcohol (charged, 150 g) was performed and completed with a conversion of 98.9% (see table 3) for the initial 2 h, and then reductive amination of dodecylaldehyde (charged 150 g) was performed for the following 2 h. Dotted line indicates one time addition of the aldehyde, and a solid line after two hours indicates the continuous addition of the aldehyde at 3.0 ml/min (0.82 mol/h). ↓ indicates the addition of the aldehyde at one time. DMA and hydrogen were fed at 21–22 NL/h; and 18 NL/h, respectively. It can be seen from the figure and table that for reductive amination of dodecylaldehyde, added at one time (dotted line), an amine yield gradually increased, but only to 42.7% with a conversion of 85.6% for 2 h.

Selectivity for DMTA was only 43.1%, and that for aldol was 25.6% which is much higher than that (0.04%) for one-pot amination of dodecyl alcohol. Dodecyl alcohol formed by hydrogenation of dodecylaldehyde was not detected apparently, because it might be consumed rapidly by one-pot amination. Didodecylmethylamine (DDMA) content was 17.5%, much higher than for one-pot amination of dodecyl alcohol. Reductive amination was completely stopped after two hours with a conversion of 85.6% probably by some poisoning due to adsorption of aldols. It can be understood from these observations that significant amount of by-products such as aldols and DDMA was formed in reductive amination of dodecylaldehyde added at one time. Initial reaction rate for amine formation was 44.5 mol/h/g-mole-Cu, one fourth of one-pot amination of dodecyl alcohol.

These observations demonstrated that there is an essential difference between one pot amination of

Table 3
Comparison of reductive amination of dodecylaldehyde and one-pot amination of dodecyl alcohol using Cu/Ni/Ba colloidal catalyst

	Conv. (%)	Amine yield (%)	DMTA (%)	Alc (%)	RCHO (%)	DDMA (%)	Aldol (%)	Wax z (%)	Initial amination rate (mol/h/mole-Cu)
<one-pot amination of dodecyl alcohol>									
	98.9	97.1	97.1	1.1	0	1.7	0.04	0.02	176.1
<reductive amination of dodecylaldehyde>									
RCHO charged									
at-one-time	85.6	42.7	43.1	0	14.4	17.5	25.6	0.22	44.5
continuously	100	79.5	80.1	0	0	8.5	11.8	0.32	–

All the data are based on those of figure 2; Cu:Ni:Ba = 5:1:1; Cu. cone., 10z ppm.

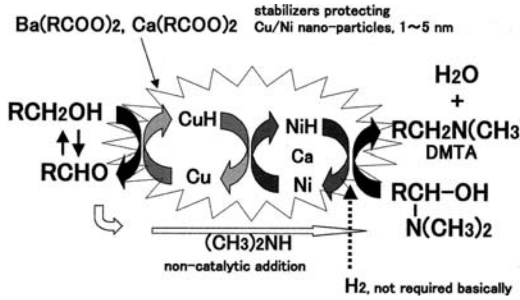
dodecyl alcohol containing active hydrogen with in a molecule and reductive amination of aldehyde having no active hydrogen within the molecule. On the other hand, when dodecylaldehyde was charged continuously (solid line from two hours) at 3.0 ml/min (0.82 mol/h), an amine yield was increased to 79.5% which is about twice of one time addition of the aldehyde.

Aldol content was decreased to 11.8% Which is less than half for one time addition of dodecylaldehyde, but the content is still much higher than that (0.04%) for one-pot amination of dodecyl alcohol. It was concluded from these observation that one-pot amination of dodecyl alcohol is essentially different from reductive amination of dodecylaldehyde in terms of a source for active hydrogen within a starting molecule. It was also concluded that in one-pot amination of dodecyl alcohol, synergism by the combination of copper and nickel is coupled with a source for active hydrogen in dodecyl alcohol, and it produced much higher efficiency than conventional reductive amination of dodecylaldehyde in the presence of hydrogen which has to be separately activated. More detailed studies on these difference may be performed in a future research, but our observations demonstrated the difference between one-pot amination of alcohols and reductive amination of aldehydes for the first time.

3.5. *Proposed catalytic cycle for one-pot amination of alcohols using*

From these essential observations and discussions on Cu/Ni-based catalyst in a colloidal state, we proposed a catalytic cycle in Scheme 1 for one-pot amination of alcohols with dimethylamine using Cu/Ni-based catalyst especially in a colloidal state stabilized by barium stearate, and named it as "Self-supplying System for Active Hydrogen" generated by the combination of Cu/Ni-based catalyst and alcohols which has a source for active hydrogen with the molecule.

The reaction system using Cu/Ni/Ba catalyst is homogeneous in terms of a reactant, active hydrogen and catalyst, which is completely different from heterogeneous catalytic reaction system. It can be said that in one-pot amination of alcohols,aldehydes as real reactants are produced as they are consumed, which prevents liberation of excess free aldehydes, resulting in significant decrease in byproducts such as aldols to increase objective product with a high yield (98% at maximum).



Scheme 1. Proposed catalytic cycle for one-pot amination of alcohols with dimethylamine using Cu/Ni/Ba colloidal catalyst.

After our original basic studies at the end of 70s [4,6], several articles on Cu/Ni-based catalyst for one-pot amination of fatty alcohols were published [5,7]. However, in these articles, there is no discussion on difference between one-pot amination of alcohols and reductive amination of aldehydes.

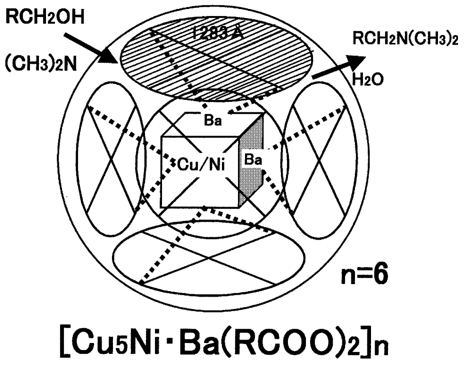
Present articles described existence of self-supplying system for active hydrogen and essential difference between one-pot amination of alcohols and reductive amination of aldehydes for the first time, and these basic observations by the combination of copper and nickel were patented early at the end of 70s [4,6].

3.6. *On the structure of Cu/Ni-based colloidal catalyst*

TEM images of Cu/Ni/Ca/Ba colloidal catalyst were reported elsewhere [9]. Cu/Ni nanoparticles with a diameter of 1 ~ 5 nm were observed, but coagulation of fine particles by ethanol precipitation was observed. In the present studies we reconsidered structure of the Cu/Ni-based nanoparticles stabilzed by stabilizers with a following optimum composition.

$$\mathrm{Cu}(0) : \mathrm{Ni}(0) : \mathrm{Ba}(\mathrm{RCOO})_2 = 5 : 1 : 1$$

$$\mathrm{Cu}(0) : \mathrm{Ni}(0) : \mathrm{Ca}(\mathrm{RCOO})_2 : \mathrm{Ba}(\mathrm{RCOO}) = 5 : 1 : 1 : 1$$



Scheme 2. A model structure for a Cu/Ni-based nanoparticle such as Cu/Ni/Ba and Cu/Ni/Ca/Ba Colloidal catalyst. Cu, Ni and Ca form fcc lattice resulting in alloy formation.

Simple calculation of number of metal atoms (Cu, Ni) based on a fcc lattice structure (cubic closest-packing) with an empty volume of 26%, for a Cu/Ni two-component nanoparticle with the optimum Cu/Ni mole ratio of 5:1 and a diameter of 1 nm, showed that a, Cu/Ni-based nanoparticle is a heptamer or octamer of a basic unit such as Cu/Ni/Ba$(RCOO)_2$ or Cu_5Ni/$Ca(RCOO)_2$/$Ba(RCOO)_2$. With an assumption of C_{2v} symmetry and a molecular size (25 Å) for barium stearate [12] existed on the surface of a Cu/Ni nanoparticle with a diameter of 1nm. apparent outer surface area of nanoparticle. $[Cu_5Ni/Ba(RCOO)_2]n$ ($n = 7$–8) was calculated to be 4874 Å^2. On the other hand, base area (indicated by shade in scheme 2) of a circular cone formed by free rotation of barium stearate molecule around the molecular axis was calculated to be 1283 Å^2. Therefore number of barium stearate molecule, which can be existed without steric hindrance on the surface of a Cu/Ni nanoparticle with a dameter of 1 nm, was estimated to be at least four (4874 Å^2/1283 Å^2). A model structure for a Cu/Ni-based nanoparticle stabilized by barium stearate is shown in scheme 2. In the scheme metallic copper and nickel have fcc lattice structure, therefore, they can form a binary alloy in any compositions. Furthermore, metallic calcium also has a fcc structure, therefore, formation of an alloy such as $CaNi_5$ as a hydrogen absorbing material also might be possible. Detailed characterization of separated Cu/Ni-based catalyst has to be performed in future for detailed understand in future for detailed understanding of structure.

3.7. *Other basic functions typical of Cu/Ni-base catalyst*

Here, we described other basic functions and characteristics of Cu/Ni-based catalyst observed especially in a colloidal state, a highly dispersed state of Cu/Ni-based nanoparticles.

3.7.1. *Optimization of Ni/Cu ratio for the catalytic system*

After finding SiO_2 and nickel stearate as additive to prevent sintering of reduced copper as a main catalyst for one-pot amination of fatty alcohols, we confirmed the importance of nickel to significantly increased catalytic activity, and performed optimization of copper/nickel stearates catalyst. For the two-component system in our original studies [4], amount of nickel stearate (g) was ranged from 0 to 3 g for a constant amount of cupric stearate (3.0 g, 4.77×10^{-3} mol) for 300 g (1.613 mol) of dodecyl alcohol to make dehydrogenation activity of copper constant. In a preceding publication [7] based on our original studies [4], Abe et al. also examined the effect of Ni/Cu ratio on catalytic activity by changing amount of nickel stearate and

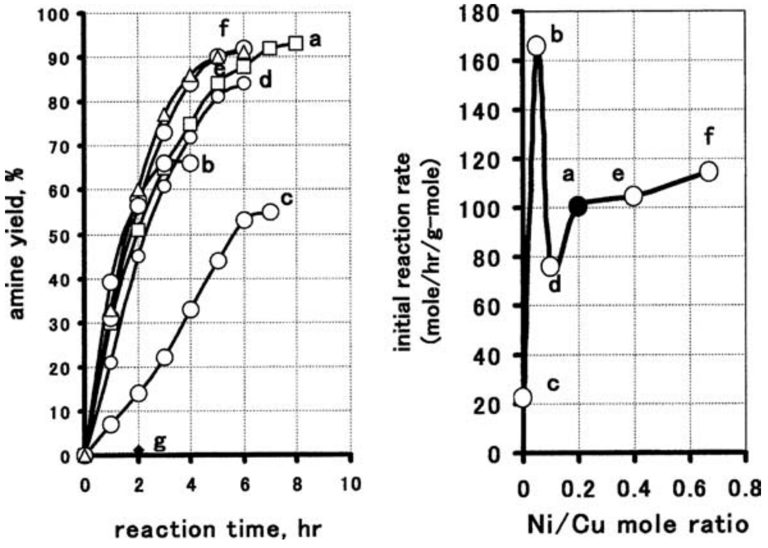


Figure 3. Effect of Ni/Cu mole ratio of copper/nickel stearates catalyst on catalytic activity for one-pot amination of dodecyl alcohol and dimethylamine. H2/DMA-feed rate, 60/18 NL/h.

cupric stearate at the same time at a constant total weight of the two stearate Therefore, it can be considered that in Abe's experiment, dehydrogenation activity by copper was different in each Cu/Ni-ratio. Our original results at a constant amount of cupric stearate obtained in 1977 [4] is shown in figure 3.

Ni/Cu mole ratio was ranged from 0 (c, reference) to 0.05 (b), 0.1 (d), 0.2 (a), 0.4 (e), 0.67 (f),and 0∞ (g, only nickel stearate). The left figure shows reaction profiles for each catalyst with different Cu/Ni mole ratio, and the right one shows dependence of initial reaction rate, expressed in mol/h/g-mole-Cu for amine formation, on Ni/Cu mole ratio. It can be seen from the left figure that cupric stearate without incorporation of nickel stearate (c) showed lower catalytic activity with serious sintering at 6 h, and only nickel stearate without incorporation of cupric stearate (g) showed no catalytic activity. It can be seen from the right figure that incorporation of small amount of nickel stearate with cupric stearate remarkably increased initial reaction rate (b), eight-fold higher than that for cupric stearate catalyst without incorporation of nickel stearate (c). However, as shown in the left figure, the amination reaction completely stopped at three hours by serious sintering with an amine yield of 66 (b). With further increase in Ni/Cu mole ratio, initial reaction rate once decreased (d), and then increased again, and amination reaction was completed with an amine yield of more than 90% (a, e, f). From these observations we selected 0.2 (a) for an optimum Ni/Cu mole ratio which gave an amine yield of 93% for 8 h, although Ni/Cu ratio of 0.05 (b) showed a higher initial activity.

In Abe's experiments, the point b in the right figure was not observed and Ni/Cu mole ratio of 0.36 showed a maximum activity and their optimum Ni/Cu ratio is located between (a) and (e) in figure 3.

Initial reaction rates for each Ni/Cu mole ratio were not presented [7]. It was concluded from these observations that incorporation of nickel stearate is important to increase catalytic activity.

3.7.2. Function of fatty acid residue for Cu/Ni stearates catalyst

What we thought next is the significance of fatty acid residue of the stearate catalyst. The simple question forced the authors to investigate the function of free stearic acid by using acetylacetonates of copper and nickel as catalyst materials and stearic acid instead of using stearates of copper and nickel. Effect of free stearic acid on catalytic activity of mixed acetylacetonates of copper and nickel is shown in figure 4.

Function of stearic acid in Cu/Ni-based colloidal catalyst. dodecylalcohol 300 g; Cu conc. 2000 ppm vs alcohol; H2/DMA-feed rate 60/18 NL/h;reaction temp, 210 °C.

The left figure shows reaction profiles for various amount of stearic acid added, and the right one was ranged from 0 (a) to 0.5 (b), 1.0 (c), 2.0 (d), 4.0 (e), 6.0 (t) for a mixture of cupric acetylacetonate (2.5 g) and nickel acetylacetonate (0.25 g), and the corresponding mole% of stearic acid vs cupric acetylacetonate were 0, 19, 37, 73, 146 and 220, respectively. It can be seen from the figure that mixed acetylacetonates of copper and nickel without adding stearicacid showed no catalytic activity (a). However, when amount of stearic acid. was increased from 0 to 19 mol% (b), dark reddish active colloidal catalyst, as obtained when using stearate of copper and nickel, was produced and amination reaction was effectively proceeded. It can be seen from the right figure that initial amination rate was remarkably increased by incorporation of stearic acid (b). Further increase in amount of stearic acid significantly increased

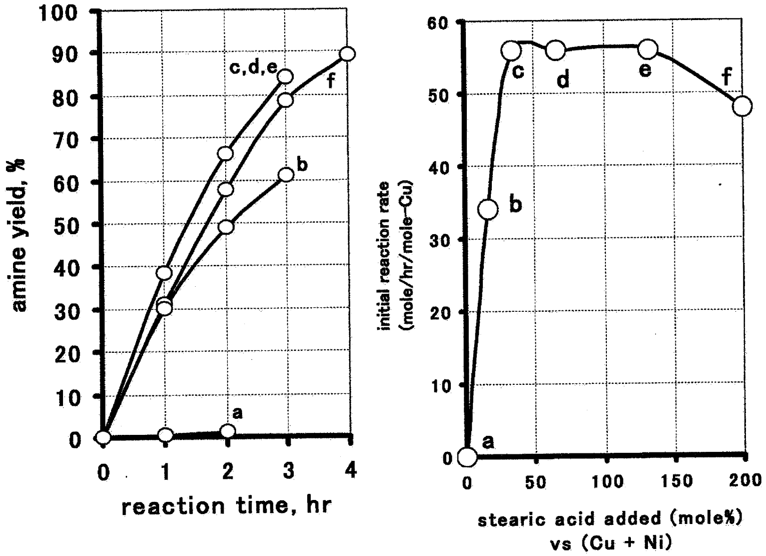


Figure 4. Function of stearic acid in Cu/Ni-based colloidal catalyst. Cu conc. 2000 ppm vs alcohol; H2/DMA-feed rate 60/18 NL/h.

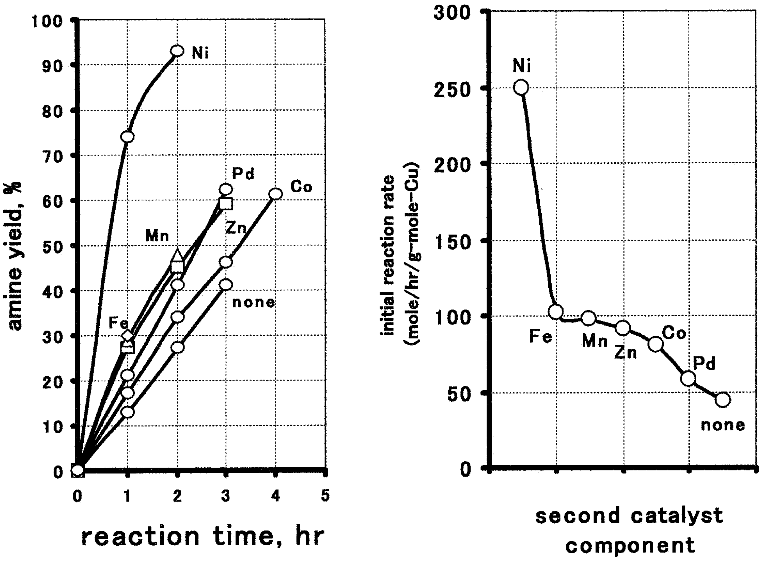


Figure 5. Optimization of a second catalyst component. Cu:second catalyst component:Ba mole ratio = 5:1:1.

catalytic activity, and a maximum catalytic activity was obtained at a stearic acid mole% of 37 (c). However, further increase in stearic acid did not show higher catalytic proceeded activity, and then catalytic activity was decreased slightly (f), It was understood from these observations that a mixture composed of acetylacetpnates of copper and nickel also can be used as effective catalyst materials as long as sufficient amount of stearic acid is incorporated.

It was concluded from these observations that stearic acid is an indispensable catalyst component, and that it functions as a stabilizer to prevent copper sintering or coagulation of the Cu/Ni two-component nanoparticles. However the following question arose. "Free stearic acid separately added will be consumed by esterification with starting alcohols existed in excess, resulting in complete consumption of the stabilizer followed by deterioration of the Cu/Ni-based colloidal catalyst finally" This simple question forced the author to use stearic acid as a salt of alkali or alkali-earth metal ions which are not reduced under the reducing amination conditions for their standard electrode potential of about −2.8 V. This is the way how the Cu/Ni-based catalyst stabilized by barium, stearate was developed [4]

3.7.3. Optimization of a second catalyst component

For detailed optimization of a second catalyst component (*co-catalyst*) for the catalytic system, effect of incorporation of various VIII-group metal stearates with Cu/Ba colloidal catalyst on catalytic activity was investigated. As second catalyst components, manganous stearate, ferric stearate, zinc stearate, cobaltous stearate palladium, acetylacetonate were used. The result is shown in figure 5. Left figure shows reaction profiles when using Cu/Ba colloidal catalyst incororated by one of the various second catalyst components. Right figure shows comparison of initial reaction rate for each three-component catalyst.

It can be seen from the figure that nickel stearate showed the highest activity. It was concluded that nickel is the best land indispensable second catalyst component. Incorporation of one of stearates of Mn, Fe, Co, Zn also increased catalytic activity to some extent, but catalytic activity was much lower than that of Cu/Ni based catalyst. Incorporation of palladium, acetylacetonate, instead of nickel stearate, did not show higher catalytic activity than Cu/Ni/Ba catalyst. When silver laurate was used instead of cupric stearate, catalytic activity of Ag/Ni/Ba colloidal catalyst was one fourth of Cu/Ni/Ba catalyst.

It was concluded from these observations that copper and nickel form the only one combination for the catalytic system which gives the highest catalytic activity.

3.7.4. Optimization of the Cu/Ni-based catalytic system stabilzed by barium stearate

Optimization of the Cu/Ni/Ba colloidal catalyst was performed finally. The result is shown in Figure 6.

The left figure shows the optimization of nickel stearate and barium stearate for the copper-based colloidal catalyst. The right one show the significant increase in catalytic activity by incorporation of nickel stearate and barium stearate with cupric stearate, and comparison with copper–chromite catalyst. It can be seen from the left figure that optimum mole ratio of Cu/Ni/Ba colloidal catalyst was Cu:Ni:Ba = 5:1:1 in our studies at the end of 70s [4,6], and same result was obtained by Abe's additional experiment based [7] on our original research. Initial reaction rate for Cu/Ni/Ba, Cu/Ni, Cu/Ba and Cu colloidal catalyst in the right figure were 250, 122, 44 and 27 mol/h/-mole-Cu, respectively, for amine formation. Catalytic activity of

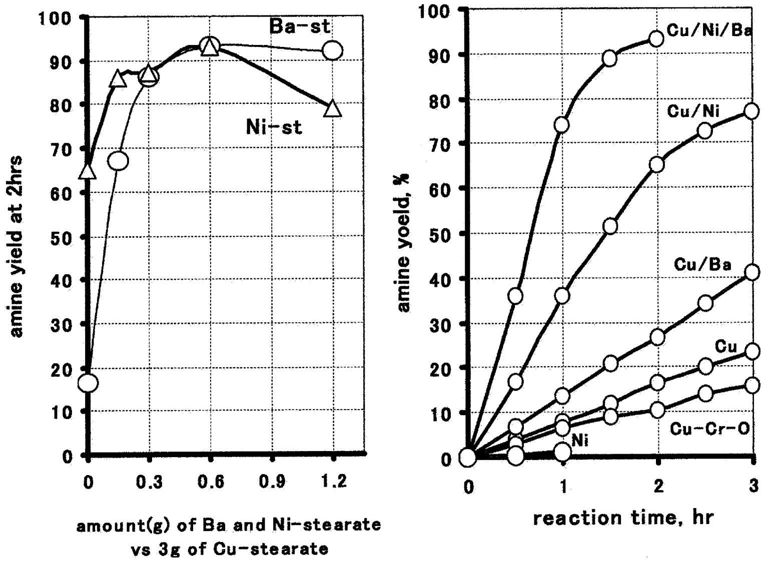


Figure 6. Optimization of the Cu/Ni/Ba stearate catalyst.

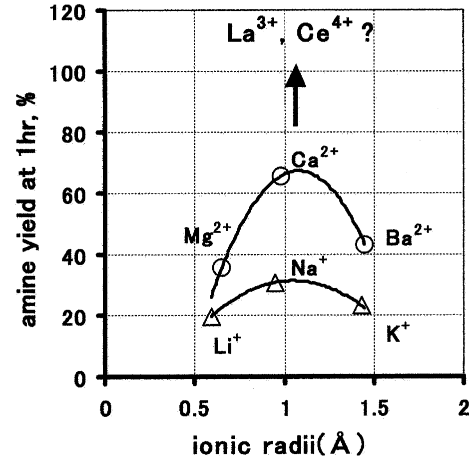


Figure 7. Dependence of catalytic activity of Cu/Ni-based catalyst on ion of stabilizers in one-pot amination of low reactive DIADOL-135 (oxo-alcohol) with dimethylamine. Reprint from figure 3 of. ref. [9].

Table 4
Catalytic activity of copper-based colloidal catalysts incorporated by calcium stearate for one-pot amination of DIADOL-135 with dimethylamine

	Initial amination rate(mol/h/g-mole-Cu)	
Catalysts	Normal-isomers	Branched-isomer
Cu/Ni/Ca/Ba	175	143
Cu/Ni/Ca	160	129
Cu/Ni/Ba	114	34
Cu/Ni	93	32

cupric stearate catalyst was ten-fold increased by incorporation of Ni as dehydrogenation catalyst and barium stearate as a stabilizer for the Cu/Ni-based nanoparticles (1–5 nm).

3.8. *On stabilizers, key components for Cu/Ni-based catalyst in a colloidal state*

In development of Cu/Ni/Ba colloidal catalyst for one-pot amination of dodecyl alcohol (straight-chain alcohol), difference in performance of stabilizers such as stearates of alkali and alkali-earth metals was not clearly observed. However, significant difference was observed, for the first time, in one-pot amination of low reactive oxo-alcohols such As. DIADOL-135 produced by Mitsubishi Kagaku in Japan, and it was published elsewhere [9]. Figure 3 of ref. [9] is shown in figure 7 with proposed ions for another advanced stabilizers. The figure indicates that divalent ions (alkali-earth) produced two-fold higher performance than monovalent ions (alkali metal), and that metal ions such as Ca^{2+} and Na^{+}, both of which have an ionic radii of 1 Å, produced highest performance in each metal group. Therefore, it was considered that lanthanide ions such as La^{3+} and Ce^{4+} might produce much higher activity for Cu/Ni-based colloidal catalyst, because they also have an ionic radii of about 1 Å and that standard electrode potential (E^{0}_{25}, a measure of non-reducibility) of La^{3+} and Ce^{4+} are −2.52 and −2.48 V, respectively, which are comparable to those of Ca^{2+} (−2.87 V) and Na^{+} (−2.71 V).

It was also considered that the higher a valence state of a metal ion of a stabilizer is, the more the number of fatty acid residue of a stabilizer is, which might produce higher stability for finer nanoparticles, resulting in much higher catalytic activity for Cu/N-based catalyst. These will be investigated in future studies.

Anyway, it should be noted that incorporated of calcium stearate with Cu/Ni produced remarkable increase in catalytic activity. For one-pot amination of DIADOL-135 (branched isomers, 50%) with dimethylamine, initial reaction rates for several amination of

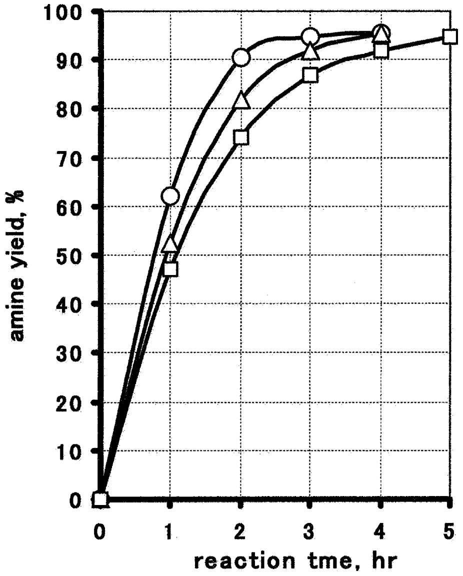


Figure 8. Catalytic activity of Cu/Ni/Ca/Ba colloidal catalyst for one-pot amination of dodecyl alcohol with dimethylamine. ○, (Cu, 200 ppm, 220 °C); △, (Cu, 200 ppm, 210 °C); □ (Cu. 100 ppm, 220 °C).

normal-isomers and branched isomers were estimated for several Cu/Ni-based catalyst. The results are shown in table 4.

It can be understood from the table that by incorporation of calcium stearate with Cu/Ni, initial reaction rate especially for the amination of branched isomers was remarkably increased, four-fold higher than Cu/Ni/Ba colloidal catalyst, and at further increase in catalytic activity is obtained by additional incorporation of barium stearate as a stabilizer. figure 8 shows application of Cu/Ni/Ca/Ba colloidal catalyst [9] for one-pot amination of dodecyl alcohol and dimethylamine.

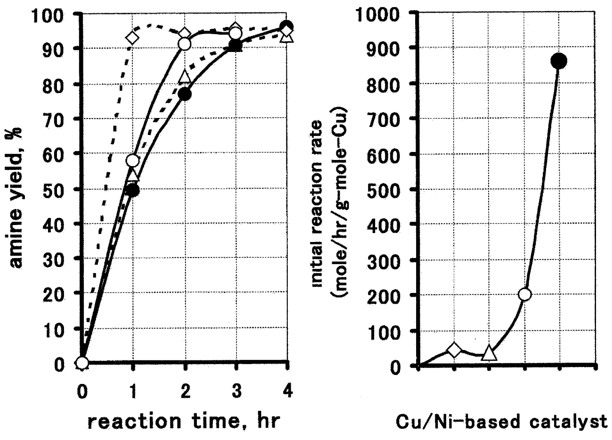


Figure 9. Comparison of catalytic activity of Cu/Ni-based catalyst in colloidal state and a solid state for one-pot amination of dodecyl alcohol and dimethylamine. ●, Cu/Ni/Ca/Ba(Cu, 200 ppm); ○, Cu/Ni/Ba(Cu, 1000 ppm); △, Cu/Ni/SiO_2(Cu, 5000 ppm)[2]; □, Cu/Ni/Zn/$CaCO_3$(7300 ppm)[5b]. reaction temp, 210 °C. For Cu/Ni/Zn/$CaCO_3$, reaction temp is 220 °C.

It can be seen from the figure that amination reaction was completed with a copper concentration of only 100–200 ppm. A maximum amine yield of 98% was obtained at a Cu concentration of 200 ppm and 210 °C. The lower the catalyst concentration is, the higher an amine yield is. Initial reaction rate for the amintion reaction using Cu/Ni/Ca/Ba [9] and Cu/Ni/Ba colloidal catalyst were 1700 and 340 mol/h/mole-Cu, respectively, and catalytic activity of Cu/Ni/Ca/Ba colloidal catalyst was five-fold higher than Cu/Ni/Ba colloidal catalyst in one-pot amination of normal chain alcohols.

Comparison of catalytic activity of Cu/Ni-based colloidal catalyst and Solid ones, Cu/Ni/SiO_2 [2] and Cu/Ni/Zn/CaC03 [5b] for one-pot amination of dodecyl alcohol and dimethylamine is shown in figure 9. Left figure shows reaction profiles and right one shows comparison of initial reaction rate for these catalysts. It can be seen from the right figure that Cu/Ni-based catalyst in a colloidal state showed remarkably higher activity than that of solid ones, which demonstrated that colloidal state, or a highly dispersed state, directly relates with higher catalytic activity. Especially, catalytic activity of Cu/Ni/Ca/Ba colloidal catalyst was extremely higher These observations demonstrated the significance of incorporation of calcium stearate with Cu/Ni-based catalyst especially in a colloidal state. Calcium stearate in Cu/Ni/Ca/Ba colloidal catalyst was partially reduced in amination reaction, which was observed in the development of Cu/Ni/Ca/Ba colloidal catalyst [9], and this is a reason why barium stearate was additionally incorporated to produce higher stability for the catalytic system.

Corresponding effect was not observed for corresponding solid catalyst by incorporation of calcium stearate. It was considered that in colloidal catalytic system, catalyst materials are activated in a homogeneous state, resulting in the formation of reduced state of Ca^{2+} [9] as well as Ni^{2+} [7,14] probably catalyzed by reduced copper. However, it can be considered that for solid catalyst, reduction of these elements is not easy in a heterogeneous state, and are existed mainly in an oxidized state [5,7] The authors think that a hydrogen absorbing alloy such as $CaNi_5$ might be formed in a reducing amination conditions, and that it might strengthen "Self-supplying system for active hydrogen" produced by the combination of copper and nickel. All of nickel, copper, calcium and cerium have fcc lattice structure in a metallic state, so they can form alloys in any combinations. Therefore, it can be thought that incorporation of lanthanides such as La^{3+} or Ce^{4+} especially in a colloidal state might produce much higher catalytic activity than Cu/Ni/Ca/Ba in terms of higher valence and possibility for formation of hydrogen absorbing alloy. Detailed studies have to be performed in future.

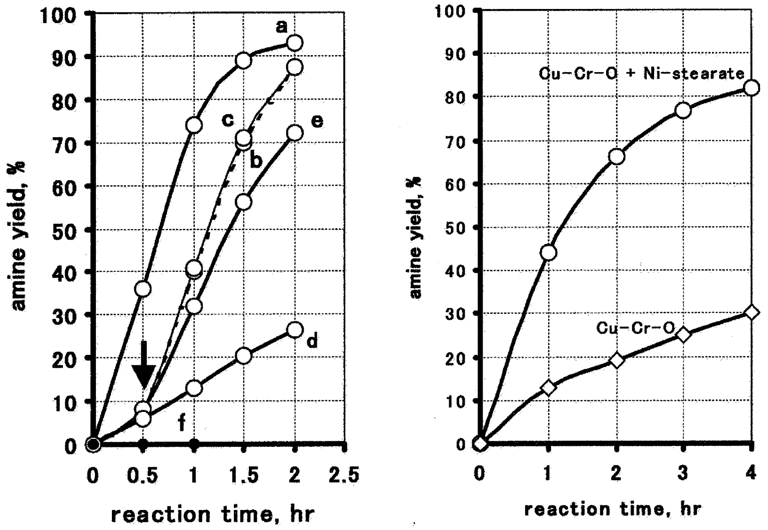


Figure 10. Effect of addition of nickel stearate during amination of dodecyl alcohol and dimethylamine. left figure:colloidal catalyst, Cu, 1000 ppm, Cu:Ni:Ba = 5:1:1. (a) nickel stearate(reference); (b) nickel acetylacetonate; (c) nicke stearate; (d) none (cupric stearate only); (e) nickel dimethylglyoxime; (f) nickel dimethyldithiocarbamate. The arrow indicates the addition point of a nickel component. Right figure: solid catalyst, Cu 5000 ppm; ○, copper-chromite + nickel stearate; ◇, copper-chromite, copper-chromite + Ni/SiO_2.

3.9. Effect of additional Ni-component during amination reaction

Effect of addition of Ni-component during one-pot amination of dodecyl alcohol and dimethylamine is shown in figure 10.

Effect of addition of nickel stearate during amination of dodecyl alcohol and dimethylamine. Left figure: colloidal catalyst. Cu, 1000 ppm. Cu:Ni:Ba = 5:1:1. a, nickel stearate (reference); b; nickel acetylacetonate; (c), nickel stearate; (d), none (cupric sterte only); (e), nickel dimethylglyoxime; (f), nickel dimethyldithiocarbamate. The arrow indicates the addition point of a nickel component. right figure: solid catalyst, Cu 5000 ppm; ○, copper-chromite + nickel stearate; ◇, copper-chromite, copper-chromite + Ni/SiO_2.

Left figure shows effect of addition of nickel stearate at half an hour after starting the amination using Cu/Ba colloidal catalyst without nickel-component (b,c,e), and right figure shows effect of incorporation of nickel stearate with copper-chromite catalyst and that of incorporation of NiO/SiO_2 with copper-chromite. It can be seen from the left figure that catalytic activity of Cu/Ba colloidal catalyst was significantly increased immediately after-addition of nickel inner complexes such as nickel-acetylacetonate (b), nickel-dimethylglyoxime (e) as well as nickel stearate (c). Initial reaction rate for the amination reaction after adding Ni-component was comparable to that of a reference (a) in which a mixture of three stearates of copper, nickel and barium was activated at the same time. For nickel-dimethyldithiocarbamate (f), colloidal catalyst was not formed and catalytic activity was not observed at all, because sulfur of the carbamate is one of catalyst poison for Cu/Ni-based catalyst. It was concluded from these observations that active specie of the Cu/Ni-based catalyst is easily produced in a colloidal state immediately after the addition of a nickel component. On the other hand, it can be seen from the right figure that incorporation of nickel stearate as a mechanical mixture increased catalytic activity of copper-chromite catalyst more than four-fold. However, when nickel oxide supported on SiO_2 was added to copper-chromite catalyst, significant increase in catalytic activity was not observed at all. It was concluded from this observation that a nickel adatom structure or a Cu/Ni alloy may be formed on a surface of reduced copper immediately after *in-situ* reduction of nickel stearate catalyzed by reduced copper. These observations indicate structural information of Cu/Ni-based catalyst, therefore, detailed characterization is required for detailed understanding of structure of Cu/Ni-core in the catalytic system.

4. Conclusions

One-pot amination of dodecyl alcohol with dimethylamine using Cu/Ni/Ba colloidal catalyst proceeded without charging bulk hydrogen with an amine yield of more than 90%, which indicates the existence of "Self-supplying system for active hydrogen" based on dehydrogenation of a starting alcohol over reduced copper. However, in reductive amination of dodecylaldehyde using the same catalyst, a lower amine yield (40–80%) was obtained with significant formation of aldols. Essential difference between one-pot amination of alcohols having active hydrogen and reductive amination of aldehydes was demonstrated for the first time. Combination of cupper for dehydrogenation and nickel for hydrogenolysis especially in a colloidal state was essential for effective generation of the synergism. Remarkable performance by incorporation of calcium in one-pot amination of normal-chain alcohols and superiority of colloidal catalyst over corresponding solid catalyst in catalytic activity was demonstrated for the first time.

In-situ characterization of the Cu/Ni/Ca/Ba catalytic system and its theoretical consideration are required in future studies for detailed understanding of the function of calcium and for further advancement of the Cu/Ni-based catalyst. Finally, importance of stabilizers as key components for increased catalytic activity of Cu/Ni-based colloidal catalyst was discussed.

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