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Cu/Ni colloidal dispersions stabilised by calcium and barium stearates for the amination of oxo-alcohols

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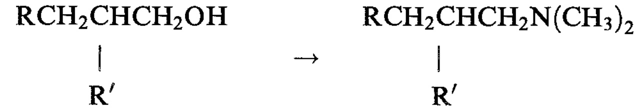
Bimetallic Cu/Ni colloidal dispersions (the core catalyst) stabilised by a combination of calcium and barium stearates as protective colloids (catalyst C) showed a remarkable catalytic activity – several times higher than that of the core catalyst stabilised by barium stearate only (catalyst A) – for the amination reaction of low reactive oxo-alcohols, having steric hindrance by branched alkyls, with dimethylamine to prepare N,N-dimethyl tertiary amines. Application of the catalyst C for the same amination reaction of dodecyl alcohol could be performed at a lower catalyst concentration of even 100 ppm based on copper at 220°C with a tertiary amine yield of 92% in a three hours' reaction. The reaction mixture containing catalyst C formed a gel at room temperature and formed a stable homogeneous solution with acetone as a polar solvent. It is postulated that water-repellency of calcium stearate and further incorporation of barium stearate as a second promoter yields a doubly stabilised structure for the core catalyst resulting in a remarkable increase in catalytic activity.

Keywords: Cu/Ni colloidal dispersion; barium stearate; calcium stearate; protective colloid; amination of oxo-alcohols; tertiary amine

1. Introduction

The development and application of bimetallic Cu/Ni colloidal dispersions (the core catalyst) stabilised by carboxylates of alkali or alkali earth metals, especially barium stearate as an effective protective colloid (catalyst A), for the amination reaction of fatty alcohols with dimethylamine (DMA) and the superiority of the catalyst A (Cu/Ni/Ba colloidal catalyst) over the conventional copper based solid catalysts, such as copper chromite, were originally patented in 1978 [1,2] and enabled the industrial application of the catalyst A for the alcohol based direct production of N,N-dimethyl-long-alkyl tertiary amines, important intermediates for surface active agents. Later, the catalytic activity and some characterisation of catalyst A were reported [3]. In the initial stage of catalyst development using straight chain alcohols, the difference in performance among stearates of alkali (Na) and alkali earth metals (Mg, Ca, Ba) as protective colloids was found to be small. However, the low reaction rate (long reaction time) observed when using catalyst A for the same amination reaction of synthetic oxo-alcohols containing branched alkyls functioning as steric hindrances, forced the authors to reinvestigate the catalytic system, especially the protective colloids controlling the stability of the core catalyst. The present study describes how the new catalytic system (catalyst C), with the core catalyst stabilised by a combination of calcium and barium stearates, for the amination reaction of oxo-alcohols with DMA was developed and shows its superiority over the catalyst A. A TEM observation of catalyst C and its proposed structure is also presented.



$$RCH_2\underset{\underset{R'}{|}}{C}HCH_2OH \rightarrow RCH_2\underset{\underset{R'}{|}}{C}HCH_2N(CH_3)_2$$

oxo-alcohol, $R' = C_1{-}C_7$

2. Experimental

2.1. Materials

Synthetic oxo-alcohols for the amination reaction with DMA were DIADOL-135 from Mitsubishi Chemical Corporation, OXOCOL-1415, 1215 and 1213 from Nissan Chemical Industries and DOBANOL-25 from Mitsubishi Petrochemical Company Limited. KALCOL-20 of Kao's dodecyl alcohol (linear alkyl) was used as a reference. Oxo-alcohols were composed of branched and linear isomers and showed some distribution in chain length. The hydroxy value (OHV), the content of branched isomers and the chain length of the oxo-alcohols used for the amination reaction are listed in table 1 with the calculated maximum tertiary amine values (Ter.AmV_{100}) corresponding to a 100% yield based on OHV. In catalyst development DIADOL-135, which showed the highest content of branched isomers and the lowest reactivity among the five oxo-alcohols, was used. Cupric stearate was purchased from Tokyo

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Table 1
Commercially available oxo-alcohols for amination reaction

Oxo-alcohols	Chain length	Content of branched isomers (%)	OHV	Calculated max. tertiary amine values based on OHV (Ter.AmV$_{100}$)
DIADOL-135	C_{13}, C_{15}	50	261.9	232.6
OXOCOL-1415	C_{14}, C_{15}	40	252.6	225.2
OXOCOL-1215	C_{12}–C_{15}	40	273.5	241.7
OXOCOL-1213	C_{12}, C_{13}	40	290.3	255.7
DOBANOL-25	C_{12}–C_{15}	20	270.7	240.5
dodecyl alcohol	C_{12}	0	300.0	262.2

Chemical Industry Co. Limited and was recrystallised from dioxane three times before use. Nickel stearate, barium stearate and calcium stearate were purchased from Tokyo Chemical Industry Co. Limited and were used as obtained. Liquefied DMA was purchased from Nitto Kagaku, and hydrogen from Kaito Sangyo.

2.2. Reaction setup

The reaction setup is shown in fig. 1. A 1 ℓ four-neck round bottom flask equipped with a stirrer, a temperature indicator and controller, inlet and outlet lines for DMA gas and hydrogen gas, flow meters for DMA and hydrogen gases and a condensor to separate oily materials and reacted water were used. Liquid DMA stored in an autoclave was used as the DMA source.

2.3. Reaction method

A typical reaction method will be described for the bimetallic Cu/Ni colloidal dispersion stabilised by the combination of calcium and barium stearate (catalyst C). 300 g of a starting alcohol, 3.0 g of cupric stearate (0.30 g based on Cu), 0.60 g of nickel stearate (0.056 g based on Ni), 0.60 g of calcium stearate and 0.60 g of barium stearate at an optimum mole ratio (Cu : Ni : Ca : Ba = 5.00 : 1.01 : 1.04 : 0.89) were charged to the reactor. 3.0 g of cupric stearate and 0.6 g of nickel stearate is the optimised standard composition for the bimetallic Cu/Ni colloidal dispersion, the core catalyst in the present study. This composition of catalyst sources for 300 g of starting alcohol was used in the present study unless otherwise noted.

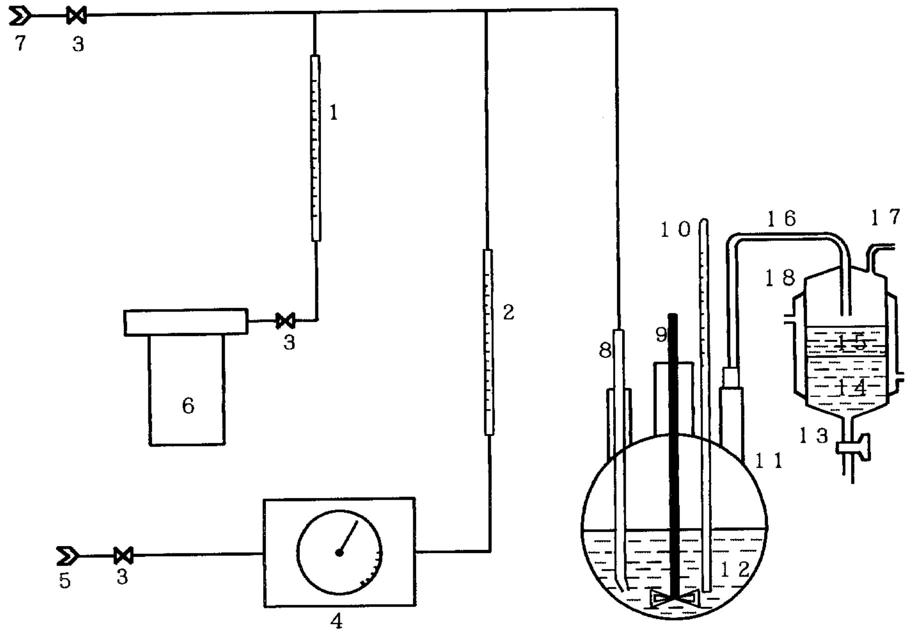


Fig. 1. Reaction setup. (1) Gas flow meter for dimethylamine; (2) gas flow meter for hydrogen, (3) valve, (4) integrated gas flow meter, (5) hydrogen source, (6) dimethylamine container, (7) nitrogen source, (8) inlet of mixed gas, (9) stirrer, (10) thermometer, (11) 1 ℓ four-neck flask, (12) reaction mixture containing alcohol and catalyst, (13) stopper, (14) reacted water, (15) oily materials (a part of the reaction mixture), (16) outlet of reacted gas and reaction mixture, (17) outlet of reacted gas, (18) condensor.

Heating was performed to achieve a reaction temperature of 210°C under a hydrogen flow of 30 ℓ/h at atmospheric pressure and a stirring rate of 1000 rpm. During heating the metal carboxylates were completely dissolved to a greenish blue homogeneous alcohol solution. The greenish blue color characteristic of Cu^{2+} began to change from about 150°C to pale green → pale yellow → colorless and, finally, instantly turned to reddish brown showing that reduction of Cu^{2+} to Cu^0 through Cu^+ has proceeded by hydrogen. A homogeneous bimetallic Cu–Ni colloidal dispersion stabilised by both calcium and barium stearate as protective colloids (catalyst C) was thus prepared in situ in the reaction mixture. DMA was fed as a mixed gas with hydrogen at a flow rate of 26 ℓ/h at atmospheric pressure. The hydrogen flow rate was kept at 30 ℓ/h. The total gas flow rate was 56 ℓ/h. Samples of the reaction mixture were taken from the reactor every hour and analysed.

2.4. Analysis of a reaction mixture

Oxo-alcohols have complex compositions due to the distribution in chain length and existence of branched isomers. This resulted in some difficulties in applying gas-chromatography for the estimation of the composition of a reaction mixture containing unreacted alcohols and formed amines. Therefore an absolute content of formed amines, expressed by "amine values", was evaluated by the conventional acid–base titration method using HCl. The "total amines value" (To.AmV) was defined as the sum of all the amines (primary, secondary and tertiary) in a unit weight (1 g) of a sample and was expressed in a KOH weight (mg) which was equivalent to the amount of hydrochloric acid needed to neutralise the amines. The "tertiary amine value" (Ter.AmV), which showed the content of only tertiary amines in a sample, was obtained after masking of primary and secondary amines by acetylation. These two amine values, To.AmV and Ter.AmV, were used to estimate amine yields and tertiary amine yields.

For estimation of amine yields, To.AmV divided by the calculated maximum tertiary amine value corresponding to a 100 yield (Ter.AmV_{100}, based on OHV of the starting alcohols in table 1) and multiplied by 100 was used:

$$\text{amine yield (\%)} = \text{To.AmV}/\text{Ter.AmV}_{100} \times 100\,. \quad (1)$$

Eq. (1) also shows the initial yield (%) of objective tertiary amines, because primary and secondary amines as by-products due to disproportionation of DMA were less than 1% in the initial stage of the amination reactions. In calculation of the precise yields of the objective N,N-dimethyl-long-alkyl tertiary amines, the mono-alkyl components were separated by distillation and an Ter.AmV of the distillate and the distillation yield (wt%) were used as follows:

$$\text{tertiary amine yield (\%)} = \text{Ter.AmV}/\text{Ter.AmV}_{100} \times \text{distillation yield (wt\%)}\,. \quad (2)$$

These two values were used in the following discussion.

2.5. Separation of the colloidal catalyst C from a reaction mixture

Separation of a homogeneous colloidal catalyst from a reaction mixture is generally difficult. However, the Cu/Ni based colloidal catalyst in a reaction mixture was separated by precipitating with polar solvents, such as methyl alcohol, ethyl alcohol and acetone. In the case of methyl alcohol a black sponge-like material was observed at the bottom of the sample tube. In the case of ethyl alcohol a dark purple, very light precipitate was floating in the mixture. In the case of acetone a reddish brown stable homogeneous solution was obtained and catalyst separation was not observed. Therefore, methyl alcohol and ethyl alcohol were selected as precipitation solvents for the colloidal catalyst. The precipitated catalysts were washed with the solvents ten times by decantation and dried under nitrogen flow.

3. Result and discussion

3.1. Catalytic activity of a Cu/Ni core catalyst stabilised by barium stearate (catalyst A) for the amination of oxo-alcohols with DMA

Catalytic activity of a Cu/Ni core catalyst stabilised by barium stearate (catalyst A) was examined for the amination reaction of the three oxo-alcohols (DIADOL-135, OXOCOL-1213 and DOBANOL-25) and dodecyl alcohol as a reference. Branched isomer contents of the four alcohols were 50, 40, 20 and 0%, respectively. The result is shown in fig. 2. It is obvious

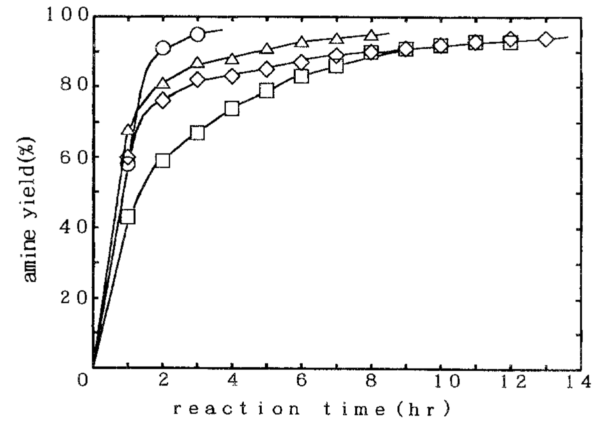


Fig. 2. Catalytic activity of the catalyst A for commercially available oxo-alcohols. (□) DIADOL-135, (◇) OXOCOL-1213, (△) DOBANOL-24, (○) dodecyl alcohol.

from this figure that after 1 h, the reaction rate of the oxo-alcohols gradually decreased and the order of their reactivities coincided with that of their contents of branched isomers. Dodecyl alcohol, a linear alcohol, was most reactive with a reaction time of 3 h. Among the oxo-alcohols investigated DIADOL-135 showed the maximum content of branched isomers, 50%, and showed the longest reaction time. For the oxo-alcohols, initially the contained linear isomers reacted mainly. Therefore the initial reaction rates were comparable to that of dodecyl alcohol. However, after 1 h the reaction rate decreased to 1/16–1/50 of the initial value due to the reaction of the branched isomers. It was concluded from these observations that the reaction rate depends on the content of branched isomers and that catalyst A shows insufficient activity (longer reaction time) for the amination reaction of oxo-alcohols. Therefore the development of the new catalytic system was performed using the lowest reactive DIADOL-135. Before catalyst screening using DIADOL-135, the effect of chain length of barium carboxylate (stearyl and behenyl) and the effect of the added amount of nickel stearate and the catalyst amount were examined for catalyst A, but none of them showed significant difference in catalytic activities.

3.2. Comparison of stearates of Li^+, Na^+, K^+ as alkali metals and Mg^{2+}, Ca^{2+} and Ba^{2+} as alkali earth metals as protective colloids

For the Cu/Ni core catalyst, the stability of the catalytic system was the key factor controlling the catalytic activity. Therefore the performances of stearates of alkali metals (Li^+, Na^+, K^+) and alkali earth metals (Mg^{2+}, Ca^{2+}, Ba^{2+}) as protective colloids were compared using DIADOL-135. Fig. 3 compares the initial catalytic activities at 1 h for each protective colloid. It shows that calcium stearate was most effective and superior to barium stearate which was originally selected as the best protective colloid for the core catalyst. Here the catalyst B, the core catalyst stabilised by calcium stearate, was born. From the figure it can be seen that the performance of the divalent metal stearates is higher than that of monovalent metal stearates and that the stearates of calcium and sodium showed the maximum activity in each group. The ionic radii of calcium and sodium are about 1, 0.99 and 0.95 Å, respectively. The authors suggested that the ionic radii of about 1 Å for calcium and sodium were the origin of maximum performance in each metal group. This specific size of an ion might have some relation with the specific structure of a catalyst system. Amination reactions of low reactive DIADOL-135 revealed the difference in performance of protective colloids clearly for the first time, which was unclear in the amination reactions of straight chain alcohols.

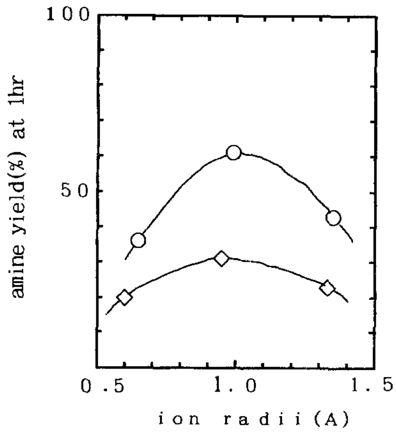


Fig. 3. Dependence of the initial catalytic activity for the amination of DIADOL-135 on ionic radii of alkali and alkali earth metals in stearates.

3.3. Selection of a calcium carboxylate

The effect of the chain length and the optimum amount of calcium carboxylate were examined to select the optimum calcium carboxylate for the core catalyst. Fig. 4 shows the effect of the chain length of calcium carboxylate on catalytic activity at 1 h. It is obvious from the figure that among the four calcium carboxylates – laurate, palmitate, stearate and behenate – stearate showed the highest performance. The effect of chain length of barium carboxylate is also compared in fig. 4. It also shows that stearate was most effective. From these observations it was concluded that the bimetallic Cu/Ni colloidal dispersions stabilised by calcium stearate (catalyst B) was a good starting catalyst for the amination of oxo-alcohols. The optimum amount of calcium stearate for the core catalyst composed of 3.0 g of cupric stearate and 0.6 g of nickel stearate was examined varying its amount (0, 0.3, 0.45, 0.60, 0.75, 0.9, 1.2 g). 0.6 g of calcium stearate was the optimum value and showed the highest catalytic activity, 89%.

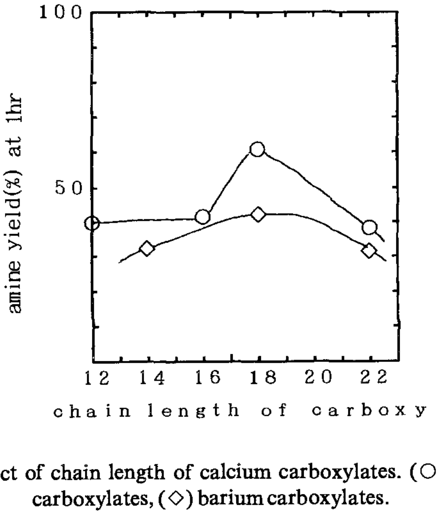


Fig. 4. Effect of chain length of calcium carboxylates. (○) Calcium carboxylates, (◇) barium carboxylates.

3.4. The second stabiliser for catalyst B

However, in the investigation of the concentration effect of catalyst B, it was found that decolorization of the reaction mixture occurred at a low catalyst concentration of 250 ppm based on copper. Coagulation of the catalyst system and copper coating inside the pyrex reactor were observed. These phenomena showed that sintering of the catalyst B, especially the copper component, had been proceeding during the amination reaction. Therefore it was concluded that the catalyst B should be further stabilised by a second protective colloid. Among the second stabilisers investigated barium stearate was found the most effective. Fig. 5 compares the catalytic activity of the core catalyst, catalyst A, catalyst B and catalyst C. It can be clearly observed that the catalytic activity of the core catalyst is increased by incorporation with calcium stearate (catalyst B) and is further increased by further incorporation with barium stearate (catalyst C). Superiority of catalyst C over catalyst A could be clearly observed for the amination of DIADOL-135, which contained the highest amount of branched isomers among the oxo-alcohols investigated. Catalyst C was very stable throughout the amination reaction and the sintering phenomenon which was typical to catalyst B was not observed even at a low catalyst concentration of 100 ppm based on copper. Here, the bimetallic Cu/Ni colloidal dispersion doubly stabilised by incorporation of both calcium and barium stearate, catalyst C, was born.

3.5. Catalytic activity of catalyst C

The catalytic activity of catalyst C for the amination reaction of the five oxo-alcohols in table 1 was examined and compared with that of catalyst A.

The result is shown in fig. 6 (6a for OXOCOL-1415, 6b for DIADOL-135, 6c for OXOCOL-1215, 6d for OXOCOL-1213 and 6e for DOBANOL-24). Superiority of the catalyst C, especially a higher reaction rate in the last stage of the reactions, was clearly observed for oxo-alcohols, especially OXOCOL-1415, DIADOL-135 and OXOCOL 1215. For DOBANOL-25 the branched isomer content was 20%, so the activity difference between catalysts A and C was small. Reaction times and tertiary amine yields for catalysts A and C are compared in table 2. The main difference between the two catalyst is that catalyst C showed a higher reaction rate at the same concentration of a Cu/Ni core catalyst as observed in fig. 6. This promotion in catalytic activity for catalyst C was brought about by incorporation of both calcium and barium stearates as protective colloids. However, tertiary amine yields for catalysts A and C showed comparable values except for OXOCOL-1213. This was also the case for dodecyl alcohol as long as the catalyst concentration was 1000 ppm based on copper. Lower tertiary amine yields for oxo-alcohols compared to that for dodecyl alcohol were ascribed to higher contents of higher molecular weight materials (amines, alcohols) for these oxo-alcohols.

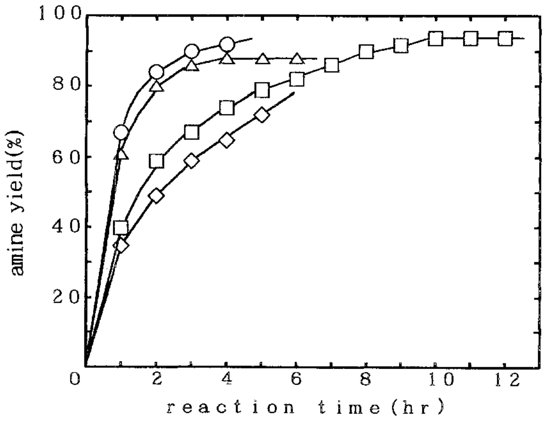


Fig. 5. Comparison of the catalytic activities of catalysts A, B, C and the core catalyst. (□) Catalyst A, (△) catalyst B, (○) catalyst C, (◇) core catalyst.

This might be decreased if the amination reaction was carried out at a lower temperature (< 210°C) under controlled feed of DMA. It was concluded from these observations that catalyst C mainly contributed to the increase in reaction rate, but did not increase the yield under the present conditions. Application of catalyst C for the amination reaction of dodecyl alcohol was performed.

A tertiary amine yield of 93% was obtained in a 5 hours' reaction performed at 220°C with a catalyst concentration as low as 200 ppm based on copper.

The corresponding yield of about 60–70% was obtained when catalyst A was used. A remarkable higher catalytic activity compared to that for catalyst A was clearly observed. The superiority of catalyst C over catalyst A for amination of dodecyl alcohol was further characterised by its lower catalyst concentration, which participated in decreasing the quantity of undesirable by-products.

3.6. Some specific physical phenomena of catalysts B and C

A reaction mixture containing catalyst C or B specifically formed a gel at room temperature. This gel showed water-repellency and formed a stable homogeneous solution with acetone as a polar solvent, which was not the case for the other catalysts. It is known that calcium stearate is used as a water-repellent reagent. The authors think that calcium stearate and barium stearate as protective colloids function in a different way in the catalytic system containing the Cu/Ni core. Among the divalent alkali earth metals Mg, Ca and Ba, Ca showed the highest performance and its ionic radius is 1 Å. However, sintering was observed for catalyst B at the low concentration of 250 ppm. This shows that destruc-

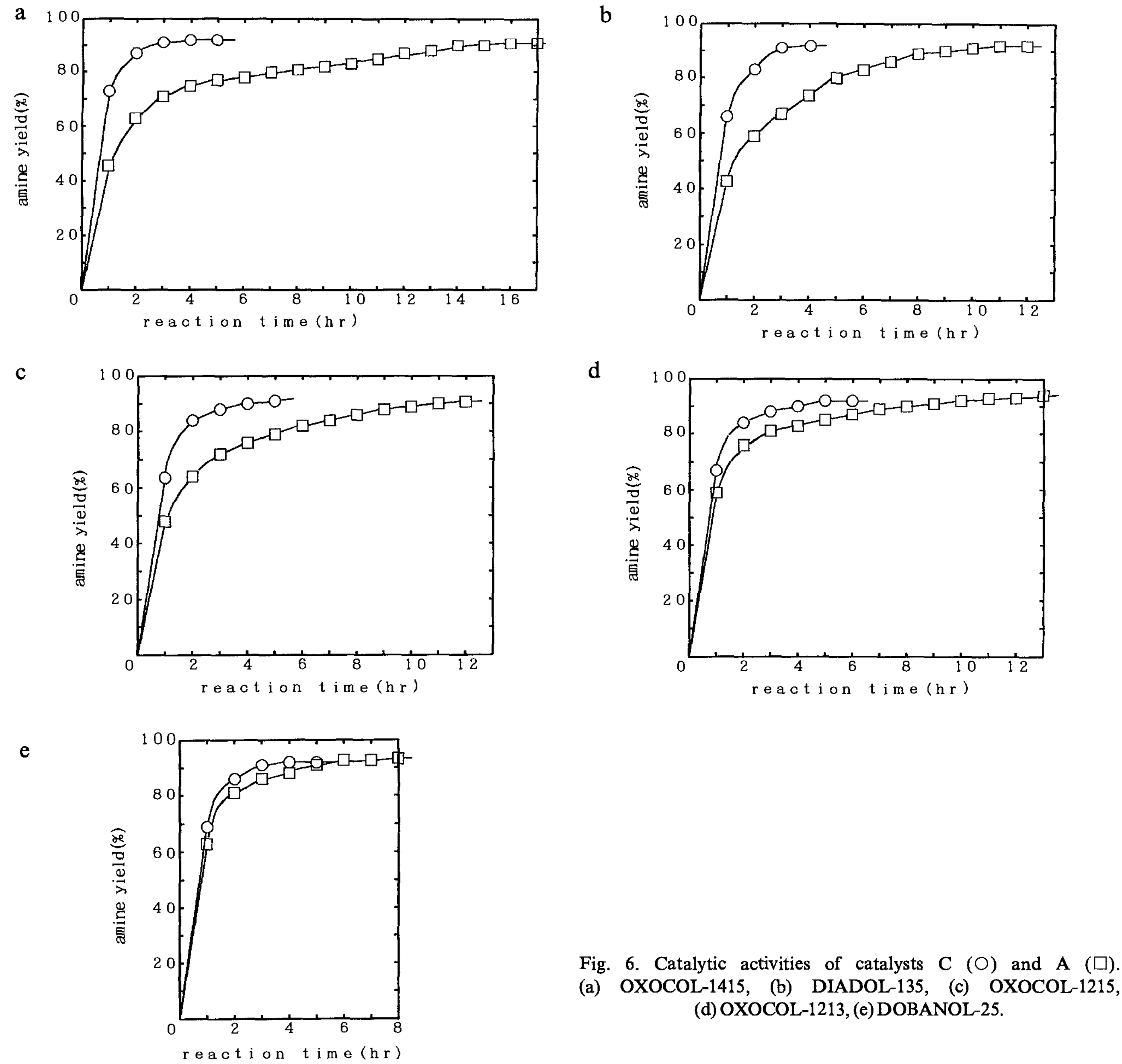


Fig. 6. Catalytic activities of catalysts C (○) and A (□). (a) OXOCOL-1415, (b) DIADOL-135, (c) OXOCOL-1215, (d) OXOCOL-1213, (e) DOBANOL-25.

Table 2
Amination of oxo-alcohols

Oxo-alcohols	Catalyst[a]	Reaction time (h)	Tertiary amine yield (%)
DIADOL-135	A	12	84
	C	4	84
OXOCOL-1415	A	17	85
	C	4	87
OXOCOL-1215	A	12	84
	C	5	85
OXOCOL-1213	A	12	87
	C	5	78
DOBANOL-25	A	8	89
	C	4	89
dodecyl alcohol	A	5	92
	C	3	92

[a] A: catalyst A (stearates of copper, nickel and barium are 3.0, 0.6 and 0.6 g, respectively for 300 g of alcohol); C: catalyst C (stearates of copper, nickel, calcium and barium are 3.0, 0.6, 0.6 and 0.6 g, respectively for 300 g of alcohol).

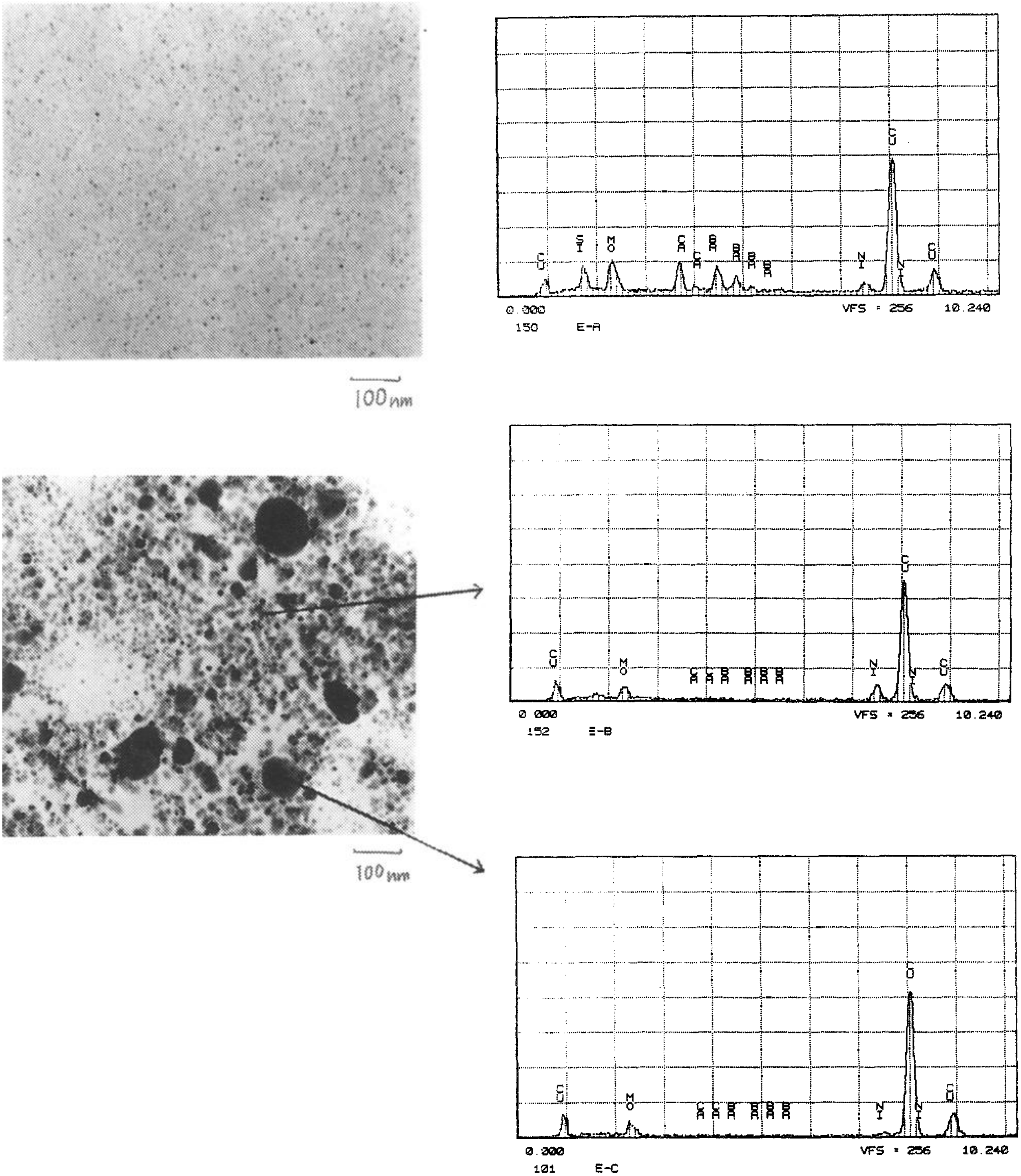


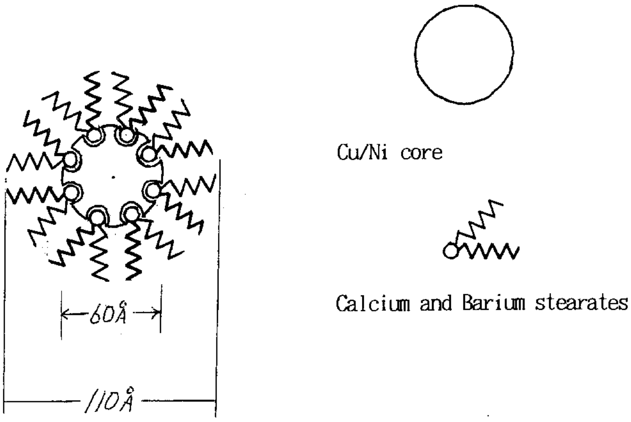
Fig. 7. TEM images of EDS analyses of separated catalysts of the colloidal catalyst C.

tion of the structure of the core catalyst stabilised by the protective colloid accompanied the amination reaction. The authors think that these phenomena may imply formation of a ternary alloy of the Cu/Ni core and calcium. These observations and consideration forced us to apply barium stearate as a second stabiliser.

As a result decolorization of the reaction mixture and coating of metallic copper inside the reactor, usually observed as sintering phenomena of the catalyst B, were completely inhibited resulting in an increase in catalytic activity.

3.7. TEM images of catalyst C and its model structure

TEM observation of catalyst C, Cu/Ni binary colloi-



Scheme 1. Model structure of catalyst C, Cu/Ni binary dispersion stabilised by a combination of barium and calcium stearates.

dal dispersion stabilised by the combination of calcium and barium stearates, was performed.

TEM images of the catalyst separated by ethyl alcohol are shown in fig. 7. The separated catalyst was composed of fine particles with a diameter of less then 6 nm (upper figures) and larger particles with a diameter of 10–100 nm (lower figures). Larger particles were formed by decomposition of the four-component colloidal system and agglomeration of the metallic components during separation and washing treatment. EDS analyses showed that the fine particles were composed of the four components, Cu, Ni, Ca and Ba with an atomic ratio of 5.00 : 0.30 : 0.84 : 0.61, respectively. The initial atomic ratio of Cu : Ni : Ca : Ba was 5.00 : 1.01 : 1.13 : 0.97, respectively. On the other hand, EDS analyses of the larger particles showed the absence of Ba and Ca components, indicating the complete destruction of the four-component colloidal system. In an actual reaction system, a reaction mixture containing catalyst C was completely transparent. Therefore the actual particle size of the colloidal catalyst must be much smaller than 6 nm. The catalyst concentration based on copper in the reaction mixture was as low as 100–600 ppm. Therefore observation of TEM images of a colloidal catalyst in a frozen reaction mixture was difficult.

The atomic composition of the protective colloids (Ca and Ba stearates) of catalyst C in a reaction mixture was 26 mol% and the observed atomic composition for the separated catalyst was 21 mol%. It is reported that the molecular size of barium stearate was 25 Å [4] and that calcium stearate may have almost the same size. In TEM observations, the particle size of the metallic Cu/Ni core was observed. A W/O type micelle structure composed of protective colloids and a Cu/Ni core (< 60 Å) were suggested as a model for colloidal catalyst C. With these considerations the particle size of catalyst C was estimated to 110 Å or less including an outer region composed of protective colloids. Scheme 1 shows the proposed model of catalyst C, a Cu/Ni core stabilised by calcium and barium stearates as protective colloids. The Cu/Ni core region exists in hydrophilic atmosphere due to formed water, which accelerates the decomposition of the Cu/Ni core. Incorporation of protective colloids, especially calcium stearate, might produce water-repellency in the core region. However, calcium stearate alone could not show enough stabilising performance and the second stabiliser, barium stearate was indispensable.

4. Conclusions

It was concluded from these observations and considerations that the remarkable increase in catalytic activity of catalyst C was brought about by the synergism of the two protective colloids, calcium and barium stearates, functioning as a water-repellent reagent and a stabiliser for the Cu/Ni core, respectively. The possibility of the existence of Cu/Ni/Ca three-component metallic clusters will be elucidated in a future study.

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