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Characterization of Highly Selective Cu-Ni Amination Catalysts

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The characterization of Cu-Ni amination catalysts has been done by using TEM, XPS, and EXAFS. The Cu-Ni catalyst whose nickel atoms were hard to be reduced even at high temperatures under a hydrogen atmosphere gave high selectivity in the reaction between dodecyl alcohol and dimethylamine to produce N,N-dimethyldodecylamine.

Long chain aliphatic tertiary amines, especially N,N-dimethylalkylamines (DMAA), are one of the most important intermediates which are derived to produce cationic surfactants, amphoteric surfactants and amine oxides.1)

DMAA is able to be synthesized directly from aliphatic alcohols and amines over amination catalysts, such as Cu-Ba,2) Cu-Ni,3) and so forth. Among them, the Cu-Ni catalyst supported on zeolite (13X) gave extremely high activity and selectivity in the reaction between dodecyl alcohol and dimethylamine to produce N,N-dimethyldodecylamine.3) However, the preparation methods of Cu-Ni catalysts gave large effects on the catalytic activity and selectivity in this reaction. We, in this paper, discuss the correlation between the states of Cu-Ni catalysts

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which have been analyzed by using TEM (JEOL JEM-2000FX), XPS (ULVAC PHI ESCA 5400) and EXAFS (RIGAKU DENKI RU-300) and the catalytic properties of those catalysts.

Cu-Ni (4:1 by metal weight) catalysts supported on zeolite were prepared by two methods. The first one was prepared as follows: (1) coprecipitation at constant pH (= 7) by adding a mixture of aqueous solutions of copper and nickel nitrates and aqueous sodium carbonate solution to water slurry of the same amount of zeolite (13X) as copper and nickel metals, (2) filtration, washing, drying (373 K, 10 h) and calcination (873 K, 1 h). Over the catalyst, copper and nickel metals were dispersed on zeolite homogeneously, which was analyzed by TEM, hereafter denoted as the Cu-Ni catalyst (homo).

The second one was prepared by adding aqueous sodium carbonate solution to an aqueous mixed solution of copper and nickel nitrates with zeolite followed by filtration, washing, drying, and calcination.3) In this case, copper and nickel metals over the catalyst existed heterogeneously around zeolite which was also analyzed by TEM, hereafter denoted as the Cu-Ni catalyst (hetero).

Table 1 shows the catalytic properties of Cu-Ni catalysts in the reaction of dodecyl alcohol and dimethylamine to produce N,N-dimethyldodecylamine (DMDA).3) The reactant composition was analyzed by gas chromatography with OV-17 column. The Cu-Ni (hetero) gave much higher selectivity to DMDA than the Cu-Ni (homo). In case of the Cu-Ni (homo), N,N-didodecylmethylamine was produced as a main by-product, which was produced by the reaction between dodecyl alcohol and methylamine formed by the disproportionation of dimethylamine. So the Cu-Ni catalyst (hetero) seems to be less active in the disproportionation reaction of dimethylamine than the Cu-Ni catalyst (homo).

Table 1. Reactant Composition after the Reaction between Dodecyl Alcohol and Dimethylamine over Cu-Ni Catalysts[a)]

Catalyst	N,N-Dimethyl-dodecylamine	N,N-Didodecyl-methylamine	Non-Reacted Dodecyl alcohol	Aldol
Cu-Ni(homo)	93.6	4.8	1.5	0.1
Cu-Ni(hetero)	97.0	1.9	1.2	0.0

a) Reaction was carried out at 473 K for 5 h under an atmospheric pressure using 1.0 wt% (vs. dodecyl alcohol) of catalysts.

To elucidate the difference of catalytic property between them, the binding energies for copper and nickel of catalysts were measured by XPS as shown in Table 2. The binding energy of C 1s (285.0 eV) was taken as the standard. It was found that the binding energy of Ni $2p_{3/2}$ of the Cu-Ni catalyst (hetero) is clearly higher than that of the catalyst (homo). And in case of the catalyst (hetero), Na^+ exists on the surface of the catalyst. According to the previous work[4)] Ni^{2+} of NiO gives the peak at 854.5 eV. When NiO contains excess oxygen atoms, the peak of Ni $2p_{3/2}$ shifts to 855.8 eV. The catalyst (hetero) seems to contain some amounts of Ni^{3+} or otherwise to be the formation of a sodium complex such as Na_2NiO_2.

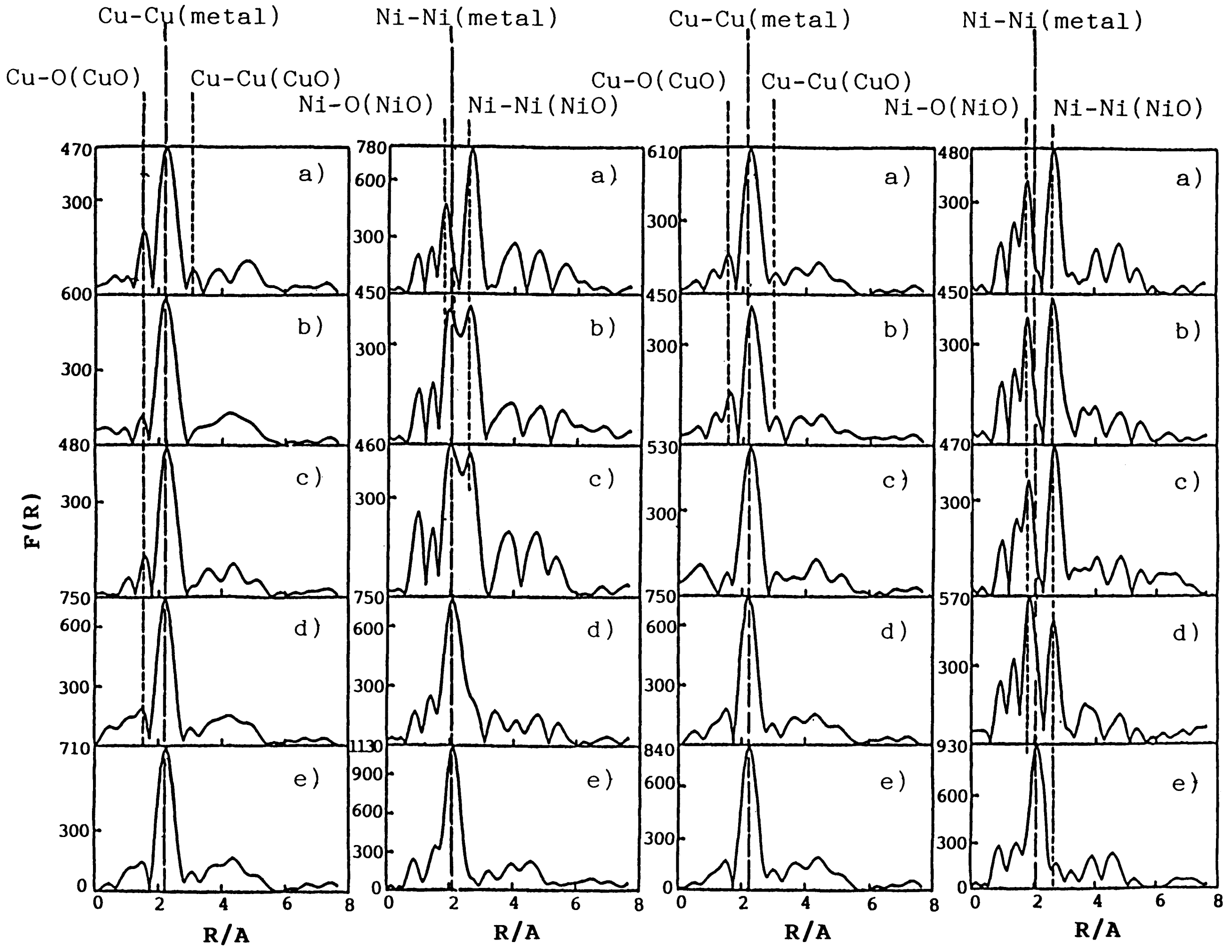
Table 2. AES and XPS Data of Non-Treated Cu-Ni Catalysts

Catalyst	Binding energy/eV					
	Cu LVV Auger	Cu $2p_{3/2}$	Ni $2p_{3/2}$	O 1s	Na 1s	Si 2p
Cu-Ni (homo)	335.6	933.7	854.1	535.2 533.3		102.0
Cu-Ni (hetero)	335.3	933.5	855.5	535.5 533.7	1072.1	101.8

Figure 1 shows the results of the Fourier transforms of EXAFS for two Cu-Ni catalysts after various hydrogen treatments. It was found that when the Cu-Ni catalysts were not treated by hydrogen, CuO and NiO particles were separately supported on zeolite in both Cu-Ni catalysts.

When the Cu-Ni catalysts were treated under hydrogen atmosphere at elevated temperatures, Cu in both catalysts was easily reduced at 373 K. It is noted that Ni of the catalyst (homo) begins to be reduced at 573 K while that in the catalyst (hetero) is hard to be reduced even at 773 K for 1 h. The formation of some sodium-nickel compound is expected for the stabilization. The difficulty to reduce nickel oxide gives high catalytic performance in the DMDA production reaction.

This fact indicates that reduced nickel metal catalyzes the disproportination reaction of dimethylamine to produce trimethylamine and methylamine, which furthermore reacts with dodecyl alcohol to form N,N-didodecylmethylamine.



(1) Cu of Cu-Ni catalyst (homo) (2) Ni of Cu-Ni catalyst (homo) (3) Cu of Cu-Ni catalyst (hetero) (4) Ni of Cu-Ni catalyst (hetero)

Fig. 1. Fourier transform of Cu-Ni catalysts after various hydrogen treatments (The phase shift is not taken into consideration).
a) non-treated, b) at 373 K for 1 h, c) at 573 K for 1 h, d) at 773 K for 1 h, and e) at 773 K for 5 h.

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