Catalytic Amination of Octanol for Synthesis of Trioctylamine and Catalyst Characterization

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Abstract Synthesis of trioctylamine by the amination of octanol and ammonia under atmospheric pressure over an excellent Ni–Cu catalyst supported on diatomite is studied in this article. The key factor for the synthesis is the preparation of catalyst with a high activity and selectivity. The activity and selectivity can be adjusted by varying the Ni to Cu ratios. The optimum molar ratio of Ni to Cu was 1.25:1. For the catalyst with a Ni/Cu ratio of 1.25:1, the conversion of octanol and the selectivity of trioctylamine reached 100 and 97.3%, respectively, at 5 h. The reaction of dioctylamine with octanol was the rate-determining step for the formation of trioctylamine. The Physical properties of catalysts, such as particle size, Brunauer–Emmett–Teller (BET) surface area, valence state of catalyst elements, morphology and reduction properties of catalysts were investigated by using X-ray diffraction, nitrogen adsorption–desorption isotherms (BET), X-ray photoelectron spectroscopy, Transmission electron microscopy, and temperature programmed reduction, respectively. The reaction scheme of catalytic amination of octanol with ammonia was discussed.

Keywords Ni/Cu · Catalytic amination · Octanol · Trioctylamine · Characterization

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1 Introduction

Long-chain alkyl tertiary amines including mono-, di-, and tri-alkyl tertiary amines ($RNMe_2$, R_2NMe and R_3N, respectively), as important intermediates for cationic surfactants, amphoteric compounds and important organic intermediates, have extensive applications. These derivatives of tertiary amines can be used as detergents, fabric softener, antistatic agents, bactericides, cosmetic additives and so forth. Especially, tri-alkyl tertiary amines can be used as extraction agents to recover various metal ions and acids from water solutions and as phase transfer catalysts accelerating the reaction rates of some reactions [1–3]. Catalytic amination of fatty alcohols is a major process for the preparation of these amines at present. Studies on catalysts and synthetic processes for mono- and di-alkyl tertiary amines have been performed for a long time, and have been reported widely [1, 3–7]. Cu/Ni-based catalysts show excellent performances for the preparation of mono- and di-alkyl tertiary amines [8–13]. Performances of Cu–Ni catalysts can be adjusted by varying Cu/Ni ratios or by adding a third element. Reported catalysts so far for the preparation of mono- and di-alkyl tertiary amines contain more Cu than Ni [3–13]. In Cu-rich-Cu/Ni-based catalysts, Cu is a main catalyst element, and Ni is an effective promoter. It has long been believed in general that Cu/Ni-based catalysts with Cu-rich compositions for the effective amination of fatty alcohols with Me_2NH are also effective for the amination of fatty alcohols with $MeNH_2$ and NH_3, and those catalysts with Ni-rich compositions are not applicable to the synthesis of R_2NMe [8] and R_3N [2]. Up to now, very few articles were reported about catalysts for the synthesis of tri-alkyl tertiary amines [2, 14]. Tri-alkyl tertiary amines contain a bulky group (three long alkyl-chains) with a steric-hindrance. Therefore, more active

catalysts than those used for the preparation of mono- and di-alkyl tertiary amines are required.

Based on these backgrounds, the present study described the more effective amination catalysts for the synthesis of tri-long-alkyl tertiary amines. The catalysts used in the present study are diatomite-supported Ni–Cu catalysts with various Ni/Cu ratios. Being different from the reported catalysts so far for the synthesis of mono- and di-alkyl tertiary amines, the catalysts used for the synthesis of tri-alkyl tertiary amines in the present study was Ni-rich new compositions for Cu/Ni-based catalysts. This difference, based on a synergism of Cu and Ni, resulted in a significant increase in activity and selectivity. The excellent results of our present study opened, for the first time, a new field of Cu/Ni-based catalysts against the conventional Cu-rich catalysts. In this paper, characterization of the developed catalysts was performed in term of particle size, Brunauer–Emmett–Teller (BET) surface area, valence state of catalyst elements, morphology, and reduction properties by Transmission electron microscopy (TEM), X-ray diffraction (XRD), BET, X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR) analysis. The reaction scheme was also discussed.

2 Experimental

2.1 Materials

Octanol with a purity of >99% was purchased from Beijing Chemical Plant in China. NH_3 with a purity of >99% was purchased from Taiyuan Fertilizer Plant in China. H_2 with a purity of >99.5% was purchased from Taiyuan Steel Plant in China. Reagent grade of cupric nitrate, nickel nitrate, and sodium carbonate were purchased from Tianjin Chemical Plant in China. Diatomite powder was purchased from Yunnan Aid-Filter Agent Plant in China.

2.2 Catalyst Preparation

The catalysts were prepared by a conventional co-precipitation method. A calculated amount of diatomite powder and deionized water were mixed in a beaker and heated to 45 °C under agitation. The solutions of Cu–Ni nitrates and Na_2CO_3 were simultaneously added dropwise to the slurry. The pH of the slurry had to be maintained at 9 by adjusting the feed rates of the two solutions. The temperature was kept at 45 °C for 2 h under agitation. Then, the slurry was filtered, and the filtered cake was washed with deionized water until the pH of the washing water becomes neutral (pH 7), and then, the washed cake was filtered, dried at 120 °C, calcinated at 450 °C for 3 h, and pulverized to be used.

2.3 Reaction Method

2.3.1 Reaction apparatus

A four-necked 500-mL round bottom flask equipped with a stirrer, a thermometer, a gas inlet tube, and a reflux condenser with a water separator was used to separate formed water and an organic phase.

2.3.2 Procedure

Octanol (150 g) and catalyst (2.0 g) were placed into the flask. H_2 was fed into the reaction system at a flow rate of 0.4 L/min under agitation. The temperature of the reactor was raised to 170 °C and held at the temperature for 40 min for catalyst reduction. Then the mixture of NH_3 and H_2 (40%/60%, vol/vol) was fed into the reactor at a rate of 0.7 L/min. The condensed water was separated from the reaction system and organic phase was returned to the reactor to complete the reaction. The reaction temperature was raised to 230 °C gradually. Samples for analysis were taken every hour during the reaction.

2.4 Analysis

Samples from the amination reaction were analyzed by GC-HP6890 (J&W GC, USA) gas chromatograph to obtain a composition of a reaction mixture. Column: DB-1701 (30 m × 0.32 mm × 0.25 μm); column temp.: 80–250 °C (8 °C/min); detector: FID; carrier gas: He 20 mL/min.

2.5 Catalyst Characterization

TEM grids were prepared by dispersing the fresh calcined catalysts into redistilled water by ultrasonication and then placing a drop of the catalyst dispersion into lacey carbon grids. After evaporation of the water, micrographs were collected on a JEM-1011 (JEOL Ltd., Japan), with a 200-kV electron source. Several TEM images were recorded at various locations on the sample and at different magnifications to confirm that the structures observed were present throughout the catalyst. For each catalyst representative images are presented in the figures.

The XRD data were gathered on a MiniFlex II (Rigaku, Japan) with monochromatic Cu Kα radiation in the range of $2\theta = 10–70°$. Diffraction patterns were obtained for selected calcined catalysts. The catalyst powders were secured onto a glass slide with double-sided sticky tape.

Nitrogen adsorption–desorption isotherms (BET) was measured using an ASAP 2010 (Micromeritics, USA) at liquid nitrogen temperature. All samples were degassed at 100 °C under vacuum for 8 h.

TPR was performed with an AutoChem2910 (Micromertics, USA). 10% H_2-Ar gas was fed into the catalyst sample at 25 mL/min, temperature was raised to 550 °C in 10 °C/min constantly from room temperature.

XPS spectrum was measured with a V.G. MiltiLab 2000 (V.G. Analytical, United Kingdom) with Al Kα as the excitation source. The electron binding energy scale was calibrated by assigning 284.6 eV to the Cls peak position. Firstly the catalyst was reduced at 170 °C for 40 min under H_2 atmosphere, and then XPS was measured.

3 Results and Discussion

3.1 The Activity and Selectivity of Ni–Cu Catalyst

Seven catalysts with different Ni/Cu molar ratios were prepared and tested in the amination reaction according to the methods in Sects. 2.2 and 2.3, respectively. The relationship between the trioctylamine contents of the samples and reaction time for each catalyst is shown in Fig. 1. The trioctylamine content can be taken as a measure of the catalyst selectivity.

It can be seen from Fig. 1 that for the catalysts containing only Cu or only Ni (single element catalysts), the trioctylamine contents at 5 h were 13.0 and 4.9%, respectively, while for other catalysts with the Ni/Cu ratios, 2:1, 1.5:1 and 1:1, the trioctylamine content at 5 h reach about 92.0%.

The optimum Ni/Cu molar ratio was 1.25:1, and the trioctylamine content at 5 h was 97.3% (maximum). It was understood from these observations that coexistence of Ni and Cu is essential for the generation of effective activities of the Ni/Cu-based catalysts for the synthesis of R_3N, and
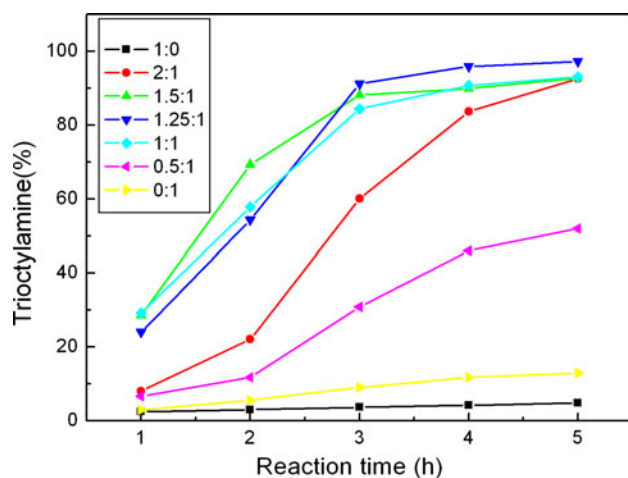

Fig. 1 The dependence of the trioctylamine content on the Ni/Cu ratio of various diatomite-supported catalysts used in the amination of octanol and NH_3
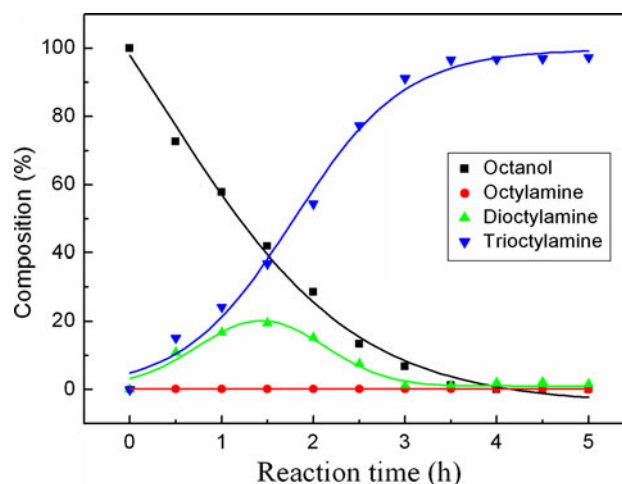

Fig. 2 The time course of the amination reaction of octanol with NH_3 over the optimized Ni/Cu catalyst supported on diatomite (Ni/Cu molar ratio, 1.25:1)

that a synergism of Ni and Cu obviously exists in the Ni/Cu-based catalysts. The amination of octanol with ammonia is a consecutive reaction, via the formation of octylamine and dioctylamine, to form trioctylamine. The time course of the amination reaction of octanol with NH_3 over the optimized Ni/Cu-catalyst (Ni/Cu molar ratio, 1.25:1) is shown in Fig. 2. Various intermediate species such as octylamine and dioctylamine were observed.

It can be seen from Fig. 2 that only 0.07% of octanol remained at 4 h, and it disappeared completely at 5 h. The concentration of unreacted octanol can be taken as a measure of catalyst activity. These results indicate that the Ni/Cu-based catalyst with the optimum Ni:Cu ratio of 1.25:1 shows a very high activity. The octylamine content keeps an extremely low value in the amination reaction, indicating that octylamine was converted to dioctylamine very fast, and that this step is not the rate-determining step for the trioctylamine formation. The formation curve for the dioctylamine in the figure is typical consecutive reaction in which the content of the intermediate product (R_2NH) showed a maximum value. A similar result for the existence of a primary amine (dodecylamine) in an extremely low concentration was also reported by Abe [2] for the amination of dodecyl alcohol with ammonia over a Cu-rich-Cu/Ni-based catalyst with an amination of R_2NH to R_3N as a rate-determining step. It was concluded from these observations that the reaction from dioctylamine to trioctylamine is the rate-determining step of the formation of trioctylamine.

3.2 Reaction Mechanism

The amination mechanism of alcohols to mono-alkyl tertiary amines ($RNMe_2$) was reported elsewhere [6–8, 15].

A simple amination mechanism for alcohols to tri-alkyl tertiary amines (R_3N) was postulated in the article [2]. Based on the experimental results of our present studies, discussion and the reference papers, we proposed a detailed reaction mechanism for the amination of alcohols to tri-alkyl tertiary amines, as shown in Scheme 1.

The amination reaction is composed of ten steps: catalytic dehydrogenation of the alcohol to the alkyl aldehyde (1); addition of NH_3 to the formed aldehyde (2); hydrogenolysis of the NH_3-aldehyde adduct to form RNH_2 and water (3, 4). After RNH_2 is formed, it further reacts with alkyl aldehyde to form dialkylamine (5–7). Similarly, dialkylamine reacts with alkyl aldehyde to form the final target product, trialkylamine (8–10). From the above reaction mechanism, it can be thought that an alcohol and NH_3 react to form an alkylamine firstly, and then the reaction between an alcohol and a formed alkylamine leads to the formation of dialkylamine, followed by the amination of an alcohol with dialkylamine to produce trialkylamine.

After alkylamine and dialkylamine were produced, alcohol is aminated with alkylamine or dialkylamine, not with NH_3, when NH_3 exist excessively in the reaction system.

This could be explained from the view point of kinetics: the reaction between aldehydes and alkylamines is much faster than that of aldehyde with ammonia, or alkylamines have a higher adsorption coefficient than ammonia. If amines are adsorbed more strongly on the catalyst surface, then the ammonia concentration on the surface should be low [14, 16, 17].

3.3 Catalyst Characterization

3.3.1 TEM Observation

TEM images of diatomite as a catalyst support and three diatomite-supported catalysts are shown in Fig. 3. It can be seen from Fig. 3a that the particle sizes of diatomite are about 40 nm. When the catalyst contains only CuO or NiO, the particles are about 30 nm (Fig. 3b, c). When both NiO and CuO are supported on the carrier, it can be seen from Fig. 3d that the catalyst particle diameters decreased to about 5–6 nm. CuO and NiO form very fine nanoparticles,

Scheme 1 Proposed reaction mechanism for the amination of alcohols and NH_3 to tri-alkyl tertiary amines
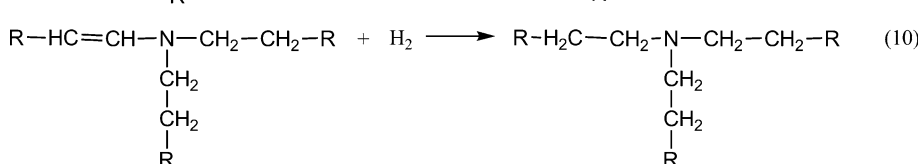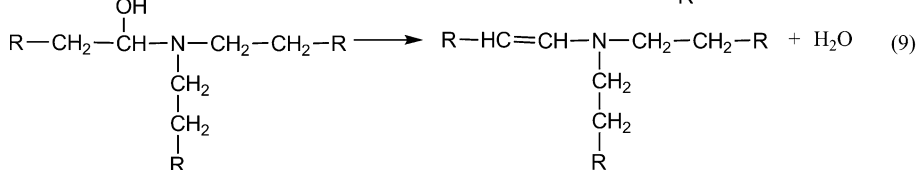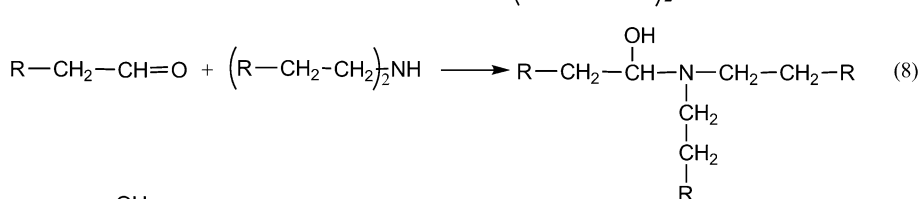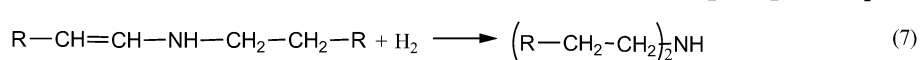
$$R-CH_2-CH_2-OH \longrightarrow R-CH_2-CH{=}O + H_2 \tag{1}$$

$$R-CH_2-CH{=}O + NH_3 \longrightarrow R-CH_2-\underset{\overset{|}{OH}}{CH}-NH_2 \tag{2}$$

$$R-CH_2-\underset{\overset{|}{OH}}{CH}-NH_2 \longrightarrow R-HC{=}CH-NH_2 + H_2O \tag{3}$$

$$R-HC{=}CH-NH_2 + H_2 \longrightarrow R-H_2C-CH_2-NH_2 \tag{4}$$

$$R-CH_2-CH{=}O + R-H_2C-CH_2-NH_2 \longrightarrow R-CH_2-\underset{\overset{|}{OH}}{CH}-NH-CH_2-CH_2-R \tag{5}$$

$$R-CH_2-\underset{\overset{|}{OH}}{CH}-NH-CH_2-CH_2-R \longrightarrow R-CH{=}CH-NH-CH_2-CH_2-R + H_2O \tag{6}$$

$$R-CH{=}CH-NH-CH_2-CH_2-R + H_2 \longrightarrow \left(R-CH_2-CH_2\right)_2 NH \tag{7}$$

$$R-CH_2-CH{=}O + \left(R-CH_2-CH_2\right)_2 NH \longrightarrow R-CH_2-\underset{\overset{|}{OH}}{CH}-\underset{\underset{\underset{R}{|}}{\underset{CH_2}{|}}{\underset{CH_2}{|}}}{N}-CH_2-CH_2-R \tag{8}$$

$$R-CH_2-\underset{\overset{|}{OH}}{CH}-\underset{\underset{\underset{R}{|}}{\underset{CH_2}{|}}{\underset{CH_2}{|}}}{N}-CH_2-CH_2-R \longrightarrow R-HC{=}CH-\underset{\underset{\underset{R}{|}}{\underset{CH_2}{|}}{\underset{CH_2}{|}}}{N}-CH_2-CH_2-R + H_2O \tag{9}$$

$$R-HC{=}CH-\underset{\underset{\underset{R}{|}}{\underset{CH_2}{|}}{\underset{CH_2}{|}}}{N}-CH_2-CH_2-R + H_2 \longrightarrow R-H_2C-CH_2-\underset{\underset{\underset{R}{|}}{\underset{CH_2}{|}}{\underset{CH_2}{|}}}{N}-CH_2-CH_2-R \tag{10}$$
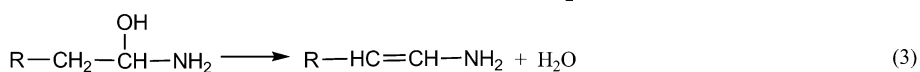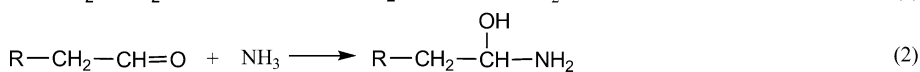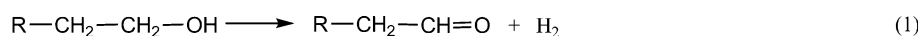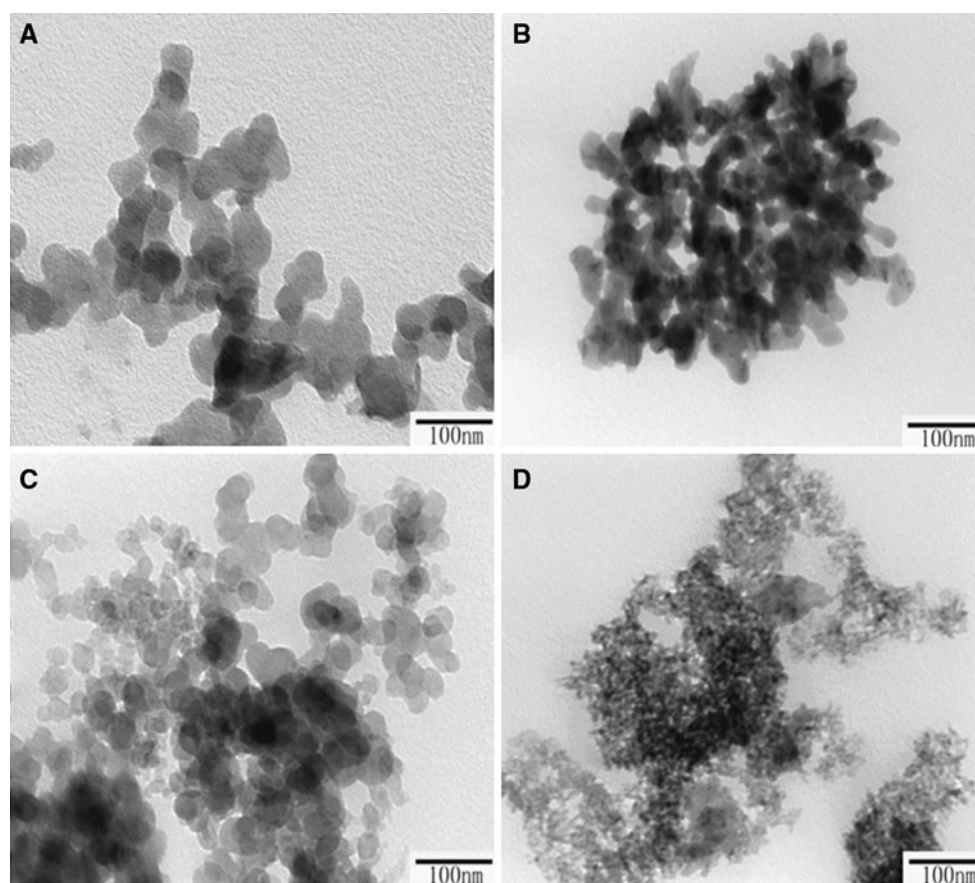
Fig. 3 TEM images of the carrier and catalysts. **a** The carrier diatomite, **b** Cu catalyst, **c** Ni catalyst, and **d** 1.25:1 Ni–Cu catalyst

resulting in generation of effective performance of the catalyst for the synthesis of trioctylamine.

3.3.2 XRD Measurement

The XRD patterns of the carrier and three catalysts are shown in Fig. 4. The diatomite as a catalyst support (a) shows two diffraction peaks at $2\theta = 15$–$25°$ (broad)

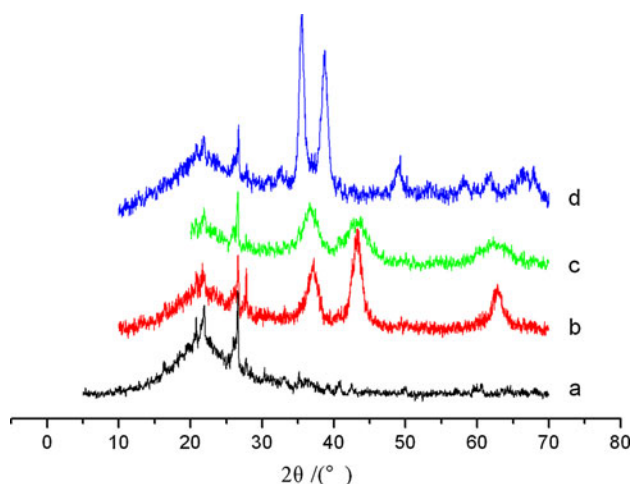**Fig. 4** XRD patterns of carrier and catalysts. *a* diatomite, *b* Ni catalyst, *c* 1.25:1 Ni–Cu catalyst, and *d* Cu catalyst

and 25–27° (sharp). The NiO catalyst supported on diatomite (b) shows three diffraction peaks at $2\theta = 35$–$40°$, 40–45°, and 60–65° [18]. The CuO catalyst (d) shows two strong and sharp diffraction peaks at $2\theta = 35$–$40°$ [18], indicating the presence of larger particles of CuO compared to those of NiO. When NiO and CuO are combined (c), only NiO diffraction peaks are observed and the half width of the diffraction peaks becomes slightly greater. It indicates the presence of a higher dispersion of NiO in the Ni–Cu catalyst (Ni/Cu, 1.25:1). On the other hand, in the Ni/Cu-based two-component catalyst (c), diffraction peaks of CuO disappear, which means that CuO is highly dispersed on the carrier. These XRD results coincide with the TEM results.

3.3.3 N_2 Adsorption–Desorption Isotherms

N_2 adsorption–desorption isotherm tests were conducted to investigate changes in the pore structures of catalysts. N_2 adsorption–desorption isotherms of three catalysts are shown in Fig. 5. According to the International Union of Pure and Applied Chemistry (IUPAC) classification [19], the isotherms showed a typical Type IV model.

The specific surface areas were evaluated using BET method [20]. Pore size distribution (PSD) was calculated
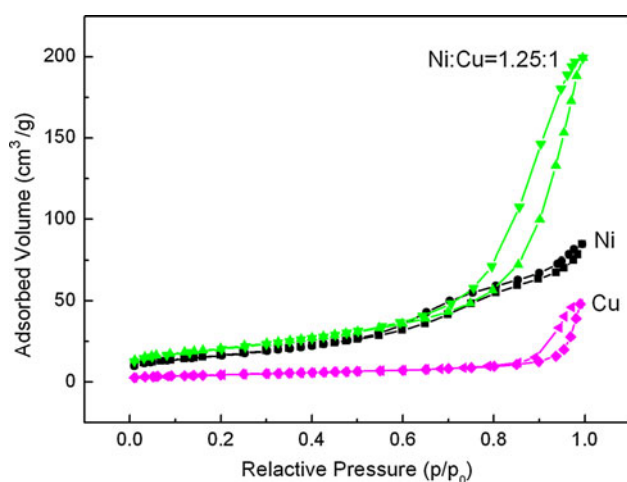
Fig. 5 N_2 adsorption–desorption isotherms of catalysts

Table 1 N_2 adsorption and desorption data

Catalyst (Ni:Cu)	BET surface area ($m^2 \, g^{-1}$)	Volume of pores ($cm^3 \, g^{-1}$)	BJH pore diameter (Å)
Diatomite	5.33	0.01	88.61
1:0	57.80	0.12	72.19
2:1	65.59	0.23	123.21
1.5:1	61.84	0.24	141.59
1.25:1	72.71	0.29	146.03
1:1	58.48	0.28	177.76
0.5:1	24.17	0.05	86.45
0:1	15.73	0.06	176.46

using the Barrett–Joyner–Halenda (BJH) method [21] based on the adsorption branch of the isotherm, and the pore size was estimated from the peak position of the distribution curve. The pore volume was taken at the $P/P_0 = 0.990$ point. The BET surface area, total pore volume, and pore size are summarized in Table 1.

As shown in Table 1, the BET surface area and the pore volume of the 1.25:1 Ni–Cu catalyst became larger compared to those of diatomite and other catalysts. It can be considered that the larger surface area of the two-component catalyst is the one of the factors for the more effective amination of octanol with NH_3 due to the higher dispersion of metal nanoparticles on the catalyst surface and a significant change in pore structure of diatomite.

3.3.4 TPR Test

TPR of the three catalysts (Cu, Ni, 1.25:1Ni–Cu) were carried out to investigate reduction temperatures of them, and the results are shown in Fig. 6. In the figure, a shows the reduction process of $Ni^{2+} \rightarrow Ni^0$ of the Ni/diatomite
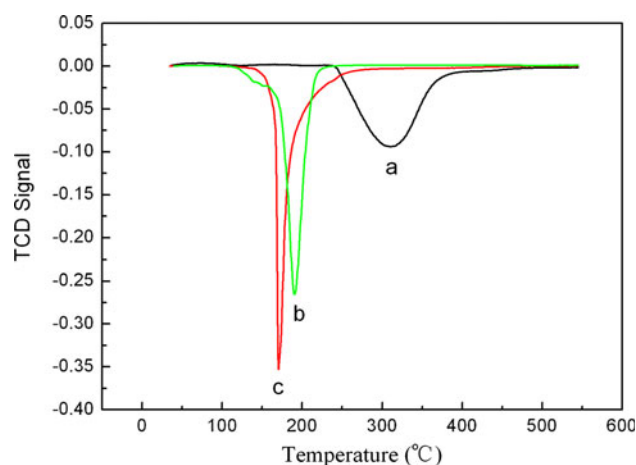

Fig. 6 TPR of the three catalysts. *a* Ni catalyst, *b* Cu catalyst, and *c* 1.25:1 Ni–Cu catalyst

catalyst containing only Ni. The reduction temperature was 311 °C [21–24]. b shows the reduction process of $Cu^{2+} \rightarrow Cu^0$ of the Cu/diatomite catalyst containing only Cu. The reduction temperature was 190 °C. These results indicated that the reduction of Ni^{2+} is more difficult than that of Cu^{2+}. c shows the reduction process of the Ni/Cu catalyst (Ni/Cu, 1.25:1). The reduction temperature was the lowest, 170 °C. A decrease in the reduction temperature for **c** might be brought about by a strong synergism due to the coexistence of Ni and Cu.

3.3.5 XPS Study

XPS measurement of seven catalysts with different Ni/Cu ratios (mol) were performed, and surface compositions (Ni mol %, Cu mol %) of the catalysts were estimated based on XPS peak areas of $Ni2p_{3/2}$ and $Cu2p_{3/2}$ and sensitivity factors (Ni, 4.044; Cu, 5.321) by using the following equations [25].
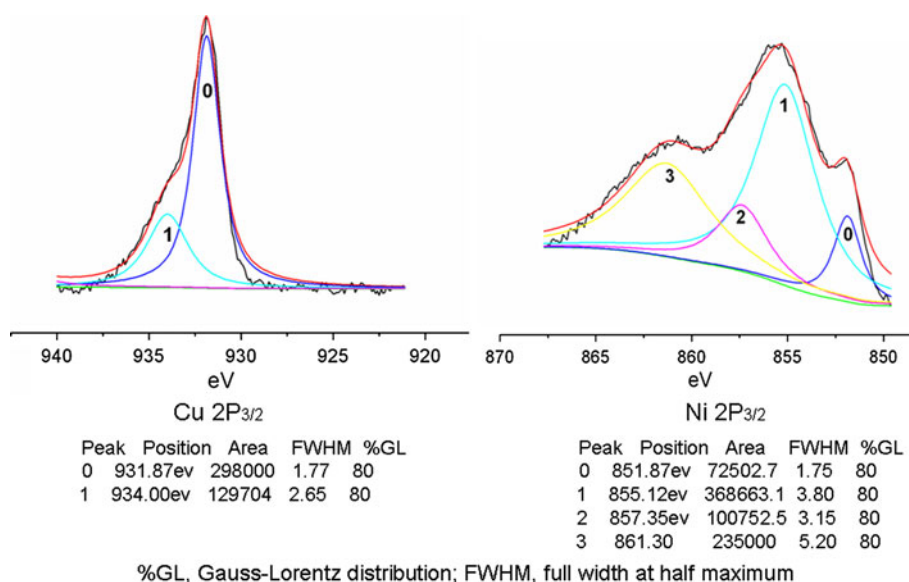
$$n(Ni)\% = \frac{\frac{A_{Ni}}{4.044}}{\frac{A_{Ni}}{4.044} + \frac{A_{Cu}}{5.321}} \times 100\%$$

$$n(Cu)\% = \frac{\frac{A_{Cu}}{5.321}}{\frac{A_{Ni}}{4.044} + \frac{A_{Cu}}{5.321}} \times 100\%$$

As a result, the Ni mol % and Cu mol % of the surface of the optimum catalyst were 76.2, 23.8%, respectively, and surface enrichment with Ni was observed on the catalyst surface. The surface Ni/Cu ratio of the optimum catalyst was 3.2:1, indicating that Ni was easily concentrated on the catalyst surface. It was concluded from these observations that a catalyst with a Ni-rich surface composition and a synergism of Ni and Cu are essential factors for the selective synthesis of trioctylamine by the stepwise amination of octanol and ammonia.

Deconvolution (peak separation with curve fitting based on Gauss–Lorentz distribution (GL % = 80%)) of the XPS

Fig. 7 Peak separation of the XPS Cu $2P_{3/2}$ and Ni $2P_{3/2}$ spectra of the optimum catalyst (Ni/Cu, 1.25:1)

Cu $2P_{3/2}$

Peak	Position	Area	FWHM	%GL
0	931.87ev	298000	1.77	80
1	934.00ev	129704	2.65	80

Ni $2P_{3/2}$

Peak	Position	Area	FWHM	%GL
0	851.87ev	72502.7	1.75	80
1	855.12ev	368663.1	3.80	80
2	857.35ev	100752.5	3.15	80
3	861.30	235000	5.20	80

%GL, Gauss-Lorentz distribution; FWHM, full width at half maximum

peaks of Cu $2P_{3/2}$ and Ni $2P_{3/2}$ of the optimum catalyst (Ni/Cu ratio, 1.25:1), which was reduced with H_2 at 170 °C for 40 min, was performed, and the result is shown in Fig. 7.

In the left figure, peak 0 and peak 1 indicate Cu^0 and Cu^{2+}, respectively. In the right figure, peak 0 indicates Ni^0, and peaks 1, 2 and 3 indicate the main peak, shoulder peak and shake-up peaks of Ni^{2+}, respectively.

The relative area of peak 0 to the total area of the four peaks can be taken as the reduction degree of Cu or Ni. It can be seen from the figure that reduction of Cu and Ni of the optimum catalyst was not completed.

The contents of Cu^0 and Ni^0 were 69.7 and 9.3%, respectively. This result indicates that most Cu was existed as Cu^0, and most Ni was existed as Ni^{2+} on the catalyst surface.

These results on the reduction degrees of copper and nickel of the Cu/Ni-based two-component solid catalyst are similar to those of reported Cu/Ni-based catalysts so far [1, 4, 5, 9]. Best of our knowledge, detailed study to investigate the relationship between the reduction degree of copper and the activity of Cu/Ni-based two component catalysts used for the amination reaction has not been reported so far. However, importance of the existence of high valence state of nickel such as Ni^{2+}, and Ni^{3+} for the prevention of the disproportionation of formed amines and the effect of the reduced nickel (Ni^0) on the promotion of the disproportionation of amines are reported [1, 4, 5, 9].

4 Conclusions

Trioctylamine was synthesized by the reaction of octanol and ammonia over Ni-rich Ni/Cu catalysts supported on diatomite under atmospheric pressure. It was confirmed that the amination of octanol with dioctylamine is the rate-determining step for the formation of trioctylamine, which is the same result reported by Abe on the amination of dodecyl alcohol with ammonia to tridodeylamine over a Cu-rich-Cu/Ni-based solid catalyst.

The catalyst with a Ni–Cu molar ratio of 1.25:1 is the optimum for this amination reaction. Characterization of the diatomite-supported Ni/Cu catalysts were performed in terms of the valence states and reduction properties of catalyst elements (Ni, Cu), particle size, and catalyst morphology by using TEM, XRD, XPS, BET and TPR.

It was concluded that a Ni-rich surface composition (Ni, 76.2 mol %; Cu, 23.8 mol %) and coexistence of Ni and Cu are the essential factors for the effective and selective synthesis of trioctylamine by the amination of octanol and ammonia over the diatomite-supported Ni/Cu-based catalysts.

It was also concluded that some activation (increases in BET surface area and pore diameter) of catalysts induced by the loading of Ni and Cu is another factor for the increased activity and selectivity of the optimum catalyst.

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