

Dendrimer-Encapsulated Copper Cluster as a Chemoselective and Regenerable Hydrogenation Catalyst

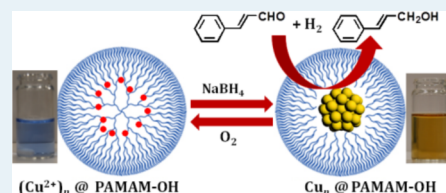
Prasenjit Maity,[†] Seiji Yamazoe,[†] and Tatsuya Tsukuda^{*,†}

[†]Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

S Supporting Information

ABSTRACT: A copper cluster encapsulated within a poly(amidoamine) dendrimer with hydroxyl surface groups (PAMAM–OH) acted as a chemoselective catalyst for hydrogenation of carbonyl and olefin groups in water. The activity was dependent on the molar ratio of Cu^{2+} and PAMAM–OH used in the synthesis, which was ascribed to the size-specific chemical properties of Cu clusters. The dendrimer-encapsulated Cu cluster was oxidized into Cu^{2+} ions under aerobic conditions, but could be regenerated by reduction with NaBH_4 for catalytic application.

KEYWORDS: Cu clusters, dendrimer, water medium, chemoselective hydrogenation



Recently, growing attention has been directed toward reducing the use of precious metals in catalysis because of their limited availability from natural resources. Much effort has been made to replace the platinum group metals with the first-row transition metals (Cu, Ni, Co, Fe) in the forms of ions and zerovalent metals in homogeneous and heterogeneous catalysis, respectively.^{1,2} However, practical use of these metals in heterogeneous catalysts is hampered because of their instability under ambient conditions. For example, Cu nanoparticles (NPs) stabilized by organic polymers or immobilized on solid supports are easily oxidized into CuO or Cu_2O NPs under ambient conditions,^{3–6} with a few exceptions in which they are transformed into Cu^{2+} ions.^{7–9}

One realistic solution to this problem is to utilize the oxidized NPs (CuO and Cu_2O) for catalysis.^{10–13} Another solution is to utilize Cu NPs as catalysts under an anaerobic or reductive atmosphere. Indeed, Cu NPs (>10 nm) have been used as catalysts for reduction of a dye by hydrazine⁹ and aromatic nitro compounds¹⁴ and azides¹⁵ by ammonium formate, hydrogenation of nitrophenol¹⁶ and CO_2 ,^{17–19} and in the water–gas shift reaction.²⁰ Cu NPs have also been used for other types of reactions, such as Suzuki–Miyaura cross-coupling,²¹ alkyne coupling,²² and dehydrogenation of tetrahydroquinoline²³ and alcohols²⁴ under inert atmosphere.

To the best of our knowledge, there have been no systematic studies on the catalytic properties of Cu NPs, mainly because of their instability. Much less is known for smaller Cu clusters, although their size-controlled synthesis and size-dependent optical properties have been reported recently.^{25–28} The present work focuses on catalytic properties of small Cu clusters for hydrogenation reactions, one of the most fundamental transformations.^{29–31} Although bare Cu cluster ions (Cu_n^+) isolated in the gas phase do not react with H_2 because of the presence of an activation barrier,^{32,33} theoretical calculations predict that H_2 is dissociated at a corner Cu atom and forms hydrides on the cluster surface.^{34,35} Encouraged by

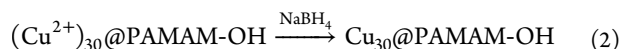
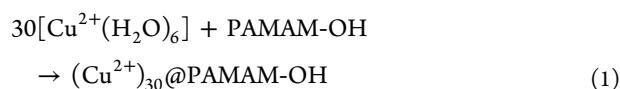
this prediction, we studied hydrogenation of various functional groups, such as $\text{C}=\text{C}$, $\text{C}=\text{O}$, and NO_2 catalyzed by small Cu clusters. We chose a poly(amidoamine) dendrimer with hydroxyl surface groups (PAMAM–OH) as a stabilizer because of the following features, as reported by Crooks:⁷ (1) the size of the clusters can be tuned by controlling the average number of Cu precursor ions coordinated within the dendrimer; (2) the Cu clusters formed in PAMAM–OH are not oxidized into copper oxides under ambient conditions, but are reversed into Cu^{2+} . In this paper, we demonstrate chemoselective hydrogenation of $\text{C}=\text{O}$ groups over $\text{C}=\text{C}$ and NO_2 groups catalyzed by PAMAM–OH-encapsulated Cu clusters in water under mild conditions. The activity was dependent on the size of the Cu clusters and generation of PAMAM–OH. Cu clusters regenerated from the oxidized Cu^{2+} could be reused as catalysts without loss of activity or selectivity.

The synthesis method of Cu clusters is similar to that reported by Crooks.^{7,36} In brief, the synthesis of Cu_n clusters with a formal size $n = 30$ within PAMAM–OH(G6), which will be referred to as $\text{Cu}_{30}@\text{PAMAM-OH(G6)}$, is described below. First, to a 10 mL aqueous solution (0.46 mM) of PAMAM–OH(G6), a 2.75 mL aqueous solution of CuSO_4 (50 mM, 30 equiv with respect to PAMAM–OH) was added. Coordination of Cu^{2+} to the amine sites within PAMAM–OH (G6) was confirmed by the blue shift of the optical absorption peak from 805 to 605 nm (eq 1).^{7,36} Finally, $\text{Cu}_{30}@\text{PAMAM-OH(G6)}$ was obtained by adding a 1 mL aqueous solution of NaBH_4 (0.69 M, 5 equiv with respect to Cu^{2+}) under vigorous stirring at room temperature (eq 2).

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The formation of $\text{Cu}_{30}\text{@PAMAM-OH(G6)}$ was recognized by the abrupt change of color of the solution from blue to deep brown. The absence of the surface plasmon band at $\sim 580 \text{ nm}$ ^{5,7,25–27} implied that the resulting clusters were very small. TEM images of $\text{Cu}_{30}\text{@PAMAM-OH(G6)}$ showed no particles, whereas those of $\text{Cu}_{60}\text{@PAMAM-OH(G6)}$ indicated the formation of particles with a diameter of $1.2 \pm 0.3 \text{ nm}$, which were possibly oxidized during preparation of the specimens.³⁶

The as-prepared $\text{Cu}_{30}\text{@PAMAM-OH(G6)}$ was used to study catalytic hydrogenation of various functional groups, such as $\text{C}=\text{C}$, $\text{C}=\text{O}$, and NO_2 . The results are summarized in Table 1. $\text{Cu}_{30}\text{@PAMAM-OH(G6)}$ efficiently catalyzed hydrogenation of a range of carbonyl substrates to the corresponding alcohols in aqueous–organic biphasic medium (entries 1–7). Various olefins were also hydrogenated to the corresponding saturated alkanes (entries 8–11), but the activity was much lower than that for carbonyls. Control experiments showed that both H_2 and Cu_{30} clusters are required for these reactions (entry 6); neither residual NaBH_4 contained in aqueous dispersion of as-prepared $\text{Cu}_{30}\text{@PAMAM-OH(G6)}$ nor unreduced $(\text{Cu}^{2+})_{30}\text{@PAMAM-OH(G6)}$ catalyzed the reduction. Nitrobenzene was totally inactive toward hydrogenation under identical conditions (entry 12).

The remarkable difference in catalytic activity of Cu clusters toward the three functional groups motivated us to study chemoselective hydrogenation of selected substrates: 4-nitrobenzaldehyde, 3-nitrostyrene, and cinnamaldehyde. As expected, 4-nitrobenzaldehyde and 3-nitrostyrene were hydrogenated selectively to 4-nitrobenzylalcohol (entry 13) and 3-nitroethylbenzene (entry 14), respectively. Selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) remains a challenge, since the $\text{C}=\text{C}$ bond is thermodynamically more easily hydrogenated than the $\text{C}=\text{O}$ bond. Pt or Ru-based catalysts have been conventionally used to achieve high selectivity and reasonable activity,^{37–40} whereas Jin recently demonstrated that $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ acted as a highly selective catalyst.⁴¹ Hydrogenation of CAL by $\text{Cu}_{30}\text{@PAMAM-OH(G6)}$ yielded COL as a major product (86% selectivity) and 3-phenyl propanol (HCOL) as a byproduct (13% selectivity) (entry 15) at 25°C . The absence of hydrocinnamaldehyde suggests that HCOL is formed via sequential hydrogenation of COL. The selectivity for COL was increased from 86% to 93% by reducing the temperature from 25 to 10°C (entry 15). To the best of our knowledge, this is the first demonstration of the Cu cluster-catalyzed selective hydrogenation of an α,β -unsaturated aldehyde, suggesting that Cu clusters can activate molecular hydrogen, probably via dissociative adsorption on the surface.^{34,35}

Cluster size, that is, the number of constituent atoms, is a crucial parameter for rational design of cluster-based catalysts.^{42–44} We prepared a series of Cu clusters, $\text{Cu}_n\text{@PAMAM-OH(G6)}$, with formal sizes $n = 10, 20, 30, 40, 50,$ and 60 by controlling the average number of the Cu^{2+} precursors accommodated in each PAMAM-OH.⁷ Their catalytic activity was compared for hydrogenation of 2-hexanone under identical conditions. In all the cases, 2-hexanone

Table 1. Catalytic Hydrogenation by $\text{Cu}_{30}\text{@PAMAM-OH(G6)}$.^a

Entry	Substrate	Conversion (%)	Product	Selectivity (%)
1		95		100
2		88		100
3		90		100
4		99		100
5		99		100
6		99 0 ^b 0 ^c		100 – –
7		99		100
8		22		100
9		20		100
10		15		100
11		18		100
12		0		–
13		88		100
14		12		100
15		99 67 ^d	 COL HCOL	86 93 ^d 13 7 ^d

^aReaction conditions: amount of Cu in catalyst, $4.6 \mu\text{mol}$; amount of substrate, 0.23 mmol ; volume of water, 5 mL ; pressure of H_2 , 3 MPa ; temperature, 25°C ; stirring rate, 900 rpm ; reaction time, 6 h for entries 1–7, 14, 15 and 12 h for entries 8–13. ^bIn the absence of H_2 , but with 5 equiv of NaBH_4 . ^c $(\text{Cu}^{2+})_{30}\text{@PAMAM-OH(G6)}$ as catalyst. ^dTemperature, 10°C ; pressure of H_2 , 1 MPa ; reaction time, 30 min .

was obtained as the unique product. As shown in Figure 1a, the conversion decreases with an increase in the molar ratio, $[\text{Cu}^{2+}]/[\text{PAMAM-OH(G6)}]$. To obtain insight into the size-specific catalysis, a turnover frequency (TOF) per surface atom was estimated by assuming that (1) the number of surface atoms in the size range studied increases linearly with size at the same rate as cuboctahedral or icosahedral magic clusters (Au_{13} and Au_{55}),³⁶ (2) the rate constant is estimated from the conversion after 0.5 h by assuming first-order kinetics, and (3) the surface coverage of Cu_n by the dendrimer is neglected. The

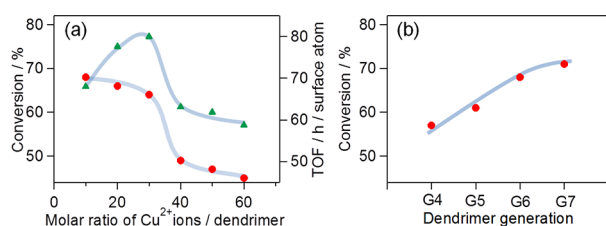
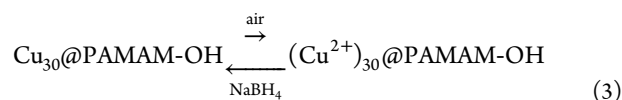


Figure 1. (a) Conversions (red) and TOF values (green) for hydrogenation of 2-hexanone as a function of the molar ratio of $[\text{Cu}^{2+}]/[\text{PAMAM-OH}(\text{G}6)]$. (b) Conversion for hydrogenation of 2-hexanone as a function of $\text{Cu}_{10}@\text{PAMAM-OH}$ generation. The curves are guides for the eye. In both cases, the experimental conditions are the same as in Table 1, with a reaction time of 30 min.

TOF values thus estimated are plotted in Figure 1a, showing a volcano-shaped behavior.

The effect of the generation of PAMAM-OH on catalytic activity was also examined. Figure 1b plots the conversion of 2-hexanone by $\text{Cu}_{10}@\text{PAMAM-OH}(\text{G}n)$ as a function of dendrimer generation. The catalytic activity increases monotonically with the generation. This trend is in sharp contrast to that reported for hydrogenation reactions catalyzed by Pd clusters in PAMAM-OH($\text{G}n$); steric crowding on the dendrimer periphery, which increases with generation, hinders access of the substrate to Pd clusters.⁴⁵ We ascribe the trend in Figure 1b to more efficient condensation of organic substrates into the dendrimer cavity in water due to increased hydrophobicity with generation; a similar effect has been proposed for organic reactions in water.^{46–48}

The Cu clusters formed within PAMAM-OH were easily oxidized into Cu^{2+} when exposed to air.^{7,36} The absorption peak at 605 nm indicates that the Cu^{2+} ions were more strongly coordinated by amine sites in PAMAM-OH than by water solvents. This spontaneous conversion into $(\text{Cu}^{2+})_{30}@\text{PAMAM-OH}(\text{G}6)$ allows us to regenerate $\text{Cu}_{30}@\text{PAMAM-OH}(\text{G}6)$ by NaBH_4 reduction (eq 3). This shuttle chemistry between $(\text{Cu}^{2+})_{30}@\text{PAMAM-OH}(\text{G}6)$ and $\text{Cu}_{30}@\text{PAMAM-OH}(\text{G}6)$ could be repeated quantitatively.



In sharp contrast, the Cu clusters stabilized by PVP were irreversibly transformed into Cu_2O NPs when dispersed in water under aerobic conditions.³⁶ We could not regenerate the Cu(0) clusters by adding NaBH_4 to these Cu_2O NPs. We compared the catalytic performances of the regenerated $\text{Cu}_{30}@\text{PAMAM-OH}(\text{G}6)$ with the original ones using hydrogenation of 2-hexanone as a test reaction. The conversion was constant, even for the fifth regenerated $\text{Cu}_{30}@\text{PAMAM-OH}(\text{G}6)$.³⁶

In summary, we have developed a catalytic system by employing PAMAM-OH-dendrimer-encapsulated, size-controlled Cu clusters as a chemoselective and regenerable hydrogenation catalyst. The catalytic activity was dependent on the formal cluster size and generation of the dendrimer.

EXPERIMENTAL METHODS

Preparation of $\text{Cu}_{30}@\text{PAMAM-OH}(\text{G}6)$. To a 10 mL aqueous solution of PAMAM-OH dendrimer (0.46 mM) was added 2.75 mL of an aqueous solution of CuSO_4 (50 mM), and the resulting mixture was stirred for 15 min at room temperature. Next, 1 mL of an aqueous solution of NaBH_4

(0.69 M) was added under vigorous stirring at room temperature. The final volume was adjusted to 150 mL by adding water.

Catalytic Test. A 5 mL aqueous solution of $\text{Cu}_n@\text{PAMAM-OH}$ ($n = 10, 20, 30, 40, 50$, and 60) containing 4.6 μmol of Cu was placed in a Teflon tube reactor with a magnetic stirrer bar inside. A 0.23 mmol portion of substrate (substrate/catalyst = 50) was added to this solution. The Teflon tube reactor was placed inside an autoclave, and H_2 gas was purged through it three times to remove the air present inside. The final H_2 pressure was maintained at 3 MPa. The reaction was continued at 25 °C with a stirring rate of 900 rpm. After a given time (30 min, 6 h, or 12 h), the Teflon tube reactor was removed, and the reaction mixture was transferred to a conical flask. From the deep brown color of the solution, it was evident that the Cu^0 clusters were stable under the prescribed reaction conditions. Next, 10 mL of ethyl acetate was added, and the mixture was stirred for 20 min to extract the reactants and products. During this time, the color of the aqueous phase changed to deep blue, indicating the oxidation of $\text{Cu}_n@\text{PAMAM-OH}(\text{G}6)$ to $(\text{Cu}^{2+})_n@\text{PAMAM-OH}$ (Supporting Information Figure S4). The ethyl acetate phase was analyzed using a Shimadzu gas chromatograph (GC 14A) with a FID detector. A silica capillary column (RTX 1) with dimensions of 30 m \times 0.53 mm was used for the present study.

ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures and characterization results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tsukuda@chem.s.u-tokyo.ac.jp

Notes

The authors declare no competing financial interest.

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