The catalytic activity of alloy nanoparticles depends on the particle size and composition ratio of different metals. Alloy nanoparticles composed of Pd, Pt, and Au are widely used as catalysts for oxidation reactions. The catalytic activities of Pt and Au nanoparticles in oxidation reactions are known to increase as the particle size decreases and to increase on the metal-metal interface of alloy nanoparticles. Therefore, multimetallic nanoclusters (MNCs) around 1 nm in diameter have potential as catalysts for oxidation reactions. However, there have been few reports describing the preparation of uniform alloy nanoclusters. We report the synthesis of finely controlled MNCs (around 1 nm) using a macromolecular template with coordination sites arranged in a gradient of basicity. We reveal that Cu-Pt-Au MNCs supported on graphitized mesoporous carbon show catalytic activity that is 24 times greater than that of a commercially available Pt catalyst for aerobic oxidation of hydrocarbons. In addition, solvent-free aerobic oxidation of hydrocarbons to ketones at room temperature, using small amounts of a radical initiator, was achieved as a heterogeneous catalytic reaction for the first time.

INTRODUCTION
Oxidative transformation of raw materials into useful intermediates has long been pursued by researchers in the field of catalytic chemistry (1). The oxidation of hydrocarbons to more functional compounds, such as alcohols and ketones, is an important organic transformation. These reactions have traditionally used dangerous solvents and additives and explosive oxidants (2–7). Solvent-free aerobic oxidation of organic compounds has recently been reported as a useful oxidative transformation of organic compounds (8–10). Noble metal nanoparticles composed of Pd, Pt, Au, and alloy nanoparticles supported on metal oxides are commonly used in these catalytic systems (8–14). Subnanoclusters (under 1 nm), in particular, have been reported as remarkable active species for oxidative transformation due to the specific reactive sites of their metal surfaces (15, 16). In this context, multimetallic nanoclusters (MNCs) have much potential as high-performance catalysts because of their particular merits, which include larger surface areas, active metal-metal interfaces, and specific reactive sites, but the catalytic activity of 1-nm MNCs has not been investigated thus far due to difficulties in the synthesis of MNCs of finely controlled size and metal composition ratio (17–19). Phase transitions with mass selection of clusters have thus far been the only synthetic method for subnanosized clusters, with a narrow size distribution at the atomic level (15, 16, 20). However, the application of this synthetic method to the synthesis of MNCs is difficult in principle. In addition, even if many kinds of metals are mixed at the nanoscale, mixed nanoclusters (NCs) often undergo phase separation due to lattice mismatch or other factors (21), and electronic interactions between different metals are lost. The efficient realization of synergistic effects between different metals in catalytic reactions is an important theme in catalytic chemistry. Here, mixing three kinds of metals at the boundary of nanoscale and subnanoscale has been accomplished, and we consider them as precisely constructed MNCs. The synthetic challenge was realized by using a macromolecular template method, with a dendrimer bearing coordination sites for metal ions. Dendrimer template synthesis of NCs has attracted much attention as a new research direction in catalytic chemistry (22–28). For the synthesis of finely controlled NCs, this method meets two significant requirements (27, 28): (i) The template molecule, which has a defined number of coordination sites for metal ions, regulates the size of the NCs after reduction of the precursor coordinating metal ions, and (ii) the dendrimer prevents aggregation of the NCs because of its dense tree-like structure, which encapsulates the NCs, and its coordination sites, which stabilize them but with enough surface accessibility for reactants in the catalytic reaction process. This is because it has coordination sites to stabilize MNCs, plus sufficient room due to its rigid π-conjugated structure. One particular dendrimer used in this research, fourth-generation dendritic polyphenylazomethine with a tetraphenylmethane core (TPM-DPA G4), has a specific ability to define the number and composition of metal types at the atomic level through layer-by-layer stepwise complexation of imine sites with metal ions (Figs. 1 and 2) (27, 29, 30). Previously, we developed synthetic methods for NCs of Rh, Pt, and Au with controlled atomicity after the reduction of precursor dendrimer complexes (27, 31). The presence of each of these NCs was confirmed by high-angle annular dark-field–scanning transmission electron microscopy (STEM) analysis and electrospray ionization mass spectrometry. However, there are no reports of the synthesis of finely controlled 1-nm MNCs composed of at least three types of metal. Here, we report their synthesis and an investigation of their catalytic activities in aerobic oxidation reactions.

RESULTS
Preparation and characterization of MNCs
Here, we aimed to synthesize finely controlled MNCs composed of Pt, Au, and Cu. Cu is much cheaper than the noble metals and have efficient catalytic properties for various oxidative transformations of organic compounds (32). The first step in synthesizing the MNCs was to confirm the formation of finely controlled dendrimer complexes as

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Cu–Pt–Au MNC precursors. Heterometal assembly of imine units on a phenylazomethine dendrimer with FeCl₃, GaCl₃, VCl₃, and SnCl₂ was demonstrated in our previous study (28, 30). The phenylazomethine dendrimer has a basicity gradient in the layers of imine units; the inner imines show greater basicity than the outer imines (29, 30). The manner of complexation between the imine units of the phenylazomethine dendrimer and the metal ions is dominated by the Lewis acidity of the metal ions and Lewis basicity of the imine sites on each layer. Metal ions with the highest Lewis acidity coordinate to the imines of the innermost layer, which show the highest Lewis basicity thermodynamically. This stepwise complexation was confirmed by ultraviolet-visible (UV-vis) spectroscopic titration, in which four independent isosbestic points appeared and the metal ion stoichiometries of the isosbestic points were consistent with the number of imine sites on each layer. Agreement between the number of metal equivalents and the number of imine sites indicated stepwise radial complexation from the inner imine layer to the outer imine layer of the phenylazomethine dendrimer.

Previous studies determined that the coordination constants of CuCl₂, PtCl₄, and AuCl₃ with the imine groups are $1.84 \times 10^3$, $1.4 \times 10^4$, and $4.2 \times 10^4 \text{ M}^{-1}$, respectively (31, 33). On the basis of the idea that the metal chloride with stronger Lewis acidity prefers to bind to the inner layers, AuCl₃ is expected to bind to the innermost layer, whereas CuCl₂ is expected to bind to the outermost layer. This assumption was supported by the UV-vis titration experiment. After the addition of 12 equivalents (equiv) of AuCl₃, isosbestic points were observed at 354.0 nm for 0 to 4 equiv of AuCl₃ and at 355.5 nm for 4 to 12 equiv of AuCl₃, which corresponded to the complexation of the first and second layers. Subsequently, after addition of 16 equiv of PtCl₄ and 32 equiv of CuCl₂, the isosbestic points shifted to 373.0 nm for 0 to 16 equiv of PtCl₄ and to 365.0 nm for 0 to 32 equiv of CuCl₂. These processes correspond to the stepwise complexation of the third and fourth layers, respectively (fig. S1). However, the bindings of CuCl₂ to the outer layers are not stoichiometric due to the weak binding. The titration experiment demonstrated that the complexation still continued at the nominal equivalent point where every imine site is filled by the metal chloride. Therefore, it should be noted that the stoichiometry of Cu is not strictly determined under the present conditions. Despite this uncertain relationship, the dendrimer reactor method still has a significant advantage in synthesis of finely controlled Cu–Pt–Au MNCs compared to conventional methods. Chemical reduction of the metalodendrimer complexes by sodium borohydride yielded MNCs, which were used in a catalytic reaction as heterogeneous catalysts supported on graphitized mesoporous carbon (GMC) (34). GMC stabilizes MNCs even at 90°C under O₂ at atmospheric pressure, preventing the MNCs from aggregating (fig. S2).
confirming the presence of finely size-controlled metal NCs of 1.3 ± 0.2 nm on GMC. STEM–energy-dispersive x-ray spectroscopy (EDX) analysis and chemical mappings of the MNCs showed the coexistence of Cu, Pt, and Au atoms in each individual metal cluster (figs. S3 and S4). X-ray photoelectron spectroscopy (XPS) analysis of Cu32Pt16Au12 MNCs showed peaks at 933.0 eV (Cu 2p3/2), 72.8 eV (Pt 4f7/2), and 84.3 eV (Au 4f7/2). In the XPS spectrum of monometallic Cu NCs, Cu60 [the divalent peak area of Cu 2p3/2 (933.7 eV)] is almost three times larger than zerovalent or monovalent peak area of Cu 2p3/2 (932.9 eV) (figs. S5 to S10). In contrast, XPS spectra of MNCs composed of Cu and other noble metals, such as Cu32Pt28, Cu32Au28, and Cu32Pt16Au12, show greater amounts of monovalent or zerovalent Cu on the MNCs (fig. S5 and table S1). The peak area ratios of [Cu(0) + Cu(I)] to Cu(II) in Cu60, Cu32Pt28, Cu32Au28, and Cu32Pt16Au12 NCs in the Cu 2p region of the XPS spectra are 0.36, 0.59, 0.81, and 2.17, respectively. Note in particular that the [Cu(0) + Cu(I)] to Cu(II) peak area ratio of Cu32Pt16Au12 NCs is the state between Cu2O and CuO (fig. S11). The edge energies and edge shapes of Cu32Pt16Au12 are different from those of Cu60 NCs (table S1). The fact that lower-valent copper species [Cu(0) and Cu(I)] are stabilized to a significant extent by alloying with other noble metals, such as Ag, Pt, and Au, thereby preventing the oxidation of these low-valent Cu atoms to divalent species, has been reported previously (35, 36). X-ray absorption fine structure (XAFS) analyses were conducted to investigate the interatomic distances, near-neighbor coordination numbers, and valence state of Cu32Pt16Au12 NCs. In Cu K-edge x-ray absorption near-edge structure spectra of Cu foil, Cu2O, CuO, and Cu32Pt16Au12 (figs. S11), the edge energies and edge shapes of Cu32Pt16Au12 are different from those of Cu2O and CuO. In addition, the oxidation state of Cu species in Cu32Pt16Au12 is the state between Cu2O and CuO (37, 38). Coordination numbers and metal-metal bond distances in extended XAFS (EXAFS) analyses indicate the existence of Cu–O bonds, Cu–M (M = Pt/Au) bonds, and M–M bonds (M = Pt/Au), and the formation of small nanoparticles of Cu32Pt16Au12 was confirmed by the low coordination number as compared with bulk metal (figs. S11 to S13 and table S2) (39).

Catalytic aerobic oxidation of hydrocarbons

After characterization of the MNCs, we investigated their catalytic activity in the oxidation of hydrocarbons using molecular oxygen as an oxidant under atmospheric pressure. Both air (ca. 20% O2) and pure oxygen in a balloon were used for the reaction. The catalytic activity was examined on the basis of aerobic indane oxidation as a model reaction. The turnover frequency (TOF) values for product formation (ketone) per total number of metal atoms (Cu, Pd, Pt, and Au) in each cluster are shown in Fig. 4. For comparison, we also investigated the catalytic activities of various types of metals, such as commercially available Pt nanoparticle supported on activated carbon and alloy nanoparticle catalysts composed of Pd and Au, which are successful catalytic systems for aerobic oxidation (9, 10, 12). Remarkably, Cu32Pt16Au12 MNCs exhibited a catalytic activity almost 5 times greater than those of the Pd–Au catalysts and 24 times greater than that of a commercially available Pt catalyst under the same reaction conditions, and this synergistic effect was not observed in a mixture of copper and other noble metal clusters that were prepared separately. The formation of organic hydroperoxides, alcohols, and ketones was confirmed by 1H nuclear magnetic resonance (NMR) analysis (Scheme 1). Previous research demonstrated that organic hydroperoxides are thermally converted to the corresponding alcohols and ketones during the process of GC (gas chromatography) analysis (40). A report on the oxidation of indane compared catalytic activities with an internal standard by GC analysis (14). Therefore, we compared the catalytic activities on the basis of the conversion from indane by calculating the total amounts of organic hydroperoxides, alcohols, and ketones. The resulting catalytic activity of Cu32Pt16Au12 MNCs was 1433 (total metal atom−1 hour−1) TOF at 90°C under pure O2 (fig. S14). To the best of our knowledge, this catalytic activity is the highest among existing catalysts for aerobic oxidation of hydrocarbons under mild conditions (14). Conversion to ketone from certain hydrocarbons, such as tetralin (1,2,3,4-tetrahydronaphthalene), was found to occur only when the reaction was catalyzed by bi- or trimetallic MNCs. In contrast, the commercially available Pt catalyst exhibited no catalytic activity at all for oxidation of tetralin at 90°C under a pressure of 1 atm of O2 (fig. S15). Note that the Cu32Pt16Au12 trimetallic catalyst was also effective for aerobic oxidation of primary carbon-hydrogen bonds, such as xylene (table S3).

To reveal the origin of this remarkable catalytic activity, we first investigated the catalytic mechanism of the oxidation reaction. The reaction pathway was unclear because of the instability of the organic hydroperoxide intermediate. Over the time course of this reaction, 1H NMR analysis detected organic hydroperoxide first, followed by alcohol and ketone. The addition of TEMPO [2,2,6,6-tetramethylpiperidine 1-oxyl; 1 mole percent (mol %)] or hydroquinone to the reaction mixture as a radical scavenger resulted in obstruction of ketone formation and hydroperoxide production at 90°C under air. These results indicate that the organic hydroperoxide is produced via a radical intermediate (Scheme 2) (41). We consider that this oxidation of an alkane to the final ketone product could result from two possible reaction paths after the formation of the organic hydroperoxide intermediate: (i) transformation of the organic hydroperoxide to an alcohol, followed by oxidation to the corresponding ketone in a stepwise manner Scheme 3), or (ii) direct transformation of the hydroperoxide to a ketone (Scheme 4). To decide between these paths, indanol was used as a starting material under the
same reaction conditions (90°C under air). However, indanol was not transformed to the corresponding ketone at all. On the basis of these experimental results, we concluded that the catalytic system under discussion mainly involved direct transformation from peroxide to ketones. This is a remarkable difference with respect to conventional catalysts. In general, oxidation from alcohols to ketones under aerobic conditions is much faster than oxidation from the corresponding alkanes to ketones (14). These results provide insight into the development of a new selective catalyst for oxidation of alkanes without oxidation of the hydroxyl group of alcohols. When a monometallic catalyst was used, an organic hydro-

![Fig. 3. Preparation of MNCs supported on GMCs. (A) Schematic representation of the synthesis of Cu_{24}Pt_{16}Au_{12}@TPM-DPA G4/GMC by layer-by-layer stepwise complexation with metal ions followed by chemical reduction. (B) Atomic resolution high-magnification STEM images of MNCs on GMCs.](image-url)
The composition ratio of the catalysts on their activity was investigated. The transformation from organic hydroperoxide to ketone. The effect of the atomic alloying of Cu with other noble metals promotes the transformation of other metals. The different tendency also supports the mechanism that our catalytic system is not a transformation from alcohols to ketones (Scheme 3) but a direct transformation from hydroperoxide intermediates to ketones (Scheme 4). These results suggest that both catalytic transformations may have the proper reactive interfaces. However, the origin of the remarkable catalytic activity of these interfaces and the acceleration of catalytic activity under O₂ after the addition of a third metal are still unclear, and additional mechanistic studies are ongoing.

MNC catalysts were applied to oxidation reactions of hydrocarbons under ambient conditions. Cu-X (X = Pt/Au) MNCs showed remarkable catalytic activity for oxidation of hydrocarbons at room temperature with a catalytic amount of tert-butyl hydroperoxide (TBHP) as a radical initiator. In this reaction, only MNCs exhibited catalytic activity for the transformation of organic hydroperoxides to ketones; non-noble metal NC or commercially available catalyst exhibited this activity (Fig. 5). This is the first report, as far as we are aware, of solvent-free catalytic aerobic oxidation of hydrocarbons to ketones at room temperature with a radical initiator. Note that this oxidation reaction proceeds smoothly under neutral conditions. These results demonstrate the remarkable synergistic effects of 1-nm MNCs composed of Cu and other noble metals for oxidation reactions of hydrocarbons.

DISCUSSION

We demonstrated the synthesis of MNC catalysts using a dendrimer template. Remarkable synergistic effects were observed for Cu–Pt–Au MNCs in the solvent-free oxidation of benzylic C–H bonds under air and under an O₂ atmosphere. In addition, these catalysts showed significant catalytic activities even at room temperature with a catalytic radical initiator. Mechanistic examination revealed that synergistic effects were involved, in particular, in the transformation from the peroxide intermediate to ketone on the interface between Cu(0)/Cu(I) and other noble metals. This discovery of positive synergistic effects from metal–metal interactions gives new insight into the design of next-generation high-performance catalysts for aerobic oxidation of unreactive substrates.

MATERIALS AND METHODS

Chemicals

TPM-DPA G4 (Fig. 2) was synthesized according to previously described methods (45). Pt/C [10 weight % (wt %)] in Figs. 4 and 5 are platinum on carbon extent of labeling: 10 wt % loading and matrix-activated carbon support, which is explained as the catalyst for hydrogenation reactions of various organic compounds and oxidation reactions of alcohols purchased from Aldrich. GMCs [99.95% trace metal basis; <500-nm particle size (dynamic light scattering); 1.887 g cm⁻³; pore volume (typical), 0.342 cm³ g⁻¹] are purchased from Aldrich. Chemicals were purchased from catalytic activity of Cu-Au bimetallic nanoparticles for aerobic oxidation of carbon monoxide after oxidation of Cu(0)/Cu(I) to Cu(II). The reactive site for the transformation of organic hydroperoxide to ketone in this reaction was assumed to be the interface between Cu(0)/Cu(I) and other noble metals. On the other hand, Zhao et al. (44) reported interesting metal–transition metal oxide interfacial effects on the selective oxidation of alcohols. Here, they also investigated the relation of the composition ratio of the catalyst and the catalytic reactivity to produce ketones from alcohols. Remarkably, their results are opposite to ours, showing that the catalytic performances are improved at a high ratio of the transition metal oxide to other metals. The different tendency also supports the mechanism that our catalytic system is not a transformation from alcohols to ketones (Scheme 3) but a direct transformation from hydroperoxide intermediates to ketones (Scheme 4). These results suggest that both catalytic transformations may have the proper reactive interfaces. However, the origin of the remarkable catalytic activity of these interfaces and the acceleration of catalytic activity under O₂ after the addition of a third metal are still unclear, and additional mechanistic studies are ongoing. The MNC catalysts were applied to oxidation reactions of hydrocarbons under ambient conditions. Cu-X (X = Pt/Au) MNCs showed remarkable catalytic activity for oxidation of hydrocarbons at room temperature with a catalytic amount of tert-butyl hydroperoxide (TBHP) as a radical initiator. In this reaction, only MNCs exhibited catalytic activity for the transformation of organic hydroperoxides to ketones; non-noble metal NC or commercially available catalyst exhibited this activity (Fig. 5). This is the first report, as far as we are aware, of solvent-free catalytic aerobic oxidation of hydrocarbons to ketones at room temperature with a radical initiator. Note that this oxidation reaction proceeds smoothly under neutral conditions. These results demonstrate the remarkable synergistic effects of 1-nm MNCs composed of Cu and other noble metals for oxidation reactions of hydrocarbons.

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Kanto Kagaku Co. Ltd., Tokyo Chemical Industry Co. Ltd., Wako Pure Chemical Industries Ltd., or Aldrich and used without further purification (solvents for the UV-vis titration and the preparation of metal NCs were of dehydrated grade). For the measurement of catalytic activities, hydrocarbons were used after distillation under reduced pressure because their purity has significant influence on catalytic activities.

**General methods**

UV-vis absorption spectra (fig. S1) were recorded during the titration experiments on a spectrophotometer (UV-3150PC, Shimadzu) using a quartz cell with a 1-cm optical path length. Stirring (700 rpm) of the oxidation reaction was done using the Zodiac Personal Organic Synthesizer (CCX-3200) at 298 or 363 K. NMR spectra were measured using the Bruker AVANCE III 400 at 400 MHz for $^1$H with tetramethylsilane (0.00 ppm) as the internal standard.

Atomic resolution high-magnification STEM images (Fig. 3B and figs. S3 and S4) were obtained using an instrument (ARM200F, JEOL) with a CEOS-ASCOR Cs-corrector and a cold field-emission gun operated at 80 kV. For STEM measurement, copper grids with either a plastic (collodion) or carbon substrate for Fig. 3B were purchased from Oken Shoji. The microscope was equipped with dual JEOL silicon drift detectors (100 mm² each) for the EDX analysis. Molybdenum grid coated with thin carbon film was used for STEM-EDX measurement.

XPS analyses in fig. S5 and in figs. S6 to S10 were measured using the ESCA 3400 (Shimadzu) and ESCA1700R (ULVAC-PHI), respectively. For the XPS measurement (figs. S5 to S10), C1s (284.5 eV) peak of a glassy carbon substrate was used as a reference for the binding energy. Peak separations of [Cu(0) + Cu(I)] to Cu(II) in Cu_{60}, Cu_{32}Au_{28}, Cu_{32}Pt_{28} and Cu_{32}Pt_{16}Au_{12} NCs in the Cu_{2p} region of the XPS spectra were carried out in previous reports (36, 46, 47).

XAFS was measured in the transmission mode at the BL9A and BL12C beamlines at the High Energy Accelerator Research Organization Institute of Materials Structure Science Photon Factory (KEK IMSS PF) (figs. S11 to S13 and table S2). Synchrotron radiation from the storage ring was monochromatized with Si111 channel-cut crystals. The angle of the monochromator was calibrated using Cu, Au, and Pt foil. Ionization chambers, as detectors to monitor the incident ($I_0$) and transmitted x-rays ($I_0$), were filled with N$_2$ and 50% Ar–50% N$_2$ mixed gas for Cu K-edge XAFS, respectively. For Pt L$_3$ and Au L$_3$-edge XAFS, the ionization chambers were filled with 15% Ar–85% N$_2$ mixed gas for $I_0$ and 100% Ar for $I$. All measurements were conducted at room temperature.

**Typical procedures**

**UV-vis spectroscopic titration**

Solutions of TPM-DPA G4 (acetonitrile/chloroform, 1:1; 2.46 µM), AuCl$_3$ (acetonitrile; 4.07 mM), PtCl$_4$ (acetonitrile; 3.09 mM), and CuCl$_2$ (acetonitrile; 3.44 mM) were prepared in volumetric flasks under nitrogen. The TPM-DPA G4 solution (3.0 ml) was added to a quartz cell, followed by the addition of metal salt solution (that is, 1 equiv for TPM-DPA G4). The UV-vis spectra were measured before and after the addition of metal salts. Measurements were repeated after each addition of metal salt solution to achieve UV-vis titration.

**Cu$_{32}$Pt$_{16}$Au$_{12}@TPM-DPA G4/GMC**

All processes were conducted under a dry nitrogen atmosphere. AuCl$_3$ solution (3.0 mM in acetonitrile) of 12 equiv for the TPM-DPA G4, PtCl$_4$ solution (3.0 mM in acetonitrile) of 16 equiv, and CuCl$_2$ solution (3.0 mM in acetonitrile) of 32 equiv were added to the solution of TPM-DPA G4 (3.0 µM) in acetonitrile/chloroform (1:1) in a vial inside a glove box. After stirring for 30 min, 60 equiv relative to all metal of a sodium borohydride solution (0.53 M in methanol) was added to the solution.
Just after the addition of the sodium borohydride, GMC was added to the solution of Cu32Pt16Au12@TPM-DPA G4. After adding GMC, the suspensions of Cu32Pt16Au12@TPM-DPA G4/GMC were stirred for an hour. The amount of GMC was adjusted to 1.0 wt % on the basis of the total mass of Pt and Au. For synthesis of Pd28Au32 in Fig. 4, [(CH3CN)4Pd](BF4)2 was used as a bimetallic cluster precursor. The other metal NC catalysts were synthesized under the same condition, changing only the molar ratios of metal chlorides to the dendrimer.

**Aerobic oxidation reactions**

The suspension Cu32Pt16Au12@TPM-DPA G4 was then vigorously stirred for 1 min, and 0.0056 mol % (Cu + Pt + Au) relative to hydrocarbon was added to a flask using a micropipette, followed by vacuum drying overnight. Hydrocarbons (400 μl) were then added to the flask. The reaction mixture was stirred at 700 rpm for 6 hours at 90°C under air or on a balloon filled with O2 gas (1 atm). The reaction progresses were then monitored by 1H NMR after 6 hours, with anisole added to the flask as internal standard.

**Aerobic oxidation reactions with radical initiator at room temperature**

The suspension Cu32Pt16Au12@TPM-DPA G4 was then vigorously stirred for 1 min, and 0.0056 mol % (Cu + Pt + Au) relative to hydrocarbon was added to a flask using a micropipette, followed by vacuum drying overnight. Hydrocarbons (400 μl) were then added to the flask. After adding 1 mol % of TBHP relative to hydrocarbon to the flask, the reaction mixture was stirred at 700 rpm for 24 hours at 25°C under air. The reaction progresses were then monitored by 1H NMR after 24 hours, with anisole added to the flask as internal standard.

**XAFS data analysis**

XAFS analyses were carried out using REX2000 software (Rigaku Co.), as previously reported (48). The theoretical phase shifts and backscattering amplitude functions used in the curve fitting were obtained by using the FEFF code (49) via Cu bulk (for Cu-Cu), Pt bulk (for Pt-Pt), Au bulk (for Au-Au), Cu2O (for Cu-O), AuPt (50), CuPt (51), and CuAu (52) alloy crystallographic parameters. Although the structures and lattice mismatch of bimetallic alloys can be determined by directly using XAFS, the limitation of Pt and Au L2-edge XAFS is that the small energy separation (ca. 350 eV) in Pt and Au L2-edge XAFS results in overlapping XAFS oscillation. Therefore, reliable curve fitting analyses of PtAu bimetallic system of Cu-Pt-Au becomes difficult (53, 54).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/7/e1700101/DC1

**REFERENCES AND NOTES**


Finely controlled multimetallic nanocluster catalysts for solvent-free aerobic oxidation of hydrocarbons
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