Smart Nanocatalysts with Streamline Shapes

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ABSTRACT: Particulate catalysts with streamline shapes have important impacts on fluid-related reactions, and they need to be properly characterized. However, utilization of streamline-shaped catalysts for heterogeneous catalysis has remained an unexplored area due to the lack of easy-to-use techniques to produce such shaped catalysts, especially at the small length scale of the submicron to micron regime. Herein, we report our recent development of a class of prototype nanocatalysts with streamline shapes. In this research, the kinetic control is adapted to obtain streamline-shaped supports, followed by functionalizing such supports with catalytically active metal nanoclusters (e.g., Au, Pd, Pt, and Ag or their combinations) in a stepwise manner. Advantages related to the streamline morphology of catalysts have been demonstrated with a number of solid–solution systems such as alcohol oxidation, olefin hydrogenation, and Suzuki–Miyaura coupling. We believe these findings will promote new research on the design and synthesis of functional materials with additional fluid-advanced features.

INTRODUCTION

When an object moves through a viscid fluid, it experiences a drag force, which usually consists of pressure drag and frictional drag (scaling with the Reynolds number).1,2 It is broadly accepted that the shape of a particle has a great effect on the amount of drag produced. A streamline body represents a superior geometry since it faces minimum fluid resistance; well-known examples of this type are submarines in seawater or airplanes in air. Systems of heterogeneous catalysis can be viewed as dispersed solid–liquid (or solid–gas) flows. It has been well established that an optimal shape configuration of catalysts can promote the transport processes and thus enhance catalytic activity in the fixed bed reactors.3 However, to date, no studies have been attempted to adopt streamline catalysts in liquid phase heterogeneous catalytic reactions. This is perhaps due to the lack of easy-to-use techniques to produce catalyst particles with a streamline morphology.

As shown in Figure 1a, streamline catalyst particles may align themselves according to a solvent flow, just like a school of fish swimming against the current, and the fast movement of fluid over the particles (equivalent to the fast motion of particles) benefits a rapid mass exchange, which may exert a strong impact on their performance. The velocity vector plots and pressure fields for catalyst objects with various geometric shapes operating in a water flow can be described conveniently by computational fluid dynamics (CFD) simulation (ANSYS Fluent 15.0 software), as illustrated in Figure 1b–f and Figures S1–S3. As shown, the more streamline the particle is, the lower the disruption of the flow patterns and a higher flow rate on the particle surface are found. The computational results show that a streamline body gives the lowest drag (i.e., pressure drop), followed by sphere, circular cone, cube, and the last is a flat plate.

Figure 1. Geometric consideration (also see Figures S1–S3) and synthesis of streamline catalysts. (a) The alignment of streamline catalyst particles in the presence of solvent flow. (b–f) Velocity vector plots of catalyst objects with various body shapes (flow rate 0.1 m s⁻¹ (water) and temperature 25 °C). Geometrical shapes investigated include streamline body, cube, circular cone, flat plate, and sphere, which share the same projected frontal area. Color-code is used to indicate the strength of the flow velocity. (g) Schematic illustration of stepwise preparations of TCOS support and the derived catalysts (see Supporting Information).

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Generally, a lower drag endows catalyst particles with a greater fracture resistance during the reaction, whereas the tubular, cylindrical extrudates have the disadvantage of low crushing strength and abrasion resistance.\textsuperscript{4} We observe that there are narrow elongated wake regions right after the nonstreamline particles, as formed of a swirling or eddy flow. It should be pointed out that fluid–particle mass transfer in the wake region is very low because the flow is separated from the body surface (the phenomenon is termed as separation of boundary layer).\textsuperscript{5} In contrast, the uniformity of the velocity fields is clear after passing through the streamline particle, and hence the separation of flow is eliminated, suggesting a full usage of catalyst surface. What is more, another advantage of streamline catalysts is that they have a larger active surface per unit volume than their spherical counterparts and can load more active sites for catalysis. In a simple estimation, it is calculated that streamline catalysts can give 16% more surface area than a spherical catalyst of equivalent volume (see Table S1). Therefore, it is highly desirable to add streamline features to catalysts and elucidate the impact of particle shape on their catalytic performance.

\section*{Results and Discussion}

Herein, as depicted in Figure 1g, we report our present work on using core–satellite structured Cu\textsubscript{2}O@Au nanospheres as a template/precursor for hydrolysis and polycondensation of 3-mercaptopropyl trimethoxysilane (MPTMS) to construct tadpole-shaped copper organosilicate (denoted as TCOS, Table S2 and Figure S4). The sol–gel derived TCOS materials have a streamline shape. First, monodisperse Cu\textsubscript{2}O nanoparticles with an average size of 126 nm (please see Supporting Information for details, Figure S5) were synthesized as a template for Au deposition. Because the standard reduction potential of AuCl\textsubscript{4}\textsuperscript{-}/Au (1.00 V vs standard hydrogen electrode (SHE)) is higher than that of Cu\textsuperscript{2+}/Cu\textsubscript{2}O (0.22 V vs SHE),\textsuperscript{6} Au nanoparticles (size of 5.1 ± 0.7 nm) can be deposited on Cu\textsubscript{2}O crystals by spontaneous galvanic replacement at ambient temperature, resulting in a composite material of surface decorated Cu\textsubscript{2}O@Au (Figures S6 and S7). In general, the sol–gel process of organosilane RSi(OR\textsubscript{3})\textsubscript{3} (e.g., MPTMS) is based on the hydrolysis and followed by condensation under acidic or alkaline conditions.\textsuperscript{7} Rather surprisingly, we found that Cu\textsubscript{2}O@Au nanoparticles can act as catalysts for the sol–gel reaction of MPTMS and thereby construction of polysilsesquioxane frameworks. Most intriguingly, the product (i.e., TCOS) has a streamline shape (Figure 2a–f and Figures S8 and S9), which is the streamline geometry we described in Figure 1b. The monodisperse TCOS particles, with ca. 100% morphological yield, have a maximal head width of ca. 380 nm and a tail that tapers along its longitudinal axis of ca. 800 nm. Their tilted diameter increases abruptly (from 0 to 330 nm) and then gradually decreases (from 330 to 0 nm) from head to tail along the longitudinal axis (stereographs of atomic force microscopy (AFM) in Figure 2b and Figure S10), resembling the vivid appearance of a tadpole. Three main compositional characteristics are found in the TCOS product (Figure 2f and Figures S11–S13): (i) copper was distributed across the entire structure, accounting for 19% by weight (inductively coupled plasma (ICP) measurement), (ii) the streamline structure contained organic groups (including sulfur element), originated from mercaptopropyl groups of MPTMS, and (iii) gold element existed largely in the globose head of this streamline body, with a mass percentage of 2% (ICP measurement); thus, hereafter, TCOS can also be read as M\textsubscript{A}@TCOS (M\textsubscript{A} = Au, unless otherwise specified). Additionally, we further optimized synthetic parameters (e.g., reaction temperature, duration, and precursor concentration) in order to produce TCOS samples in good quality (Figures S16–S18) and a high morphological yield (~100%, Figure S9). For instance, the average tail length of TCOS can be varied from 0.3 to 1.25 μm simply by adjusting the concentration of MPTMS in synthesis.

Although extensive research has been pursued in the synthesis of organosilica (also known as polysilsesquioxane),\textsuperscript{8–11} no control over product shapes has been achieved owing to the difficulty in auto-organization of the sol–gel process at a mesoscopic length scale (10–1000 nm). Moreover, typically, the organosilica network with hydrocarbon groups exhibits hydrophobic properties.\textsuperscript{12} However, a highly hydrophilic surface was formed in our TCOS system (water contact angle of 38°; Figure 2g). As proven by X-ray diffraction (XRD) analysis (Figure S19), all Cu\textsubscript{2}O phase was absent in the TCOS product, suggesting the total transformation, but the Au phase was still preserved. The TCOS has a layered structure with discernible clay-like reflections. The $d$-spacing of the layered structure determined to be 1.62 nm is interpreted as the sum of the tetrahedral siloxane layer thickness plus the interlayer distance created by the alkylthiol spacers (refer to the structural models in Figure S19c, where the alkyl chains are in bilayer arrangements).\textsuperscript{8,14} On the other hand, the 0.42 nm periodicity displayed in the XRD pattern can be attributed to alkylthiol chains packing within the layer (via van der Waals interactions).\textsuperscript{14,15} The observed reflections are generally
broad, suggesting some degree of intralayer disorder/defects due to the sorption of copper ions. Furthermore, evidence for copper coordination with the alkylthiolate group through forming covalent Cu–S bonds is provided by X-ray photoelectron spectroscopy (XPS) characterization (Figures S20–S25). In contrast, no XPS signal due to Au was observed in the TCOS sample, indicating that Au nanoparticles (located in the head portion) were totally confined underneath the copper organosilicate layer, as also evidenced from their corresponding high-resolution transmission electron microscopy (HRTEM) images in Figure S26. Furthermore, XPS spectra in Figure S21 and Figure S24 indicate that the copper species mainly exist as Cu(I). A small amount of Cu(II) should be attributed to the spontaneous surface galvanic replacement reaction during the preparation of Cu2O@Au. It was found that Cu(I) was quite stable in our synthetic solution because thiolates were able to stabilize Cu+ ions by protecting them from further oxidation to Cu(II). Fourier transform infrared spectroscopy (FTIR) spectrum (Figure S27) of TCOS shows that the Cu(I)–O vibrational band (at 630 cm⁻¹) in the Cu2O template disappeared completely and a new organosilicate phase (featured with alkylsiloxane network) formed, consistent with the conclusion derived from XRD analysis. Specifically, the thiol groups (S–H stretching vibration, 2557 cm⁻¹) in TCOS are missing, again supporting the binding of thiol group to copper. In addition, solid-state ²⁹Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy (Figure S28) confirms the presence of organosiloxane units [(OSi)m(OH)1–m, m = 1–3] in the TCOS, which reveals two distinct resonances: the peaks at ~67 and ~58 ppm were assigned to the fully condensed T₃ and the partially condensed T₂ species, respectively, also indicating that Si–C bonds were not cleaved during the reaction. Besides, the organic constituents of TCOS were also determined by thermogravimetry and FTIR (combined TGA–FTIR; Figure S29). The mesoporosity of TCOS was confirmed by N₂ physisorption measurements. The N₂ sorption isotherm (Figures S30 and S31) of TCOS displays type IV hysteresis, which shows a large BET surface area of 234 m²·g⁻¹, a total pore volume of 0.42 mL·g⁻¹, and well-defined mesopores with an average pore size of 3.7 nm (BJH model). In addition, the shape of TCOS can be maintained even after hydrothermal treatments (160 °C for 24 h, Figure S32) or calcination under air (500 °C for 6 h, Figure S33); it is indeed structurally and thermally robust.

To shed light on the formation mechanism of singular TCOS and to understand the role of Cu₂O@Au precursor, two solid analogues were also made in this work. Copper organosilicate (COS) was prepared in a similar manner as the TCOS, but bare Cu₂O particles (i.e., without gold) were used instead. Our TEM images and energy-dispersive X-ray spectroscopy (EDX) elemental maps show that the COS is in a flexible sheet form with irregular shapes (Figures S34 and S35). In addition to the COS, an organosilica sample was also obtained directly from the hydrolysis of MPTMS using triethylamine as a base catalyst. As shown in Figures S36 and S37, the as-synthesized organosilica particles are spherical in shape (similar to Stöber silica). The hydrophobic surfaces of these two solid analogues are evident from the water contact angles of 84° (COS) and 140° (organosilica) in Figure 2h,i. Importantly, the dynamic viscosity of TCOS in ethanol (suspension concentration: 0.5 g·L⁻¹) was determined as 1.171 cP (at 25 °C), which was smaller than the values of COS (1.178 cP) and organosilica (1.191 cP) in ethanol. Again, XRD results indicate that the d-spacing values of the layered structure in TCOS (1.62 nm) were relatively larger than that of organosilica (1.12 nm), due to the incorporation of copper ion in the organic layer (Figure S19). It is worth noting that the space difference is close to two times of the theoretical value of Cu–S bond (2.2 Å). The enlargement of interlayer spacing will affect the porosity of TCOS; indeed, the TCOS samples are more porous, compared with COS (BET surface area of 58 m²·g⁻¹), organosilica (3 m²·g⁻¹), and the Stöber silica (16 m²·g⁻¹).

On the basis of the above characterizations, the origin of the streamline shape is unlikely to lie in thermodynamics but on reaction kinetics, as illustrated in Figure 3a. First, Cu₂O acted as a catalyst for the hydrolysis and polycondensation of MPTMS. We found that the catalytic effect of Cu₂O is induced by releasing protons in solution via the metal–thiol complexation RSH + Cu⁺ → RSCu(1)+H⁺, as evidenced by the solution pH value changes from 6.7 to 4.3 after mixing Cu₂O with MPTMS. These protons will promote the construction of the organosilicate framework through three steps: hydrolysis of MPTMS to form the silanol species RSi(OH)₃ followed by a chain bilayer self-organization process, and then Si–O–Si condensation. The released H⁺ can also directly etch Cu₂O phase via Cu₂O + 2H⁺ → 2Cu⁺ + H₂O. It has been reported that the stability of Cu₂O crystal planes in weak acid solution follows the order {100} >> {111} > {110}. In our present work, the pristine Cu₂O spheres were quite reactive as they were aggregated from small crystallites. To validate the effect of this surface reactivity, we selected the {100}-faceted Cu₂O (i.e., nanocubes) to replace the spherical Cu₂O and used the resultant Cu₂O@Au as a catalyst for the reaction by using TCOS (having long and short tails) and spherical Cu₂O@Au@mSiO₂ as catalysts. The kinetic data without using catalysts are also plotted (line (4)) for comparison. Insets show the corresponding TEM images and structural models of the particles.
as a precursor. Nevertheless, we found that the product Cu$_2$O@Au@organosilica from this process still maintained the cubical shape with some interior voids (Figures S38 and S39). Because the [100] crystal planes are more stable, less Cu$^+$ ions can be liberated in the latter case and the deposition of pure organosilica is kinetically preferred. To further address the formation process, time-dependent pH change upon the synthesis was recorded in Figure 3a, which provides significant insight into the Cu$_2$O etching behavior. In particular, the pH value decreases drastically at the onset of MPTMS addition, and then it proceeds for two stages of decrease before it stabilizes. Decorating the Cu$_2$O spheres with Au nanoparticles seems to be efficient in preventing Cu$^+$ ions from rapid leaching. As MPTMS approaching the Cu$_2$O spheres, Cu$^+$ would be liberated. Because of uneven distribution of Au nanoparticles on the Cu$_2$O spheres, the reaction was always commenced at a surface spot where the Au nanoparticles were less dense (i.e., the Cu$_2$O was less protected). Therefore, MPTMS and H$^+$ could break through the layer of Au nanoparticles and result in a breach on the Cu$_2$O surface (refer to the models in Figure 3a). The breaching process on the surface was actually captured in our TEM observation, especially at a low reaction temperature (Figure S17a–c). We noted that the side view of distribution of Au nanoparticles in TCOS appears as a 270° arc in the TEM image (inset, Figure 3a). The second stage pH-decrease corresponded to the formation of breaches. As such, the anisotropic growth of copper organosilicate was induced. Further growth and shape-control of the organosilicate phase would then be driven by the minimum free-energy structures accessible in the stirred solvent (Figure 1a), which spontaneously adopted the streamline geometry as a result of minimizing fluid resistance (Figure 1b). In terms of elaborated lamellar mesophase, the steric and fluid resistance (Figure 797) experiences a lower drag than the spheres, leading to a higher relative swimming speed in the stirred reaction medium, and (ii) the active metal (Au nanoparticles) located in the Au@TCOS head tended to be refreshed more continuously during the reactions, thereby facilitating the mass exchange for reactant and product species on the active sites of the catalyst surface.

As described earlier, the scientific interest in the streamline materials is placed on their lower drag in flowing fluids. In this regard, M$_x$@TCOS (M$_x$ = Au, Pd, and Pt) samples can serve as smart nanocatalysts because the head portion (M$_x$) is catalytically active while the TCOS body ensures a minimum fluid resistance. To demonstrate such advantages, we used Au@TCOS for catalytic reduction of 4-nitrophenol to 4-aminophenol. As compared in Figure 3b,c and Figure S48, the catalysts with varied geometrical shapes possess different activities: Au@TCOS (long tail) > Au@TCOS (short tail) > spherical counterpart. In terms of rate constants, assuming a pseudo-first-order reaction, Au@TCOS with a long tail (0.224 min$^{-1}$) is about two times their spherical counterpart (0.118 min$^{-1}$). These findings are understandable: (i) Au@TCOS experienced a lower drag than the spheres, leading to a higher relative swimming speed in the stirred reaction medium, and (ii) the binary metal (Au nanoparticles) located in the Au@TCOS head tended to be refreshed more continuously during the reactions, thereby facilitating the mass exchange for reactant and product species on the active sites of the catalyst surface.

It is important to recognize that M$_x$@TCOS (M$_x$ = Au, Pt and Pd) themselves own a high degree of mesoporosity as well as thiol functionality which provides strong affinity to other noble metals (M$_y$). Therefore, streamline M$_x$@TCOS can be assembled into even more complex nanocatalysts, M$_x$@TCOS@M$_y$ on which multiple metal components M$_y$ can be further integrated on their external surfaces. Using Au@TCOS as a primary support, our investigation has shown that noble metal clusters of Au, Pd, Pt, and Ag can be further deposited on the M$_x$@TCOS via in situ reduction of metal precursors (e.g., HAuCl$_4$, H$_2$PdCl$_4$, H$_2$PtCl$_6$, and AgNO$_3$) with sodium borohydride as a reducing agent, giving rise to a wide array of M$_x$@TCOS@M$_y$ (M$_x$ = Au and M$_y$ = Au, Pd, Pt, and Ag). For instance, in Au@TCOS@Au sample, the formed Au nanoclusters (diameter: 1.7 ± 0.2 nm) were dispersed uniformly on the surface of TCOS (TEM images; Figure 4f and Figures S49–S51). The (111) lattice fringes of Au are clearly visible (d$_{111}$ = 0.23 nm). Similarly, other M$_x$@TCOS@M$_y$ (M$_x$ = Au and M$_y$ = Pd, Pt, and Ag) catalysts with excellent controllability were also prepared (Figures S52–S54). EDX elemental mappings in Figure 4a–d clearly indicate the presence of the respective metals on the entire TCOS surface. In addition, we found that increasing the concentration of metal precursor yielded larger sized metal clusters (Figures S55–S57), due to a fixed amount of thiol groups available for binding the metals. Under the optimal condition, the average size of Pd, Pt, and Ag nanoclusters immobilized on TCOS support was 1.6 ± 0.3, 2.1 ± 0.9, and 2.1 ± 0.3 nm, respectively. Reexamination of the XPS S 2p spectra shows that the relative intensity ratio of S metal to S–H increased drastically after the metal anchorage (Figure S58). The actual metal loadings in the final catalytic were analyzed with the ICP method, which revealed a metal content of 9.85, 4.16, 8.77, and 3.55 wt % for Au, Pd, Pt, and Ag, respectively. Chemical states of metal in M$_x$@TCOS@M$_y$ catalysts were also investigated by XPS (Figure 4g and Figure S59). For all the noble metal species, two symmetrical 3d or 4f core level peaks were observed, and no other components could be deconvoluted, revealing that the ionic metals were completely reduced to their metallic states. For example, the binding energies of Au 4f$_{7/2}$ and 4f$_{5/2}$ were 84.2 and 87.9 eV, respectively, which can be assigned to only Au(0). Moreover, binary Au/Pd clusters, ternary Au/Pd/Ag clusters, and quaternary Au/Pd/Ag/Pt clusters could also be deposited by
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On the basis of this work alone, we have studied a great number of noble metals that can work as multifunctional catalytically active metal surfaces (especially for MB). Along with free of using any capping agents, which ensures the presence of catalytically active metal surfaces (especially for MB). Along with images, XPS spectra, and catalytic data in Supporting Information. Coupling of iodobenzene and phenylboronic acid. See more TEM characterizations in Figures S60. Quaternary Au/Pd/Ag/Pt clusters on the TCOS and other elemental mapping (see Figure 4e for EDX elemental maps of Table S2) were validated by using TEM, STEM, and EDX TCOS@MB, where MB = Au+Pd+Ag+Pt catalysts (Table S3).

In summary, the roles of particle geometry on fluid-related gas–solid and solid–solution systems are fundamentally important. Our current work represents the first example of synthetic preparation of streamlined nanocomposites (e.g., with a tadpole morphology) with complex chemical compositions in a tailorable fashion. Significantly, such streamline-shaped nanocatalysts indeed can reduce fluid resistance and have elucidated their structural benefits in catalytic applications compared to other commonly used counterparts. Therefore, we envision that future development of streamline-based hybrid materials (e.g., TCOS), in combination with various functional nanostructured materials (e.g., MA and MB in MA@TCOS@MB), will play a greater role in the design and synthesis of new generation catalysts or sorbents for multiphase processes. Apart from the heterogeneous catalysis studied in the current work, sorptive separation and chemical sensing could also be future research topics using this class of materials.

CONCLUSIONS

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00216. Detailed synthetic procedures and additional experimental results of studied samples, including Tables S1–S11 and Figures S1–S67 (PDF).
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Notes

The authors declare no competing financial interest.