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Porous and hollow metal-layer@SiO₂ nanocomposites as stable nanoreactors for hydrocarbon selective oxidation \dagger

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Porous and hollow metal-layer@SiO₂ nanocomposites (metal = Au, Ag, Cu) have high catalytic activity and stability for cyclohexene selective oxidation.

In recent years, nanocomposite catalysts with tunable particle size, shape and composition have attracted considerable research interest because of their improved physical and chemical properties over those of their components.¹⁻⁸ Metal (such as Au, Ag, Cu) nanoparticles with high surface-to-volume ratio have received increasing attention due to their great catalytic performance in hydrogenation, oxidation, and reduction reactions compared to their bulk materials.⁹⁻¹² Starting with metal nanoparticles, two- and three-dimensional model catalysts have been developed that are composed of nanoarrays on a flat substrate and nanoparticles dispersed in a high-surface-area shell with core–shell structures, respectively.^{13–18} These model catalytic systems have enabled systematic investigations of the effects of particle size, shape and composition on catalytic properties. However, metal nanoparticles still tend to aggregate and sinter, leading to a rapid decay in catalytic abilities.^{19,20}

A nanoreactor, a miniaturized reaction vessel retaining a catalyst inside, has great potential for improved chemical transformations by protecting the catalyst from environmental influences and confining reagents and catalysts within the nanospace for a prolonged period of time.^{21–24} On the other hand, the bulk porous metal (Au) structure also shows good catalytic properties.^{25,26} Combining the space confinement of nanoreactor and the porous metal structure will be an efficient way not only to overcome the disadvantage of dispersed metal nanoparticles but also to improve the catalytic activity and stability. In light of this, the porous and hollow core–shell nano-structure should be regarded as an ideal model nanoreactor to realize the above idea. In this system, the hollow and porous metal layer (Au, *etc.*) as a core and the porous shell (SiO₂, *etc.*) as a catalyst support could enhance the catalytic performance by suppressing catalyst

sintering, improving charge transfer, and promoting the catalyst stability.^{25,26}

Here, we demonstrate a facile approach for the controllable preparation of porous and hollow metal (Au, Ag, Cu)-layer@SiO₂ nanocomposites (see ESI† for experimental details). These nanocomposites, used as solvent-free nanoreactors, show high catalytic activity for the selective oxidation of cyclohexene (cyclohexene conversion of 58.41% (Au), 48.03% (Ag) and 32.99% (Cu) based on cyclohexene) at 60 °C using H₂O₂ as an oxidant. Furthermore, the Au-layer@SiO₂ nanocomposites as nanoreactors are stable enough during the 5 times recycling without exhibiting any significant changes of the catalytic activity and selectivity.

The synthetic strategy of porous and hollow metal (Au, Ag, Cu)layer@SiO₂ nanoreactors is based on a three-step process shown in Scheme 1. First, negatively charged uniform polystyrene (PS) spheres (shown in Fig. S1†) with sulfate functional groups on the surfaces were dispersed into HAuCl₄, AgNO₃ (adding ascorbic acid) and Cu(NO₃)₂ (adding NaBH₄) aqueous solutions to obtain PS@metal (metal = Au/Ag/Cu) core-shell composites, respectively.²⁷ Here, the metal shell of the PS@metal composites is a porous layer. Second, the PS@metal particles were mixed with tetrabutyl orthosilicate (TEOS) for sol-gel reaction to obtain PS@metal@SiO₂ triple-layer core-shell hybrid microspheres (typical scanning electron microscopy (SEM) images shown in Fig. 1). Third, the as-synthesized PS@metal@SiO₂ nanocomposites were added to isopropanol solution to remove the



Scheme 1 Schematic procedure for the fabrication of porous and hollow metal-layer@SiO₂ nanoreactors.

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Fig. 1 SEM and TEM (inset) images of (a) PS@Au@SiO₂, (b) PS@Ag@SiO₂, (c) PS@Cu@SiO₂ triple-layer core-shell spheres. (Scale bar: 40 nm.)

PS core and then the metal (Au, Ag, Cu)-layer@SiO₂ nanoreactors (metal weight content: Au ~4.5%, Ag ~3.2%, Cu ~1.9%) were obtained.

Fig. 2a presents a typical SEM image of the resulting porous and hollow Au-layer@SiO2 nanoreactors. It can be seen that all Aulayer@SiO₂ nanoreactors have an average diameter of ca. 300 nm with a narrow size distribution, and these nanoparticles are spherical with smooth surfaces. Transmission electron microscopy (TEM) images of these Au-layer@SiO2 nanoreactors (Fig. 2b) show complementary contrast, apparently confirming the formation of a uniform hollow Au-layer and a SiO₂ shell. The energy dispersive X-ray (EDX) spectrometry analysis (Fig. 2b inset) of Au-layer@SiO₂ nanoreactors confirms their compositions. We can see that, except for the Cu and C peaks coming from the use of copper grid covered with a carbon film, the Au, Si and O diffraction peaks corresponding to the Au-layer and the SiO₂ shell can be clearly observed. Fig. 2c shows the typical TEM image of a single Au-layer@SiO₂ nanoparticle. It can be observed that the hollow Au-layer with a thickness of 5-10 nm was covered by a uniform shell of SiO₂ with a thickness of \sim 40 nm. Fig. 2d–g show the EDX elemental mapping of the Au-layer@SiO₂ nanoparticle, which indicates that the Au and Si, and O elements are



Fig. 2 Structure and morphology of porous and hollow Au-layer@SiO₂ nanoreactors: (a) SEM image, (b) TEM image (inset: EDX pattern), (c) TEM image of a single Au-layer@SiO₂ nanoparticle, and corresponding elemental mapping images of (d) C, (e) Au, (f) Si and (g) O. (Scale bar: 20 nm.)

well-dispersed within the inside layer and the covered shell, respectively. These EDX elemental mapping images shown here are the direct evidence for the formation of a hollow Au-layer@SiO₂ structure. The signals of the C element in Fig. 2d are attributed to the carbon film coated on the copper grid. The SEM, TEM and EDX elemental mapping images of Ag-layer@SiO₂ and Cu-layer@SiO₂ are shown in Fig. S2 and S3,† confirming that the uniform hollow Ag-layer@SiO₂ and Cu-layer@SiO₂ nanostructures were obtained, respectively.

To testify whether the core-shell structures of PS@Au@SiO₂ and porous and hollow Au-layer@SiO₂ nanocomposites have the porous characteristics, Brunauer–Emmett–Teller (BET) gas adsorption measurements (Fig. 3) were conducted at liquid N₂ temperature (77 K). The adsorption–desorption isotherm and the pore size distribution curve of (PS@Au)@SiO₂ (Fig. 3a and b) can be identified as type IV, and the hysteresis loop in the adsorption–desorption isotherms is the characteristic of mesopores.^{7,28} However, after removing the PS core, the isotherms of Au-layer@SiO₂ (Fig. 3c and d) have the typical features of macroporous materials.^{29,30} These results show that both the SiO₂ shell and the Au-layer are porous and not compact. Based on the above evidence, we can conclude that porous and hollow metal-layer@SiO₂ nanoreactors have been successfully synthesized.

The typical catalytic performance of the porous and hollow metal (Au, Ag, Cu)-layer@SiO₂ nanoreactors over cyclohexene selective oxidation was checked at 60 °C using H₂O₂ as an oxidant. The detailed conversion of cyclohexene and selectivity of oxidation products are shown in Tables S1 and S2.† As shown in Fig. 4a and Table S1,† Au-layer@SiO₂ nanoreactors as catalysts yielded the highest conversion of 58.41% of cyclohexene, while Ag-layer@SiO₂ and Cu-layer@SiO₂ nanoreactor catalysts gave the cyclohexene conversion of 48.03% and 32.99%, respectively. In the following experiments, the catalytic performance of Au-layer@SiO₂ nanoreactors for the selective oxidation of cyclohexene is further studied, and the detailed results are shown in Fig. 4b and Table S2.† We can see that both the conversion of cyclohexene and the selectivity of 1,2-cyclohexanediol increased with the increasing reaction time, while the selectivity of cyclohexene oxide decreased. After 24 h, the conversion



Fig. 3 Nitrogen adsorption–desorption isotherm of (a) $(PS@Au)@SiO_2$ and (c) porous and hollow Au-layer@SiO_2. Pore size distribution curve of (b) $(PS@Au)@SiO_2$ and (d) porous and hollow Au-layer@SiO_2.



Fig. 4 Profile of porous and hollow metal-layer@SiO₂ nanoreactors as catalysts on selective oxidation of cyclohexene: (a) the relationship between the conversion of cyclohexene and reaction time with different metal (Au, Ag Cu)-layer@SiO2 nanoreactors as catalysts. (b) The relationship between the conversion of cyclohexene/selectivity of different products and reaction times with porous and hollow Au-layer@SiO2 as a catalyst. (c) The relationship between the conversion of cyclohexene/ selectivity of different products and recycling times with porous and hollow Au-layer@SiO2 as a catalyst. (d) XRD patterns of porous and hollow Au-layer@SiO2 nanoreactors before reaction (dark line) and after 1 (red line), 2 (blue line) and 5 (dark cyan line) times recycling. Inset: enlarged XRD patterns of Au-layer@Si porous and hollow O2 nanoreactors before and after 1 (red line), 2 (blue line) and 5 (dark cyan line) times recycling. (e) TEM images of porous and hollow Au-layer@SiO₂ nanoreactors as catalysts after 5 times recycling experiments (60 °C and 24 h). (f) TEM image of a porous and hollow Au-layer shell after removal of the SiO₂ of Au-layer@SiO₂ nanoreactors (after 5 times recycling).

of cyclohexene and selectivity of 1,2-cyclohexanediol reached 58.41% and 70.20%, respectively, while the selectivity of cyclohexene oxide fell to 22.63% from 91.61%. The results indicate that epoxide is formed initially as a primary product, and other products are formed as a consequence of sequential oxidation. The relationship between the conversion and selectivity of cyclohexene for different products and reaction time with Ag-layer@SiO2 and Cu-layer@SiO2 nanoreactors as catalysts are shown in Fig. S4a and b,† respectively. The turnover frequency (TOF) was employed to evaluate the catalytic activities, which was calculated by determining the moles of product formed (or reactant consumed) per unit time per mole of available active sites on the catalyst.31,32 As shown in Table S1,† the change in TOF suggests the selective oxidation of cyclohexene over these metal (Au, Ag, Cu)-layer@SiO₂ catalysts to be qualified as structuresensitive.14 Based on the above experimental results, it can be concluded that the activity order of the three kinds of nanoreactors was: Au-layer@SiO₂ > Ag-layer@SiO₂ > Cu-layer@SiO₂, due to the catalytic performance of the corresponding metal-layer. To examine the key role of the nanospaces in the metal-layer@SiO₂ nanoreactors, a series of control experiments over cyclohexene selective oxidation were carried out, employing $PS(@metal@SiO_2 (metal = Au, Ag, Cu)$

as catalysts. As shown in Fig. S5 and Table S1,† the PS@metal@SiO₂ as catalysts yielded the conversion of 9.57% (Au), 7.87% (Ag) and 5.40% (Cu), respectively, which were much lower than that produced by metal-layer@SiO₂ [58.41% (Au), 48.03% (Ag) and 32.99% (Cu)], respectively. This is the direct evidence that the catalytic activity of the metal-layer@SiO₂ is mainly determined by the presence of the centre nanospaces.

In addition to catalytic activity, the stability of catalysts is another important issue for their practical applications. Therefore, we carried out repeated experiments (5 times) on cyclohexene selective oxidation with Au-layer@SiO₂ as a catalyst. As shown in Fig. 4c and Table S3,† the Au-layer@SiO₂ nanoreactors are stable enough during the repeated experiments without exhibiting any significant loss of catalytic activity and selectivity. Crystalline structures and morphologies of Au-layer@SiO₂ after 5 times recycling on cyclohexene selective oxidation were also studied. The XRD pattern of the Au-layer@SiO₂ samples (Fig. 4d and inset) at the end of the repeated experiment is almost identical to that of the as-prepared Au-layer@SiO₂ nanoreactors. Furthermore, compared with the fresh catalysts (Fig. S6a†), no evident morphology changes can be observed in the TEM results (Fig. 4e and S7†).

On the other hand, in order to further confirm the porous and hollow shell structure of the Au layer, HF (0.5%) was used to remove the SiO₂ shell of Au-layer@SiO₂. As shown in Fig. S6b,† the obtained sample exhibits a typical porous (or discontinuous) hollow shell structure. To further confirm the stability of the nanoreactors, we also removed the SiO₂ shell of Au-layer@SiO₂ (after 5 times recycling) to check the structure of the Au-layer shell (Fig. 4f). Compared with the fresh catalysts (Fig. S6b†), there is no obvious change observed in TEM image of the discontinuous Au hollow shell, which is also agreed with the XRD analysis. All the above results further indicate that these Au-layer@SiO₂ nanocomposites possess excellent stability for hydrocarbon selective oxidation, which should be attributed to the presence of the discontinuous hollow shell of Au in Au-layer@SiO₂ nanoreactors.^{25,26}

Based on the above experimental results, the superior catalytic performance of metal-layer@SiO2 composites is due to the structural features of the composite nanoreactors. First, the reagents can be absorbed by the SiO_2 shell, then diffuse through the SiO_2 shell and the metal-layer, being enriched within the centre nanospaces, as the SiO₂ shell and the metal-layer are not compact. The concentration of reagents around the metal-layer in the nanoreactor leads to a higher reaction rate. Second, the thin layer of mesoporous silica is only 40 nm, indicating a very short diffusion course for both reactants and products. Such a short diffusion course is beneficial for heterogeneous catalysis. Third, based on the presence of the porous and hollow metal layer within the SiO₂ shell, the loss of metal nanoparticles due to frictional or other mechanical forces can be avoided and the possible aggregation occurring in metal-layer@SiO₂ nanoreactors can remarkably decrease to greatly enhance the catalytic activity and stability. These three aspects together account for the porous and hollow metal-layer@SiO2 nanoreactors with excellent catalytic activity and stability for hydrocarbon selective oxidation.

Conclusions

We demonstrate a facile chemical method for controllable synthesis of the porous and hollow metal-layer@SiO₂ nanoreactors (metal = Au, Ag, Cu). Such nanoreactors can be regarded as novel solvent-free

catalysts for the selective oxidation of cyclohexene using H_2O_2 as an oxidant at 60 °C. The high catalytic activity and stability of this kind of nanoreactor is mainly due to the porous and hollow metal layer within the porous SiO₂ shell. The present work also provides an exciting prospect for the application of new porous and hollow metal-layer based core–shell nanoreactors in catalytic reactions.

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