Diffusion-controlled synthesis of Cu-based catalysts for the Rochow reaction

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ABSTRACT The properties of materials are strongly dependent on their structures. The diffusion effect is a main kinetic factor that can be used to regulate the growth and structure of materials. In this work, we developed a systematic and feasible strategy to synthesize Cu₂O solid spheres and hexahedrons by controlling the diffusion coefficients. These Cu₂O products can be successively transformed into corresponding Cu hollow spheres and hexahedrons as well as CuO porous spheres and hexahedrons by controlling hydrogen diffusion in hydrazine hydrate solution and controlling oxygen diffusion in air, respectively. The formation of these transformations was also discussed in detail. Tested for Rochow reaction, the as-prepared Cu₂O solid and CuO porous spheres exhibit higher dimethyldichlorosilane selectivity and Si conversion than Cu hollow spheres, which is attributed to the active sites for CH₃Cl adsorption formed in Cu_xSi phase after the removal of oxygen atoms in Cu₂O and CuO in the formation of dimethylchlorosilane. The present work not only develops a feasible method for preparing well shape-defined Cu₂O solid spheres and hexahedrons but also clarifies the respective roles of Cu, Cu₂O and CuO in dimethyldichlorosilane synthesis *via* Rochow reaction.

Keywords: cuprous oxide, hollow spheres, porous spheres, surface oxygen vacancies, Rochow reaction

INTRODUCTION

Controllable synthesis of materials with well-defined shapes has attracted immense research interest in recent years, due to the unique morphology-dependent physical and chemical properties [1–4]. The diffusion effect in controllable synthesis is a main kinetic factor for regulating materials structure in materials science fields

[5,6]. Very recently, various materials with controlled shapes such as snow-like vaterite [5] and silver dendritic [7] have been successfully synthesized by controlling chemical diffusion and reaction kinetics. Cuprous oxide (Cu₂O), an important metal oxide that possesses unique optical and electrical properties [8], has been widely applied in various fields such as catalysis [9,10], sensors [11], and energy conversion and storage [12]. In the last several years, the controllable synthesis of Cu₂O micro- and nano-sized crystals with a vast array of architectures, including core-shell Cu₂O spheres [13], hollow Cu₂O spheres [14], and porous Cu₂O spheres [15] has been achieved using electrodeposition method, thermal relaxation method, sonochemical method, vacuum evaporation method, γ -irradiation method, and liquid-phase reduction method [16–18]. Additionally, metallic copper (Cu) and copper oxide (CuO) with various structures have also received intense attention, as they can be used in catalysis, sensors, and electronics [19–26]. However, the aforementioned synthesis approaches often involve the use of surfactants, template, and high temperature and pressure to obtain morphology-controllable Cu₂O structures, which undoubtedly increases the synthesis cost and thus limits their large-scale production. Therefore, it is highly desired to develop a feasible and green method to fabricate shape-controlled Cu₂O *via* adjusting diffusion parameters.

Rochow reaction is the so-called direct process employed in industry to produce methylchlorosilanes, in which silicon (Si) reacts with chloromethane (CH₃Cl) over the Cu-based catalysts [27]. Metallic Cu [28] and copper compounds such as Cu₂O [29], CuO [30], CuCl [31], and Cu-Cu₂O-CuO composites [32] are known to be

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catalytically active for this reaction with the assistance of some promoters. The selective synthesis of dimethyldichlorosilane ($(\text{CH}_3)_2\text{SiCl}_2$, M2) from this reaction is most desirable in the organosilane industry. Therefore, many efforts have been made to develop efficient Cu-based catalysts to improve M2 selectivity and yield [33,34]. Previously, we explored a series of model catalysts for Rochow reaction, and observed that Cu_2O and CuO were more active than metallic Cu [28–30], but the true role of oxygen species was not clear yet because of the high complexity of the reaction and the irregularity in morphology of the catalyst particles. It is reported that the surface oxygen vacancies are the most relevant surface defects in metal oxides, which may assist in band bending and subsequent electron-hole pair separation in various applications, especially in catalysis [35–37]. Also, first quantum-mechanical and density functional theory studies have revealed that surface oxygen vacancies can impact the function of Cu atoms [38,39]. It is expected that a systematic comparison of the catalytic activity between Cu, Cu_2O and CuO catalysts with the same shape will simply the issue and possibly provide better understanding to the role of oxygen species and the catalytic mechanism through clarifying the role of the surface oxygen vacancies.

Here, we report a simple well-controlled synthesis of Cu_2O solid spheres and hexahedrons by controlling the diffusion coefficients, including adjusting solvents, reactant concentration, and temperature. Subsequently, the Cu hollow spheres and CuO porous spheres are prepared by diffusion-controlled reduction of Cu_2O with hydrazine hydrate solution and oxidation of Cu_2O in air. Compared with the hollow Cu sphere catalyst used for M2 synthesis *via* Rochow reaction, the Cu_2O solid spheres and CuO porous spheres show enhanced M2 selectivity and Si conversion. The role of oxygen species and the reaction mechanism were discussed accordingly.

EXPERIMENTAL

Materials synthesis

Synthesis of Cu_2O solid spheres

The synthesis conditions used in this work are summarized in Table S1. In a typical synthesis, 2.0 g of copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, analytical reagent (AR), Sinopharm Chemical Reagent Co., Ltd) was dissolved in a mixture of 40.0 mL deionized water and 40.0 mL methanol. Upon heating to 70°C, 2.8 g of sodium hydroxide (NaOH , AR, Sinopharm Chemical Reagent Co., Ltd) and

2.4 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$, AR, Sinopharm Chemical Reagent Co., Ltd) were added into the solution with stirring. The mixture was stirred for another 60 min at 70°C, and then cooled to room temperature. The resulting precipitate was collected by centrifugation, washed with distilled water and absolute ethanol for several times, and finally dried under vacuum at 80°C for 24 h.

Synthesis of CuO porous spheres

The obtained Cu_2O solid spheres were oxidized in air to prepare CuO porous spheres. Typically, 0.5 g of Cu_2O solid spheres was placed in a square crucible, which was then put in a corundum tube in a tube furnace. The sample was oxidized in air (50.0 mL min^{-1}) at 350 °C for 6 h, then cooled to room temperature naturally.

Synthesis of Cu hollow spheres

The obtained Cu_2O solid spheres were reduced with hydrazine hydrate solution to prepare Cu hollow spheres. Typically, 0.5 g of Cu_2O solid spheres was placed in a beaker with 50 mL of deionized water, followed by the addition of 0.5 mL of hydrazine hydrate (80 wt.%). The reaction was carried out at room temperature for 12 h. The resulting precipitate was collected by centrifugation, washed with distilled water and absolute ethanol for several times, and finally dried under vacuum at 80°C for 24 h.

Materials characterization

X-ray diffraction (XRD) were recorded on a PANalytical X'Pert PRO MPD using the Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The microscopic feature of the samples was characterized by a field-emission scanning electron microscopy (FESEM) with energy-dispersive X-ray spectrometer (EDX) (JSM-7001F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) (JEM-2010F, JEOL, Tokyo, Japan) operated at 200 kV. Thermal gravimetric (TG) analysis was carried out on an EXSTAR TG/DTA 6300 (Seiko Instruments, Japan) at a heating rate of 2°C min^{-1} in air (200 mL min^{-1}) from 30 to 900°C. H_2 -temperature programmed reduction (H_2 -TPR) measurements were carried out on an automated chemisorption analyzer (ChemBET pulsar TPR/TPD, Quantachrome). 0.10 g of Cu_2O particles was initially loaded in a quartz U-tube. Prior to the measurement, the sample was degassed at 200°C for 4 h under helium. When the temperature was dropped to 20°C, the gas was switched to 9.9 vol.% H_2/Ar . Finally, the sample was heated from 20 to 500°C under 9.9 vol.% H_2/Ar with a flow rate of 30 mL min^{-1} .

Catalytic measurement

The evaluation of catalyst was carried out with a typical fixed-bed reactor [33]. 10.0 g of Si powder (20–50 mesh, provided by Jiangsu Hongda New Material Co., Ltd.) and 0.5 g of Cu₂O, together with 0.05 g of zinc (Zn, AR, Sinopharm Chemical Reagent Co., Ltd) as the promoter, were ground homogeneously to form a contact mass, which was then loaded into a glass reactor. The reactor system was purged with purified N₂ for 0.5 h followed by heating to 325°C within 1 h under a N₂ flow rate of 25 mL min⁻¹. Subsequently, N₂ was turned off, and CH₃Cl gas with a flow rate of 25 mL min⁻¹ was introduced into the reactor to react with Si followed by heating to 325°C. After a given period of 24 h, the reaction was stopped. The gas products were cooled into a liquid phase with the circulator bath controlled at -5°C by a programmable thermal circulator (GDH series, Ningbo Xinzhi Biological Technology Co., LTD). The products in the liquid solution were quantitative analyzed by gas chromatograph (GC-7890A, Agilent Technologies) equipped with a KB-201 capillary column (60 m) and a thermal conductivity detector (TCD). Gas chromatography-mass spectrometry (GC-MS, QP2010, Shimadzu) was used for identification of the products, which contained methyltrichlorosilane (CH₃SiCl₃, M1), dimethyldichlorosilane ((CH₃)₂SiCl₂, M2), trimethylchlorosilane ((CH₃)₃SiCl, M3), methylchlorosilane (CH₃SiHCl₂, M1H), dimethylchlorosilane ((CH₃)₂SiHCl, M2H), low boiler (LB) and high boiler (HB). The selectivity was calculated by the peak area ratio (in mass percentage; peak area calibrated with response factor). The Si conversion was determined by the ratio of mass difference of Si powder (before and after the reaction) and the mass of Si (before the reaction) (Formula 1).

Here $m_{\text{Si, before}}$ and $m_{\text{Si, after}}$ represent the mass of Si powder before and after the reaction, respectively. The amount of unreacted Si after the reaction was measured by inductively coupled plasma optical emission spectrometer (ICP-OES). The calibration was done with commercial multi-element standard solutions. Prior to ICP-OES analysis, the waste contact masses were completely dissolved with HF/HNO₃ solution and evaporated to almost dryness. Then, the concentrated solutions were diluted with a 2% HNO₃ solution. Si element was measured for three times to determine standard deviations.

RESULTS AND DISCUSSION

Previous reports have demonstrated that the diffusion rate and reaction parameters are the most important

factors in the synthesis materials with well-defined shape [5,7]. The solvent, reactant concentration, and reaction temperature have strong impact on the diffusion coefficients of reactant, whereas the reaction order and reducing agent affect the reaction processes. Therefore, to obtain well-defined Cu₂O particles with uniform morphology and size, we systematically investigated the effects of diffusion and reaction parameters, as shown in Fig. S1.

Diffusion-controlled synthesis of Cu₂O hexahedron and Cu₂O spheres

Effect of the concentration of precursor solution and the solvents

Fig. 1a shows the XRD patterns of Cu₂O hexahedrons and Cu₂O spheres obtained in pure water (S1) and a methanol/water mixture (S2), respectively. In both cases, the diffraction peaks at 29.5°, 36.3°, 42.2°, 61.3°, and 73.5° are observed and indexed to the lattice planes of (110), (111), (200), (220), and (311) of cubic Cu₂O (JCPDS No. 00-005-0667), respectively. Using Debye-Scherrer formula based on the (111) peak at 36.3°, the calculated average crystal size of Cu₂O is 35.6 and 42.6 nm for the Cu₂O hexahedrons and Cu₂O spheres, respectively. The SEM image reveals that S1 (Fig. 1b) is composed of only regular and dense hexahedrons with smooth surface and diameter of about 1–2 μm. As the concentration of precursor solution decreases, a mixture of Cu₂O hexahedrons and spheres with a diameter of about 0.5–2 μm is obtained (S3, Fig. 1c). From the inset of Fig. 1c, it is clearly seen that the hexahedrons have cavernous surfaces. However, with increasing the solution component concentration, a large portion of non-uniform Cu₂O particles is formed (Fig. S2). When methanol is added in preparing S1, well-dispersed Cu₂O solid spheres (S2) with a diameter of about 1–3 μm are obtained (Fig. 1d–f). In the cases of adding ethanol (S6), glycol (S7) and glycerol (S8), non-uniform Cu₂O spheres mixed with smaller irregular nanoparticles were synthesized (Fig. S3). In addition, the influence of component concentration of the prepared solution in mixed methanol/water solvent was also investigated and the results are shown in Fig. S4.

According to Wilke and Chang Equation, the order of diffusion coefficients in various solvents is as follows: water > methanol + water > ethanol + water > glycol + water > glycerol + water [40,41]. The above results suggest the diffusion coefficients have a strong influence on the morphology of Cu₂O particles, and the uniform and pure Cu₂O solid hexahedron and spheres can be prepared

Figure 1 XRD patterns of Cu_2O hexahedron and Cu_2O spheres (a), SEM images of Cu_2O particles obtained in different solvents: water (S1, S3) (b, c), water + methanol (S2) (d, e), and TEM image of Cu_2O spheres (S2) (f).

only with proper diffusion coefficients. In the synthesis process of Cu_2O , the reactant and the initially formed small nanoclusters and nanoparticles can diffuse quickly in water, but it becomes slower in methanol, ethanol, glycol, and glycerol gradually. Thus, the Cu_2O morphology evolution should be the result of the different diffusion coefficients obtained by changing the concentration of the prepared solution and reaction solvent, which influence the ion transfer rate in solution.

To further confirm the influence of diffusion coefficients on Cu_2O particles forming, we performed a series of control experiments by varying the solvent ratios. As mentioned above, when pure water is used as the solvent (S3), only are Cu_2O hexahedrons with a diameter of about $1\ \mu\text{m}$ obtained (Fig. 1c). After adding 10 mL of methanol (S9, water:methanol = 70:10), there is no obvious change in the size of the Cu_2O products compared with S2, but the shape becomes irregular and some Cu_2O spheres appear (Fig. 2a). With the addition of more methanol (S10, water:methanol = 60:20; S8, water:methanol = 50:30), non-uniform and irregular Cu_2O particles are formed (Fig. 2b, c); meanwhile, more particles become the spherical structure. Upon further adding methanol to 50 mL (S12, water:methanol = 30:50), the obtained products are composed of porous spheres with a diameter of about $1\text{--}2\ \mu\text{m}$ (Fig. 2d). The diffusion coefficient of methanol/water mixture decreases first with addition of the methanol in the concentration of 0–40 mol.%, but in-

Figure 2 SEM images of the products obtained at different volume ratios of water : methanol: 70 : 10 (S9) (a), 60 : 20 (S10) (b), 50 : 30 (S11) (c), and 30 : 50 (S12) (d).

creases again with further increase of methanol (40–100 mol.%). For example, the diffusion coefficient for pure water is $2.275 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$, 10% of methanol is $1.656 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$, 30% of methanol is $1.273 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$, 50% of methanol is $1.341 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$, and 70% of methanol is $1.566 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$ at 298 K [42,43]. Accordingly, the Cu_2O hexahedrons become spheres with the decrease of diffusion coefficient, then porous spheres with the increase of diffusion coefficient.

Effect of the reaction temperature

Fig. 3 shows the SEM images of Cu_2O particles obtained

at different temperatures. It can be seen that sample S13 obtained at 50°C has a spherical morphology with a size distribution of 1–3 μm (Fig. 3a), and the surface of spheres is smooth. Similar results are observed for the samples obtained at 60 and 70°C (S14 and S2) (Figs 3b and 1e), which are all Cu_2O spheres with relatively uniform morphology. However, when the temperature reaches 80 and 90°C, the obtained sample S15 and S16 exhibit a non-uniform particle size distribution as compared to those of S2, S13, and S14 (Fig. 3c, d). It should be pointed out that at these temperatures, the products are composed of mainly Cu_2O particles and small portion of Cu particles according to the XRD results (Fig. S5). Hence, the reaction temperature between 50 and 70°C should be suitable for the preparation of homogeneous Cu_2O spheres. The diffusion coefficients of methanol/water mixtures rises gradually with the increase of the temperature, e.g., the diffusion coefficients of water is $1.298 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 278 K and $2.275 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K, while that of 50% of methanol + 50% of water is $0.741 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 278 K and $1.341 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K [42,43]. Similarly, the diffusion coefficients of the solute in methanol + water mixtures should also rise with the increase of reaction temperature.

Effect of adding reactant sequence and different reducing agents

The effect of reactant addition sequence and different reducing agents were investigated. The formation of Cu_2O spheres involves the formation of CuO nanoparticles and their reduction, as shown in Equations 1–3:

Compared with the uniform Cu_2O spheres obtained in the case of glucose (Fig. 4a) (S2), smaller Cu particles are directly prepared using ascorbic acid (Fig. 4b) (S17) and

Figure 3 SEM images of Cu_2O particles obtained at different reaction temperature: 50°C (S13) (a), 60°C (S14) (b), Cu and Cu_2O particles obtained at 80°C (S15) (c), 90°C (S16) (d).

hydrazine hydrate (Fig. 4c) (S18) as the reducing agent. Three solvents (pure water, water + methanol, and water + ethanol) were used to study the influence of the reaction processes on the Cu_2O shape by reactant addition sequence. When $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{C}_6\text{H}_{12}\text{O}_6$ were first added, Cu_2O nanoparticles were initially formed but without formation of the black CuO nanoparticles which was revealed from the evolution of the solution color. After adding NaOH, the fast formed black CuO nanoparticles were quickly reduced to form non-uniform Cu_2O particles in pure water (S19) (Fig. S6a), in water + methanol (S20) (Fig. S6b), and in water + ethanol (S21) (Fig. S6c). When $\text{C}_6\text{H}_{12}\text{O}_6$ and NaOH were first added, none of products was obtained. After adding $\text{Cu}(\text{CH}_3\text{COO})_2$, the black CuO nanoparticles were quickly formed, followed by a rapid reduction of CuO to Cu_2O nanoparticles and further self-assembly to non-uniform Cu_2O microparticles in pure water (S22) (Fig. S6d), in water + methanol (S23) (Fig. S6e) and in water + ethanol (S24) (Fig. S6f). All of these six samples are Cu_2O particles according to the XRD patterns (not shown here). Thus, the reaction processes have strong influence on the shape of Cu_2O products.

Figure 4 SEM images of the obtained Cu_2O particles using glucose as reducing agent (S2) (a), the obtained Cu particles using ascorbic acid (S17) (b), and hydrazine hydrate (S18) (c) as reducing agent, and XRD patterns of these samples in water and methanol (d).

Figure 5 XRD patterns of the samples (a), SEM images of $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres obtained by reduction with hydrazine hydrate for 4 h (b) and 8 h (c), Cu hollow spheres obtained by reduction with hydrazine hydrate for 12 h (d and e), TEM images of $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres obtained by reduction with hydrazine hydrate for 8 h (f).

Diffusion-controlled synthesis of Cu hollow and CuO porous spheres as well as Cu and CuO hexahedrons

The formation of Cu hollow spheres and CuO porous spheres is illustrated in Equations 5 and 6, respectively.

When the Cu_2O solid spheres are reduced with hydrazine hydrate for 4 and 8 h, the $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres are obtained (Fig. 5b, c). SEM-EDX line-scan analysis (Fig. S7a) shows the presence of both Cu and O elements with an atomic ratio of 90:10 for $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres. By comparing the Cu and O elements atomic ratio, which is 65:35 in Cu_2O spheres (Fig. S7b), part of Cu_2O is reduced to Cu in the $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres, indicating the formation of a structure containing a Cu_2O core and a Cu shell. From the XRD patterns of Fig. 5a, the Cu content in $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres is rising with the increase of the reduction time. When the reduction time is prolonged to 12 h, all of the Cu_2O solid spheres become Cu hollow spheres, as verified by both SEM images (Fig. 5d, e) and XRD patterns (Fig. 5a). The TEM image (Fig. 5f) further confirms that the $\text{Cu}_2\text{O}@\text{Cu}$ core-shell structure was formed when Cu_2O was reduced for 8 h. The formation of hollow Cu spheres may be related to the generation and release of N_2 molecules.

The porous CuO spheres were prepared by oxidizing the obtained Cu_2O spheres in air. Fig. 6a shows the XRD

patterns of the Cu_2O spheres, $\text{Cu}_2\text{O}@\text{CuO}$ core-shell spheres and CuO porous spheres. When the Cu_2O spheres were oxidized in air at 350°C for 2 h, the $\text{Cu}_2\text{O}@\text{CuO}$ core-shell spheres were formed, as shown in Fig. 6b, c. Further increasing the oxidation time to 4 h, uniformly core-shell structured $\text{Cu}_2\text{O}@\text{CuO}$ spheres were obtained (Fig. 6d, f). SEM-EDX spectrum and line scan show the presence of both Cu and O elements with an atomic ratio of 54:46 in $\text{Cu}_2\text{O}@\text{CuO}$ core-shell spheres, indicating that some of Cu_2O spheres were oxidized to CuO forming $\text{Cu}_2\text{O}@\text{CuO}$ core-shell structure (Fig. S7c). Finally, the regular porous CuO spheres were prepared when Cu_2O spheres were oxidized for 6 h, as shown in Fig. 6g, h. The observed lattice spacing of 0.25 nm corresponds to the ($\bar{1}11$) plane of monoclinic CuO, as shown in high resolution TEM (HRTEM) image of Fig. 6i. The formation of porous CuO spheres can be attributed to the air forming void space among CuO nanoparticles. Additionally, the Cu and CuO hexahedron were also successfully obtained by reduction and oxidation of Cu_2O hexahedron (Fig. S8).

The formation process of Cu_2O solid spheres, Cu hollow spheres and CuO porous spheres

According to the above observations, the formation of $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres and Cu hollow spheres can be illustrated in Fig. 7a, which involves dissociation of N_2H_4 , removal of O atoms from Cu_2O and generation of

Figure 6 XRD patterns of the samples (a), SEM images of $\text{Cu}_2\text{O}@\text{CuO}$ core-shell spheres obtained by oxidation in air at 350°C for 2 h (b), and 4 h (d and e), CuO porous spheres obtained by oxidation in air at 350°C for 6 h (g), TEM images of $\text{Cu}_2\text{O}@\text{CuO}$ core-shell spheres obtained by oxidation in air at 350°C for 2 h (c), and 4 h (f), CuO porous spheres obtained by oxidation in air at 350°C for 6 h (h) and HRTEM image of CuO porous spheres (i).

H_2O via H atom diffusion. At the initial stage of the reduction, the surface of the Cu_2O crystals contacts with N_2H_4 to form lattice defects, then Cu_2O reacts with H atoms in N_2H_4 to form N_2 and H_2O [44]. The dissociated H atoms from N_2H_4 further penetrate into the Cu_2O lattices, the inner Cu_2O diffuses out to react with N_2H_4 ; the driving force for out-diffusion originates from concentration gradient. This involves a solid-phase diffusion process, which is the so-called Kirkendall effect [45]. Ultimately, Cu_2O is converted to Cu completely forming Cu hollow spheres. Hence, by tuning the reduction time, it is able to control the content of Cu_2O and Cu, and the interior structure of the $\text{Cu}_2\text{O}@\text{Cu}$ core-shell spheres. In the oxidation processes (Fig. 7b), the diffusion of oxygen occurs at the Cu_2O –oxygen interface to form CuO developing from the surface to interior. At the beginning of oxidation, the surfaces of Cu_2O spheres are firstly oxidized to CuO . The continuous oxidation could be extended from the outer surface to the interior space. Finally, porous CuO spheres resulting from Kirkendall

effect are formed until all Cu_2O are consumed and completely transformed to CuO by reacting with oxygen [46–48]. Cu_2O oxidation can be also contributed to lattice diffusion. Thus, by tuning the oxidation time, it is able to control the content of both Cu_2O and CuO as well in the $\text{Cu}_2\text{O}@\text{CuO}$ core-shell spheres. In a word, the variation of the products in hollow or porous structure can be attributed to Kirkendall effect, the gas (N_2 and O_2) void and the atoms diffusion effect. The diffusion of atoms in different compositions occurs where the void is present, leaving room for other atoms to move in.

Catalytic properties of Cu, Cu_2O , and CuO as Cu-based catalysts for the Rochow reaction

Fig. 8 and Table S2 show the catalytic performance of Cu, Cu_2O , CuO spheres and hexahedrons as Cu-based catalysts for Rochow reaction at 325°C . It can be seen that CuO and Cu_2O catalysts exhibit a Si conversion, which is 30.6% for CuO spheres, 35.4% for CuO hexahedrons, 23.2% for Cu_2O spheres and 29.4% for Cu_2O hexahe-

Figure 7 Schematic illustration of the reduction and oxidation processes of Cu_2O spheres to form Cu hollow spheres and CuO porous spheres.

Figure 8 Selectivity for M2 and conversion of Si for Cu , Cu_2O , CuO spheres and hexahedrons for Rochow reaction. Error bars, standard deviation of triplicated wells. The catalytic measurements were independently repeated three times to obtain three M2 selectivity and Si conversion for each catalyst.

drons, higher than those of Cu spheres (20.8%) and Cu hexahedron (23.1%). More importantly, CuO and Cu_2O show higher M2 selectivity as well, which is 78.6% for CuO spheres, 80.6% for CuO hexahedron, 63.4% for Cu_2O spheres and 70.6% for Cu_2O hexahedron, as compared to those of Cu spheres (56.2%) and Cu hexahedron (57.5%). As we know, a high M2 selectivity and yield are highly desirable in the organosilane industry. Our results demonstrate that the synthesized CuO and Cu_2O catalysts possess much better catalytic activity for M2 synthesis than Cu catalysts with a similar morphology. It should be pointed out that the Cu_2O hexahedrons show much higher dimethyldichlorosilane selectivity and Si conversion than Cu_2O spheres, which is probably because the former has stronger reducibility. This has been verified by the H_2 -TPR characterization, which shows that the maximum reduction peak for Cu_2O hexahedron is lower

than that for Cu_2O spheres (Fig. S9).

The measured XRD patterns of the contact masses using Cu hollow spheres, Cu_2O solid spheres, and CuO porous spheres as catalysts after a reaction of 24 h are shown in Fig. 9a. It can be seen that, the reacted contact masses are composed of Si and Cu , but of no Cu_2O and CuO species due to the reaction of CH_3Cl with the lattice oxygen from Cu_2O and CuO forming Cu in the induction period [33]. An enlargement of the XRD patterns in the range of 40° – 50° (Fig. 9b) shows the presence of Cu_xSi species in all the reacted contact masses, and higher intensities of Cu_xSi are observed in the cases of $CuO + Si$ and $\text{Cu}_2\text{O} + Si$ than that in $Cu + Si$, suggesting that pure CuO and Cu_2O catalysts are more active in generating Cu_xSi than the pure Cu catalyst. In Rochow reaction, the Cu_xSi species are regarded as the real catalytic active species, on which, M2 is selectively produced [49]. Ele-

Figure 9 XRD patterns of reacted contact masses for Cu hollow spheres, Cu₂O solid spheres, CuO porous sphere catalysts after reaction of 24 h (a), and SEM image, elemental mapping images of Si, Cu, Zn, and SEM-EDX spectra of contact masses using CuO porous sphere catalyst (b).

Figure 10 The illustration of the catalytic mechanism using CuO (or Cu₂O) forming surface oxygen vacancies and Cu_xSi (a) and using Cu forming Cu_xSi without surface oxygen vacancies (b), and the formation processes of (CH₃)₂SiCl₂ on high active surface oxygen vacancies (c).

mental mapping images of Si, Cu, Zn, and SEM-EDX spectra of contact masses using CuO porous spheres as the catalyst indicate the uniform distribution of the elements Si, Cu, and Zn on the reaction interface, as shown in Fig. 9c.

Defects such as oxygen vacancies play a crucial role in the surface properties of transition metal oxides. As we know, the loss of an oxygen atom from Cu₂O and CuO generates an oxygen vacancy. Surface oxygen vacancies are the most relevant surface defects in metal oxides, and they participate in a large number of chemical reactions [35,50]. Although the exact mechanism of Rochow reaction over Cu-based catalysts is still unclear, previous studies have shown that CH₃Cl first adsorbs on the surface to form Cu_xSi active phase, then reacts with Si atoms to form M2 [26,30,33,49]. Based on the catalytic results and the aforementioned analysis, a mechanism of surface oxygen vacancies as important catalytic sites for Rochow reaction is first proposed and illustrated in Fig. 10. The reaction of CH₃Cl with the lattice oxygen from Cu₂O and CuO generates surface oxygen vacancies and Cu_xSi when using Cu₂O and CuO catalysts (Fig. 10a). However, only

Cu_xSi phase without surface oxygen vacancies is formed when using Cu catalyst (Fig. 10b). The diffusion of a CH₃Cl molecule is typically rapid and in equilibrium. Thus, the highly active surface oxygen vacancies in Cu_xSi are preferential adsorption sites for CH₃Cl molecules [33,51,52]. Upon adsorption on the Cu_xSi surface, the CH₃Cl molecule can readily dissociate into electronegative Cl⁻ and electropositive CH₃⁺, which are then drawn by the high active surface oxygen vacancies to the reaction sites [24,30]. Subsequently, the electropositive Cu⁺ in Cu_xSi absorbs electronegative Cl⁻, while electronegative Si⁻ in Cu_xSi absorbs electropositive CH₃⁺, and finally, the electronegative Cl⁻ transfers to and combine with Si forming M2 *via* a exothermic process (Fig. 10c).

CONCLUSIONS

In summary, we demonstrated a diffusion-controlled synthesis route to prepare well-defined Cu₂O solid spheres by controlling the diffusion coefficients through adjusting the solvents, reactant concentration, and reaction temperature. Subsequently, the Cu hollow spheres and CuO porous spheres were prepared by controlled

hydrogen diffusion reduction of Cu_2O in hydrazine hydrate solution and controlled oxygen diffusion oxidation of Cu_2O in air, respectively. As compared to the Cu hollow spheres, both the Cu_2O solid and CuO porous spheres can greatly enhance the M2 selectivity and Si conversion in Rochow reaction, which is possibly due to the generated highly active surface oxygen vacancies in the Cu_xSi phase. The work not only demonstrates a new approach to the development of novel Cu-based catalysts with high activity, but also provides deep understanding of the roles of Cu, Cu_2O and CuO in Rochow reaction.

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Author contributions Ji Y, Wang X and Su F conceived the idea of the project. Liu H conducted the synthesis of materials. Liu H, Li J and Zhong Z performed the characterizations and catalytic tests. Ji Y, Wang X and Su F analyzed the data. Liu J, Ji Y, Wang X, Zhang Z and Su F drafted the manuscript. Liu H and Li J contributed equally to this work. All authors participated the general discussion of the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper.

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扩散控制合成Cu基催化剂及其Rochow反应性能研究

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摘要 大多数材料的功能和性质取决于它们的结构, 而扩散机制是调控材料生长和结构的一个主要动力学因素. 本工作提出了一条系统且可行的策略即通过控制扩散系数来制备Cu₂O固体球和六面体, 且这些Cu₂O产物可以分别通过水合肼溶液中氢原子扩散控制和空气中氧原子扩散控制, 转变成相应的Cu中空球和六面体, 以及CuO多孔球和六面体. 此外, 对转变过程的微观机制作了详尽的讨论; 用固定床评价了这些材料在用来合成有机硅行业广泛使用的单体的Rochow反应中的催化性能. 结果表明, 相较于Cu中空球, Cu₂O固体球和CuO多孔球表现出了更高的二甲基二氯硅烷选择性和硅粉原料转化率, 这主要归因于在形成Cu_xSi活性相的过程中, Cu₂O和CuO中的晶格氧去除以后形成的表面氧缺陷可以作为反应物CH₃Cl的吸附活性位. 该工作不仅提出一种制备规整Cu₂O固体球和六面体的可行方法, 而且揭示了Rochow反应合成单体二甲基二氯硅烷中Cu, Cu₂O和CuO各自的催化作用.