Supporting Information

Flower-like CuO microspheres with enhanced catalytic performance for dimethyldichorosilane synthesis

Zailei Zhang,^{a,b}, Hongwei Che,^a Yingli Wang,^a

Jiajian Gao,^a Xilin She,^b Jin Sun,^b Ziyi Zhong,^c and Fabing Su*^a

^a State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of ¹⁰ Sciences, Beijing, China 100190, Tel.: +86-10-82544850, Fax: +86-10-82544851, E-mail address: fbsu@mail.ipe.ac.cn.

^b College of Chemical and Environmental Engineering, Qingdao University, Qingdao, China 266071.

^c Institute of Chemical Engineering and Sciences, A*star, 1 Pesek Road, Jurong Island, Singapore 627833.

15 Experimental Section

Materials

5

The flower-like CuO microspheres were prepared by a hydrothermal method as shown in Scheme S1. To optimize the synthesis conditions and investigate the product formation mechanism, as compiled in Table 1, synthesis parameters such as the reaction temperature, time, the reactant amount, solvent ratio and the type of ²⁰ copper source were changed individually while keeping all other experimental parameters unchanged. In a typical synthesis, for an example (C3 in Table 1), 1.0 g of copper nitrate (Cu(NO₃)₂•H₂O, A.R., Sinopharm Chemical Reagent Co., Ltd) were first dissolved in 50.0 mL of absolute alcohol (CH₃CH₂OH, A.R., Sinopharm Chemical Reagent Co., Ltd) to form a solution in a beaker, and then 30 mL of ammonia water (25 - 28 %) (NH₃•H₂O, A.R., Sinopharm Chemical Reagent Co., Ltd), and 5.0 g of sodium nitrate (NaNO₃, A.R., Sinopharm Chemical Reagent Co., Ltd), were added respectively. After stirring for 10 min to form a clear solution, the resulting

5

solution was transferred into 100 mL stainless-steel autoclaves lined with poly(tetrafluoroethylene) (PTFE, Telfon). The autoclave was sealed and maintained at 130 °C for 18 h, and then cooled down to room temperature. The resulting precipitate solid was collected by centrifugation, washed with distilled water and absolute ethanol, and finally dried in vacuum at 60 °C for 8 h.



Scheme S1. Illustration of synthesis process.

Sample	copper nitrate (g)	ethanol (mL)	water (ml)	ammonia water (mL)	sodium hydroxide (mL)	sodium nitrate (g)	reaction temperature (°C)	reaction time(h)
C1	1.0	50	0	30	10	5	80	18
C2	1.0	50	0	30	10	5	100	18
C3	1.0	50	0	30	10	5	130	18
C4	1.0	50	0	30	10	5	160	18
C5	1.0	50	0	30	10	5	130	5 min
C6	1.0	50	0	30	10	5	130	15 min
C7	1.0	50	0	30	10	5	130	30 min
C8	1.0	50	0	30	10	5	130	1
C9	1.0	50	0	30	10	5	130	2
C10	1.0	50	0	30	10	5	130	4
C11	1.0	50	0	30	10	5	130	30
C12	1.0	50	0	30	10	5	130	48
C13	0.2	50	0	30	10	5	130	18
C14	0.5	50	0	30	10	5	130	18
C15	2.0	50	0	30	10	5	130	18
C16	1.0	50	0	10	10	5	130	18
C17	1.0	50	0	50	10	5	130	18
C18	1.0	50	0	30	5	5	130	18
C19	1.0	50	0	30	20	5	130	18
C20	1.0	50	0	30	10	0	130	18
C21	1.0	50	0	30	10	2	130	18
C22	1.0	50	0	30	10	7	130	18
C23	1.0	50	0	30	10	10	130	18
C24	1.0	40	10	30	10	5	130	18
C25	1.0	30	20	30	10	5	130	18
C26	1.0	20	30	30	10	5	130	18
C27	1.0	10	40	30	10	5	130	18
C28	1.0	5	45	30	10	5	130	18
C29	1.0	0	50	30	10	5	130	18
C30*	1.0	50	0	30	10	5	130	18
$C31^{*}$	1.0	50 50	0	30	10	5	130	18
C32.	1.0	50	0	30	10	5	130	10
C33*	1.0	50	0	30	10	5	130	18
C34 ⁺	1.0	50	0	30	10	5	130	18
C35 ⁺	1.0	50	0	30	10	5	130	18
C36 ⁺	1.0	50	0	30	10	5	130	18
C37 ⁺	1.0	50	0	30	10	5	130	18
$C38^+$	1.0	50	0	30	10	5	130	18

Table S1. The synthesis conditions used for preparing flower-like CuO microspheres.

* Note: the copper precursor used in C30, C31, C32, and C33 is CuCl₂, Cu(CH₃COO)₂, CuSO₄, and CuCl, respectively. ⁺ Note: the salts used in C34, C35, C36, C37 and C38 is KNO₃, NaCl, KCl, CH₃COONa and Na₂CO₃ respectively, instead of NaNO₃.

Material Characterization

5

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO MPD using the K α radiation of Cu ($\lambda = 1.5418$ Å). The microscopic feature of the samples was observed by field-emission scanning electron microscopy (SEM) (JSM-6700F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) (JEM-2010F, JEOL, Tokyo, Japan). The pore nature of the samples was investigated using physical adsorption of N₂ ^s at liquid-nitrogen temperature (-196 °C) on an automatic volumetric sorption analyzer (NOVA3200e, Quantachrome). Prior to the measurement, the sample was degassed at 200 °C for 5 h under vacuum. The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05 - 0.2. Pore size distribution (PSD) curve was derived from the Barrett–Joyner–Halenda (BJH) method using adsorption branch. The pore size was estimated from the maximum position of the BJH-¹⁰ PSD curve. Temperature programmed reduction (TPR) measurements were carried out on Automated chemisorption analyzer (ChemBET pulsar TPR/TPD, Quantachrome). First, 0.05 g of CuO was loaded in a quartz U-tube. Prior to the measurement, the sample was degassed at 200 °C for 30 min under helium. When the temperature dropped to 20 °C, the gas was changed to 9.9 % H₂/Ar. Finally, the sample was heated from 20 °C to 800 °C with 10 °C/min under 9.9 % H₂/Ar with a gas flow of 30 mL/min.

15 Measurement of catalytic property

The evaluation of catalyst was carried out with a typical MCS lab fixed-bed reactor.¹ 10.0 g of Si powder (20 - 50 mesh, provided by Jiangsu Hongda New Material Co., Ltd) and 1.0 g of CuO or commercial copper catalyst (Cu-Cu₂O-CuO, provided by Jiangsu Hongda New Material Co., Ltd) together with 0.1 g of Zinc (Zn, A.R., Sinopharm Chemical Reagent Co., Ltd) used as a promoter were mixed homogeneously to form a contact mass, ²⁰ which was then loaded in the glass reactor. The reactor system was first purged with purified N₂ for 0.5 h and then heated to 325 °C within 1 h under a N₂ flow rate of 25 mL/min. Subsequently, N₂ was turned off and MeCl gas (provided by Jiangsu Hongda New Material Co., Ltd.) with a flow rate of 25 mL/min was introduced into the reactor to react with Si at 325 °C. After a period of 24 h, the reaction was stopped. The gas product was cooled down to liquid with the circulator bath controlled at 5 °C by a programmable thermal circulator (GDH ²⁵ series, Ningbo xinzhi biological technology Co., LTD). The waste contact mass (solid residue after reaction) containing unreacted Si powder and Cu+Zn compounds was weighed for calculating Si conversion. Liquid collected in a glass container was analyzed with Agilent Technologies 7890A GC System. The Rochow reaction is briefly illustrated in the figure below:

Si + MeCl
$$\xrightarrow{\text{copper catalyst}}_{300-350 \circ C}$$
 $(CH_3)_3SiCl_{(CH_3)_2SiCl_2}$
 CH_3SiCl_3 (S1)
 CH_3HSiCl_2
 $(CH_3)_2HSiCl_3$ (S1)
 CH_3HSiCl_2
 $(CH_3)_2HSiCl_3$
 CH_3HSiCl_2
 $(CH_3)_2HSiCl_3$

The MCS product mainly contained M1, M2, M3, and is normally more than 95 wt % of total reaction product amount.² Thus, to simplify the calculation, other trace products and the change in catalyst were ignored, and the Mi (i = 1, 2, 3) selectivity and Si conversion were derived from the following formulas:

⁵ Selectivity of Mi (S_{Mi}) =
$$\frac{\text{mole}_{Mi}}{\sum_{i=1}^{3} \text{mole}_{Mi}} \times 100\%$$
 (i = 1,2,3) (S2)

Conversion of Si (C_{Si}) = $\frac{\text{weight}_{\text{contact mass before reaction}} - \text{weight}_{\text{contact mass after reaction}} \times 100\%$ (S3) weight Si before reaction



Fig. S1 SEM images of flower-like CuO microspheres obtained at different reaction temperatures: (a) s 80 °C (C1), (b) 100 °C (C2), (c) 130 °C (C3), and (d) 160 °C (C4).

For reactions carried out at 80 °C (C1) and 100 °C (C2), the solution after a filtration step is blue color, which is the same as that of the precursor solution, and the yield of CuO is much small, indicating an incomplete reaction. In contrast, for reactions carried out at 130 °C (C3) and 160 °C (C4), the solution after filtration is transparent, suggesting the complete conversion of the copper precursor to CuO. Thus, a reaction temperature of 130 - 160 °C is recommended.



Fig. S2 SEM images of flower-like CuO microspheres obtained at different reaction times: (a) 5 min (C5), (b) 15 min (C6), (c) 30 min (C7), (d) 1h (C8), (e) 2 h (C9), (f) 4 h (C10), (g) 18 h (C3), (h) 30 h ¹⁰ (C11), and (i) 48 h (C12).

For reaction times less than 4 h (C5, C6, C7, C8, C9, and C10), the solution after filtration is blue color, indicating an incomplete reaction in the reactor. For reaction times more than 4 h (C3, C11, and C12), the solution after filtration is colorless, suggesting the complete conversion of the copper ¹⁵ precursor to CuO. Therefore, 18 h of reaction time is preferred.



Fig. S3 SEM images of the CuO microspheres obtained at different copper nitrate amounts: (a) 0.2 g (C13), (b) 0.5 g (C14), (c) 1.0 g (C3), (d) 2.0 g (C15), and (e) TEM images and (f) on the edge of (b) 0.5 g (C14), (j) the HRTEM image of (f).

To study the uniform morphology of CuO microspheres, the sample (C3) done 1.0 g with copper nitrate amount was chosen for further investigation.



Fig. S4 SEM images of CuO microspheres obtained at different ammonia water amounts: (a) 10 mL

(C16), (b) 30 mL (C3), and (c) 50 mL (C17).



Fig. S5 SEM images of CuO microspheres obtained at different sodium hydroxide amounts: (a) 5 mL (C18), (b) 10 mL (C3), and(c) 20 mL (C19).

Based on the observations of Fig. S4 and S5, 30 mL of ammonia water and 10 - 20 mL of sodium hydroxide amounts are suitable for obtaining homogeneous flower-like CuO microspheres.



Fig. S6 SEM images of the CuO samples obtained at different sodium nitrate amounts: (a) 0.0 g (C20), (b) 2.0 g (C21), (c) 5.0 g (C3), (d) 7.0 g (C22), and (e) 10.0 g (C23).

⁵ From above SEM images, sodium nitrate amount with 2.0 - 10.0 g could be used for obtaining uniformly flower-like CuO microspheres.



Fig. S7 SEM images of CuO microspheres formed at different initial solvent volume ratios (water: alcohol): (a) 10:40 (C24), (b) 20:30 (C25), (c) 30:20 (C26), (d) 40:10 (C27), (e) 45:5 (C28), and (f) 50:0 (C29).

Above SEM images show that the flower-like CuO microspheres with different micro-sizes could be obtained at the wide range of initial solvent volume ratios in the presence of alcohol. The agglomeration occurred without using alcohol (see Fig. S7-f).



Fig. S8 SEM images of CuO formed at different copper sources: (a) CuCl₂ (C30), (b) Cu(CH₃COO)₂ (C31), (c) CuSO₄ (C32), and (d) CuCl (C33).

Above SEM images show that the flower-like CuO microspheres with different microsizes could be obtained using different copper sources $CuCl_2$ (C30), $Cu(CH_3COO)_2$ (C31), and $CuSO_4$ (C32). However, for CuCl, flower-like composite microspheres (C33) containing CuO and Cu₂O was obtained and this was confirmed by its XRD pattern (not shown here). Further study is underway.

10



⁵ **Fig. S9** SEM images of CuO formed at different salts: (a) NaNO₃ (C3), (b) KNO₃ (C34), (c) NaCl (C35), (d) KCl (C36), (e) CH₃COONa (C37), and (f) Na₂CO₃ (C38).

From above SEM images, we can find the strong effect of these mineralizers (NaNO₃, KNO₃, NaCl, KCl, CH₃COONa and Na₂CO₃) on the morphology and particle size of CuO products and particularly NaNO₃ actually appears crucial for the formation of microspheres with a narrower size distribution. ¹⁰ Not only NaNO₃ but also KNO₃, NaCl, and KCl play an important role as mineralizers. However, the exact mechanism is still not fully understood and further studies are needed in the future.



Fig. S10 SEM image of commercial CuO particles as a representative catalyst.



Fig. S11 N₂ adsorption-desorption isotherms (a) and XRD patterns (b) of flower-like CuO microspheres and commercial CuO particles. (For clarity, the isotherm of C16, C14, C4, C3, C2, and ⁵ C1 was vertically shifted for 30, 60, 90, 120, 150, and 180 cm³/g, respectively.)

Samples	$S_{BET} (m^2/g)$	Average crystal size (nm)
C1	23.2	22.3
C2	25.4	23.1
C3	10.6	23.4
C4	5.6	25.4
C14	26.3	23.1
C16	8.9	20.6
C25	21.6	24.1
commercial CuO	0.2	50.8

Table S2. Surface area and average crystal size of CuO samples.



Fig. S12 XRD patterns of contact masses before reaction (a: C1+Si, b: C2+Si, c: C3+Si, d: C4+Si, e: C14+Si, f: C16+Si, g: C25+Si, and h: commercial CuO+Si).

Contact mass is the solid mixture of the reactant Si and the copper catalyst together with its promoter. ⁵ Before reaction, fresh contact masses exhibit similar XRD profile.



Fig. S13 H₂-TPR curves of CuO samples.

For some of the flower-like CuO microspheres samples, the H₂ consumption peak is located at about 200 - 325 °C (C1, C2, C3, C14, and C25), while that of the other samples (C4, and C16) is ⁵ located at about 250 - 360 °C. In contrast, the commercial CuO particles give a main reduction peak at about 400 - 530 °C, and a small reduction peak at about 300 - 350 °C. The maximum reduction peak for the flower-like CuO microspheres is lower by nearly 200 °C than the commercial CuO particles, suggesting that flower-like CuO microspheres were more readily reduced. Above TPR curves demonstrate that the flower-like CuO microspheres have a higher reductive activity than that of ¹⁰ commercial CuO particles.

References

- 1 L. N. Lewis, W. V. Ligon and J. C. Carnahan, Silicon Chem., 2002, 1, 23.
- ¹⁵ 2 C. P. H. Lyons and G. S. Roussillon, USP-4661613, 1987.