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# Copper nanoparticles socketed *in situ* into copper phyllosilicate nanotubes with enhanced performance for chemoselective hydrogenation of esters<sup>†</sup>

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Copper nanoparticles exsoluted *in situ* under reducing atmosphere at elevate temperature are socketed into the parent copper phyllosilicate nanotubes (CSNTs) and exhibit excellent catalytic performance and superior stability for the selective hydrogenation of various esters to alcohols.

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chemoselective hydrogenation of The esters into corresponding alcohols is a basic reaction in chemical production, which is widely used in producing various industrial products, including high-quality polyesters, chemicals, and fuels.<sup>1–3</sup> For example, recent progress shows that the chemoselective hydrogenation of dimethyl oxalate (DMO) derived via a syngas route may lead to a new nonpetroleum based synthesis procedure for the production of ethylene glycol (EG), methyl glycolate (MG) and ethanol.<sup>4,5</sup> The inexpensive Cu-based catalyst is proven to be highly active for the chemoselective hydrogenation of esters to alcohols.<sup>6–8</sup> However, the conventional Cu-based catalyst presents a decreasing tendency during hydrogenation reactions, because of the loss of active Cu surface sites through migration and aggregation of Cu nanoparticles and the changes in valence state of surface Cu species under reaction conditions.9,10 Several methods have been introduced to stabilize the Cu species, such as the introduction of additives and formation of alloys.<sup>11–16</sup> Moreover, Yue et al.<sup>17</sup> reported a copperimpregnated CSNTs for the hydrogenation of DMO to ethanol with high efficiency and steady performance, given that the confinement effect of nano-sized channels on Cu particles could provide the largest amount of surface  ${\rm Cu}^0$  and  ${\rm Cu}^*.$  Correlatively, Zhang et al.  $^{18}$  designed an anti-sintering nickel phyllosilicate nanotubes and used for reforming reactions. The phyllosilicate nanotubes could effectively maintain the Ni particle size during reaction. It has been reported that in situ exsolution strategy can generate stronger metal-oxide

interfaces compared with conventional deposition method and thus can be applied to prepare stable and active supported catalysts.<sup>19</sup> Additional examples of the metallic nanoparticles *in situ* exsoluted from perovskite parents inhibited nanoparticles agglomeration and exhibited excellent activity and stability in electrochemical reaction.<sup>20–23</sup> Berg et al.<sup>24</sup> revealed the *in situ* formation of copper nanoparticles on a silica support under the H<sub>2</sub> atmosphere from homogeneous copper phyllosilicate platelets precursor using transmission electron microscopy (TEM). Nevertheless, the structure and performance of the copper nanoparticles exsoluted and socketed *in situ* into the parent CSNTs under reducing atmosphere at elevate temperatures have not been reported so far.

In this work, we employ the as-prepared CSNTs as precursor to prepare a new type of Cu-based catalyst CSNTs-T, (T represents the reduction temperature) through the in situ exsolution strategy under reducing atmosphere. Almost quantitative conversion and high selectivity to corresponding alcohols are obtained over the optimized catalyst CSNTs-623 for the selective hydrogenation of various esters. In addition, the catalytic performance of CSNTs-623 has no obvious deterioration after the reaction on stream for as long as 1000 h. Characteristic studies using several spectroscopic techniques reveal that the catalyst CSNTs-623 possesses high dispersion, strong metal-support interactions, and Cu favourable ratio of active Cu species, thereby exhibiting excellent performance for the chemoselective hydrogenation of various esters into corresponding alcohols.

The CSNTs were prepared by a modified hydrothermal method based on literature<sup>25</sup> (See ESI<sup>+</sup> for details of synthesis of all materials, catalytic activity testing, and characterization techniques). As shown in Fig. 1A, CSNTs have uniform thin nanotube morphologies, and the diameter of the nanotubes is approximately 10 nm with a wall thickness of 1–2 nm. XRD results confirm the formation of a copper phyllosilicate phase. The characteristic diffractions of CSNTs (Fig. 1B), centred at 20=11.19°, 19.94°, 21.82°, 30.81°, 35.02°, 57.48°, and 62.44°, are attributed to the chrysocolla phases (JCPDS No. 027-0188). After the reduction, the Cu<sup>2+</sup>/Cu<sup>+</sup> in CSNT crystal lattice was reduced to Cu<sup>0</sup> while SiO<sub>2</sub> appeared in the surrounding. The XRD peaks of chrysocolla phase were partly substituted by a couple of new peaks corresponding to metallic Cu. The

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average diameter of Cu nanoparticles is approximately 4.6 nm (Fig. 1C). Strong metal-support interactions restricted the accumulation of copper nanoparticles in the reduction, which is attributed to the intrinsic lattice structure. The schematic illustration of the formation of CSNTs (Fig. 1D) implies that Cu nanoparticles are strongly anchored by the layered structure at a suitable reduction temperature.



Fig. 1 (A) TEM image of CSNTs; (B) XRD patterns of CSNTs and CSNTs-623; (C) TEM image of reduced CSNTs; (D) Schematic illustration of the formation of CSNTs.

 Table 1
 Cu LMM XAES
 deconvolution results of CSNTs under a different reduction temperatures

Catalyst	K. E.ª / eV		A. P. <sup>b</sup> / eV		v <sup>c</sup> /o/		
	Cu⁺	Cu <sup>0</sup>	Cu⁺	Cu <sup>0</sup>	∧ <sub>Cu+</sub> / %		
CSNTs	914.2	918.0	55616.7	_	100		
CSNTs-523	914.1	918.0	29907.6	17556.7	63.0		
CSNTs-623	914.2	918.0	28960.5	14948.9	65.9		
CSNTs-723	914.0	918.0	14451.8	8551.6	62.8		
CSNTs-773	914.3	918.3	24438.2	19718.5	55.3		
CSNTs-823	914.2	918.2	11709.2	15145.5	43.6		
$^a$ Kinetic energy. $^b$ Auger parameter. $^c$ Ratio between Cu $^+$ and (Cu $^++Cu^0$ ) by deconvolution of Cu LMM XAES spectra.							

To understand the status of Cu nanoparticles exsoluted *in* situ during the reduction, the CSNTs were reduced in  $5\%H_2-95\%N_2$  at different temperatures to afford the catalyst CSNTs-*T*. The physiochemical properties of CSNTs-*T* are illustrated in Table S1 (ESI<sup>†</sup>). The BET surface area decreased from 486.9 to 404.5 m<sup>2</sup> g<sup>-1</sup> with the increasing reduction temperature ranging from 523 K to 823 K. Similar change trend was observed in V<sub>p</sub> and D<sub>p</sub> data. This phenomenon implies that the nanotube structure is partially destroyed in the reduction process when the temperature is higher than 773 K, as confirmed by the TEM image in Fig. S1 (ESI<sup>+</sup>). However, the XRD profiles of CSNTs-*T* in Fig. S2 (ESI<sup>+</sup>) do not show significant difference in the Cu nanoparticle size of CSNTs-*T*. The mean particle sizes are approximately 5 nm. Two types of Cu species could be identified (Fig. S3, ESI<sup>+</sup>). The kinetic energy of approximately 914 eV and 918 eV (Table 1) are attributed to

the Cu<sup>+</sup> and Cu<sup>0</sup> species according to literature, <sup>12</sup> respectively. It has been reported that copper phyllosilicate could produce stable Cu<sup>+</sup> species on its surface in the hydrogenation reaction and enhance the dispersion and metal-support interactions significantly.<sup>26</sup> In present work, the ratio of Cu<sup>+</sup> species in CSNTs-*T* maintained up to 60% when the reduction temperature was below 723 K; and rapidly decreased to 43.6% while increasing the reduction temperature to 823 K. The characterization results reveal that the CSNTs-*T* catalyst reduced at a range of 523 K to 723 K may possess an excellent thermal stability.

The selective hydrogenation of dimethyl 1,4-cyclohexane dicarboxylate (DMCD) is selected as the first probe reaction to investigate the Cu-based catalysts. As shown in Scheme 1, DMCD hydrogenation is a multi-steps reaction. One ester group of DMCD is hydrogenated to form methyl 4carboxylate hydroxymethylcyclohexane (MHMCC) as intermediate, then the MHMCC is hydrogenated continuously to produce CHDM as the target product. The overhydrogenolysis of CHDM may generate 4-methvlcyclohexanemethanol (MCHM) as a by-product. As the target product of DMCD hydrogenation, 1,4-cyclohexane dimethanol (CHDM) can be used to produce high-quality and nontoxic polyester fibres with higher corrosion resistance and melting point than ethylene glycol.<sup>27–29</sup> A series of Cr-free Cu-based layered double hydroxides (LDH) catalysts investigated by Li et al. $^{30-32}$  displayed excellent catalytic performance of DMCD hydrogenation, which was mainly attributed to the presence of highly dispersed and stable active metallic copper species in LDH precursors. However, the lifetime of these catalysts does not satisfy to industrial requirement. Deactivation is mainly caused by the aggregation of Cu nanoparticles during the reaction process. As shown in Table 2, the DMCD conversion maintained up to 99% when the reduction temperature of CSNTs was below 623 K. The DMCD conversion and CHDM selectivity decreased while further increasing the reduction temperature. A similar variation of turnover frequency (TOF) value was observed. Combining the XPS result in Table 1 can lead to the speculation that the ratio of  $Cu^{\dagger}$  species in CSNTs-T is the key factor for influencing the catalytic performance. The catalyst with a proper  $Cu^+$  ratio of approximately 60% exhibited the best catalytic performance in the selective hydrogenation of DMCD to CHDM.

For comparison, the Cu-based catalysts with similar metal content were prepared by deposition-precipitation, ureaassisted gelation, and ammonia evaporation hydrothermal methods, labelled as D-Cu/SiO<sub>2</sub>, U-Cu/SiO<sub>2</sub>, and A-Cu/SiO<sub>2</sub>, respectively. The layer structure of copper phyllosilicate exists in A-Cu/SiO<sub>2</sub> as shown in Fig.S8 (ESI<sup>+</sup>).<sup>26</sup> Subsequently, copper phyllosilicate disappeared after reduction at 623 K, which was consistent with literature results.<sup>11</sup> All samples had the similar metal content of approximately 30%, as demonstrated by XRF (Table S1, ESI<sup>+</sup>). CSNTs-623 exhibited the highest  $S_{BET}$  of 469.1  $m^2~g^{-1}$  , and the largest  $V_P$  of 1.15  $cm^3~g^{-1}$  compared with the comparison catalysts, mainly due to the existence of the nanotube structure. Fig. 2A displays the hydrogen temperature program reduction (H<sub>2</sub>-TPR) profiles of the four Cu-based catalysts. The D-Cu/SiO<sub>2</sub>, U-Cu/SiO<sub>2</sub>, and A-Cu/SiO<sub>2</sub> showed a reduction peak at 471 K, 493 K, and 503 K, respectively; whereas the reduction of copper species over CSNTs occurred at a higher temperature of 508 K, revealing metal-support interactions in CSNTs. All these characterizations indicate that

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the nanotube structure of CSNTs is beneficial to the dispersion of Cu species. In Fig. 2B, the CSNTs-623 achieved almost 100% DMCD conversion and 96.3% CHDM selectivity under the optimal conditions (Liquid hourly space velocity (LHSV) = 1.0 h<sup>-</sup> <sup>1</sup>), which was superior to that of the other catalysts. Excellent catalytic performance is achieved at a relative low LHSV value mainly due to the high ratio of surface active sites to reactant molecule. As LHSV increases, the retention time of DMCD molecule on catalyst surface is too short to reaction, which leads to a decrease of hydrogenation rate. The result is that both DMCD conversion and CHDM selectivity decreased with an increase of selectivity to MHMCC. However, the CSNTs-623 maintained both the conversion and selectivity up to 90% with an LHSV as high as 4  $h^{-1}$ . In contrast, the other three catalysts rapidly deactivated under the same reaction conditions. The CSNTs-623 exhibited the maximum TOF value of 19.8 h<sup>-1</sup> which is nearly five times higher than that of D-Cu/SiO<sub>2</sub> (Fig. S4, ESI<sup>+</sup>). Thus, the *in situ* exsolution of Cu nanoparticles in the CSNT crystal lattice improved not only the catalytic performance, but also the stability of the catalyst.



Scheme 1 The reaction pathway for selective hydrogenation of DMCD to CHDM.

**Table 2** Catalytic performance of CSNTs-T for the selective hydrogenation of DMCD to CHDM<sup>a</sup>

Catalyst	TOF	Conversion	Selectivity / %		
Catalyst	/ h <sup>-1</sup>	/ %	CHDM	MHMCC	MCHM
CSNTs-523	20.1	99.1	96.3	2.8	0.9
CSNTs-623	19.8	100	96.3	3.2	0.5
CSNTs-723	17.5	89.7	92.6	5.1	2.3
CSNTs-773	12.7	83.2	87.5	11.1	1.4
CSNTs-823	10.8	70.3	82.5	15.5	1.5

<sup>a</sup> Reaction conditions:  $P(H_2) = 5.0$  MPa, T = 493 K,  $H_2/DMCD$  molar ratio = 260, and LHSV = 1.0 h<sup>-1</sup>. <sup>b</sup> The TOF value was calculated by Cu dispersion when the conversion was controlled under 30%.



**Fig. 2** (A) H<sub>2</sub>-TPR profiles of (a) CSNTs, (b) as-prepared A-Cu/SiO<sub>2</sub>, (c) as-prepared U-Cu/SiO<sub>2</sub>, and (d) as-prepared D-Cu/SiO<sub>2</sub>. (B) Catalytic performance of (a) CSNTs-623, (b) A-Cu/SiO<sub>2</sub>, (c) U-Cu/SiO<sub>2</sub>, and (d) D-Cu/SiO<sub>2</sub> for the selective hydrogenation of DMCD to CHDM under

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To further investigate the stability of CSNTs-623, the thermal stability of the DMCD hydrogenation reaction over four catalysts was evaluated according to our prior literature<sup>13</sup> and the results are shown in Table S2 (ESI<sup>+</sup>). The space time yield (STY) of the fresh catalyst at 493 K was calculated, and then the temperature was rising to 623 K for 24 h. Finally, the reaction temperature was adjusted to 493 K, and the STY after thermal treatment was obtained. The ratio of these two STY values reflects the thermal stability of catalysts. The STY<sub>T</sub>/STY<sub>F</sub> ratios for the D-Cu/SiO<sub>2</sub>, U-Cu/SiO<sub>2</sub>, and A-Cu/SiO<sub>2</sub> catalysts were 0.55, 0.88, and 0.93, respectively, whereas CSNTs-623 achieved up to 0.99. After thermal treatment, the catalytic performance of DMCD hydrogenation over CSNTs-623 did not significantly decline.



**Fig. 3** Long-term performance of DMCD hydrogenation over CSNTs-623. Reaction conditions:  $P(H_2) = 5.0$  MPa, T = 493 K,  $H_2/DMCD$  molar ratio = 260, and LHSV = 1.0 h<sup>-1</sup>.

The XRD and XPS measurements were conducted to investigate the difference of catalysts after thermal treatment. As shown in Fig. S5 (ESI<sup>+</sup>), the Cu nanoparticles sintered obviously after thermal treatment except for CSNTs-623, which is consistent with TEM images (Fig. S6, ESI<sup>+</sup>). The Cu<sup>+</sup> ratios were calculated according to Fig. S7 (ESI+) and are illustrated in Table S3 (ESI<sup>+</sup>). CSNTs-623 had the highest initial  $Cu^{+}$  ratio of 65.9%, compared with D-Cu/SiO<sub>2</sub> (50.2%), U-Cu/SiO<sub>2</sub> (54.8%), and A-Cu/SiO<sub>2</sub> (60.6%). After the thermal treatment, the Cu<sup>+</sup> ratios of D-Cu/SiO<sub>2</sub>, U-Cu/SiO<sub>2</sub>, and A-Cu/SiO<sub>2</sub> decreased, whereas the CSNTs-623 maintained its Cu<sup>+</sup> ratio of 61.4%. Cu active sites in the hydrogenation of esters showed a synergetic effect between  $Cu^{+}$  and  $Cu^{0}$ , that is, the dissociative activation of  $H_2$  molecules on  $Cu^0$  and  $Cu^+$  species as electrophilic or Lewis acid sites that can polarize the carbonyl group via the lone pair electron on oxygen.<sup>33</sup> Above all, the Cu nanoparticle size and Cu<sup>+</sup> ratio are two key factors which influenced the catalytic performance and stability of Cubased catalysts in the hydrogenation of DMCD. The strong metal-support interactions of CSNTs-623 prepared by in situ exsolution strategy are proved to effectively maintain Cu nanoparticle size and Cu<sup>+</sup> ratio during the reaction. The long term performance of CSNTs-623 was evaluated under optimal reaction conditions and is shown in Fig. 3. CSNTs-623 exhibited almost a full conversion and up to 95% CHDM selectivity over

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1000 h. The designed CSNTs-623 catalyst with proper Cu<sup>+</sup> ratio and nanoparticle size exhibited excellent catalytic performance and superior stability, mainly due to the strong metal-support interactions by the *in situ* exsolution of Cu nanoparticles from the nanotube structure of CSNTs.

The selective hydrogenation of other esters to corresponding alcohols was also investigated under optimal reaction conditions (Table 3). The hydrogenation of diethyl malonate yielded a 98.4% conversion and 79.9% 1,3-propanediol selectivity. Almost a full conversion and more than 98% selectivity was obtained when using ethyl acetate and DMO were used as substrates.

In summary, a facile hydrothermal approach is developed to prepare CSNTs with uniform thin nanotube morphology. Then the CSNTs-T catalyst prepared by in situ exsolution strategy exhibits excellent catalytic performance and superior stability for DMCD hydrogenation reaction compared with the Cu/SiO<sub>2</sub> catalysts synthesized by traditional methods. The yield of CHDM remains up to 95% during 1000 h under optimal reaction conditions. The reduction temperature significantly influences the  $Cu^+/Cu^0$  ratio on CSNTs-T. The suitable temperature ranges from 523 K to 723 K, affording the surface  $Cu^{\dagger}$  concentration more than 60%. Further increasing the reduction temperature the nanotube structure of CSNTs can cause partial destruction. Thus, the in situ exsolution of Cu nanoparticles from CSNTs with highly metal dispersion and strong metal-support interactions are beneficial to maintain its particle size and  $\mathrm{Cu}^{^+}$  species during reaction. The reduced CSNTs catalyst shows potential applications in hightemperature hydrogenation reactions. The approach is envisioned to fabricate other nano-socketed materials using corresponding precursors such as Co phyllosilicate for catalytic applications.

 Table 3
 Catalytic performance of selective hydrogenation of esters

 over CSNTs-623
 CSNTs-623

Ester	Р/	T/	Product	Conversion	Selectivity
	MPa	К		/%	/%
Diethyl malonate <sup>a</sup>	5	483	1,3- Propanediol	98.4	79.9
Ethyl acetate <sup>b</sup>	3	493	Ethanol	99.2	98.5
Dimethyl oxalate <sup>c</sup>	3	453	Ethylene glycol	99.6	98.3

Reaction conditions: <sup>a</sup>  $H_2$ /ester molar ratio = 250, and LHSV=0.6 h<sup>-1</sup>. <sup>b</sup>  $H_2$ /ester molar ratio = 80, and LHSV = 1.0 h<sup>-1</sup>. <sup>c</sup>  $H_2$ /ester molar ratio = 60, and LHSV=1.2 h<sup>-1</sup>.

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## **Graphical abstract**

# Copper nanoparticles socketed *in situ* into copper phyllosilicate nanotubes with enhanced performance for chemoselective hydrogenation of esters

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