

# High-Performance Catalysts Derived from Cupric Subcarbonate for Selective Hydrogenation of Acetylene in an Ethylene Stream

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A high-performance base metal catalyst for acetylene selective hydrogenation was prepared from cupric subcarbonate  $(Cu_2(OH)_2CO_3)$  by thermal treatment with an acetylene-containing gas followed by hydrogen reduction. The characterization results revealed that the copper catalyst was composed of interstitial copper carbide  $(Cu_xC)$  and metal Cu, which were embedded in porous carbon matrix. The  $Cu_xC$  crystallites, which showed outstanding hydrogenation activity, were derived from the hydrogen reduction of copper (II) acetylide  $(CuC_2)$  which was generated from the reaction between acetylene and  $Cu_2(OH)_2CO_3$ . The Cu particles and porous carbon were

# Introduction

Ethylene is mainly produced by naphtha cracking and is used as a basic petrochemical raw material for synthetic resins, such as polyethylene. For polymer-grade ethylene, acetylene impurity must be reduced below an acceptable level (5 ppm) to protect the downstream polymerization catalyst and to avoid ungraded polymer products.<sup>[1-4]</sup> In industry, the preferred method of removing the acetylene impurity in ethylene stream is by selective hydrogenation of acetylene to ethylene product.<sup>[5,6]</sup> The most commonly used catalyst is the low-surface-area alumina-supported Pd catalyst modified by Ag.<sup>[7,8]</sup> In addition, Ga,  $^{[9-11]}$  Zn,  $^{[12-14]}$  Au,  $^{[15-17]}$  Cu,  $^{[18-21]}$  and In $^{[22,23]}$  are also used as the promoters. Recently, Liu et al.<sup>[24,25]</sup> and McCue et al.<sup>[26]</sup> reported that palladium sulfide and palladium phosphides exhibited excellent ethylene selectivity at complete acetylene conversion above 125°C. In general, one major disadvantage associated with precious metal catalysts is the high cost.

Ni-based catalysts have been extensively explored for replacing supported Pd catalysts.  $^{\left[ 27-31\right] }$  However, Ni-based cata-

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generated from the unavoidable thermal decomposition of  $CuC_2$ . The prepared Cu-derived catalyst completely removed the acetylene impurity in an ethylene stream with a very low over-hydrogenation selectivity at 110°C and atmospheric pressure. No obvious deactivation was observed in a 180-h test run. In the Cu-derived catalyst,  $Cu_xC$  served as the catalytic site for H<sub>2</sub> dissociation, Cu mainly functioned as the site for selective hydrogenation of acetylene, whereas the porous carbon matrix posed a steric hindrance effect on the chain growth of linear hydrocarbons so as to suppress the undesired oligomerization.

lysts deactivate quickly during the acetylene hydrogenation due to the vigorous formation of oligomers.<sup>[32,33]</sup> In addition, Febased,<sup>[34,35]</sup> Cu-based<sup>[36-38]</sup> and CeO<sub>2</sub>-based<sup>[39-41]</sup> catalysts were also reported to perform well in selective hydrogenation of acetylene. For example, Cu catalysts were intrinsically selective to alkene in alkyne hydrogenation due to the marked difference of adsorption energy between alkyne and the corresponding alkene.<sup>[7,42,43]</sup> However, Cu catalysts are much less active than Pd catalysts in hydrogenation, and, as a result, the selective hydrogenation of acetylene over Cu catalysts often takes place at higher temperatures. Acetylene is prone to oligomerize to produce green oil at high temperatures, and the oligomers will foul the catalyst surface, thus leading to rapid catalyst deactivation.<sup>[7,44]</sup> Bridier et al<sup>[45]</sup> reported that CO-modified Cubased catalyst displayed an enhanced propene selectivity and suppressed the formation of oligomers. They proposed that the addition of CO altered the surface structure of Cu irreversibly, resulting in smaller Cu ensembles and minimizing the C-C coupling reaction. Another effective approach to suppressing the formation of oligomers is to lower the reaction temperature. McCue et al.<sup>[46]</sup> and Kyriakou<sup>[47]</sup> reported that the Pd-promoted Cu catalysts exhibited outstanding performance in selective hydrogenation of acetylene at low temperatures, by taking advantage of the high ethylene selectivity of Cu and the high activity of Pd.

In our previous investigation, a new interstitial copper carbide (Cu<sub>x</sub>C) was synthesized by reducing copper (I) acetylide (Cu<sub>2</sub>C<sub>2</sub>) in H<sub>2</sub> at 180 °C.<sup>[48]</sup> The DFT calculation results indicated that the Cu<sub>x</sub>C was more active than the Cu catalyst in H<sub>2</sub> dissociation. The Cu<sub>2</sub>O-derived catalyst, consisting of Cu<sub>x</sub>C and Cu, was remarkably active, selective, and stable in acetylene selective hydrogenation in an ethylene stream. In the present work, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> was used to prepare the catalysts for



selective acetylene hydrogenation using the same method. The obtained catalysts were characterized and tested in selective hydrogenation of acetylene in ethylene stream. In addition, the stability of the catalyst was investigated.

# **Results and Discussion**

### Synthesis of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>

The catalyst precursor  $Cu_2(OH)_2CO_3$  was synthesized by a precipitation method. The effect of synthesis temperature on the morphology and structure of the synthesized  $Cu_2(OH)_2CO_3$  was investigated. The SEM observation (Figure 1a–c) revealed that the particle size of  $Cu_2(OH)_2CO_3$  increased with temperature. The morphology of  $Cu_2(OH)_2CO_3$  changed from an aggregation of nanoparticles (~25 nm) to bundles of rectangular pillars, accordingly. Figure 1d shows the XRD patterns of the  $Cu_2(OH)_2CO_3$  samples synthesized at different temperatures (25,

45 and 65 °C). At higher temperatures (45 and 65 °C), the well resolved diffraction peaks characteristic of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> (JCPDS No. 76-0660) were detected in the XRD patterns, and no other crystal phase was detectable. At 25 °C, no distinct diffraction peaks were detected, probably because the crystallite size of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> was below the detection limit or the sample was amorphous. The HRTEM image (Figure 1e) shows that the Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> sample synthesized at 25 °C consisted of nanosized polycrystallites (2~4 nm) with various orientations, suggesting that highly dispersed crystallites of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> were obtained at 25 °C. The lattice fringes with d-spacing of 0.262, 0.252, 0.247 and 0.228 nm corresponded to the (121), (240), (201) and (221) planes of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, respectively. Figure 1f presents the N<sub>2</sub> adsorption and desorption isotherms and the BET specific surface areas of the three Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> samples. With increasing synthesis temperature, the specific surface area decreased from 67 to 10 and to  $4 \text{ m}^2\text{g}^{-1}$ . It demonstrates that the synthesis temperature significantly affected the morphology and dispersion of the synthesized  $Cu_2(OH)_2CO_3$ .



**Figure 1.** SEM images of the  $Cu_2(OH)_2CO_3$  samples synthesized at (a1, a2) 25 °C, (b1, b2) 45 °C and (c1, c2) 65 °C. (d) XRD patterns of  $Cu_2(OH)_2CO_3$  synthesized at different temperatures. (e) HRTEM image of  $Cu_2(OH)_2CO_3$  synthesized at 25 °C. (f) N<sub>2</sub> adsorption-desorption isotherms and specific surface areas of  $Cu_2(OH)_2CO_3$  samples synthesized at various temperatures (25 °C, 45 °C and 65 °C.).



The Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> samples synthesized at different temperatures were used as the precursors to prepare selective hydrogenation catalysts. The preparation procedure mainly includes two steps: (1) thermal treatment with an acetylene-containing gas at 120 °C, and (2) hydrogen reduction at 150 °C. Figure 2 compares the catalytic performance of the three prepared catalysts in selective hydrogenation of acetylene in an ethylene stream. The catalyst prepared from the Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> sample synthesized at 25 °C exhibited the highest activity, achieving 100% acetylene conversion with 17% ethane selectivity at 120 °C and atmospheric pressure. The better catalyst activity might be related to the smaller particle size, higher dispersion and surface area of the Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> precursor synthesized at low temperatures, leading to the formation of highly dispersed



**Figure 2.** (a) Acetylene conversion and (b) ethane selectivity as a function of reaction temperature in acetylene selective hydrogenation on the catalysts from  $Cu_2(OH)_2CO_3$  samples synthesized at different temperatures. The  $Cu_2(OH)_2CO_3$  samples were treated with an acetylene-containing gas at 120 °C and subsequently reduced in H<sub>2</sub> at 150 °C.



Figure 3. (a) XRD pattern and (b) HRTEM image of  $Cu_2(OH)_2CO_3(T120-R150)$  prepared from  $Cu_2(OH)_2CO_3$  obtained at 25 °C.

 $Cu_xC$  phase with high hydrogenation activity. Therefore, the  $Cu_2(OH)_2CO_3$  sample synthesized at 25  $^\circ C$  was used to prepare the acetylene hydrogenation catalyst in the following investigation.

### Characterization of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>-derived catalysts

The XRD pattern of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150) (Figure 3a) indicated that all the diffraction peaks characteristic of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> disappeared after the thermal treatment and the subsequent  $H_2$ reduction. In contrast, four new peaks were detected. Among them, the sharp peaks at  $2\theta = 43.3$ , 50.4 and 74.1° were ascribed to the (111), (200) and (220) planes of metallic Cu (PDF 04-0836). The broad diffraction peak at  $2\theta = 37.2^{\circ}$  was identical to that of the (0001) plane of Cu<sub>x</sub>C reported in our previous investigation,<sup>[48]</sup> indicating the formation of the interstitial copper carbide (Cu<sub>x</sub>C) phase in Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150). The weak and broad diffraction peak indicates the Cu<sub>v</sub>C phase was highly dispersed in the catalyst. Figure 3b illustrates the HRTEM image of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150). In accordance with the XRD characterization, two types of crystal phases were observed. The lattice fringe of 0.181 nm was assigned to the (200) plane of metal Cu. The lattice fringe of 0.238 nm corresponded to the diffraction peak at  $2\theta = 37.2^{\circ}$  in the XRD pattern of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150).

The XPS spectra of  $Cu_2(OH)_2CO_3(T120-R150)$  are shown in Figure 4. The absence of the Cu  $2p_{3/2}$  peak at 934.6 eV and the satellite peak at around 945 eV of  $Cu^{2+}$  (Figure 4a) indicates that no  $Cu^{2+}$  species was present in the catalyst.<sup>[37]</sup> In addition to the Cu  $2p_{3/2}$  peak at 932.1 eV attributed to  $Cu^+/Cu^0$ , the peak at 932.8 eV located between that of  $Cu^{2+}$  and that of  $Cu^+/Cu^0$  was linked to a Cu–C bond in  $Cu_xC.^{[37,48,50]}$  The Cu species in Cu<sub>x</sub>C has a partial positive charge ( $\delta^+$ ) due to an electron density transfer from Cu to  $C.^{[51]}$  In the Cu LMM spectrum (Figure 4b), the peak could be deconvoluted to two peaks at 918.6 and 917.2 eV. The one at 918.6 eV was attributed to  $Cu^0$ , and the other one at 917.2 eV, situated between  $Cu^+$  (916.8 eV) and  $Cu^0$  (918.6 eV), could be ascribed to the  $Cu^{\delta+}$  species in  $Cu_xC.^{[48]}$  In the C 1s spectrum, a shoulder peak at 283.8 eV indicated the formation of the interstitial carbide.<sup>[48,50]</sup>



Figure 4. (a) Cu 2p, (b) Cu LMM and (c) C 1s XPS spectra of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150).



The N<sub>2</sub> adsorption-desorption isotherms and BET specific surface areas of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>, Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120) and Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150) are shown in Figure S1. When Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> was treated with the acetylene-containing gas, the specific surface area increased from 67 to 91  $m^2 q^{-1}$ . The subsequent hydrogen reduction led to a significant increase of the specific surface area (164 m<sup>2</sup>/g). When Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150) was treated in a 1.5 M HNO<sub>3</sub> solution at room temperature, the copper species were dissolved in the solution, and the specific surface area of the remaining material was 538  $m^2 g^{-1}$  (Figure S2). After the treatment, the D band  $(1360 \text{ cm}^{-1})$  and G band  $(1560 \text{ cm}^{-1})$  were detectable in the Raman spectrum (Figure S3). It suggests that a porous carbon matrix was present in the catalyst. It seems that the Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>-derived catalyst consisted of Cu<sub>2</sub>C and Cu particles which were wrapped in a porous carbon matrix.

Our previous study indicated that Cu<sub>x</sub>C was obtained by H<sub>2</sub> reduction of copper (I) acetylide (Cu<sub>2</sub>C<sub>2</sub>).<sup>[48]</sup> It was reported that Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> reacts with acetylene readily to form copper (II) acetylide (CuC<sub>2</sub>).<sup>[52]</sup> It is therefore inferred that the copper (II) acetylide (CuC<sub>2</sub>) was the precursor or intermediate in the formation of Cu<sub>x</sub>C.

A small amount of bulk CuC<sub>2</sub> was synthesized from  $Cu_2(OH)_2CO_3$  and then thermally treated at 150 °C in hydrogen to obtain CuC<sub>2</sub>(R150). HRTEM image of CuC<sub>2</sub>(R150) (Figure 5a) displayed that two types of lattice spacings corresponding to Cu<sub>x</sub>C and Cu were observed. In the XRD pattern of CuC<sub>2</sub>(R150) (Figure 5b), three strong diffraction peaks at  $2\theta = 43.3$ , 50.4 and 74.1°, which were attributed to metal Cu, and a weak peak ascribed to Cu<sub>x</sub>C, were detected, identical to the peaks in the



Figure 5. (a) HRTEM image and (b) XRD pattern of CuC<sub>2</sub>(R150).

pattern of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150). It suggests that Cu<sub>x</sub>C was produced by H<sub>2</sub> reduction of CuC<sub>2</sub> at 150 °C, reducing Cu<sup>2+</sup> in CuC<sub>2</sub> to Cu<sup> $\delta$ +</sup> in Cu<sub>x</sub>C. In parallel, metal Cu and carbon material were produced by decomposition of CuC<sub>2</sub> because of its considerably low thermal stability. It is, therefore, proposed that the formation of Cu<sub>x</sub>C in Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>-derived catalyst involves the following two steps: (1) CuC<sub>2</sub> is produced by the reaction of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> with acetylene, (2) the resultant CuC<sub>2</sub> is reduced in hydrogen to generate Cu<sub>x</sub>C.

### Catalytic performance

It is known that Cu catalysts show outstanding selectivity to ethenes in selective hydrogenation of ethynes.<sup>[42,43]</sup> However, due to the low H<sub>2</sub> dissociation ability of Cu catalyst, Pd was often added to enhance the dissociation of H<sub>2</sub> at low temperatures.<sup>[46,47]</sup> On the other hand, interstitial transition metal carbides were reported to exhibit significantly higher activity in many hydrogenation reactions than their corresponding parent metals.<sup>[53–55]</sup> Recently, we reported that Cu<sub>x</sub>C exhibited considerably higher hydrogenation ability than the Cu catalyst.<sup>[48]</sup>

Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150) was tested in the selective hydrogenation of acetylene in excess ethylene in the temperature of 90-120°C at atmospheric pressure, in comparison with the Cu catalyst obtained from the same precursor by hydrogen reduction (Figure 6a). Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150) displayed an outstanding hydrogenation activity in the temperature range of 90-120°C, whereas the Cu catalyst showed extremely low hydrogenation activity in the same temperature range. In general, Cu catalysts showed marked hydrogenation activity above 150°C (Table S1). With increasing the hydrogenation temperature, the acetylene conversion increased monotonically and reached 100% above 110°C. Simultaneously, the ethane selectivity, a measure of the undesired over-hydrogenation increased with temperature. When acetylene was completely removed at 110°C, the selectivity to ethane was around 20%. When the temperature was raised to 120°C, the selectivity to ethane was still below 40%. In our previous investigation, the DFT calculation results illustrated that the Cu<sub>x</sub>C was in accordance with Cu<sub>3</sub>C(0001) in a rhombohedra-centered hex-



Figure 6. Acetylene conversion and ethane selectivity as a function of (a) reaction temperature, (b)  $H_2/C_2H_2$  ratio and (c) time on stream in acetylene hydrogenation over  $Cu_2(OH)_2CO_3(T140-R150)$ .



agonal structure, and H<sub>2</sub> preferably adsorbed on Cu<sub>3</sub>C(0001).<sup>[48]</sup> Additionally, the dissociation energy of H<sub>2</sub> on Cu<sub>3</sub>C(0001) was significantly lower than on Cu(111). In addition, the ethylene hydrogenation activity (Figure S4) on CuC<sub>2</sub>(R150) composed of Cu<sub>x</sub>C and Cu is markedly higher than that on CuC<sub>2</sub>(v150) which was decomposed to C and Cu.<sup>[52]</sup> On the other hand, the energy barriers for acetylene hydrogenation to vinylidene and then to ethylene over Cu<sub>3</sub>C(0001) were considerably higher than on Cu(111), suggesting that the Cu phase provides the main sites for acetylene hydrogenation. In the selective hydrogenation of acetylene over Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150), Cu<sub>x</sub>C lowered the energy barrier of H<sub>2</sub> dissociation and served as the site for H<sub>2</sub> dissociation at low temperature, and majority of the generated hydrogen atom spilt over to the Cu surface where acetylene was selectively hydrogenated to produce ethylene.

In industry, the ratio of hydrogen to acetylene  $(H_2/C_2H_2)$  is strictly monitored when supported Pd catalysts are used to remove acetylene impurity in ethylene.<sup>[56]</sup> High H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> ratio often leads to the formation of unselective palladium hydride phase and thus to over-hydrogenation,<sup>[8,57,58]</sup> resulting in a net ethylene loss and increasing the risk of a thermal runaway due to the high exothermicity of ethylene hydrogenation. Low  $H_2/$  $C_2H_2$  ratio decreases acetylene conversion, and facilitates the oligomerization to yield green oil which fouls the catalyst. The effect of  $H_2/C_2H_2$  ratio on the performance of  $Cu_2(OH)_2CO_3(T140-$ R150) was investigated in the range of 6-15 at 120°C and atmospheric pressure (Figure 6b). Acetylene conversion was kept constant at 100%, while the ethane selectivity increased from 10% to 39% when the  $H_2/C_2H_2$  ratio increased from 6 to 15. The wide operation window of  $H_2/C_2H_2$  ratio is favorable not only for the reactor operation, but also for the flexible choice of the front-end and the tail-end hydrogenation processes.

Fast deactivation of copper catalysts was observed in alkyne hydrogenation due to the buildup of oligomers below 160 °C.<sup>[7,45]</sup> Meanwhile, copper is often reported as the catalyst for the synthesis of carbon nanofibers by using acetylene as the gas source.<sup>[59,60]</sup> The carbon nanofibers from acetylene polymerization are accumulated on the catalyst surface and also deactivate the catalyst in acetylene hydrogenation. Therefore, the catalyst stability is of paramount importance for selective hydrogenation of acetylene on copper-based catalysts. Figure 6c demonstrated that Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150) was stable in the selective acetylene hydrogenation at 110 °C for 180 h, with complete acetylene conversion and 16% ethane selectivity. The high stability of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150) might be associated with the low reaction temperature. It was reported that the core-shell Pd@carbon nanoparticles supported on carbon nanotubes (Pd@C/CNTs) showed excellent stability in acetylene hydrogenation.<sup>[61]</sup> The formation of the porous carbon matrix in Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150) might pose steric hindrance to the chain growth of linear hydrocarbons, thus suppressing the undesired oligomerization and polymerization.

### Effect of acetylene treatment conditions

During the preparation of the hydrogenation catalyst, both the acetylene treatment and subsequent H<sub>2</sub> reduction significantly affect the contents and dispersion of Cu<sub>x</sub>C crystallites. The effect of the acetylene treatment temperature (120-180°C) on the hydrogenation performance of the catalyst reduced in H<sub>2</sub> at 150°C is shown in Figure 7. Acetylene was completely converted at 110°C and atmospheric pressure over Cu-(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150) and Cu(OH)<sub>2</sub>CO<sub>3</sub>(T160-R150), with ethane selectivities of 21% and 18%. The acetylene conversions over Cu(OH)<sub>2</sub>CO<sub>3</sub>(T120-R150) and Cu(OH)<sub>2</sub>CO<sub>3</sub>(T180-R150) were 70% and 61%, respectively. Acetylene conversion increased with reaction temperature, and complete acetylene conversion was achieved above 120 °C for each catalyst. Cu(OH)<sub>2</sub>CO<sub>3</sub>(T140-R150) exhibited the highest acetylene conversion. In the TG-DSC curve of bulk CuC<sub>2</sub> (Figure S5), an exothermic peak appeared above 160 °C, indicating that CuC<sub>2</sub> decomposed considerably to Cu and carbon above 160 °C. As a result, vigorous decomposition of the generated CuC<sub>2</sub> above 160 °C reduced formation of Cu<sub>2</sub>C active phase and enhanced the production of Cu and carbon, whereas low reaction rate at 120 °C yield less amount of CuC<sub>2</sub>.

The effect of acetylene treatment time is shown in Figure 8. The acetylene treatment time had a strong impact on the activity of the resultant catalyst. The optimal treatment time at 140 °C was 2 h.  $CuC_2$ , which is the intermediate for the production of CuxC, is thermally unstable, and prolonged treatment time led to enhanced decomposition of the in situ generated  $CuC_2$ .

It is apparent that  $H_2$  reduction of the insitu formed  $CuC_2$  was accompanied by the simultaneous decomposition of  $CuC_2$ .



Figure 7. (a) Acetylene conversion and (b) ethane selectivity as a function of reaction temperature over the  $Cu(OH)_2CO_3(Tx-R150)$  catalysts.



Figure 8. (a) Acetylene conversion and (b) ethane selectivity as a function of reaction temperature over  $Cu(OH)_2CO_3(T140-R150)$  catalysts treated with acetylene-containing gas for different times at 140 °C.



As a result, the subsequent  $H_2$  reduction determines the amount of generated Cu<sub>x</sub>C active phase and thus the hydrogenation activity of the obtained catalysts. The effect of reduction temperature on the performance of the prepared catalyst in selective hydrogenation of acetylene is shown in Figure 9. Acetylene conversion and ethane selectivity increased with reaction temperature, and complete acetylene conversion was achieved at 120°C for each catalyst. The reduction below 180°C resulted in highly active catalyst for acetylene hydrogenation, achieving 100% acetylene conversion at 110°C and atmospheric pressure. When Cu(OH)<sub>2</sub>CO<sub>3</sub>(T140) was reduced at 210°C, the acetylene conversion was around 80% under the same conditions. Reduction at higher temperature enhanced the parallel decomposition of CuC<sub>2</sub>, leading to decreased formation of Cu<sub>x</sub>C. The lower activity of the catalyst reduced at 130 °C might be linked to the lower reduction rate of CuC<sub>2</sub>. The effect of reduction time on the performance of the catalyst is presented in Figure 10. It is shown that the reduction time had a minor effect on the activity of the catalysts, probably due to the fast rate in reduction and thermal decomposition of  $CuC_2$  at 180°C.

## Conclusions

A non-precious metal catalyst for selective hydrogenation of acetylene in excess ethylene was prepared from  $Cu(OH)_2CO_3$  through thermal treatment with acetylene and subsequent  $H_2$  reduction. The catalyst was composed of  $Cu_xC$  and Cu crystallites which were highly dispersed in a porous carbon



Figure 9. (a) Acetylene conversion and (b) ethane selectivity as a function of reaction temperature over the  $Cu(OH)_2CO_3(T140-Ry)$  catalysts reduced at different temperatures.



Figure 10. (a) Acetylene conversion and (b) ethane selectivity as a function of reaction temperature over the  $Cu(OH)_2CO_3$ (T140-R180) catalysts reduced at 180 °C for different times.

matrix. The obtained catalyst was highly active, selective and stable in acetylene hydrogenation at low temperatures (~ 120 °C). The Cu phase was the main site for acetylene hydrogenation, and the Cu<sub>x</sub>C phase served as the catalytic sites for H<sub>2</sub> dissociation. In contrast to the high sensitivity to H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> for Pd-based catalysts, the ethane selectivity on the prepared catalyst was not dramatically affected by the H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> ratio in the feed in the presence of large excess ethylene. As a result, the new catalyst could be used for both the front-end hydrogenation process and the tail-end hydrogenation process without adding CO as a selectivity enhancer. The high stability of the catalyst might be ascribed to the lowered reaction temperature as well as to the formation of a porous carbon matrix which suppressed the chain growth of linear hydrocarbons by a steric hindrance effect.

# **Experimental Section**

### **Chemicals and Materials**

Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub> and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd, China, and used without further purification. Hydrogen gas and ethylene were from Dalian Guangming Gas Co., China. The acetylene-containing gas (0.50% C<sub>2</sub>H<sub>2</sub> and 99.50% Ar) for the thermal treatment and the hydrogenation feed (0.80% CH<sub>4</sub>, 0.50% C<sub>2</sub>H<sub>2</sub>, and 98.70% C<sub>2</sub>H<sub>4</sub>) were provided by Dalian Guangming Gas Co., China.

### **Preparation of catalysts**

Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> was synthesized by a fast-precipitation method according to the literature.<sup>[49]</sup> 200 mL Na<sub>2</sub>CO<sub>3</sub> solution (0.1 mol L<sup>-1</sup>) was poured into 200 ml Cu(NO<sub>3</sub>)<sub>2</sub> solution (0.1 mol L<sup>-1</sup>) at different temperatures (25, 45 and 65 °C) and stirred for 30 min. Then the precipitate was collected through filtration, washed with deionized water and ethanol for several times, and dried in a vacuum oven at 30 °C for 12 h.

The catalysts were prepared as follows. The Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> sample was heated from room temperature to the thermal treatment temperature at 3 °Cmin<sup>-1</sup> and kept for 2 h in an acetylene-containing gas (0.50% C<sub>2</sub>H<sub>2</sub> and 99.50% Ar) at 30 mlmin<sup>-1</sup>, then cooled down to room temperature. The obtained sample was denoted as Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(Tx), where x represents the thermal treatment temperature. Then Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(Tx) was reduced in 50 mlmin<sup>-1</sup> H<sub>2</sub> at a set temperature for 3 h with a heating rate of 3 °Cmin<sup>-1</sup>. The resultant hydrogenation catalyst was denoted as Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>(Tx–Ry), where y represents the reduction temperature. For comparison, a Cu catalyst was prepared from the Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> sample synthesized at 25 °C by hydrogen reduction at 400 °C and atmospheric pressure for 6 h

Bulk CuC<sub>2</sub> was prepared as follows. Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> was dissolved in ammonia solution (12.5%) at room temperature. Ar was bubbled into the blue solution at 50 ml min<sup>-1</sup> for 30 min. Subsequently, a mixture gas (10.0% C<sub>2</sub>H<sub>2</sub> in Ar at 50 ml min<sup>-1</sup>) was bubbled for 5 h. The bulk copper (II) acetylide (CuC<sub>2</sub>) was obtained by centrifugation and washed with deionized water and ethanol for several times, and then kept in water (**CAUTION: Dry CuC<sub>2</sub> is highly explosive.**). The obtained CuC<sub>2</sub> was heated in H<sub>2</sub> (50 ml min<sup>-1</sup>) or in vacuum at 150°C for 3 h, and the resultant materials were denoted as CuC<sub>2</sub>(R150) and CuC<sub>2</sub>(v150), respectively.



### **Catalyst Characterization**

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku SmartLab diffractometer with Cu K $\alpha$  radiation at a scanning rate of 8°/min between 20° and 80°. The tube voltage and current were 40 kV and 100 mA, respectively. Scanning electron microscope (SEM) observation was conducted on a SU8220 instrument operated with a beam energy of 5.0 kV. Transmission electron microscope (TEM) observation was performed on a FEI Tecnai G2 F30 microscope operated at 300 kV. Raman spectrum was recorded using a Thermo Scientific DXR Raman instrument with a 532 nm laser beam as the excitation source. TG-DSC curves were measured on TGA Q50 in N<sub>2</sub> flow at 50 ml min<sup>-1</sup> with a heating rate of 3°C min<sup>-1</sup>. Nitrogen sorption isotherms were measured at -196°C on Micromeritics Tristar II 3020 instrument. The specific surface areas was calculated according to the Brunauer-Emmett-Teller (BET) method.

#### Catalytic performance

The selective hydrogenation of acetylene in ethylene stream was performed at atmospheric pressure in a quartz tube fixed-bed reactor (10 mm i.d.).  $Cu_2(OH)_2CO_3$  sample (0.1 g) was mixed with quartz sands (0.6 g, 60–80 mesh), and sandwiched in the middle of the reactor. The acetylene hydrogenation catalyst was prepared in situ, prior to selective hydrogenation.

The acetylene hydrogenation reaction was performed in the temperature range of 90–120 °C with a mixture gas of 93% feed gas and 7% H<sub>2</sub>. The total flow was 10 ml/min. The outlet gas composition was analyzed by an online gas chromatography (GC A90, ECHROM) equipped with an FID detector and a capillary column (Agilent HP-AL/S,  $30 \text{ m} \times 0.535 \text{ mm} \times 15.00 \mu\text{m}$ ). Methane was used as the internal standard for GC analysis. Because it is extremely difficult to determine the increment of ethylene in the presence of over 90% ethylene, the selectivity to undesired ethane was used to measure the selectivity of the catalyst. Acetylene conversion and ethane selectivity were calculated as follows (Equation 1 and Equation 2).

$$C_{2}H_{2} \text{ conversion (\%)} = \frac{[C_{2}H_{2}]_{\text{inlet}} - [C_{2}H_{2}]_{\text{outlet}}}{[C_{2}H_{2}]_{\text{inlet}}} \times 100$$
(1)

$$C_{2}H_{6} \text{ selectivity (\%)} = \frac{\left[C_{2}H_{6}\right]_{outlet}}{\left[C_{2}H_{2}\right]_{init} - \left[C_{2}H_{2}\right]_{outlet}} \times 100$$
(2)

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## **Conflict of Interest**

The authors declare no conflict of interest.

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