Combustion Products of Calcium Carbide Reused by Cu-Based Catalysts for Acetylene Carbonylation

Yongkang Sun, Junming Zeng, Jie Zhang, Jun Yang, Weixin Qian, Feng Yu, Bin Dai,* and Jiangbing Li*

Cite This: ACS Omega 2020, 5, 27692−27701

ABSTRACT: Sustainable development is a worldwide concern. This work mainly focuses on the reuse of the combustion products of calcium carbide and the influence of different kinds of copper on the acetylene carbonylation reaction. A series of catalysts were prepared by heating the precursors under various atmospheres (air, hydrogen, and nitrogen). The X-ray diffraction and the X-ray photoelectron spectroscopy have been analyzed regarding copper species composition and content in catalysts. The result of the Cu+-promoted reaction was in good agreement with the conducted density functional theory analysis, and we speculate that Cu+ promotes the transfer of electrons in the reaction. Transmission electron microscopy and elemental mapping evaluation confirmed the difference in Cu dispersion. Characterization of catalysts using temperature programmed desorption and pyridine Fourier-transform infrared revealed differences in their acidity. Acidity was found to be favorable for acetylene carbonylation. Selectivity and yield of the CuAlZn-LDO(N) catalyst at 225 °C were 73 and 70%, respectively, and the catalyst showed good stability over two consecutive cycles of reuse.

1. INTRODUCTION

The preparation of calcium carbide (CaC₂) in an industrial setting typically involves reacting coal and calcium oxide in an electric smelting furnace. In the recent years, CaC₂ has become a significant important organic raw material for the production of acetylene.1−4 The use of CaC₂ is an attractive approach that provides ideas for the preparation of acetylene from nonoil resources. The presence of large amounts of CO in the CaC₂ combustion products enables application of this process in various green chemistry strategies. The Reppe reaction of acetylene with CO or hydrogen-containing compounds (such as water, etc.) is the most important process in the production of carboxylic acid monomers.5,6 Products of carbonylation, such as acrylic acid (AA) and its derivatives, are widely used for the production of polymers, including plastics,7 synthetic rubbers,8 and fibers.9−17 Therefore, the use of waste gas will allow the utilization of CO as a benign C1 feedstock to produce more sustainable chemical compounds (AA),10 and the strategy is in compliance with world demand for sustainable development.11

The majority of common catalysts for acetylene carbonylation are metal halogenides.12,13 Moreover, different homogeneous catalysts have been used for this process; however, the separation of the catalysts from the reaction solvent is often challenging. Thus, according to the principles of green chemistry, heterogeneous catalysts are considered as more efficient and environmentally friendly systems. Various Cu catalysts have been employed for acetylene carbonylation reactions.14 Particularly, Cu-based oxide catalysts have attracted significant attention due to their environmentally friendly characteristics, excellent redox capabilities, and low cost.15,16 Consequently, in recent years, new Cu-based catalysts have been developed. A previous study reported an ion exchange reaction in which various ions were exchanged for Cu species.17 Nevertheless, a big disadvantage of the ion exchange processes is the upper limit of the Cu-loading amount, which is very difficult to determine accurately. Layered double hydroxides (LDHs) are layered structure materials,18 which can be roasted to obtain layered double oxides (LDOs). Different functional materials, such as metal nanoparticles or mixed metal oxides with high dispersion and thermal stability, can be obtained from LDHs.19−21 The preparation of such structures typically involves a topological transformation over an oxide matrix.22,23 The aforementioned functional materials can be used as effective catalysts owing to their highly ordered structures comprising layers of alternate cations.24−27 Moreover, due to the existence of acid cations interacting with the Al and Cu species in LDHs,28 it is important to regulate the acidic and basic sites in the structure.

Received: September 2, 2020
Accepted: October 5, 2020
Published: October 14, 2020
It is noteworthy that the performance of a catalyst not only does depend on the employed metal precursors but also is affected by the catalyst postprocessing method. In this work, CuAlZn-LDHs were synthesized and calcinated in the presence of different gases to evaluate the catalyst synthesis procedure. The catalytic performance of the developed materials for acetylene carbonylation was investigated. Catalytic Cu species exhibiting different valence states were obtained by passing the precursors through a roasting gas. It was found that the presence of Cu⁺ was favorable for improving the reactivity. Furthermore, regulating the amount of various Cu species in the precursors was achieved using different roasting conditions. The roasting gas also affected the interspersion of the Cu ions. Specifically, higher dispersion of roasted Cu was observed under a nitrogen atmosphere. Importantly, the synthetic procedure was relatively and the developed catalyst showed stable catalytic performance after three consecutive reaction cycles.

2. RESULTS AND DISCUSSION

2.1. Chemical Component. Structure is an important aspect affecting the catalyst performance; therefore, the crystal structures of the synthesized materials were characterized by X-ray diffraction (XRD). Figure 1a illustrates the XRD patterns of CuZnAl-LDH, CuZnAl-LDO(A), CuZnAl-LDO(N), and CuZnAl-LDO(H) composites. In the CuZnAl-LDH pattern, the sharp peaks corresponding to the hydrotalcite phase at diffraction angles of 2θ = 11.6, 23.3, 34.5, and 60.1° were attributed to the basal planes (003), (006), (009), and (110), respectively. Similar patterns were previously reported for hydrotalcite-type structures; thus, it was confirmed that the material was successfully prepared. Notably, the highest intensity was detected for the roasting peaks corresponding to CuZnAl-LDH, which indicated the presence of perfect crystalline phases in the composite. The comparison found of the structures revealed that following calcination of CuAlZn-
LDH at 300 °C, the layered structure of the LDH precursor was damaged and the crystallinity of the catalyst significantly reduced. Concurrently, the catalyst will also undergo a structural collapse after calcination under different atmospheres, and the supported Cu ions were converted into different Cu species. For instance, in the XRD patterns of both CuZnAl-LDO(A) and CuZnAl-LDO(N), the signals detected at 2θ = 35.5 and 38.6° were attributed to crystalline CuO, which suggested that the catalyst produced CuO upon calcination under air and nitrogen. Moreover, the peaks at 2θ = 43.3, 50.4, and 74.1° in the diffractogram of the catalyst roasted under a hydrogen atmosphere were ascribed to Cu0, which was produced by the reduction of a Cu-containing compound by the gas. No other Cu species were detected, indicating that any additional Cu-based compounds present in the sample were smaller than the gauging limit of XRD or that they existed as noncrystalline species. Figure 1b demonstrates that compared with CuZnAl-LDO(N), the CuO crystals were hardly detected in the recycled catalysts RN1, RN2, and RN3. Because the reaction was conducted under reduction conditions in the presence of CO and acetylene, it is speculated that CuO was transformed into other species. The amount of coke in catalysts was measured by thermogravimetric analysis (TGA) (Figure 1c,d). The sample mass decreases with increasing temperature, and only three recycle samples had DTG signals; it was obvious that coke was formed during acetylene carbonylation.

The morphology of the synthesized CuAlZn-LDO material was analyzed by transmission electron microscopy (TEM). The results obtained for CuZnAl-LDO(A), CuZnAl-LDO(N), and CuZnAl-LDO(H) calcined under the air, nitrogen, and hydrogen atmosphere are demonstrated in Figure 2a,c,e, respectively. As it can be seen, the calcined LDH samples exhibited layered particles. In addition, plate-like crystals were observed which implied a gradual transformation of LDH to LDH structures. It was also determined that the sheet-like morphology was maintained. Figure 2c shows that the catalyst displayed a uniform distribution of the metal. In contrast, significant metal accumulation can be observed in Figure 2e. To evaluate the distribution of metals in more detail, we subsequently performed elemental mapping analysis on the samples. Figure 2b,d,f demonstrates the individual distribution of the active Cu component. In CuZnAl-LDO(N), no small Cu clusters were found without agglomeration of the particles, and the Cu species were highly dispersed due to the use of different calcination gases. Table 1 summarizes the data obtained from the ICP and CO pulse adsorption analyses. It can be seen that the actual loads of CuZnAl-LDO(A), CuZnAl-LDO(N), and CuZnAl-LDO(H) were 21.4, 21.3, and 28.3%, respectively. The data obtained from the CO pulse adsorption evaluation clearly demonstrated that the maximum dispersion of CuZnAl-LDO(A), CuZnAl-LDO(N), and CuZnAl-LDO(H) was 12.2, 14.7, and 8.2%, respectively. These results were consistent with the outcomes of the scanning electron microscopy and elemental mapping analysis. Thus, it was determined that compared to CuZnAl-LDO(A) and CuZnAl-LDO(H), the CuZnAl-LDO(N) catalyst displayed the best dispersion.

The chemical states of Cu in the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy (XAES) (Figure 3). As demonstrated in Figure 3a, the obtained XPS spectrum exhibited broad and asymmetrical peaks. Hence, we speculated that various Cu species, such as Cu2+ and CuO, existed in the prepared catalysts. The Cu 2p binding energies were corrected for the C 1s binding energies of 284.8 eV. In the spectrum of CuZnAl-LDO(A), the main peak at 935.1 eV was attributed to Cu2+, while the peak at 933.7 eV was ascribed to CuO. In the CuLM characterization, the existence of CuO and Cu2+ in CuZnAl-LDO(A) was also confirmed by the peaks at 918.1 and 915.7 eV, respectively. Moreover, analysis of CuZnAl-LDO(N) revealed a main peak at 935.1 eV corresponding to Cu2+ and peak at 933.7 eV which was attributed to CuO. The comparison of CuZnAl-LDO(N) with CuZnAl-LDO(A) also showed the presence of an additional peak 932.4 eV, which we ascribed to Cu2+ or CuO. The Cu2+ and CuO species could be distinguished by CuLM Auger electron spectroscopy analysis. In addition to the peaks at 915.2 and 917.6 eV, the signal at 913.8 eV was detected, which was attributed to Cu2+. Furthermore, the spectrum of CuZnAl-LDO(H) exhibited characteristic peaks at 935.2 and 932.2 eV. Following the above analysis, we considered the performance of Cu2+ and CuO. A new peak with the binding energy of 934.2 eV was detected, which was ascribed to Cu2+. In CuLM, in addition to the Cu2+ and CuO peaks at 915.7 and 916.8 eV, respectively, a new peak at 918 eV was observed, which corresponded to Cu2+. The presence of Cu2+ was also detected in the CuZnAl-LDO(H) XRD sample. Thus, the existence of three different valence Cu species in CuZnAl-LDO(H) was determined. The Cu content was subsequently quantitatively determined by dividing the XPS or XAES spectra of Cu 2p3/2 into several Gaussian curves. The summary of the surface composition and the relative content of different Cu species are shown in Table 2. The data were calculated according to the relative peak area. The contents of Cu2+ in the CuZnAl-LDO(A), CuZnAl-LDO(N), and CuZnAl-LDO(H) catalysts were determined at 42.0, 14.8, and 45.0%, respectively. Moreover, the contents of CuO in the CuZnAl-LDO(A) and CuZnAl-LDO(N) catalysts were established at 58.0 and 23.5%, respectively. In CuZnAl-LDO(N), the content of Cu2+ was determined at 61.7%, which was higher than in the other two catalysts. Combined with the acetylene conversion indicated results, it was found that Cu2+ was the main active site of Cu-based catalysts for acetylene carbonylation. Figure 3b demonstrates the chemical states of Cu in the CuZnAl-LDO(N) catalysts. In contrast with peaks to CuZnAl-LDO(N), three types of Cu species were present in Cu50ZnAl-LDO(N) and Cu2ZnAl-LDO(N). This suggests that the adjustment of the Cu ratio under nitrogen firing conditions did not affect the Cu valence. However, based on the data shown in Table 2, the contents of Cu2+ in the Cu50ZnAl-LDO(N) and Cu2ZnAl-LDO(N) catalysts were 25 and 22.6%, respectively. This implies that the content of Cu2+ was regulated by the Cu metal ratio in the precursor. The Brunauer-Emmett-Teller (BET) surface area (Table 3)
decreased from 76.24 to 80.32 m²/g, and there is not much difference in the catalysts.

Table 2. Content of Various Cu Species in the Studied Catalysts

| catalysts          | Cu²⁺ (%) | CuO (%) | Cu⁺ (%) | Cu⁰ (%) | Cu₂O (%) |
|--------------------|----------|---------|---------|---------|----------|
| CuZnAl-LDO(A)      | 42.0     | 58.0    |         |         |          |
| Cu₀.₅ZnAl-LDO(A)   | 40.0     | 60.0    |         |         |          |
| Cu₂ZnAl-LDO(A)     | 61.3     | 38.7    |         |         |          |
| Cu₀.₅ZnAl-LDO(N)   | 45.6     | 24.9    | 25.0    |         |          |
| CuZnAl-LDO(N)      | 14.8     | 23.5    | 61.7    |         |          |
| Cu₂ZnAl-LDO(N)     | 27.8     | 49.6    | 22.6    |         |          |
| Cu₀.₅ZnAl-LDO(H)   | 8.6      | 71.2    | 20.2    |         |          |
| CuZnAl-LDO(H)      | 45.0     | 50.4    | 4.6     |         |          |
| Cu₂ZnAl-LDO(H)     | 19.4     | 59.5    | 21.1    |         |          |

Table 3. BET Surface Area in the Studied Catalysts

| catalysts | S_BET (m²/g) |
|-----------|-------------|
| CuZnAl-LDO(A) | 78.78     |
| CuZnAl-LDO(N) | 76.24     |
| CuZnAl-LDO(H) | 80.32     |

Temperature programmed desorption (TPD) of ammonia was used to measure the Lewis acidity of the prepared catalysts. The peaks corresponding to desorbed ammonia at three temperature-correlated areas indicated the presence of weakly, moderately, and strongly acidic sites. The amount of desorbed NH₃ exhibited a linear relationship with the number of acidic sites, which was determined from the peak areas of the TPD profiles. Figure 4 shows the presence of weakly and moderately acidic sites in the studied series of catalysts. The NH₃ desorption peak of CuZnAl-LDO(N) is significantly higher than those of CuZnAl-LDO(A) and CuZnAl-LDO(H), suggesting that CuZnAl-LDO(N) possesses more acidic sites for NH₃ adsorption. In addition, two desorption peaks were detected in the profile of CuZnAl-LDO(A). The first desorption peak was observed in the range of 300–400 °C and was attributed to a moderate acid. The second peak in the range of 500–600 °C corresponded to a strong acid. Furthermore, the CuZnAl-LDO(H) sample also displayed two desorption peaks. The first peak was detected between 350 and 400 °C and was ascribed to a moderate acid. The second desorption peak was observed in the range of 500–600 °C and corresponded to a strong Lewis acid. Similarly, the CuZnAl-LDO(N) sample exhibited two desorption peaks, one in the range of 300–400 °C and another in the range of 500–600 °C, which were attributed to moderate and strong acids, respectively. These outcomes indicated extensive distribution of moderately and weakly acidic sites in the catalyst. Moreover, the existence of the acidic sites was related to the contribution of different metal oxides. Compared with the CuZnAl-LDO(A) and CuZnAl-LDO(H) catalysts, the number of moderately and strongly acidic centers in CuZnAl-LDO(N) increased, which was certainly a result of the presence of Cu species. We subsequently conducted comprehensive analysis of
the IR spectra of pyridine adsorbed on the catalysts to further characterize the types of acidic sites and to confirm the acid concentrations.

To gain more insights into the changes in the Brønsted (B) and Lewis (L) acid sites, the properties of the catalysts were investigated based on the interactions between the samples and the probe molecules of the pyridine IR spectra. The Fourier-transform infrared (FT-IR) spectra of the catalysts using pyridine as the probe molecule were obtained in the temperature range of 200–350 °C. The calculated B and L acid amounts are summarized in Table 4. The characteristic IR band at 1540 cm⁻¹ was attributed to the pyridine ions in the B acid sites, while the band at approximately 1450 cm⁻¹ corresponded to pyridine bonded to the L acid centers. In CuZnAl-LDO(N), the B acid sites exhibited a peak at 1540 cm⁻¹. Furthermore, the peak at 1490 cm⁻¹ was ascribed to both B and L acid sites. The peaks at 1450 and 1610 cm⁻¹ corresponded to the L acid sites. The obtained results indicated that the amounts of acidic sites, that is, B, L, and total acid amounts are summarized in Table 4. The characteristic IR bands at 1540 cm⁻¹ were attributed to pyridine ions in the B acid sites, and the band at approximately 1450 cm⁻¹ corresponded to pyridine bonded to the L acid centers.

The first-principle density functional theory (DFT) calculations were performed employing the projector-augmented wave (PAW) method. The exchange functional was treated using generalized gradient approximation of the Perdew–Burke–Ernzerhof functional. The cut-off energy of the plane wave basis was set at 500 eV to optimize the atom and cell calculations. The vacuum spacing in the direction perpendicular to the plane of the catalyst was at least 12 Å. The Brillouin zone integration was performed using 4 × 4 × 1 Monkhorst–Pack k-point sampling for a primitive cell. The self-consistent calculations employed a convergence energy threshold of 10⁻⁸ eV. The equilibrium lattice constants were optimized with the maximum stress on each atom within 0.05 eV/Å. The Hubbard U (DFT + U) corrections for 3d transition metals were conducted according to previously reported methods. In the current study, the reaction barrier was calculated based on the transition state approach. Figure 6a illustrates detailed one-dimensional potential energy diagrams including three kinds of Cu valence states as well as the geometries of the transition states in Figure 6c. It was determined that the acetylene molecule was adsorbed on the surface of the Cu atom. In addition, the unsaturated carbon atom of acetylene was bonded to the carbon atom of the CO molecule. This step absorbed heat, and the potential barrier for the reaction on the surface of Cu⁺ was established at 38.54 kcal mol⁻¹. Moreover, the potential barriers for the reactions on the surfaces of Cu²⁺ and Cu⁰ were determined at 49.97 and 57.98 kcal mol⁻¹, respectively. Subsequently, the water molecules introduced hydroxyl moieties, generating AA on the Cu atoms on the surface of the adsorbed states. Notably, the surface of monovalent Cu displayed the lowest potential barrier. The high content of Cu⁺ correlates with lowest energy barrier. Based on the activity of the catalysts shown in Figure 8, CuZnAl-LDO(N) exhibited the most optimal performance. We speculated that high contents contributed to a reduction in the energy barrier for acetylene carbonylation, thus promoting the reaction. Scheme 1 shows possible mechanism, and we speculated that Cu⁺ promoted electron transfer from acetylene to carbonyl nickel.

2.2. Catalytic Activity. 2.2.1. Effect of Roasting Temperature on the Activity of Hydrotalcites. The effect of roasting temperature on the carbonylation of acetylene over CuZnAl hydrotalcite catalysts were investigated in the temperature range of 300–600 °C. Figure 7a shows the AA activity as a function of the catalyst roasting temperature. In range of 300–600 °C, there was negligible variation in the AA selectivity and yield. Hence, from the energy saving perspective, the optimum roasting temperature was 300 °C. The effect of temperature (205, 215, 225, and 235 °C) on the activity of the CuZnAl-LDO/NiBr₂ system is demonstrated in Figure 7b. Increasing temperature resulted in an initial increase of the catalytic activity, which then gradually decreased. The highest activity was obtained at 225 °C. In Figure 7c, when water is 20 mL, yield and selectivity of AA are best, so we believe that 20 mL of water best fit for the reaction. In Figure 7d, when quality of CuZnAl-LDO(N) is 0.2 g, selectivity and yield are 73 and 70%, respectively.

2.2.2. Comparison of the Catalytic Performance. The catalytic performance of the catalysts for acetylene carbonylation reaction was investigated after 30 min at 225 °C. Figure 8a shows the catalytic performance of CuZnAl-LDO(A), CuZnAl-LDO(H), and CuZnAl-LDO(N). The AA selectivity was <65% for both CuZnAl-LDO(A) and CuZnAl-LDO(H)
catalysts. On the other hand, the AA selectivity of CuZnAl-LDO(N) was 74%. Calcination under different atmospheres also affected the catalytic performance of catalysts. The findings of our study suggested that CuZnAl-LDO(N) could be applied as a highly efficient catalyst for acetylene carbonylation. The catalytic activity of CuZnAl-LDO(N) is summarized in Figure 8b. It is noteworthy that the performance of the materials changed at increased Cu⁺ ratios. Overall, CuZnAl-LDO(N) which exhibited the highest content of Cu⁺ displayed the best activity (Table 2). Hence, it was concluded that high content of Cu⁺ promoted acetylene carbonylation of acetylene catalyst.

2.2.3. Performance of the Recycled Catalysts. The stability of catalysts is an important factor for their practical applications. In the present study, we carried out recyclability tests to evaluate the performance of CuZnAl-LDO(N). The recovered catalyst material was recovered from the reactor by filtration and washed with deionized water prior to drying at room temperature. The results of the catalyst recyclability test are demonstrated in Figure 9. For CuZnAl-LDO(N), the selectivity and yield remained nearly unchanged after the first two cycles, with <4% loss of activity. On the other hand, AA showed an approximately 10% decrease in activity after the third cycle. The recovery and reusability of the catalyst with good catalytic performance are advantageous for its potential practical applications.

3. CONCLUSIONS

In the present work, ternary CuZnAl-LDO(N) hydrotalcite-like materials were prepared employing a simple synthetic method using different roasting temperatures. The synthesized materials used as catalysts for the acetylene carbonylation reaction. Both series of Cu (Cu⁺, Cu²⁺, and Cu⁰) contribute to the reaction and the high performance of CuZnAl-LDO(N) was attributed to the high content of (Cu⁺) in the catalyst. After calcination under a nitrogen atmosphere, increased dispersion of Cu and a larger amount exposed active sites and acid centers were determined in the CuZnAl-LDO(N) catalyst. It was also found that the acidic sites played an important role in the activity. Importantly, the cycle stability test results confirmed the reusability of the catalyst without any significant loss in activity after three reaction cycles. Finally, the DFT calculations demonstrated that high content of Cu⁺ resulted in a reduction of the energy barrier for acetylene carbonylation, promoting the reaction, which was consistent with three experimental results.

4. EXPERIMENTAL SECTION

4.1. Materials. NaOH and anhydrous Na₂CO₃ were purchased from Tianjin Sheng Chemical Reagent Co., Ltd., China. Cu(NO₃)₂, Al(NO₃)₃·9H₂O, and Zn(NO₃)₂·6H₂O were obtained from Shanghai Macklin Biochemical Co., Ltd., China. All reagents were used as received.
4.2. Catalyst Preparation. The Cu Zn Al hydrotalcite with a Cu²⁺/Zn²⁺/Al³⁺ ratio of 1:1:1 was prepared by a typical coprecipitation synthesis. 30 mL of an aqueous solution containing Cu(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, and Al(NO₃)₃·9H₂O at a molar ratio of 1:1:1 was added dropwise to 12.5 mL of 1 M solution of Na₂CO₃ under vigorous stirring. The solution pH was controlled at approximately 10 using a 1 M NaOH solution. Following titration, the reaction mixture was shaken for 0.5 h. The resultant slurry was separated by filtration and then washed three times with deionized water. The material was dried in an oven at 80 °C for 5 h. Last, the obtained precursor was marked as CuZnAl-LDH. The dry precursor was subsequently divided into three parts and heated up to 300 °C at a rate of 2 °C min. The materials were subjected to different gas flows for 5 h. The precursors heated under the air, hydrogen, and nitrogen atmosphere were labeled as CuZnAl-LDO(A), CuZnAl-LDO(H), and CuZnAl-LDO(N), respectively. Moreover, the catalysts with the Cu²⁺/Zn²⁺/Al³⁺ ratio of 0.5:1:1 and 2:1:1 were prepared using the same approach as described for CuZnAl-LDO(N) and were marked as Cu₀.₅ZnAl-LDO(N) and Cu₂ZnAl-LDO(N), respectively.

Figure 7. Activity of AA as a function of temperature: the effect of the catalyst roasting temperature (a), the effect of the catalyst reaction temperature (b), the effect of the water (c), and the effect of the catalyst quality (d).

Figure 8. Catalysts activity evaluation: catalysts calcined under different atmospheres (a) and catalysts with different Cu rations (b–d).
All recovered catalysts were denoted as RNn (n being the number of used).

4.3. Catalyst Characterization. The crystal structure of the materials was determined by XRD (Philips analytical X-ray diffractometer) at a voltage of 40 kV and a current of 15 mA using a continuous scanning mode, with a scanning range of $10^\circ \leq 2\theta \leq 80^\circ$. XPS was performed utilizing the ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA). TGA was performed on a TA Instrument STA449F3 Analyzer under an air flow. TEM and elemental mapping images were obtained using a Titan G260-300 microscope operating at 200 kV. The catalysts were dissolved in a mixed-acid acidic solution, and the actual content of Cu in the prepared samples was determined by inductively coupled plasma−mass spectrometry (ICP−MS) using the Agilent ICP-OES730 series ICP spectrometer (Thermo Fisher Scientific, USA). Temperature-programmed desorption of NH3 (NH3-TPD) was conducted on AutoChem-1 III I 2920. The acidity of the prepared catalysts was evaluated by FT-IR spectroscopy using pyridine. The FT-IR measurement was performed at room temperature (25 °C). The temperature was then increased to 350 °C, at a rate of 10 °C min$^{-1}$. The sample was subjected to vacuum activation for 1 h. The background was extracted, and the sample was cooled to room temperature. The suction of pyridine was carried out for 20 min until reaching saturation. Adsorption was subsequently stopped, and the sample was placed under vacuum. Pyridine was desorbed and the samples were separately heated to 200, 300, and 350 °C. The amounts of Lewis and Bronsted acids in the three catalysts were calculated using empirical formulas, which were obtained from the correlation experiments.

4.4. Catalyst Evaluation. The acetylene carbonylation reaction was conducted in a high-pressure reaction vessel equipped with a gas inlet and outlet. The autoclave contained a burst disk, pressure gauge, and heating and agitation rate controllers. 0.1 g of each catalyst, 1.5 g of NiBr, 150 mL of tetrahydrofuran, and 20 mL of H2O were successively added into the reaction device. After purifying, the autoclave with N2, C2H2 was injected into the reactor at a volume of 4.26 L. Subsequently, CO was added into the system at a pressure of 4.0 MPa. When the temperature reached 225 °C, it was kept constant for 0.5 h. The maximum pressure during the reaction was 7 MPa. The autoclave was then cooled to 35 °C, and the exhaust gas was collected utilizing a wet gas flowmeter. Gas chromatography (GC) was used to analyze the remaining gases and liquids. The conversion of acetylene (X), selectivity (S), and yield (Y) of AA were determined according to the following equations:

$$X = \frac{n - n_1}{n} \times 100\%$$

$$S = \frac{n_3}{n - n_1} \times 100\%$$

$$Y = \frac{n_3}{n} \times 100\%$$

where n indicates the molar content of acetylene in the system; $n_1$ is the residual molar content of acetylene following the reaction; and $n_3$ denotes molar content of AA in the system after the reaction.

### AUTHOR INFORMATION

#### Corresponding Authors

**Bin Dai** — School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, China; Email: dbinly@126.com

**Jiabing Li** — School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, China; orcid.org/0000-0001-8632-8549

**Junming Zeng** — School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, China

**Jie Zhang** — School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, China

**Jun Yang** — School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, China

**Weixin Qian** — Engineering Research Center of Large Reactor Engineering, Ministry of Education, East China University of Science and Technology, Shanghai 200237, China; orcid.org/0000-0002-1049-9453

**Feng Yu** — School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, China; orcid.org/0000-0002-8140-8344

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04289

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by the International Science and Technology Cooperation Project of Shihezi University (no. GJHZ201804); the International Science and Technology Cooperation Project of Bingtuan (no. 2018BC002); the Science and Technology Innovation Talents Program of
Bingtuan (no. 2019CB025); and the Program of Science and Technology Innovation Team in Bingtuan (no. 2020CB006).

REFERENCES

(1) Yu, D.; Sum, Y. N.; Ean, A. C. C.; Chin, M. P.; Zhang, Y. Acetylide ion (C$_2$^-) as a synthon to link electrophiles and nucleophiles: a simple method for enamino synthesis. Angew. Chem. 2013, 125, S229–S232.

(2) Mataké, R.; Adachi, Y.; Matsubara, H. Synthesis of vinyl ethers of alcohols using calcium carbide under superbasic catalytic conditions (KOH/DMSO). Green Chem. 2016, 18, 2614–2618.

(3) Kaeowchawat, N.; Sukato, R.; Vicharongwongwiv; Vilaivain, T.; Sukwattanasintt, M.; Wacharasindhu, S. Direct synthesis of ary substituted pyrroles from calcium carbide: an underestimated chemical feedstock. Green Chem. 2015, 17, 460–465.

(4) Zhang, W.; Wu, H.; Liu, Z.; Zhong, P.; Zhang, L.; Huang, X.; Cheng, J. The use of calcium carbide in one-pot synthesis of symmetric diaryl ethenes. J. Chem. Commun. 2006, 46, 4826.

(5) Russell, D. H. Acetylene and carbon monoxide chemistry. J. Franklin Inst. 1950, 249, 166–167.

(6) Petrescu, L.; Fermeglia, M.; Cormos, C.-C. Life cycle analysis applied to acrylic acid production process with different fuels for steam generation. J. Cleaner Prod. 2016, 133, 294–303.

(7) Avalos, A. S.; Hakkarainen, M.; Odellius, K. Superiorly plasticized PVC/PBSA blends through crotonic and acrylic acid functionalization of PVC. Polymers 2017, 9, 84.

(8) Cabana, S.; Lecona-Vargas, C. S.; Meléndez-Ortiz, H. L.; Contreras-García, A.; Barbosa, S.; Taboada, P.; Magariños, B.; Bucio, E.; Concheiro, A.; Alvarez-Lorenzo, C. Silicone rubber films functionalized with poly(acrylic acid) nanobrushes for immobilization of gold nanoparticles and photothermal therapy. J. Drug Delivery Sci. Technol. 2017, 42, 245–254.

(9) Riccardi, C. M.; Rasi, R. M.; Kumar, C. V. Nanooaming of enzymes by intercalation into hydrotalcite. Adv. Synth. Catal. 2017, 359, 475–500.

(10) Quartinello, F.; Vainhandl, S.; Volmajer Val, J.; Farmer, T. J.; Voncina, B.; Lobnik, A.; Herrero Acero, E.; Pellis, A.; Guebitz, G. M. Synergistic enzymo-enzymatic synthesis of poly(ethylene terephthalate) from textile waste. Microb. Biotechnol. 2017, 10, 1376–1383.

(11) González-Centeno, M. R.; Chira, K.; Miramont, C.; Escudier, J.-L.; Samson, J.-M.; Ojeda, H.; Teissedre, P.-L. Disease ordering in layered double hydroxides revealed by multinuclear NMR spectroscopy. Science 2008, 321, 113–117.

(12) Weissermel, K.; Arpe, H. Industrial Organic Chemistry, 3rd ed.; Academic Press: New York, 1997; pp 92–272.

(13) Cui, L.; Yang, X.; Zhou, X.; Zeng, Y.; Wang, G. Advance in acetylene carbonylation to acrylic acid and acrylic esters. Ind. Catal. 2013, 21, 13–18.

(14) Zhang, P.; Huang, S.; Yang, Y.; Meng, Q.; Wang, S.; Ma, X. Effect of SSIE structure of Cu-exchanged β and Y on the selectivity for synthesis of diethyl carbonate by oxidative carbonylation of ethanol: A comparative investigation. Catal. Today 2010, 149, 202–206.

(15) Yu, Y.; Chen, C.; He, C.; Miao, J.; Chen, J. In situ growth synthesis of CuO@Cu2O-MOFs core-shell materials as novel low-temperature NH3-SCR catalysts. ChemCatChem 2019, 11, 979–984.

(16) Chen, Z.; Fan, C.; Pang, L.; Ming, S.; Guo, W.; Liu, P.; Chen, H.; Li, T. One-pot synthesis of high performance Cu-SAPO-18 catalyst for NO reduction by NH3-SCR. Influence of silicon content on the catalytic properties of Cu-SAPO-18. Chem. Eng. J. 2018, 348, 608–617.

(17) Xie, H.; Yi, D.; Shi, L.; Meng, X. High performance of CuY zeolite for catalyzing acetylene carbonylation and the effect of copper valence states on catalyst. Chem. Eng. J. 2017, 313, 663–670.

(18) Hudson, M. J.; Carlino, S.; Apperley, D. C. Thermal conversion of a layered (Mg/Al) double hydroxide to the oxide. J. Mater. Chem. 1995, 5, 323.

(19) Bascialla, G.; Regazzoni, A. E. Immobilization of anionic dyes by intercalation into hydrogel. Colloids Surf. A, 2008, 328, 34–39.

(20) Wang, J.; Huang, L.; Yang, R.; Zhang, Z.; Wu, J.; Gao, Y.; Wang, Q.; O’Hare, D.; Zhong, Z. Recent advances in solid sorbents for CO2 capture and new development trends. Energy Environ. Sci. 2014, 7, 3478–3518.

(21) Choi, S.; Drese, J. H.; Jones, C. W. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. ChemSusChem 2010, 2, 796–854.

(22) Li, W.; Fan, G.; Yang, L.; Li, F. Highly efficient vapor-phase hydrogenation of biomass-derived levulinic acid over structured nanowall-Like nickel-based catalyst. ChemCatChem 2016, 8, 2724–2733.

(23) Fan, G.; Li, F.; Evans, D. G.; Duan, X. Catalytic applications of layered double hydroxides: recent advances and perspectives. Chem. Soc. Rev. 2014, 43, 7040–7066.

(24) Li, F.; Duan, X. Applications of layered double hydroxides. J. Cheminf. 2006, 119, 193–223.

(25) Sideris, P. J.; Nielsen, U. G.; Gan, Z.; Grey, C. P. Mg/Al ordering in layered double hydroxides revealed by multinuclear NMR spectroscopy. Science 2008, 321, 113–117.

(26) Kannan, S.; Dubey, A.; Knözinger, H. Synthesis and characterization of CuMgAl ternary hydroxides as catalysts for the hydrogenation of phenol. J. Catal. 2005, 231, 381–392.

(27) Antonyraj, C. A.; Gandhi, M.; Kannan, S. Phenol hydrogenation over Cu-Containing LDHs and their calcined forms: profound cobalt metal influence. Ind. Eng. Chem. Res. 2010, 49, 6020–6026.

(28) Yang, R.; Gao, Y.; Wang, J.; Wang, Q. Layered double hydroxide (LDH) derived catalysts for simultaneous catalytic removal of soot and NOx. Dalton Trans. 2014, 43, 10317.

(29) Shen, L.-L.; Xia, K.; Lang, W.-Z.; Chu, L.-F.; Yan, X.; Guo, Y.-J. The effects of calcination temperature of support on Pt/Mg(Al)O catalysts for propane dehydrogenation reaction. Chem. Eng. J. 2017, 324, 336–346.

(30) Jeong, C.; Suh, Y.-W. Role of ZrO2 in Cu/ZnO/ZrO2 catalysts prepared from the precipitated Cu/Zn/Zr precursors. Catal. Today 2016, 265, 254–263.

(31) Palomino, R. M.; Ramírez, P. J.; Liu, Z.; Hamlyn, R.; Waluyo, L.; Mahapatra, M.; Orozco, I.; Hunt, A.; Simonovis, J. P.; Senanayake, S. D.; Rodrigues, J.A. Hydrogenation of CO on ZnO/Cu(100) and ZnO/Cu(111) catalysts: Role of copper structure and metal-oxide interface in methanol synthesis. J. Phys. Chem. B 2018, 122, 794–800.

(32) Nakamura, J.; Fujitani, T.; Kuld, S.; Helvég, S.; Cherkendorff, I.; Sehested, J. Comment on “Active sites for CO2 hydrogenation to methanol on Cu/ZnO catalysts”. Science 2017, 357, No. eaan8074.

(33) Melián-Cabrera, I.; López Granados, M.; Fierro, J. L. G. Reverse topotactic transformation of a Cu—Zn—Al catalyst during wet Pd impregnation: Relevance for the performance in methanol synthesis from CO2/H2 mixtures. J. Catal. 2002, 210, 273–284.

(34) Santos, J. L.; Revina, T. R.; Ivanova, S.; Centeno, M. A.; Odintzova, J. A. Gold promoted Cu/ZnO/Al2O3 catalysts prepared from hydrothermal precursors: Advanced materials for the WGS reaction. Appl. Catal., B 2017, 201, 310–317.

(35) Zheng, K.; Kang, J.; Rutkowski, B.; Gawda, M.; Zhang, J.; Wang, Y.; Fournier, N.; Sitarz, M.; Taccardi, A.; Magarin, E.; Bordiga, S.; Lamberti, C. X-ray photoelectron spectroscopy and x-ray absorption near edge structure study of copper sites hosted at the ZnO/Cu(111) interface in methanol synthesis. J. Phys. Chem. B 2005, 109, 4605–4611.

(36) Zheng, Y.; Chen, N.; Wang, C.; Zhang, X.; Liu, Z. Oleylamine-mediated hydrothermal growth of millimeter-long Cu nanowires and their electrocatalytic activity for reduction of nitrate. Nanomaterials 2018, 8, 192.
energetic data on the CO and NH$_3$ adsorption. J. Chem. Phys. 2000, 113, 9248–9261.

(39) Chen, L.; Guo, P.; Qiao, M.; Yan, S.; Li, H.; Shen, W.; Xu, H.; Fan, K. Cu/SiO$_2$ catalysts prepared by the ammonia-evaporation method: Texture, structure, and catalytic performance in hydrogenation of dimethyl oxalate to ethylene glycol. J. Catal. 2008, 257, 172–180.

(40) Cao, Z.; Zhang, X.; Xu, C.; Huang, X.; Wu, Z.; Peng, C.; Duan, A. Selective hydrocracking of light cycle oil into high-octane gasoline over bi-functional catalysts. J. Energy Chem. 2021, 52, 41–50.

(41) Li, X.; Wang, C.; Liu, S.; Xin, W.; Wang, Y.; Xie, S.; Xu, L. Influences of alkaline treatment on the structure and catalytic performances of ZSM-5/ZSM-11 zeolites with alumina as binder. J. Mol. Catal. A: Chem. 2011, 336, 34–41.

(42) Geng, Y.; Liang, W.; Liu, J.; Cao, M.; Kang, Z. Evolution of pore and fracture structure of oil shale under high temperature and high pressure. Energy Fuels 2017, 31, 10404–10413.

(43) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865–3868.

(44) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758–1775.

(45) Chadi, D. J. Special points for brillouin-zone integrations. Phys. Rev. B: Solid State 1977, 16, 1746–1747.

(46) Angelis, F. D.; Sgamellotti, A.; Re, N. Density Functional Study of the Reppe Carbonylation of Acetylene. Organometallics 2000, 19, 4104–4116.