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Article

Enhanced stability of highly-dispersed copper catalyst supported by hierarchically porous carbon for long term selective hydrogenation

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ABSTRACT

Copper based catalysts have high potential for the substituent of noble-metal based catalysts as their high selectivity and moderate activity for selective hydrogenation reaction; however, achieving further high catalytic stability is very difficult. In this work, the carbonization process of Cu-based organic frameworks was explored for the synthesis of highly-dispersed Cu supported by hierarchically porous carbon with high catalytic performance for selective hydrogenation of 1,3-butadiene. The porous hierarchy of carbon support and the dispersion of copper nanoparticles can be precisely tuned by controlling the carbonization process. The resultant catalyst carbonized at 600 °C exhibits a rather low reaction temperature at 75 °C for 100% butadiene conversion with 100% selectivity to butenes, due to its reasonable porous hierarchy and highly-dispersed copper sites. More importantly, unprecedentedly stability of the corresponding Cu catalyst was firstly observed for selective 1,3-butadiene hydrogenation, with both 100% butadiene conversion and 100% butenes selectivity over 120 h of reaction at 75 °C. This study verifies that a simply control the carbonization process of metal organic frameworks can be an effective way to obtain Cu-based catalysts with superior catalytic performance for selective hydrogenation reaction.

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1. Introduction

Unsaturated hydrocarbons, especially alkenes, have been

wildly used as raw materials in current industry for the synthesis of rubber, plastics and organic chemical materials by polymerization reaction [1]. However, various impurities are

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usually contained in the unsaturated hydrocarbons, which are mainly produced by crude oil cracking, such as acetylene impurities (1000–10000 ppm) in ethylene stream [2], butyne and butadiene (3000–8000 ppm) in butenes stream [3]. As well known, the impurities of alkynes and alkadienes can easily poison the initiators employed for the polymerization of alkenes [4]. For instance, the 2-butyne impurity in butenes feed can easily react with the Cp^*ScCH_3 [$\text{Cp}^*=(\eta^5\text{-C}_5\text{Me}_5)$] initiator, forming $\text{Cp}^*\text{Sc}(\text{CH}_3)\text{CH}=\text{CH}(\text{CH}_3)_2$, which results in a termination of the butene polymerization reaction at concentration as low as 10 ppm [5]. Thus, these impurities have to be eliminated, usually, by selective hydrogenation that can transform the impurities into the corresponding alkenes raw materials, resulting in a high carbon utilization. Since the reaction barrier value of alkenes hydrogenated to alkanes is relatively low [6], and alkenes are easily further hydrogenated to alkanes, thus high selectivity to semi-hydrogenation is one of the most important factors for an ideal catalyst [7,8]. Currently, noble metals (e.g., Pd, Pt, Au, etc.) are widely used as heterogeneous catalysts due to their high catalytic performance for hydrogenation reactions [9,10]. However, noble metallic catalysts normally have low selectivity to alkenes (70%–85%) during the catalytic selective hydrogenation reaction because of their strong hydrogen activation [10–12]. In order to increase the selectivity to alkenes, nowadays, one of the most widely used method is to modify the surficial property (i.e., electro density, the distribution of noble metal atom and so on) by introducing a second non-noble metal assistant, and forming noble/non-noble bimetallic catalysts, such as Pd-Ni[9], Pd-Cu [13–15], Pd-Co [16,17], Pd-Zn [18,19], Pt-Cu [20–23] and so on. Specifically, the Pt-Cu alloys supported on Al_2O_3 synthesized by Lucci et al. [21] have shown 99% butenes selectivity at full conversion temperature ($T_{100\%}$) in selective hydrogenation of butadiene reaction. However, the scarcity and the high cost (above 10,000 dollars per kilogram) of noble metals limit their long-term development in the field of catalysis[7]. Non-noble metals are nearly 3,000 times cheaper than noble metals, and they also have been predicted by the theoretical calculation of Norskov's group [24] that they show high potential for the substituent of noble-metal based catalysts in the reaction of selective hydrogenation [25], due to their inferior adsorption of alkynes and alkadienes.

Supported Cu catalysts show rather high potential for this type of reaction, due to their high selectivity to alkenes and moderate reaction condition. Thus, plenty of works have been focused on the exploration of Cu-based catalysts, including the synthesis method, the modification of catalytic performance and so on [24]. As for synthetic strategies, the widely used methods are ion exchange [26], wet impregnation [27], and deposition precipitation [7,8,10] and so on, which are mainly belonged to aqueous precursor solutions methods. For example, Wang have prepared Cu/ TiO_2 catalysts by deposition-precipitation with urea (DPu), and found that DPu time has a great effect on the structure of TiO_2 supported Cu species, e.g., $\text{Cu}_2(\text{OH})_3\text{NO}_3$ and CuO for DPu of 3 and 20 h, and results in a $T_{100\%}$ at 75 and 90 °C, respectively, under a constant Cu loading. However, even though supported Cu has high selectivity

with moderate $T_{100\%}$ temperature, but researchers [8] have found that it deactivates very fast due to a rapid formation of green oil layer on the surface of Cu surface, e.g., within the first 20 min of reaction for selective ethylene hydrogenation. There is a general agreement about the mechanism of deactivation, that is, the half-hydrogenated intermediate formed by selective hydrogenation can react further with hydrogen to isomerise to form a free radical which can react with more adsorbed butadiene to produce green oil [28]. According to previous studies on metallic catalysts for selective hydrogenation [5,10,21], elevating the transfer efficiency of alkenes by design of porous support could be an attractive path to promote Cu catalysts stability in selective hydrogenation.

The construction of hierarchically interconnected pores on supports conduce to enhancing catalytic performance by means of the transfer and exchange of substances with extremely high efficiency and minimum energy consumption [29,30]. In recent years, sorts of synthesis methods have been explored for the preparation of hierarchically porous materials [31]. As a substance with well-developed porosity and high-density metal content, metal organic frameworks (MOFs) exhibit a potential for using as an ideal matrix to prepare hierarchically porous carbon supported metallic catalysts [32–34]. Hierarchically porous carbon can be self-formed by the aggregation of metal NPs in the process of carbonization of MOFs, which is conducive to mass transfer efficiency [35,36]. Besides that, it has been proved that if metal ions have the reduction potential of -0.27 V or higher, the corresponding MOFs after pyrolysis always form metal nanoparticles (NPs) in a protective atmosphere, whereas metal ions with a reduction potential lower than -0.27 V form metal oxide NPs [35]. The reduction potentials of Cu^{2+} is found to be $+0.34$ V, indicating that copper ions are able to be reduced to copper under the same pyrolysis condition. Since Xu and co-workers [32] described porous carbon materials derived from MOF-5 in 2008, the utilization of MOFs as precursor for metal/metal oxide NPs inside porous carbon frameworks (M/MO@C) have attracted a great deal of research interest. Recently, Li et al. [37] have successfully prepared the pyrolysed ZIF-8 supported Cu catalyst, which was employed as the cathode catalyst for oxygen reduction reaction. Due to their high surface area and large pore volume, hierarchically porous carbon supported non-noble metallic catalysts derived from MOFs have been widely explored in electrochemical catalysis [37–39], but rarely reported in selective hydrogenation catalysis. Since Pd/Cz-MOF-253 prepared by Huang et al. [40] was first applied as solid-based catalysts for a one-pot stepwise tandem reaction of Knoevenagel condensation and subsequent hydrogenation in 2017, much attention now has gradually paid on the application of MOFs-derived catalysts in heterogeneous catalysis. The recent study has also report [41] that highly dispersed and accessible Cu/ Cu_2O heterojunctions inside porous organic matrices through pyrolysis of copper-based MOFs (i.e., ZJU-199), demonstrating excellent catalytic properties in liquid-phase hydrogenation of furfural into furfuryl alcohol.

Considering the fact that copper has high selectivity and relative high activity, however the low catalytic stability is the

critical problem to the application of selective hydrogenation reaction. Herein, copper-based MOF (i.e., HKUST-1) was selected as the matrix for preparation of monometallic Cu supported on hierarchically porous carbon by one-step in-situ carbonization. The state of Cu (i.e., particle size, valence state) and the structure of hierarchically porous carbon were explored as a function of carbonization temperature. Besides that, the catalytic activity, selectivity to alkenes and stability of the carbonized HKUST-1 were explored for selective butadiene hydrogenation reaction. After that, the relationship between the particle size of Cu and the property of supported carbon species and the catalytic performance was mainly discussed. This work could provide a promising method for the synthesis of copper-based catalysts with high catalytic performance.

2. Experimental

2.1. Materials and chemicals

All reagents and solvents of analytical grade were used as received without further purification. Copper (II) nitrate trihydrate (99%), anhydrous ethanol (99.5%) were purchased from Sinopharm Chemistry Reagent Co., Ltd. (Beijing, China). Benzene-1,3,5-tricarboxylic acid (98%) were obtained from Aladdin Industrial Corporation (Shanghai, China).

2.2. Synthesis of HKUST-1 matrix

The hydrothermal synthesis mixture for HKUST-1 was scaled up as described in the literature [42]. In detail, copper ionic solution was prepared by dissolving 3.48 g (14.4 mmol) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 48 ml of deionized water in a beaker. Then, 1.68 g (8.0 mmol) of H_3BTC was weighted and dissolved in 48 ml of anhydrous ethanol. After that, the copper nitrate solution was slowly added to H_3BTC solution, followed by continuous magnetic stirring for 20 min at room temperature. Subsequently, the blue turbid liquid was transferred into a teflon-lined autoclave and kept at 120 °C for several hours. After that, precipitation were collected by filtration and washed thoroughly with 250 ml mixture of ethanol and deionized water (% V/V of water = 50%) [43]. The blue product was dried at 120 °C overnight and stored in sealed vials for further experiments.

2.3. Preparation of D-HKUST-1-X

The HKUST-1 matrix was added into different porcelain boats. Various carbonization temperature (i.e., 350, 400, 450, 500, 600, 700, 800, 900 °C) was selected for obtaining hierarchically porous carbon supported copper catalyst. Detailly, the HKUST-1 matrix was carbonized from room temperature (RT) to the corresponding temperature under an argon flow with a heating rate of 2 °C · min⁻¹ and then kept at certain temperature for 4 h in a tubular furnace. Here, the derivatives of HKUST-1 catalysts were marked as D-HKUST-1-X (X = carbonization temperature).

2.4. Catalytic test

Selective 1,3-butadiene hydrogenation reaction on D-HKUST-1-X catalysts was carried out in a plug-flow reactor. 100 mg of catalyst was loaded in quartz tube with the internal diameter of 8 mm. Prior to the catalytic test, catalysts were in situ activated under hydrogen (50 ml · min⁻¹) from room temperature (RT) to 350 °C with a heating rate of 2 °C · min⁻¹ and then kept at 350 °C for 2 h. After cooling down to room temperature under hydrogen, a gas mixture, containing 0.3% 1, 3-butadiene, 30% propene, 20% hydrogen and balance helium, was introduced into the reactor with a total flow rate of 100 ml · min⁻¹. To simulate the real condition in industry (i.e., butadiene in an excess of butenes), small amount of butadiene (0.3%) in an excess of propene (30%) was employed as initial reactant in this laboratorial study [10]. The activities of D-HKUST-1-X catalysts were evaluated from 30 °C to the temperature at which 1,3-butadiene conversion reaches 100%, with a heating rate of 1 °C · min⁻¹. After catalytic reaction, the products were analyzed in situ by introducing the outlet gas to a gas chromatograph (GC2030Smart, FID detector) every 15 min, every 15 °C. Through the preliminary experiments [10], it has been proved that the internal and external diffusion restrictions could be ignored under this catalytic conditions and at low conversion. Moreover, the catalytic stability of D-HKUST-1-X was also analyzed at the temperature, which firstly showed a 100% butadiene conversion, for 20 h. In addition, a much longer stability time (i.e., 120 h) was also selected for verify the high stability of the D-HKUST-1-X. A short view of our strategy is depicted in Scheme 1.

Scheme 1. Illustration of the synthesis of D-HKUST-1-X catalysts for butadiene hydrogenation reaction.

2.5. Characterizations

Scanning electron microscopy (SEM) images were obtained by a JSM 7800F instrument operated at 5 kV. Transmission electron microscopy (TEM) images were acquired on a JEOL 2100 microscope (Japan) operating at an acceleration voltage of 200 kV. X-ray powder diffraction (XRD) patterns were generated by scanning 2θ with 0.05° step size and 0.5 s per step on a Rigaku D/Max2550 V diffractometer ($\text{Cu } K\alpha$ radiation, 40 kV, 40 mA). Thermogravimetric analysis (TGA) was carried out on a TGA-50 thermogravimetric analyzer. Fourier transform infrared (FTIR) measurement was operated at a Varian Excalibur Series 3100 spectrophotometer with the dried KB disk technique. The loading of copper in the D-HKUST-1-X were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP). The N_2 adsorption-desorption isotherm was measured on Micromeritics Tristar II 3020 system at -196°C . The samples were degassed at 120°C for 8 h in quartz tubes before the experiment. The surface area and pore size distribution (PSD) were depended on the Brunauer Emmett-Teller (BET) method and derived from the desorption branch of the isotherm based on the Barrett Joyner-Halenda (BJH) model. The Raman spectra were conducted on RENISHAW Raman microscope.

3. Results and discussion

3.1. Characterization of HKUST-1 matrix

The time of hydrothermal treatment for the synthesis of HKUST-1 was explored and optimized in this work as the experimental condition varies from different laboratories. Here, it was found that the particle size of HKUST-1 grew from 10 to $20\ \mu\text{m}$ (Fig. S1) with hydrothermal treatment time increasing. Besides that, a volcano distribution can be observed in the aspect of crystallinity (Fig. S2) and porous volume (Table. S1) for the sample synthesized at different times, moreover, with a well-defined octahedral crystal obtained in the condition of hydrothermal treatment at 120°C for 18 h. Thus, here this

Fig. 1. (a) SEM image of HKUST-1 matrix; (b) N_2 adsorption-desorption isotherm curve of HKUST-1 matrix with the inset showing the distribution of the pore sizes; (c) EDX mapping of copper and oxygen; (d) XRD patterns of HKUST-1 matrix.

synthesized condition was selected for the further exploration of the HKUST-1 derived carbon supported Cu catalyst. Furthermore, the specific property of the sample synthesized at 120°C for 18 h is summarized in Fig. 1. In detailed, The HKUST-1 matrix synthesized at 120°C for 18 h has a crystallite size about $15\ \mu\text{m}$ (Fig. 1(a)), high surface area (A_{BET}) of $1599\ \text{m}^2\cdot\text{g}^{-1}$, large total pore volume (V_{p}) of $0.91\ \text{cm}^3\cdot\text{g}^{-1}$ (Figs. 1(b), and S3, Table S1) and good crystallinity (Fig. 1(d)). Moreover, as shown in the energy-dispersive X-ray spectroscopy (EDX) mapping (Fig. 1(c)) that Cu ions have uniformly dispersion in the octahedral matrix, indicating the high potential of HKUST-1 matrix for the preparation of Cu-based catalyst. By the way, a few amounts of Cu_2O was also detected by XRD in the as-prepared HKUST-1, similar phase was also observed in previous study [44].

3.2. Characterization of D-HKUST-1-X

The selection of carbonization temperature was based on the weight loss of as-prepared HKUST-1 during thermogravimetric analyzer analysis, thus $350, 400, 450, 500, 600, 700, 800, 900^\circ\text{C}$ were used in this study (Fig. S4). After carbonization, the color of HKUST-1 matrix changed from blue to black as a result from the decomposition of the organic linkers in HKUST-1 (Fig. S5). According to the scanning electron microscope (Fig. 2), it can be found that the original octahedron

Fig. 2. SEM images of D-HKUST-1-X with the inset showing their high-resolution SEM images and size distributions of metal particles.

Fig. 3. (a) TEM images of the D-HKUST-1-450; Low- (b) and high-magnified (c) TEM images of the Cu nanoparticle in D-HKUST-1-450.

structure of HKUST-1 was maintained very well after carbonization, no matter the carbonization temperature is. And plenty of metallic Cu particles (i.e., bright dots) could be clearly observed in the insert graphs in Fig. 2 with an increased magnification. The distribution of Cu particle size was summarized by counting more than 200 isolated particles and presented in Fig. 2. It shows that the average Cu particle size increases gradually from 38 to 45, 50, 51, 52, 63, 87, 290 nm with the carbonization temperature increasing from 350 to 400, 450, 500, 600, 700, 800, 900 °C, respectively. Besides that, it also shows that most of Cu nanoparticles (NPs) were well encapsulated in carbon substrates at low carbonization temperature, and they were gradually exposed on the surface of carbon at high carbonization temperature. Meanwhile, the porous hierarchy structure gradually appeared in the carbonized HKUST-1 with an increase of carbonization temperature (inset Fig. 2),

Even though SEM results indicates that the average particle sizes of supported Cu are large in the carbonized HKUST-1 samples, e.g., ~50 nm in the sample carbonized at 450 °C, but the question about whether small Cu NPs also existed in the carbon matrix has also to be answered. Thus, HKUST-1 carbonized at 450 °C (D-HKUST-1-450) was selected for further transmission electron microscopy characterization (Fig. 3). As seen from Fig. 3, most particles with size around 50 nm are characterized and they seem agree with the average size summarized from SEM (Fig. 2(c)). However, plenty of small particles, with size smaller than 20 nm, were also imaged and embedded in the carbon layer. As shown in the high-resolution TEM images (Fig. 3(b), (c)), the lattice distance is determined to

be 2.1, 1.8 1.3 Å, which are corresponding to the Cu(111), Cu(200) and Cu(220), respectively. It indicates that most of Cu²⁺ in the structure of HKUST-1 have been successfully reduced to Cu. As a result, it allows to conclude that the particle size of Cu obtained by carbonization of HKUST-1 is not uniform, with large particle (~50 nm) and small ones (< 20 nm), simultaneously. Besides that, based on TEM, carbon support was found to contain a type of hierarchically meso-macroporous structures. This type of hierarchically porous structure might be generated by the agglomeration of Cu NPs during carbonization of HKUST-1, and it was also observed in previous study related to the hierarchically flower-like N-doped porous carbon materials [45].

Besides that, after carbonization at varies temperatures, the porous hierarchy and the Cu loading in HKUST-1 derived carbon supported Cu samples were further analyzed by N₂ adsorption-desorption and inductively coupled plasma optical emission spectrometry, respectively. In Fig. 4, the isotherm curves exhibit a clear hysteresis loop in the relative pressure range 0.5 ≤ P/P₀ ≤ 1.0, and it indicates that the presence of extensive mesoporous structures in all D-HKUST-1-X samples. It has to be mentioned that, as for the sample carbonized at temperature lower than 500 °C, the isotherm curves of adsorption and desorption cannot form a closed loop, which forces the N₂ adsorption/desorption test stop and no data can be obtained. The unclosed loop N₂ adsorption/desorption curve is usually caused by the exist of non-rigid porous structures or to the irreversible adsorption of molecules in open pores of approximately the same size as the molecule [46]. Here, it may suggest that there are any undecomposed organic parts in the structure of these samples, and further evidence related to the C=C, C=O, C-H band were detected by fourier transform infrared (FTIR) analysis (Fig. S6). Moreover, the detailed information is summarized in Table 1, including specific surface area (*A*_{BET}), total pore volume (*V*_p), pore diameter (*D*_p) and Cu loading (*ω*_{Cu}). As it is shown in Table 1, *A*_{BET} and *V*_p exhibit a volcano variation with the increase of carbonization temperature. Compared with other samples, the one carbonized at 600 °C (i.e., D-HKUST-1-600) exhibited a well-structured porous hierarchy, with high BET surface area of 241 m²·g⁻¹, large pore volume of

Fig. 4. N₂ adsorption-desorption isotherm curves (a) of D-HKUST-1-X, with the corresponding pore sizes distribution (b).

Table 1

Textural parameters of the D-HKUST-1-X.

Sample	A_{BET}^a ($\text{m}^2\cdot\text{g}^{-1}$)	V_p^b ($\text{cm}^3\cdot\text{g}^{-1}$)	D_p^c (nm)	ω_{Cu}^d (wt%)
D-HKUST-1-450	106	0.17	1.7, 3.8, 15.0	49.77
D-HKUST-1-500	180	0.19	1.7, 3.8, 11.8	49.95
D-HKUST-1-600	241	0.23	3.8, 11.2, 31.5	51.72
D-HKUST-1-700	194	0.20	3.8, 10.0	52.37
D-HKUST-1-800	180	0.18	3.8	48.65
D-HKUST-1-900	143	0.15	3.8	48.40

^a BET specific surface area. ^b Total pore volume. ^c Pore size calculated from BET. ^d Cu loading of samples.

0.23 $\text{cm}^3\cdot\text{g}^{-1}$ and hierarchically pores of 3.8, 11.2, 31.5 nm in size. Moreover, slight difference in Cu loadings can be obtained in the samples carbonized at different temperatures (Table 1), but they were mainly stay in the range of 50 ± 2 wt%. As for the samples pyrolyzed at low temperature, this type of difference mainly due to the undecomposed frameworks, i.e., D-HKUST-1-450 (49.77 wt%). As for the high-temperature carbonization samples, the decrease of Cu loading might be caused by the undissolved Cu particle during ICP test.

The evolution of the structure of copper species after carbonization in Ar, activation in H_2 and oxidation in air was recorded by XRD (Fig. 5). Two main species related to copper, i.e., metallic Cu and Cu_2O , can be detected in carbonized samples (Fig. 5(a)), no matter the reduction temperature is. Considering the fact that Cu_2O phase was existed in the as-prepared HKUST-1 as it was exhibited in Fig. 2(d), thus it is difficult to tell the formation of Cu_2O , but the phase of metallic Cu verifies the fact that part of Cu ions was successfully reduced. It agrees with theoretical prediction that Cu^{2+} species were supposed to be reduced to metallic Cu as the reduction potential of Cu^{2+} is 0.34 V, which is much higher than -0.27 (the reduction potential of MOF pyrolysis) [35]. As for the phase of Cu_2O formation, an additional experiment was designed by exposing carbonized HKUST-1 (e.g., D-HKUST-1-600) to air for different time, with XRD results are included in Fig. 5(b). It is found that only metallic Cu was formed after carbonized at 600 °C, and it gradually transformed to Cu_2O after exposing to air from 0.5 to 1.5 h.

Fig. 6. High-resolution XPS spectra for Cu 2p of the D-HKUST-1-X.

Since CuO is more thermodynamically stable than Cu_2O under air, thus the observation of Cu_2O , instead of CuO , formation might mean the strong interaction existed between Cu and C support in the carbonized samples. This result also indicates that the Cu_2O phase in Fig. 5(a) were mainly from the oxidation of metallic Cu as the XRD characterization was not in situ but performed under air after HKUST-1 carbonization. As a result, the formation of Cu_2O can be observed due to the strong metal support interaction (SMSI). Anyway, the oxidized copper can be transformed to metallic copper after activation at 350 °C for 2 h under H_2 .

The chemical state of copper in the carbonized samples was evaluated by XPS technique (Fig. 6). All samples displayed similar Cu 2p XPS spectra, where the two main peaks appear in the region around 933 and 953 eV, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ peaks of Cu^0/Cu^+ species, respectively. With the increase of carbonization temperature, metallic Cu became the main phase on the surface of Cu particles with a small amount of Cu^{2+} , which shows a weak peak around 934 eV. Moreover, existence of Cu^{2+} species was also further confirmed by the shake-up satellite peaks near 945 eV [47]. It was found that the content of copper oxides (i.e., Cu_2O and CuO) gradually increase, due to the oxidation of Cu particles. It highly agrees with the results obtained by XRD. Since the test was not performed in-situ after carbonization, thus, except Cu and C, the presence

Fig. 5. XRD patterns of D-HKUST-1-X (a) and a reduced D-HKUST-1-600 after exposing to air for different times (b).

of O can also be observed in the full spectra of D-HKUST-1-X (Fig. S7).

3.3. Catalytic performance of D-HKUST-1-X

Here, a temperature programmed reaction was employed for the evaluation of the catalytic activity, selectivity to butenes and summarized in Fig. 7(a), (b). In addition, isothermal reaction was further performed on the samples for the study of catalytic stability, with results presented in Fig. 7(c).

According to Fig. 7(a), the carbonization temperature has a great effect on the catalytic activity of carbon supported copper. Specifically, after carbonization at 350 °C, the catalyst has very low catalytic activity, with only ~75% butadiene conversion at temperature as high as 120 °C. This might be due to the formed Cu nanoparticles are mainly in the formed hierarchi-

Fig. 7. Catalytic performance of D-HKUST-1-X. (a) Butadiene conversion as a function of temperature; (b) Selectivity to butenes as a function of butadiene conversion; (c) Evolution of the butadiene conversion with time on stream at $T_{100\%}$ for D-HKUST-1-X ($X = 450, 500, 600$).

cally porous carbon support (Fig. 2(a)), and it resulted in a very low exposed Cu surface for catalytic reaction. Moreover, the undecomposed organic fragments on the surface of HKUST-1 may also cause that the reactants can only access to the surface of catalyst. With the increase of carbonization temperature to 450 and 600 °C, the catalytic activity increases sharply, with the full butadiene conversion ($T_{100\%}$) decreases 90 to 75 °C, respectively. Considering the fact that the supported Cu has similar average particle size (~50 nm) in the sample carbonized at 450 and 600 °C (Fig. 2), however, the intensity of C=C, C–O, C–H peaks related to the uncarbonized organic fragments in FTIR (Fig. S6) has a great decrease when carbonization temperature increases from 350 to 600 °C, it means that this type of increase in catalytic activity mainly due to the accelerated carbonization at high temperature remove the organic fragments and increase the exposure of catalytic active site. However, the catalytic activity decreases gradually with carbonization temperature keeps increase, with $T_{100\%}$ decreases to ~120 °C when HKUST-1 carbonized at 900 °C. Since the organic framework was fully carbonized, verified by FTIR (Fig. S6), the decreases of catalytic activity supposed to be mainly due to the Cu particle sized increase, i.e., ~52 and ~290 nm for the sample carbonized at 600 and 900 °C, respectively. Comparing with previous study, which show $T_{100\%}$ at 165 °C for Au-based/ Al_2O_3 [10], $T_{100\%}$ at 80 °C for the catalyst carbonized from Co-BTC [48], the copper-based catalysts synthesized through the carbonization of HKUST-1 show high catalytic activity.

As for the catalytic selectivity, it can be expressed as either selectivity to butenes or alkanes (butane + propane) formation as a mixture of butadiene and propene was employed for catalytic reaction, and the formed butene and propene may be further hydrogenated to butane and propane, respectively. Thus, here, the relationship between selectivity to butenes and butadiene conversion was selected and drawn for the evaluation of catalytic selectivity in Fig. 7(b). It can be seen that all samples have very high selectivity to butenes (> 98%). Specifically, for the samples, which were carbonized at temperature lower than 700 °C, 100% selectivity to butenes can be observed at even full butadiene conversion. Reviewing the research of previous study [49], the supported noble bimetallic catalysts, such as Au-Pd catalysts prepared through deposition of colloids stabilized by tetrakis phosphonium chloride (THPC) on Al_2O_3 support, just shows 95.7% selectivity to butenes with the full butadiene conversion ($T_{100\%}$) of 75 °C. In this work, the selectivity to butene shows slight decrease to 99.5%, 98.3% and 98.9% for the sample carbonized at 700, 800 and 900 °C, respectively. Here, D-HKUST-1-900 (as shown in Fig. S8, i.e., Raman spectra, its relative I_G/I_D ratio as high as 0.97) with good selectivity can be attributed to highly graphitized carbon species, which can conduce to the potentiation of electron mobility and stabilization of the reactive intermediates in catalysis process [50].

Based on the catalytic activity and selectivity to butenes (Fig. 7(a), (b)), three samples, which are carbonized at 450, 500 and 600 °C, respectively, are selected for the further comparison of catalytic stability as these samples show very high performance in both high catalytic activity ($T_{100\%}$ 75–90 °C) and selectivity to butenes (100% butadiene conversion at $T_{100\%}$).

Fig. 8. Evolution of the butadiene conversion with time on stream at 75 °C for D-HKUST-1-600 for 120 h.

The catalytic stability tests of these samples were carried out under a constant temperature, at which the conversion rate of 1,3-butadiene to butenes just reached 100%, obtained from catalytic activity test (Fig. 7(c)), i.e., 90, 90, 75 °C for the sample carbonized at 450, 500 and 600 °C, respectively, resulting in a similar initial butadiene conversion (100%). In Fig. 7(c), the stability of the catalysts increases with the increase of carbonization temperature. For example, at the lowest carbonization temperature (i.e., 450 °C), the initial butadiene conversion (100%) decreases gradually to ~90% after 20 h of catalytic reaction. While, as for the sample carbonized at 500 °C, only ~3% butadiene conversion decrease can be observed. Moreover, with the carbonization temperature increase to 600 °C, the butadiene conversion kept as 100% conversion after 20 h of reaction. Comprised with previous study focused on the catalytic stability of supported copper, for instance, $\text{Pt}_{0.1}\text{Cu}_{14}/\text{Al}_2\text{O}_3$ catalyst at the single-atom limit prepared by Lucci et al. [21] exhibits 98% selectivity to butenes and ~5% decrease of butadiene conversion from the original 100% after 20 h of reaction. Another Cu-based catalyst produced by Wang et al. [8], i.e., 0.88 wt% Cu/ TiO_2 catalyst shows rather low catalytic stability, with butadiene conversion decreased rather rapid from ~100% directly to ~10% in the first 2 h reaction, the carbon supported Cu catalysts synthesized by HKUST-1 carbonization show rather high stability.

To verify the high catalytic stability of the catalysts obtained by HKUST-1 carbonization, the sample carbonized at 600 °C was further tested at 75 °C (butadiene conversion just reached 100%) as long as 120 h (Fig. 8), and it was supersized to found that the catalyst was very stable, with no observation of the decrease of butadiene conversion. It also shows that the sample carbonized at 600 °C has great potential for industrial application due to its high stability, high selectivity to butenes (100% at $T_{100\%}$) and a moderate catalytic activity ($T_{100\%}$ ~75 °C). Besides, as shown in Fig. S9, SEM images of D-HKUST-1-600 after 120 h of reaction are almost identical to those of the as-prepared catalyst. Meanwhile, Cu NPs are still uniformly embedded in the carbon species with retention of their original size.

4. Conclusions

In this work, hierarchically porous carbon supported high-density and high-dispersion metallic Cu nanoparticles catalysts were obtained by the carbonization of HKUST-1

(Cu-MOF). After catalytic performance evaluation on samples carbonized at different temperatures, it was found that the catalytic performance is obviously influenced by the particle size of Cu and the porous properties, which could be suitably tuned by carbonization temperature. Particularly, the derivative of HKUST-1 carbonized at 600 °C (i.e., D-HKUST-1-600) with moderate metal size (~51.9 nm), large porous volume ($0.23 \text{ cm}^3\cdot\text{g}^{-1}$) and reasonable hierarchically porous properties, exhibits 100% butadiene conversion and 100% butenes selectivity at 75 °C. In addition, this type of hierarchically porous carbon supported highly-dispersed Cu catalyst still exhibits a rather high catalytic stability, with 100% butadiene conversion and 100% selectivity to butenes, after the testing time as long as 120 h. This study attests the fact that the potential application of hierarchically porous carbon supported non-noble metals catalysts derived from the carbonization of MOFs, especially in selective hydrogenation of unsaturated hydrocarbons reaction.

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Graphical Abstract

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Enhanced stability of highly-dispersed copper catalyst supported by hierarchically porous carbon for long term selective hydrogenationNian Hu, Xiao-Yun Li, Si-Ming Liu, Zhao Wang *, Xiao-Ke He, Yue-Xin Hou, Yu-Xiang Wang, Zhao Deng, Li-Hua Chen *, Bao-Lian Su *
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Enhanced stability of highly-dispersed copper catalyst supported by hierarchically porous carbon can be obtained by simply MOF carbonization for selective butadiene hydrogenation.

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超高稳定性的等级孔碳负载高分散铜基选择性加氢催化剂

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摘要: 负载型Pd, Pt, Au等贵金属催化剂由于具有较高活性而被广泛应用于选择性加氢催化领域, 但资源稀缺、价格昂贵等问题严重制约了其在催化领域的长远发展。目前大量研究表明, 非贵金属催化剂也具有较高的选择性催化加氢能力, 在已被报道的非贵金属加氢催化剂中, 铜基催化剂由于在选择性加氢反应中表现出较高加氢选择性和活性引起了人们的广泛关注。然而, 早期研究的负载型铜基催化剂普遍存在催化稳定性较低的问题, 所以提高铜基催化剂的使用寿命成为了问题关键。本文以铜基有机金属框架HKUST-1作为合成目标催化剂的前驱体, 首先探究了水热合成条件对HKUST-1合成结构完整性及结晶度的影响, 再通过精确调控HKUST-1的原位碳化过程, 利用金属有机框架高温分解自还原行为, 成功制备出了等级孔碳负载的高分散铜基催化剂, 并将所制备的催化剂应用于1,3-丁二烯选择性加氢反应中。扫描电子显微镜、高分辨透射电子显微镜、X射线衍射、氮气吸脱附、傅里叶红外吸收光谱、X射线光电子能谱等技术用来表征了碳化前后催化剂载体结构的变化, 铜粒子尺寸、价态及其在载体中分布的变化。文中也深入探究了以上因素对催化剂选择性催化加氢性能的影响。研究表明: 120 °C水热合成18 h能获得尺寸在15 μm左右, 结晶度高且形貌规整的HKUST-1前驱体。随后通过合理地控制金属有机框架分解过程, 可实现对碳载体的等级孔结构和活性铜纳米粒子的分散程度的精确调控, 获得高效等级孔载体结构和高分散铜位点的催化剂。不仅如此, 通过一步碳化自还原HKUST-1制备的等级孔碳负载Cu的催化性能表现出对碳化温度高度的关联性。其催化活性随碳化处理温度的升高呈现先增强后减弱的趋势, 但所有获得的催化剂对单烯烃都具有很高的选择性(>98%)。特别地, 本文发现在600 °C碳化合成的催化剂在低温75 °C反应可实现对1,3-丁二烯的100%转化, 对丁烯的选择性为100%。同时, 该催化剂在恒温75 °C下持续反应120 h以上, 其对丁二烯转化率和对丁烯选择性依然保持100%, 表现出了超高的催化稳定性和潜在的商用价值。本文展示了通过简单地调控金属有机骨架的碳化过程是获得具有优异选择性催化加氢性能的铜基催化剂的有效途径。

关键词: 等级孔结构; 催化剂; 碳载铜; 选择性加氢; 金属有机骨架

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