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Fabrication of Supported Cuprous Sites at Low Temperatures: An Efficient, Controllable Strategy Using Vapor-Induced Reduction

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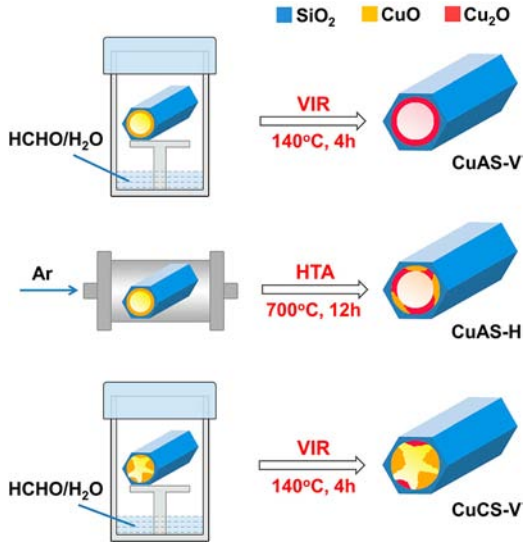
Supporting Information

ABSTRACT: Selective reduction of supported CuO to Cu_2O was realized using the strategy of vapor-induced reduction, in which $HCHO/H_2O$ vapor diffuses into the pores of the support and interacts with predispersed CuO. This new strategy allows the fabrication of supported cuprous sites at much lower temperatures within a short time, avoids the formation of Cu(0) with a Cu(I) yield of nearly 100%, and results in materials with good adsorption performance, which is impossible to achieve by conventional methods.

Because of its versatility, nontoxicity, and low cost, cuprous oxide (Cu_2O) is highly promising for diverse applications such as adsorption, photocatalysis, and sensing.[1] Much attention has therefore been given to the fabrication of cuprous sites on various supports, including alumina, silica, zeolite, and metal−organic frameworks.[2] To obtain cuprous sites, the precursor, usually cupric oxide (CuO), is introduced into the support by decomposition of a copper salt. For the fabrication of Cu_2O-containing functional materials, the subsequent conversion of the supported cupric sites to cuprous ones is considered a crucial step. To date, two approaches have been employed: (i) thermal treatment at ∼200 °C in the presence of a reducing gas (e.g., H_2 or CO) and (ii) high-temperature autoreduction (HTA) under an inert atmosphere. Only a few reports concern the use of the first approach, since the reduction process is hard to control and Cu(0) rather than Cu(I) is frequently produced, as has been well-demonstrated by H_2 temperature-programmed reduction (H_2-TPR) results in a large number of studies.[3] The second approach involving HTA can avoid the formation of Cu(0) and has been widely utilized for the preparation of Cu(I)-containing materials.[4] However, it requires high temperatures (>700 °C) and long treatment times (>12 h), which are energy-consuming and harmful to the structure of the material. Moreover, only about half of the CuO can be converted to Cu_2O using the HTA approach, which is far from satisfactory.[5] Hence, the development of an efficient, controllable method to construct supported cuprous sites is extremely desirable.

Herein we report for the first time a strategy for constructing cuprous sites on SBA-15 mesoporous silica by using vapor-induced reduction (VIR) (Scheme 1). A formaldehyde/water vapor mixture generated at elevated temperatures diffuses into the pores of SBA-15 and interacts with predispersed CuO, leading to the formation of Cu_2O. This strategy allows the reduction of CuO at temperatures as low as 140 °C, which is significantly lower than the HTA method (700 °C). More importantly, almost all of the CuO can be converted, and the yield of Cu_2O is nearly 100%. The present strategy offers an efficient and controllable way to fabricate supported cuprous sites under mild conditions, which is impossible to realize by conventional methods. We also demonstrate that the VIR-treated samples exhibited excellent performance in the adsorptive separation of ethylene and ethane that was obviously superior to the results using samples prepared by the HTA method.

Scheme 1. Conversion of Dispersed or Aggregated CuO to Cu_2O on Mesoporous Silica by the VIR and HTA Approaches



Two types of CuO-containing SBA-15 precursors, namely, CuAS and CuCS, were first synthesized by using as-prepared and calcined SBA-15, respectively [see the Supporting Information (SI) for experimental details].[5] After the introduction of CuO, the ordered mesostructure was well-preserved, as shown by low-angle X-ray diffraction (XRD) and N_2 adsorption results (Figures S1 and S2 and Table S1 in the SI). A great difference between the two types of samples was the degree of dispersion of CuO. All of the CuO was well-dispersed in the CuAS samples as a result of the confining effect

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of as-prepared SBA-15 in the synthetic process, while aggregation of CuO occurred in CuCS, as demonstrated by diffraction lines in wide-angle XRD patterns (Figure S1).[6] In contrast to the aggregated CuO, the reduction temperature of dispersed CuO was obviously lower, as shown in the H_2-TPR profiles (Figure S3). Hence, all of the CuAS samples exhibited a much lower temperature for CuO reduction than the sample CuCS(4) (where the value in parentheses indicates the Cu content in mmol/g). It was noticeable that only one H_2 consumption peak was observed for all of the samples, and the amount of H_2 consumed was in good agreement with the CuO content (Table S1). This suggests that supported CuO, regardless of the degree of dispersion, is directly reduced to metallic Cu in the presence of reducing gases.

Treatment of CuAS and CuCS using the VIR strategy resulted in the formation of CuAS-V and CuCS-V, respectively. For comparison, CuAS-H was also prepared by treatment of CuAS with the HTA method (Scheme 1). All of the CuAS-V samples showed an intense diffraction line accompanied by two weak ones in the low-angle XRD patterns (Figures 1A and S4),

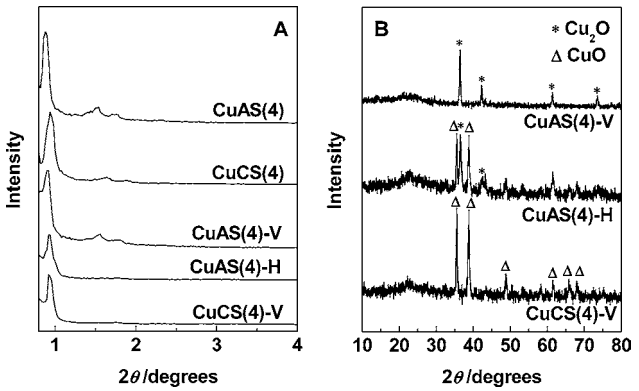

Figure 1. (A) Low-angle and (B) wide-angle XRD patterns of various samples.

which can be indexed as the (100), (110), and (200) reflections corresponding to the two-dimensional hexagonal pore regularity of the *p6mm* space group. These reflections, in combination with the transmission electron microscopy images shown in Figure S5, provide evidence of the good maintenance of mesostructure after reduction. Comparison of the samples before and after reduction showed that the intensity of the diffraction peaks of CuAS(4) was comparable to that of CuAS(4)-V. In the case of CuAS(4)-H and CuCS(4)-V, however, the (100) peak became weaker and the (110) and (200) peaks disappeared. The N_2 adsorption/desorption isotherms of the CuAS-V samples were of type IV with an H1 hysteresis loop, which is characteristic of materials with cylindrical mesopores (Figure S6). Further calculation revealed that the surface areas and pore volumes decreased progressively with increasing Cu content (Table S2). The sample CuAS(4)-V had a surface area of 400 m^2/g and a pore volume of 0.768 cm^3/g, which are apparently larger than those of CuAS(4)-H and CuCS(4)-V containing the same amount of Cu. On the basis of the above results, it is safe to say that the CuAS-V samples possessed better mesostructure than CuAS-H and CuCS-V.

The diffraction peaks in the wide-angle XRD pattern of CuAS-V were well-consistent with those of Cu_2O (JCPDS no. 65-3288; Figures 1 and S4), indicating the efficiency of the VIR strategy in the controllable reduction of CuO. However, it was hard to identify any diffraction peaks originating from Cu_2O in the pattern for CuCS(4)-V, and peaks ascribed to CuO (JCPDS no. 48-1548) became predominant. This means that the reduction of aggregated CuO is much more difficult than that of dispersed CuO. Interestingly, the crystalline phases of CuO and Cu_2O with comparable peak intensities coexisted in CuAS(4)-H. It is apparent that only part of the CuO was converted to Cu_2O using the HTA method, even though CuO was well-dispersed in the precursor.

The H_2-TPR profiles shown in Figures 2 and S7 present interesting results on the reduction of different samples

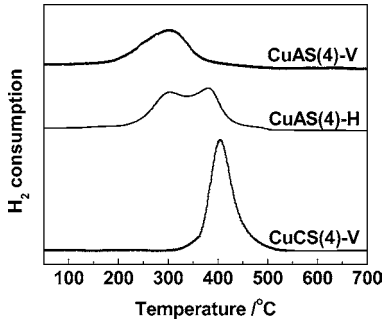

Figure 2. H_2-TPR profiles for the CuAS-V, CuAS-H, and CuCS-V samples.

prepared using the VIR and HTA methods. All of the CuAS-V samples exhibited a single peak of H_2 consumption at ~300 °C. On the basis of the aforementioned XRD results, this peak can be tentatively assigned to the transformation of Cu(I) to Cu(0). The amounts of consumed H_2 calculated from the peak areas provide further evidence of this assignment (Tables 1 and

Table 1. H_2 Consumption and Amount of Copper in Different Samples

sample	Cu content[a] (mmol/g)	H_2 consumed[b] (mmol/g)	Amount of Cu(I)[c] (mmol/g)	Cu(I) yield (%) Cu(I)/[Cu(I)+Cu(II)] from H_2 consumed[d]	from titration[e]
CuAS(4)-V	4.0	2.01	3.98	99.5	99.6
CuAS(4)-H	4.0	2.85	2.30	57.5	57.9
CuCS(4)-V	4.0	3.94	0.12	3.0	3.1

[a]Amount of Cu introduced into SBA-15. [b]Calculated from the H_2-TPR results. [c]Determined by titration. [d]Calculated from the amount of H_2 consumed and the total Cu content. [e]Calculated from the titration results and the total Cu content.

S3). For CuAS(4)-V with a Cu content of 4 mmol/g, the amount of H_2 consumed was 2.01 mmol/g. It is therefore clear that Cu(I) rather than Cu(II) was predominant in CuAS(4)-V, as otherwise the amount of H_2 consumed would have been much larger. Titration results showed that the amount of Cu(I) in CuAS(4)-V was 3.98 mmol/g. Calculations of the Cu(I) yield in CuAS(4)-V based on the amount of H_2 consumed and the titration data gave values of 99.5% and 99.6%, respectively. These results thus demonstrate that the VIR strategy can effectively reduce dispersed CuO to Cu_2O with high selectivity. The UV−vis technique was also introduced to characterize the samples before and after reduction. As shown in Figure S8, the

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UV−vis spectra of CuAS(4) and CuAS(5) presented two absorption peaks at ∼270 and ∼760 nm, which can be assigned to CuO.[7] For the samples after reduction, namely, CuAS(4)-V and CuAS(5)-V, the peaks at 270 and 760 nm were absent, while a new peak at 450 nm originated from Cu_2O emerged.[8] The UV−vis data thus confirm the results described above, pointing out the complete conversion of dispersed CuO to Cu_2O using the VIR strategy. In contrast to dispersed CuO, aggregated CuO was quite difficult to convert to Cu_2O under the same conditions. The CuCS(4)-V sample gave a peak of H_2 consumption at ∼400 °C, and the amount of H_2 consumed was calculated to be 3.94 mmol/g. Further calculations showed that the yield of Cu(I) was 3.0%, which is in line with the titration result (3.1%). Apparently, only a tiny amount of CuO in CuCS(4) was converted to Cu_2O, while CuO became more aggregated in the VIR process. This led to an increase in the reduction temperature in the H_2-TPR profiles, as can be seen by comparing the profiles for the samples before and after treatment (Figures 2 and S3). Two reduction peaks were observed for CuAS(4)-H because of the coexistence of CuO and Cu_2O. A medium amount of H_2 was consumed (2.85 mmol/g), corresponding to a Cu(I) yield of 57.5%. Such a yield is evidently lower than that for the same sample prepared using the VIR strategy (∼100%), despite the much higher temperature and longer time demanded for the HTA process.

Our materials were also applied to the adsorptive separation of C_2H_4 and C_2H_6. C_2H_4 is an important chemical with versatile applications. Conventionally, C_2H_4/C_2H_6 separation is carried out by distillation at −25 °C and 2000 kPa, which is one of the most energy-intensive processes in the chemical industry.[9] Extensive attention has recently been paid to the separation of C_2H_4 and C_2H_6 by adsorption, as this process can be performed under mild conditions.[10] Among various alternatives, supported Cu_2O is a good choice of adsorbent because of its low cost, high activity, and good reusability. The adsorption isotherms in Figure 3 show that CuCS(4)-V adsorbed 1.75 mmol of C_2H_4/g at 1000 kPa, which is close to the uptake of C_2H_6 (1.59 mmol/g). Under the same conditions, the C_2H_4 uptake increased to 2.23 and 2.63 mmol/g on CuAS(4)-H and CuAS(4)-V, respectively, while the C_2H_6 uptake remained almost constant. To provide a better understanding of the adsorption behavior, the C_2H_4/C_2H_6 selectivity was predicted using ideal adsorbed solution theory (IAST), and the results are presented in Figure 3D. The C_2H_4/C_2H_6 selectivities of the different adsorbents decreased in the order CuAS(4)-V > CuAS(4)-H > CuCS(4)-V, despite different molar fractions of the two adsorbates. To take one example, the C_2H_4/C_2H_6 selectivity was 1.7 on CuCS(4)-V at a C_2H_4 molar fraction of 0.2. A selectivity of 5.9 was obtained on CuAS(4)-H, and the selectivity was as high as 10.3 on CuAS(4)-V. Among CuAS-V samples with different Cu contents, CuAS(4)-V exhibited the best performance with regard to C_2H_4/C_2H_6 separation (Figures S9 and S10). After adsorption, regeneration of the spent CuAS(4)-V adsorbent was also conducted (Figure S11). The adsorptive capacity of the regenerated adsorbent could be well-recovered upon recycling three times. It is known that cuprous species can interact with the C═C bond in C_2H_4 through π-complexation, which gives rise to preferential adsorption of C_2H_4 over C_2H_6.[11] As a result, the content of Cu(I) in the adsorbent plays a significant role in C_2H_4/C_2H_6 separation. Of course, some other factors such as surface area and pore volume must also be taken into consideration.

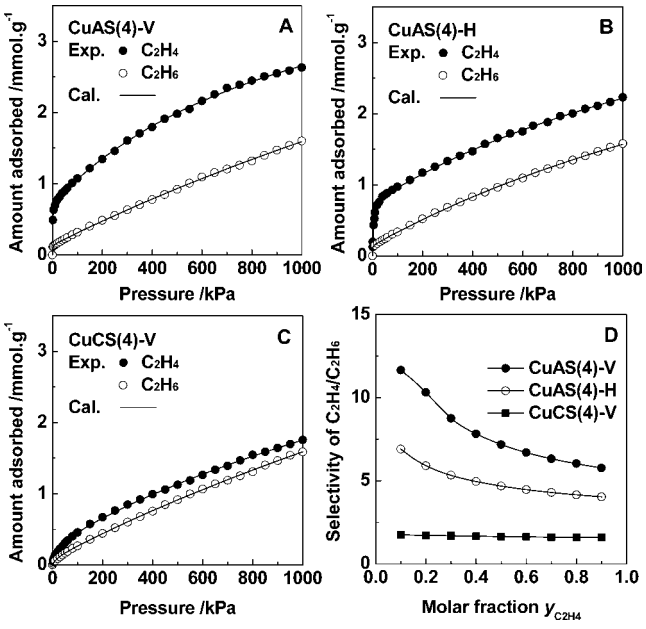

Figure 3. (A−C) Adsorption isotherms of C_2H_4 and C_2H_6 over different samples. (D) C_2H_4/C_2H_6 selectivity.

To examine the pathway for reduction, a CuAS sample treated using the VIR strategy for different times was monitored by XRD. As depicted in Figure S12, no diffraction lines were observed for the sample before treatment because CuO was well-dispersed in the pores of SBA-15. A new diffraction line derived from $Cu(OH)_2{\cdot}H_2O$ (JCPDS no. 42-0746) emerged at 1 h and disappeared at 4 h, indicating that $Cu(OH)_2{\cdot}H_2O$ is an intermediate in the reduction process. The diffraction lines of Cu_2O appeared at 2 h, and their intensity increased with increasing reaction time, corresponding to increases in the amount of Cu_2O. In terms of these investigations, the reduction pathway shown in eqs 1−3 can be proposed:

$$CuO + 2H_2O \rightarrow Cu(OH)_2{\cdot}H_2O \quad (1)$$

$$2Cu(OH)_2{\cdot}H_2O + HCHO \rightarrow HCOOH + Cu_2O + 4H_2O \quad (2)$$

$$2Cu(OH)_2{\cdot}H_2O + HCOOH \rightarrow CO_2 + Cu_2O + 5H_2O \quad (3)$$

Driven by the concentration gradient, HCHO goes into the gas phase from solution at elevated temperatures and subsequently diffuses into the pores of the mesoporous silica. The reduction reaction between HCHO and the intermediate then takes place, leading to the formation of Cu_2O and formic acid (HCOOH). In view of the reducing ability of HCOOH, the transformation of the intermediate to Cu_2O continues, accompanied by the formation of CO_2. Gas chromatography analysis indicated the presence of both HCOOH and CO_2 in the reaction mixture, thus confirming the pathway. For CuAS and CuCS samples containing identical amounts of CuO, quite different reduction behavior was observed in the VIR process. Apparently, the degree of dispersion of CuO has an important effect on the reduction. We consider that dispersed CuO, which is easily accessed by gaseous HCHO, is more readily reduced.

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Hence, the reduction efficiency is strongly dependent on the degree of dispersion of CuO.

Despite great efforts, the development of an efficient method to fabricate supported cuprous sites has remained a challenge until now. In the traditional HTA method, precursors have to be treated at high temperatures (>700 °C) for quite a long time (>12 h), which is time- and energy- consuming. The present VIR strategy allows the reduction of supported cupric species to cuprous sites at temperatures as low as 140 °C, and the whole process can be completed within 4 h, which evidently saves a great deal of time and energy. More importantly, the yield of Cu_2O is nearly 100%, without the formation of metallic Cu. Our strategy provides an efficient and controllable way to construct cuprous active sites, which is highly desired in the fields of adsorption, catalysis, sensing, and so on. Furthermore, this novel strategy should enable us to introduce various metal oxides and even metals into porous materials with a range of pore symmetries and pore sizes, which is impossible or difficult to accomplish by conventional methods.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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