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Stabilizing copper species using zeolite for ethanol catalytic dehydrogenation to acetaldehyde

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ABSTRACT

The selective dehydrogenation of ethanol to acetaldehyde is a promising route for acetaldehyde production. Although Cu-based catalysts exhibit high activity in ethanol dehydrogenation, a rapid deactivation due to Cu sintering always occurs. In this study, highly dispersed Cu species were stabilized using the silanol defects in Beta zeolite (denoted as Beta) resulting from dealumination, and applied as robust catalysts for ethanol-to-acetaldehyde conversion. Typically, a long catalyst lifetime of 100 h with an acetaldehyde yield of ~70% could be achieved over 5% Cu/Beta. The presence of Cu⁺ and Cu⁰ species and the agglomeration of Cu particles after a long-term reaction for 180 h were revealed by transmission electron microscopy, thermogravimetric analysis, and CO-diffuse-reflectance infrared Fourier transform spectroscopy, and were responsible for the deactivation of the Cu/Beta catalyst in the ethanol-to-acetaldehyde conversion.

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1. Introduction

Bio-derived ethanol is regarded as a green feedstock to produce valuable chemicals, e.g., ethene, butadiene, 1-butanol, and acetaldehyde [1,2]. Among these chemicals, acetaldehyde is an important building block for the production of acetic acid, acetate esters, and pentaerythritol [3]. In the past few decades, the bioethanol-based dehydrogenation route to produce acetaldehyde and the important hydrogen co-product has attracted significant attention.

Generally, the catalysts for alcohol dehydrogenation can be mainly divided into two types, i.e., metal (Cu, Ag, Pd, Au, etc.) and metal oxide (CuO, ZnO, MgO, Cr₂O₃, etc.) [4–15]. Among these catalysts, Cu-based catalysts exhibit very high activity and

good selectivity toward acetaldehyde, in part, because Cu can cleave C–C and C–O bonds at much lower rates than other transition metals (e.g., Pd and Pt) [16]. However, a rapid deactivation due to Cu particle sintering often occurs on Cu-based catalysts [12,17]. Hence, special attention has been paid to prevent this Cu sintering and prolong the catalyst lifetime. Some inert substances that inhibit Cu sintering have been widely used as textural promoters, and amphoteric or basic metal oxides have been proven to be beneficial for improving the dehydrogenation activity [18–21]. In addition, the effects of the Cu content and the chemical state of the active Cu species on the catalytic activity have also been investigated [16,22–27]. Bueno et al. [22] found that the selectivity for the products was related to the metal dispersion defined by the Cu content. Cassinelli et al.

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[23,24] reported that Cu⁺ cations were the most active species in the ethanol dehydrogenation reaction, whereas other groups found that the metallic Cu species were responsible for the ethanol dehydrogenation activity [16,25–27]. Furthermore, the catalytic activity and stability of the catalyst also depend on the nature of the support. A good support should ensure a suitable dispersion of the Cu active phase, possibly stabilizing it during the high-temperature reaction [28]. Inert SiO₂ [11,12], mesoporous carbon [13], silicon carbide [29], and carbon layer-coated SiO₂ [15] as well as rice husk ash [17] have already been tested as candidate supports.

In our previous work, zeolite-confined catalyst systems were successfully constructed via a post-synthesis route; they exhibited remarkable activity in ethanol-to-butadiene conversion [30–32]. The silanol groups in the hydroxyl nests of [Si]Beta zeolite acted as the exclusive anchoring sites, and could strongly anchor the cations upon calcination decomposition of the metal precursors. Considering the rapid Cu sintering of Cu-based catalysts in ethanol-to-acetaldehyde conversion, we expected that the zeolite-confined Cu/Beta zeolite catalyst will be more structurally stable against Cu sintering, and exhibit a good performance in the ethanol-to-acetaldehyde conversion. In this study, a Cu/Beta zeolite catalyst was prepared via the post-synthesis route and applied in ethanol-to-acetaldehyde conversion. The effects of the Cu contents, reaction temperatures, and Cu precursors on the catalytic performance were investigated. After optimization, a long lifetime of 100 h with an acetaldehyde yield of ~70% could be achieved over the 5% Cu/Beta zeolite catalyst. The physicochemical properties of the fresh catalysts were analyzed using X-ray diffraction (XRD), nitrogen physisorption, transmission electron microscopy (TEM), ultraviolet-visible spectroscopy (UV-Vis), and H₂-temperature-programmed reduction (H₂-TPR). The existing states of Cu species and the organic deposits occluding the catalyst as a result of the ethanol-to-acetaldehyde conversion were then characterized using TEM, thermogravimetric analysis (TGA), and CO-diffuse-reflectance infrared Fourier transform spectroscopy (CO-DRIFTS). On the basis of the catalytic and spectroscopic results, the deactivation behavior of the Cu/Beta zeolite catalyst in the ethanol-to-acetaldehyde conversion is discussed herein.

2. Experimental

2.1. Catalyst preparation

Cu/Beta zeolite was prepared via a two-step metallation procedure [30]. Firstly, the dealuminated zeolite Si-Beta zeolite was synthesized by treating commercial H-Beta zeolite ($n_{\text{Si}}/n_{\text{Al}} = 13.5$, Sinopec Co.) in 13 mol/L nitric acid aqueous solution. Thereafter, the [Si]Beta host zeolite was impregnated with Cu(Ac)₂·6H₂O. Typically, the Cu precursors were dissolved in excess water to prepare a solution, to which [Si]Beta zeolite was added under stirring for 8 h. Then, the homogenous slurry was evaporated at 80 °C and calcined at 550 °C for 6 h under flowing air. The final product was denoted as x% Cu/Beta (x

indicates the weight loadings of Cu metal).

For reference, Cu/Beta was also prepared using different Cu precursors via wet impregnation, and the obtained samples were denoted as CuCl₂-Beta, Cu(NO₃)₂-Beta, and Cu(Ac)₂-Beta (Cu loading: 5%).

2.2. Characterization of catalysts

The XRD patterns of the as-prepared catalysts were recorded on a Rigaku SmartLab powder diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), with a scanning rate of 5°/min in the 2 θ range of 5°–50°.

The surface areas and pore volumes of the calcined samples were measured using nitrogen adsorption on a Quantachrome iQ-MP gas adsorption analyzer at –196 °C. Before nitrogen adsorption, the samples were dehydrated at 300 °C for 6 h. The total surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The micropore size distribution was determined using the t-plot method.

TEM and high-resolution TEM (HRTEM) images were recorded on a JEOL JEM-2100F electron microscope at an acceleration voltage of 200 kV.

H₂-TPR experiments on the samples were carried out on a chemisorption analyzer (Chemisorb 2720, Micromeritics) with 5 vol% H₂/Ar, at a heating rate of 10 °C/min from room temperature to 500 °C. Prior to reduction, the samples (100 mg) were pretreated under Ar gas at 350 °C for 1 h.

The diffuse-reflectance UV-Vis spectra of the Cu/Beta zeolites were recorded against BaSO₄ in the region of 200–800 nm on a PerkinElmer Lambda 750 UV-Vis-NIR spectrophotometer.

¹H MAS NMR measurements were performed on a Bruker Avance III spectrometer at a resonance frequency of 400.1 MHz. The ¹H MAS NMR spectra were obtained using a single-pulse excitation of $\pi/2$ with a pulse duration of 2.6 μs and a repetition time of 20 s. All the ¹H MAS NMR studies were performed with dehydrated samples, which were treated at 450 °C in vacuum (below 10^{–2} Pa) for 12 h.

2.3. Catalyst evaluation

Ethanol-to-acetaldehyde conversion was performed in a fixed-bed reactor at atmospheric pressure, as described in our previous report. In a typical experiment, 0.4 g of the Cu/Beta catalyst (sieve fraction: 20–40 mesh) was placed in the fixed-bed reactor and treated with flowing nitrogen (20 mL/min) at 400 °C for 1 h. After cooling down to the desired temperatures, ethanol was introduced into the reactor, using a Shimadzu LC-2AT Dual Reciprocating Plunger HPLC pump, at a weight hourly space velocity (WHSV) of 1 h^{–1}. The reaction products were analyzed using an on-line gas chromatograph (Shimadzu GC-2010 plus) with a TM-Plot-Q column and a flame ionization detector (FID). The ethanol conversion and acetaldehyde selectivity were defined as follows:

$$\text{Ethanol conversion (mol\%)} = \frac{[\text{Ethanol}]_{\text{inlet}} - [\text{Ethanol}]_{\text{outlet}}}{[\text{Ethanol}]_{\text{inlet}}} \times 100\%$$

$$\text{Acetaldehyde selectivity (mol\%)} = \frac{[\text{Acetaldehyde}]_{\text{outlet}}}{[\text{Ethanol}]_{\text{inlet}} - [\text{Ethanol}]_{\text{outlet}}} \times 100\%$$

2.4. TGA and CO-DRIFTS investigations of spent Cu/Beta catalysts

TGA data were acquired using a Q600 SDT simultaneous thermal analyzer (TA Instruments). Typically, 0.1 g of spent Cu/Beta catalyst was placed in an Al₂O₃ crucible and heated up to 800 °C at a constant rate of 10 °C/min under flowing O₂/Ar (20 vol%/80 vol%, 30 mL/min).

DRIFTS measurements of the CO adsorption on the spent Cu/Beta zeolites were conducted on a spectrometer (Bruker Tensor 27), with 128 scans at a resolution of 4 cm⁻¹. The self-supporting pellets of the catalyst samples were placed into the reaction chamber, pretreated under helium flowing at 300 °C for 1 h, and subsequently cooled to 25 °C. Then, 2% CO (helium balanced) was introduced into the DRIFTS cell at a gas flow rate of 15 mL/min; subsequently, the cell temperature was increased from 25 to 50 and 100 °C. The DRIFTS spectra were obtained by subtracting the spectrum of the bare catalyst (background).

3. Results and discussion

3.1. Physicochemical properties of catalyst materials

To verify the possible structural changes during the post-synthesis procedures, the XRD patterns of the parent H-Beta and post-treated samples were collected; they are shown in Fig. 1. The typical diffraction line characteristics of the BEA topology were observed for all the samples, indicating that the primary BEA structure was well-preserved after dealumination and Cu introduction [33]. In addition, no obvious diffraction lines attributable to Cu species were observed for the Cu/Beta zeolites with low Cu contents (1%–9%), indicating that the copper species, which were either amorphous or very small, were highly dispersed within the matrix. These results are consistent with those of the N₂ adsorption-desorption analysis; no significant loss in the surface areas and micropore volumes was observed for the samples with low Cu contents (Table 1). However, upon increasing the Cu content to >20 %, characteristic peaks of CuO (35.5° and 38.9°) appeared [17],

Fig. 1. XRD patterns H-Beta, [Si]Beta, Cu/Beta and bulk CuO samples.

Table 1

Chemical composition and surface area of H-Beta, [Si]Beta and Cu/Beta samples under study.

Samples	Si/Al ^a	Cu loading ^a (wt%)	S _{BET} ^b (m ² /g)	V _{micro} ^c (cm ³ /g)
H-Beta	13.5	—	590	0.204
[Si]Beta	>1800	—	620	0.210
1%Cu/Beta	>1800	0.9	601	0.205
5%Cu/Beta	>1800	4.9	583	0.198
7%Cu/Beta	>1800	6.8	571	0.192
9%Cu/Beta	>1800	8.8	562	0.186
20%Cu/Beta	>1800	19.7	501	0.163
50%Cu/Beta	>1800	49.4	458	0.141

^a Determined by ICP-AES. ^b Determined by N₂-absorption. ^c Micropore volume was estimated by using the t-plot method.

indicating that the small crystallites of CuO gradually aggregated due to the increase in Cu content, resulting in an increase in the particle sizes. Simultaneously, the surface areas and micropore volumes of the Cu/Beta zeolites decreased obviously (Table 1).

On the basis of our previous work, the dealumination of H-Beta and incorporation of Ti, Sn, Zr, or Ce species are associated with the evolution of silanols related to the vacant sites during post-synthesis [33–36]. This phenomenon was also observed when preparing the Cu/Beta zeolites using the wet impregnation method under study. The DRIFTS spectrum (Fig. 2(a)) of the parent H-Beta exhibits two obvious characteristic bands in the hydroxyl stretching region: one band at 3740 cm⁻¹, ascribed to isolated external Si–OH groups, and another band at 3600 cm⁻¹, ascribed to the bridging hydroxyl Si–OH–Al [33]. The treatment of H-Beta with concentrated HNO₃ solution resulted in the complete disappearance of the band at 3600 cm⁻¹ associated with Si–OH–Al groups, evidencing the complete elimination of Al from the framework, which was also supported by the higher Si/Al ratio (>1800) of [Si]Beta (Table 1). Simultaneously, intensification of the band at 3735 cm⁻¹ corresponding to isolated internal Si–OH groups and the band at 3520 cm⁻¹ related to hydrogen-bonded silanol groups was clearly observed, indicating the formation of vacant T atom sites, in accordance with earlier assignments [33]. After the introduction of the Cu species, an obvious decrease in the intensity of the OH bands at 3735 and 3520 cm⁻¹ occurred. According to our previous studies [30], this observation indicated that catalyst systems of copper species confined in Beta zeolite were successfully constructed via the post-synthesis route. Upon calcination, the Cu precursors decomposed and reacted with the silanols created by dealumination. Thus, Cu functional sites could be introduced into zeolite cages, at former Al positions of the parent zeolite, to build confined catalytic reactors.

The hydroxyl groups in H-Beta, and the Si-Beta zeolites before and after the introduction of Cu species were analyzed using ¹H MAS NMR spectroscopy. As shown in Fig. 2(b), a strong signal at δ_{1H} = 1.5 ppm due to silanol groups at framework defects, and two weak resonance signals at 2.5 and 3.9 ppm ascribable to extra-framework Al–OH groups and bridging hydroxyl Si–OH–Al, respectively, appeared for the H-Beta sam-

Fig. 2. (a) DRIFT spectra in the hydroxyl stretching vibration region and (b) ^1H MAS NMR spectra of H-Beta, [Si]Beta and Cu/Beta samples; (c) UV-Vis-NIR spectra of Cu/Beta samples with different Cu contents; (d) H_2 -TPR profiles of bulk CuO and Cu/Beta zeolite samples with different Cu contents.

ple [34]. After dealumination, the band of the hydroxyl groups associated with Al species responsible for the signals at 2.5 and 3.9 ppm disappeared, and a broad signal at about 2.7 ppm due to the hydrogen bonds between some SiOH groups and neighboring framework oxygen species inside the silanol nests appeared for [Si]Beta [34]. The introduction of Cu species resulted in the disappearance of the band for silanol groups in the hydroxyl nests, leaving the band for the remaining unreacted silanols located at 1.7 ppm, in good agreement with the DRIFTS results in Fig. 2(a). On the basis of the results of DRIFTS and ^1H MAS NMR spectroscopy, the Cu/Beta-confined catalyst systems could be prepared in a way similar to that of Zn/Beta and Y/Beta in our previous work [30].

The chemical environment of the Cu species within the [Si]Beta matrix was characterized using UV-Vis-NIR spectroscopy. As shown in Fig. 2(c), two absorption bands centered at about 14000 and 48000 cm^{-1} appeared for all the Cu/Beta zeolites. The former band can be attributed to the $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transition of Cu^{2+} cations in an octahedral environment, whereas the latter can be assigned to $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$ charge transfer transitions, which are characteristic of isolated Cu^{2+} [37,38]. With an increase in the Cu loadings from 1% to 9%, the intensities of these bands gradually increased, indicating an increase in the

amount of Cu^{2+} species in the [Si]Beta matrix. Additionally, a broad band in the range of 20000–25000 cm^{-1} , attributable to the $d-d$ transition of Cu with an octahedral environment in CuO, appeared when the Cu loading increased to >5% [38,39], indicating an increase in the particle size of the Cu species; this is in good agreement with the TPR results (ut infra).

TPR experiments were performed to evaluate the reducibility of the Cu/Beta zeolites. This technique is suitable for studying low-load and highly dispersed systems whose characteristics are beyond the limits of detection of other direct structural analysis methods such as XRD [22]. Fig. 2(d) shows the TPR profiles of the bulk CuO and Cu/Beta samples with different Cu loadings. The maximum of the TPR peaks (T_{max}) of the Cu/Beta samples should have been related to the reduction of supported Cu species in different interactions with the zeolite matrix as well as to the particle size and Cu content. Bulk CuO exhibited a single hydrogen consumption peak centered at 316 °C. For the Cu/Beta samples, the reduction temperatures were significantly lowered, in good agreement with earlier reports [17,22], due to the presence of highly dispersed CuO with an octahedral environment. The broadening of the TPR peak and its shift to higher temperatures were related to an increase in the CuO particle sizes with an increase in the Cu content from 5% to

Fig. 3. (a) Ethanol conversion and acetaldehyde selectivity over Cu/Beta zeolite catalysts with different Cu contents at 300 °C with a TOS of 2 h; (b) Ethanol conversion and acetaldehyde selectivity over 5% Cu/Beta zeolite catalysts at different temperatures with a TOS of 2 h.

9%. In addition, 1% Cu/Beta exhibited a relatively higher $T_{\max}$

(301 °C) than those of the other samples. This indicated that Cu/Beta with a very low Cu content probably contained highly dispersed isolated Cu^{2+} species that strongly interacted with the support or were possibly incorporated into the zeolite framework, and were hard to reduce.

3.2. Optimization of catalysts and reaction conditions for ethanol conversion

The effects of the Cu contents, reaction temperatures, and Cu precursors on the ethanol conversion and acetaldehyde selectivity are given in Figs. 3 and 4. The Cu content of the catalyst clearly shows a strong impact on the ethanol conversion (Fig. 3(a)). Upon increasing the Cu loading from 1% to 5%, the ethanol conversion dramatically increased from 25% to 85%. However, a further increase in the Cu loading from 5% to 50% resulted in a gradual decrease in the ethanol conversion (from 85% to 48%). For comparison, the catalytic performance of bulk CuO was also studied, and a poor activity with 7% ethanol conversion and 97% selectivity toward acetaldehyde was achieved. According to earlier studies [16,22], large metal species are not conducive to ethanol conversion. This indicates that when approaching saturation of highly dispersed Cu species in 5% Cu/Beta, more Cu species will be forced to aggregate into larger CuO particles, as revealed by the XRD and H_2 -TPR results. Therefore, lower catalytic activities were observed for the Cu/Beta catalysts with higher amounts of Cu loading. In addition, an increase in the Cu loading had no significant influence on the acetaldehyde selectivity, suggesting that selective dehydrogenation of ethanol to acetaldehyde was the dominant reaction over the Cu/Beta catalysts.

Fig. 4. (a) Catalytic performance of 5% Cu/Beta prepared with different precursors in the ethanol to acetaldehyde conversion at 300 °C with a TOS = 2.0 h; H_2 -TPR profiles (b) and TEM pictures (c and d) of 5% Cu/Beta zeolites prepared with different precursors; High-resolution TEM images (f) of $\text{Cu}(\text{Ac})_2$ -Beta sample with the corresponding element mapping (g).

Fig. 3(b) shows the ethanol conversion and acetaldehyde selectivity over 5% Cu/Beta at reaction temperatures of 200–350 °C. Clearly, the ethanol conversion gradually increased from 30% to 95% with an increase in the reaction temperature from 200 to 350 °C. Simultaneously, a stable acetaldehyde selectivity of 85%–90% was maintained up to 300 °C; however, it started to decrease at 325 °C, as much more condensation products from acetaldehyde and some ethene from ethanol dehydration were produced. Therefore, 300 °C was used as the reaction temperature in subsequent studies.

Fig. 4(a) shows the effect of the Cu precursors, i.e., CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, and $\text{Cu}(\text{Ac})_2$, on the ethanol conversion and acetaldehyde selectivity over the 5% Cu/Beta catalyst at 300 °C. Obviously, the Cu precursors had a strong impact on the catalytic performance. The use of inorganic precursors, i.e., CuCl_2 and $\text{Cu}(\text{NO}_3)_2$, resulted in a lower catalytic activity, with ~50% ethanol conversion and ~80% acetaldehyde selectivity, in comparison with that achieved using the organic precursor $\text{Cu}(\text{Ac})_2$. The H_2 -TPR profiles indicated that the use of inorganic precursors would lead to the broadening of the TPR peaks and their shift toward higher temperatures (Fig. 4(b)). This suggested that the Cu species obtained from the inorganic precursors interacted more strongly with the [Si]Beta matrix or possibly had larger particle sizes. The TEM images of these Cu/Beta catalysts also indicated that the inorganic precursors could produce larger particles of Cu species (Fig. 4(c) and (d)), which were not easy to reduce and were not conducive to the ethanol-to-acetaldehyde conversion. For Cu/Beta prepared with the organic precursor, the HRTEM image showed the clear lattice fringes of the zeolite support but no evidence of large particles of Cu species on the support (Fig. 4(f)), indicating that Cu species were homogeneously dispersed in the [Si]Beta matrix. This was also supported by the corresponding element mapping results, which showed that the distribution of the Cu species was homogeneous and that no obvious Cu-containing aggregates were formed (Fig. 4(g)). Hence, a good catalytic activity could be expected and also achieved for the $\text{Cu}(\text{Ac})_2$ -Beta catalyst with a homogeneous distribution of Cu species.

3.3. Stability of optimal catalyst in ethanol conversion

Under the optimized reaction conditions (*vide supra*), i.e., 5% Cu/Beta catalyst prepared with $\text{Cu}(\text{Ac})_2$ precursor and a reaction temperature of 300 °C, the long-term stability of the catalyst was tested for 180 h, and the results are shown in Fig. 5. For comparison, the stability of bulk CuO was also studied. Using the 5% Cu/Beta catalyst, an initial ethanol conversion of 86% could be achieved, and it only dropped by ~15% after 100 h of reaction. Moreover, the acetaldehyde selectivity gradually increased from 82% to 92%, and a stable acetaldehyde yield of ~70% could be obtained during the long-term reaction for 100 h. With further progress in the ethanol-to-acetaldehyde conversion, the deactivation of the 5% Cu/Beta catalyst occurred, and the ethanol conversion gradually decreased to ~50% at a time-on-stream (TOS) of 180 h. For the bulk CuO catalyst, although a higher initial acetaldehyde selectivity of >95% could

Fig. 5. Ethanol conversion (a) and acetaldehyde selectivity (b) as well as acetaldehyde yields over 5% Cu/Beta and bulk CuO samples during the ethanol to acetaldehyde conversion at 300 °C with a TOS = 180 h.

be achieved, a rapid deactivation due to Cu sintering started to occur even at a TOS of 2.0 h, and the ethanol conversion dramatically decreased from 49% to 2% over 6 h. These results clearly indicated that Cu/Beta-confined catalyst systems were successfully constructed via the post-synthesis route, and exhibited good structural stability against Cu sintering. In addition, by increasing the WHSV from 1.0 to 4.0 h^{-1} , a high acetaldehyde productivity of 1.99 $\text{g}_{\text{Ach}}/\text{g}_{\text{cat}}/\text{h}$ with a stable acetaldehyde selectivity of 84% (see Table S1 for direct comparison with the literature) could be achieved at 300 °C over the same 5% Cu/Beta catalyst.

The 5% Cu/Beta catalyst also exhibited a remarkable activity in propanol dehydrogenation to propylaldehyde; a stable activity with ~92% propanol conversion and ~95% propylaldehyde selectivity could be achieved for a TOS of 15 h (Fig. 6). This suggested that the Cu/Beta zeolites under study were general dehydrogenation catalysts, and their use could be expanded to the selective conversion of alcohols to the corresponding aldehydes.

To verify the recyclability of 5% Cu/Beta, the spent catalyst after ethanol-to-acetaldehyde conversion for 180 h was regenerated under synthetic air at 550 °C for 4 h, and its catalytic activity was re-evaluated at 300 °C. In general, the catalytic performance of the regenerated catalyst could be well-recovered if carbon deposits were exclusively responsible for the catalyst deactivation, as shown in Fig. 7; however, a rapid deactivation occurs after a TOS of 10 h. These observations revealed that carbon deposits were associated with the deactivation of the 5% Cu/Beta catalyst under study. Other

Fig. 6. Propanol conversion and propylaldehyde selectivity over 5% Cu/Beta zeolite catalyst during the propanol to propylaldehyde conversion at 300 °C with a TOS = 14 h.

issues related to catalyst deactivation did exist; these are discussed in the next section.

3.4. Deactivation of Cu/Beta catalyst during ethanol conversion

To get more detailed information on the deactivation behaviors of the 5% Cu/Beta catalyst in the ethanol-to-acetaldehyde reaction, the existing states of Cu species and organic deposits after the reaction were investigated using TEM, CO-DRIFTS, and TGA. As shown in Fig. 8(a), the agglomeration of Cu species occurred in the deactivated catalyst; large aggregates of about 25 nm could be observed. According to earlier reports [12,17], the main reason for the deactivation of Cu catalysts is Cu sintering. Therefore, in comparison with the state of a fresh catalyst, the agglomeration of Cu species in the spent 5% Cu/Beta catalyst under study may have been a key reason for the catalyst deactivation.

The existing states of Cu species in the spent 5% Cu/Beta catalyst after ethanol-to-acetaldehyde conversion for 180 h were investigated using DRIFTS, with CO as the probe molecule. Fig. 8(b) shows the DRIFTS spectra of the spent 5%

Fig. 7. Catalytic properties of regenerated 5% Cu/Beta zeolite used as ethanol to acetaldehyde catalyst at 300 °C with a TOS of 40 h.

Cu/Beta catalyst after treatment with 2% CO (He balanced) at 25, 50, and 100 °C, followed by purging with He for 30 min. Two dominant bands at 2119 and 2170 cm^{-1} appeared for all the spent 5% Cu/Beta catalysts treated at different temperatures. The band at 2119 cm^{-1} with a shoulder at 2133 cm^{-1} could be attributed to either the Cu^+-CO carbonyl species or the atop binding of CO on Cu surface atoms [14,22,37]. However, upon increasing the treatment temperature, the intensities of the bands at 2119 and 2133 cm^{-1} significantly decreased, whereas no obvious changes occurred for the band at 2170 cm^{-1} . According to the literature, the Cu^0-CO species can be easily removed during flushing or heating, whereas the $\text{Cu}^+-(\text{CO})_x$ carbonyl species are highly resistant to He flushing or heating [22]. Therefore, the band at 2119 with a shoulder at 2133 cm^{-1} should be assigned to CO binding to Cu surface atoms. The band at 2170 cm^{-1} could be attributed to $\text{Cu}^+-(\text{CO})_2$ dicarbonyl species. These results indicated that the CuO species confined in the [Si]Beta matrix could be gradually reduced to Cu^+ and Cu^0 species during the ethanol dehydrogenation reaction. With an increase in the production of Cu^{2+} , the selectivity to acetaldehyde gradually increased, as shown by the catalytic results (Fig. 5). This indicates that the presence of Cu^+ and Cu^0 species is beneficial to the acetaldehyde selectivity; this is supported by the H_2 pretreatment results. As shown in Fig. S1, after H_2 pretreatment at 215 and 300 °C, the acetaldehyde selectivity increases to more than 90%, whereas the ethanol conversion obviously decreases. According to the TPR results (Fig. 2(d)), the 5% Cu/Beta sample treated at 215 °C should contain Cu^+ species, whereas that treated at 300 °C mainly contains Cu^0 species. This indicates that Cu^{2+} , Cu^+ , and Cu^0 species are all active in the ethanol dehydrogenation to acetaldehyde; however, the Cu^+ and Cu^0 species are beneficial to the acetaldehyde selectivity. After the emergence of Cu^0 nanoparticles due to over-reduction, metal sintering occurred, as revealed by the TEM pictures (Fig. 8(a)), leading to catalyst deactivation.

To quantify the carbon deposits formed on the 5% Cu/Beta catalyst after the ethanol-to-acetaldehyde conversion for 180 h, the weight contents of these deposits were determined using TGA in the temperature range of 25–800 °C. In general, two obvious weight losses were recognized: a low-temperature weight loss at <300 °C and a high-temperature weight loss at >400 °C. These were ascribed to volatile compounds and occluding coke compounds, respectively. According to Fig. 8(c), a small weight loss of about 0.32% due to the weakly adsorbed water and a weight loss of 3.07% attributable to the occluding carbon compounds appeared in the TGA curves. With regard to the catalytic performance of the regenerated catalyst (Fig. 7), the low weight losses of 3.07% had a minor impact on the catalyst deactivation under study. Additionally, a special wave curve with two weight gains appeared in the temperature range of 135–320 °C. According to the standard TGA curves of blank Cu and Cu_2O samples (Fig. 8(d)), the former weight gain in the temperature range of 135–225 °C should have been due to the oxidation of Cu^0 , whereas the latter in the temperature range of 300–320 °C could be assigned to the oxidation of Cu^+ species. These results indicate the presence of Cu and Cu^+ spe-

Fig. 8. TEM image and the corresponding element mapping (a), and CO-DRIFTS spectra (b) as well as TGA curves (c) of the spent 5% Cu/Beta zeolite catalyst obtained after the ethanol to acetaldehyde conversion at 300 °C with a TOS of 40 h; (d) TGA curves of the bulk Cu and Cu₂O samples.

cies in the spent 5% Cu/Beta catalyst after the reaction for 180 h, again, in good agreement with the CO-DRIFTS results (Fig. 8(b)).

To summarize the results of the TEM, CO-DRIFTS, and TGA investigations, we came to the conclusion that the highly dispersed Cu²⁺ species confined in the [Si]Beta matrix could be gradually reduced to Cu⁺ and Cu⁰ species during the ethanol-to-acetaldehyde conversion. With the emergence of Cu⁰ particles, Cu sintering would occur after the long-term reaction, causing catalyst deactivation (Scheme 1). However, in comparison with bulk CuO, the Cu/Beta-confined catalyst constructed via the post-synthesis route under study exhibited much better structural stability against Cu sintering; furthermore, a long lifetime of 100 h with an acetaldehyde yield of ~70% could be achieved.

Scheme 1. Schematic illustration of the ethanol conversion on Cu/Beta zeolite and its deactivation process.

4. Conclusions

In this work, copper species confined in [Si]Beta zeolite were prepared via a post-synthesis route and applied as catalysts for ethanol dehydrogenation to acetaldehyde. The homogeneous distribution of Cu species with tiny particles in the [Si]Beta matrix resulted in good structural stability against Cu sintering; a long lifetime of 100 h with an acetaldehyde yield of ~70% could be achieved over the 5% Cu/Beta catalyst. However, in the long-term reaction, the confined CuO species were gradually reduced to Cu⁺ and Cu⁰ species, and the agglomeration of metallic Cu particles occurred, eventually leading to catalyst deactivation.

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Graphical Abstract

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Stabilizing copper species using zeolite for ethanol catalytic dehydrogenation to acetaldehyde

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Catalyst lifetime: 100 h; Acetaldehyde yield : ~ 70 %

A Cu/Beta confined catalyst constructed via the post-synthesis route exhibited good structural stability against Cu sintering; a long lifetime of 100 h with an acetaldehyde yield of ~70% could be achieved.

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分子筛稳定的Cu物种催化乙醇脱氢制乙醛

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摘要: 生物乙醇作为一种绿色原料, 常用于制备具有更高附加值的化学品, 如乙烯、丙烯、丁二烯、1-丁醇和乙醛等。其中, 乙醛作为重要的化学原料又可以进一步转化生成乙酸, 乙酸酯和季戊四醇等。因此, 由生物乙醇脱氢制乙醛的可持续路线受到了研究者的广泛关注。在众多催化体系中, Cu基催化剂表现出较高的活性和乙醛选择性, 但Cu物种的烧结又会导致催化剂的快速失活。因此, 抑制Cu物种的烧结是提高Cu基催化剂稳定性的常用手段。本文通过后合成路线构筑了具有限域效应的Cu/Beta分子筛催化剂, 并成功应用于乙醇脱氢制乙醛反应。我们首先考察了Cu的负载量、反应温度和Cu的前驱体对反应的影响, 发现以醋酸铜为前驱体的5% Cu/Beta催化剂在乙醇脱氢制乙醛反应中表现出最佳催化性能: 催化剂寿命达到100 h, 乙醛收率稳定在70%左右(反应条件: 300 °C, WHSV=1.0 h⁻¹)。XRD, TEM, DRIFT, ¹H MAS NMR, UV-Vis以及H₂-TPR等结果表明以醋酸铜为前驱体的Cu/Beta分子筛上的主要活性中心为CuO物种, 并且该物种以高度分散的形式限域在分子筛脱铝产生的硅羟基缺陷位上。因此, 在乙醇脱氢制乙醛反应中, 限域的Cu/Beta分子筛催化剂与孤立的CuO催化剂相比, 具有优异的抗烧结能力。然而, 当反应至180 h时, 催化剂会有明显的失活现象。再生后, 尽管催化剂的初始活性能较好的恢复, 但催化剂的寿命却大大下降。我们利用TEM, TGA以及CO-DRIFTS对反应后的催化剂进行表征, 发现失活的Cu/Beta催化剂上存在Cu⁺和Cu⁰物种, 并且伴有大块烧结现象。这表明随着反应的进行, Cu/Beta催化剂上的CuO物种会逐渐还原成Cu⁺和Cu⁰物种, 而Cu⁰物种的出现又会诱导烧结现象的发生, 进而导致催化剂的失活。

关键词: 乙醇脱氢; 乙醛; 沸石分子筛; Cu基催化剂; 失活

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