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Dehydrogenation of bioethanol using Cu nanoparticles supported on N-doped ordered mesoporous carbon

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Abstract: Carbon supported Cu nanoparticles have a remarkable selectivity towards the catalytic dehydrogenation of bioethanol to acetaldehyde, which is an interesting alternative to the preparation from ethylene. In this work, we prepared a series of catalysts comprised of Cu nanoparticles supported on N-doped ordered mesoporous carbons to investigate the catalytic effect of nitrogen content. Our study shows that N-doping has a significant effect on the dispersion of Cu nanoparticles and that the highest content of N results in the highest activity. Furthermore, we show that the combined effects of strong metal-support interactions and nano-confinement is an effective method to prevent thermal and steam induced sintering. In contrast, we find no evidence that N-doping activates the substrate or change the rate-determining step. At 260 °C, the best catalyst results in >99% selectivity and a site-time yield of 175 mol_{acetaldehyde}/mol_{Cu}/h. Under these conditions, the catalysts are stable for more than 12 h using an aqueous solution of 10% ethanol as feed.

Introduction

Considering the critical need to reduce the emission of CO₂, the chemical industry must gradually rely on renewable energy and biomass rather than fossil fuel resources. One such example could be the synthesis of acetaldehyde via dehydrogenation or partial oxidation of bioethanol,^[1,2] which is an interesting alternative to the preparation from ethylene (the Wacker process). Acetaldehyde is used for the production of acetic acid, ethyl acetate, acetic anhydride, pyridine, vinyl acetate and other commercially important products.^[3,4] In the past, the dehydrogenation of ethanol to acetaldehyde was typically performed at 260–290 °C using copper chromite catalysts. Unfortunately, these catalysts suffer from co-formation of several by-products, including ethyl acetate, acetic acid and crotonaldehyde.^[5–7] Because of their high selectivity towards acetaldehyde, supported copper catalysts, such as Cu-SiC,^[5] Cu/Zeolites,^[8] Cu-SiO₂,^[9,10] Cu-Al₂O₃,^[11] Cu-ZnO-Al₂O₃,^[12] Cu/carbon,^[13] or Cu/GO,^[14] have therefore sparked renewed interest. Cu supported on carbon materials are currently among the most selective catalysts^[13,15] because of the relatively inert carbon surface, which limits secondary reactions such as esterification, aldol condensation or ketonization.^[9] However, the weak metal-support interactions and the relatively low melting point of copper make the carbon-supported catalysts particularly

prone to sintering. Furthermore, copper easily gets oxidized in air, which results in fast deactivation.^[16–20] Encapsulation of nanoparticles to a confined space has proven to be a promising way to stabilize nanoparticle during catalytic reactions.^[19] Additionally, the inert surface of mesoporous carbon can help minimize side reactions to increase the selectivity towards acetaldehyde.^[9,13]

It has previously been shown that N-doping can increase the metal-support interactions between the metal nanoparticles and the carbon support.^[20,21] For instance, Bulushev et al. reported N-doping of carbon and the use of the material as a support for Cu nanoparticles in the catalytic decomposition of formic acid.^[22] The use of graphitic-nitrogen for the stabilization of Cu nanoparticles in different N-doped carbon supports such as polyacrylonitrile-based porous carbon (PPC), commercial microporous carbon (CMC) are also reported for dehydrogenation of ethanol to acetaldehyde. Morales et al. reported Cu supported on graphite and reduced graphene oxide functionalized with nitrogen groups for bioethanol as feed.^[14] However, the nature and catalytic effect of N-doping on activity and stability of Cu nanoparticles are still not fully understood.

In order to investigate the effect of N-doping, we supported Cu-nanoparticles on three ordered mesoporous carbon materials with different N-content. We then tested the catalysts for the Cu-catalyzed dehydrogenation of bioethanol to acetaldehyde to compare the catalytic activity, selectivity and stability over time. The influence of N-doping on the activation energy of catalysts and reaction mechanism were also studied using Arrhenius plot and in-situ DRIFTS. Additionally, the catalytic activity of commercially available Cu supported on activated carbon (3Cu/AC) were also studied to compare the performance of the synthesized catalysts. In contrast to the ordered mesoporous carbon support, the carbon support in 3Cu/AC is microporous.^[23,24]

Three ordered mesoporous carbon with different N-loading were synthesized by changing the carbon-nitrogen precursors. They are abbreviated as NMC-0, NMC-2 and NMC-7, where 0, 2 and 7 refers to the approximate percentage of nitrogen. Figure 1 shows the synthesis of the three ordered mesoporous carbons with different carbon-nitrogen precursors. Synthesis of NMC-7 uses 3-aminophenol (3-AMP) and hexamethylenetetramine (HMTA) as the precursors responsible for the high N-content of

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Figure 1. Synthesis route of Cu/NMC-0, Cu/NMC-2 and Cu/NMC-7.

ordered mesoporous carbon.^[25] In NMC-2 synthesis, 3-AMP was replaced with resorcinol (with no N-functional group) whereas both 3-AMP and HMTA was exchanged with N-free reagents such as resorcinol, formaldehyde (FA) and Na_2CO_3 for the synthesis of NMC-0.

Results and Discussion

Commercially available copper on activated carbon support was used as a reference to compare the performance of the synthesized materials. Figure 2 shows the N_2 physisorption isotherms of the as-synthesized mesoporous carbon supports and copper on activated carbon. As expected, the physisorption isotherm of the NMCs showed the characteristic type IV isotherm with a H4 hysteresis loop, which is typically associated with capillary condensation in mesoporous materials.^[26,27] The hysteresis loop closes around $p/p_0 = 0.3, 0.38$ and 0.45 for NMC-0,

NMC-2 and NMC-7 respectively. The high uptake at low p/p_0 shows the presence of microporous textures in ordered mesoporous carbon.^[28] Physisorption analysis of the commercial copper on activated carbon catalyst (3Cu/AC) showed a typical type I isotherm with no significant mesoporosity. As expected, the specific surface area and porosity decreased for all catalysts after loading with Cu nanoparticles, see Table 1. The surface area increased in the order of $\text{NMC-7} < \text{NMC-0} < \text{NMC-2}$, which indicates some

Table 1. N_2 Physisorption Data for synthesised materials.

Catalyst	$V_{\text{total}}^{[a]}$ (cm^3g^{-1})	$V_{\text{micro}}^{[b]}$ (cm^3g^{-1})	$S_{\text{BET}}^{[c]}$ (m^2g^{-1})
NMC-0	0.411	0.17	590
3Cu/NMC-0	0.388	0.12	512
NMC-2	0.478	.11	602
1Cu/NMC-2	0.458	0.09	542
3Cu/NMC-2	0.296	0.15	504
8Cu/NMC-2	0.275	0.15	476
NMC-7	0.529	0.09	578
1Cu/NMC-7	0.349	0.11	484
3Cu/NMC-7	0.323	0.10	413
8Cu/NMC-7	0.319	0.08	400
3Cu/AC	0.584	0.16	811

[a] V_{total} determined from the adsorption isotherm branch at around $p/p_0 = 0.95$.

[b] V_{micro} calculated by the t-plot method.

[c] S_{BET} calculated from BET surface area plot.

Figure 2. N_2 Physisorption isotherm of mesoporous carbon supports and 3Cu/AC.

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changes in the textural properties of the different NMC. [29,20] The pore size distribution of all materials is shown in Figure S1. The results show that NMC-2 and NMC-7 are quite similar with a narrow pores size distribution around 5-6 nm, while NMC-0 has a broader size distribution around 10 nm in diameter.

Table 2 shows the carbon and nitrogen content of the support materials determined by elemental analysis. Nitrogen content of NMC-7 is approximately 9.4 wt% while that of NMC-0 is 0.4 wt%. The metal loading in the catalyst were measured by ICP-OES to confirm that the amount of copper precursor used during the synthesis was appropriate. The result confirms the copper loading in the three materials, 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/NMC-7 to be 2.94, 2.95, 2.8 wt % respectively.

Table 2. Elemental CHN analysis of mesoporous carbon support.

Catalyst	Carbon (%)	Nitrogen (%)	Hydrogen (%)
3Cu/NMC-0	89.9	0.4	9.7
3Cu/NMC-2	86.1	1.5	12.4
3Cu/NMC-7	84.1	9.4	6.5

Figure 3(a) shows the XRD pattern of the prepared catalysts and 3Cu/AC and Figure 3(b) zoom in the Cu(111) peak in three as-synthesized catalysts. Materials with same copper loading (3wt%), 3Cu/NMC-0, 3Cu/NMC-2, 3Cu/NMC-7 and 3Cu/AC shows the characteristic XRD pattern of Cu(111) plane at $2\theta = 43.2^\circ$. However, the intensity of the peak decreases with increase in the N-content of mesoporous carbon. We attribute this to the highly dispersed copper particle on the N-doped carbon. [30,31] In addition to Cu(111) peak, a weak diffraction peak was observed corresponding to $\text{Cu}_2\text{O}(111)$ for 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/AC. However, no XRD pattern were observed for mesoporous carbon and therefore confirms the amorphous nature of the ordered mesoporous carbons (Figure S2). Figure S3 shows the XRD pattern of various metal loading on NMC-2 and NMC-7 such as 1 and 8 wt% of copper. In general, the intensity of the Cu(111) peak at 43.2° increases

Figure 3. a) XRD Pattern of 3Cu/NMC-0, 3Cu/NMC-2, 3Cu/NMC-7 and 3Cu/AC b) Cu(111) zoom in.

Figure 4. SEM Images of a) 3Cu/NMC-0, b) 3Cu/NMC-2, c) 3Cu/NMC-7 and d) 3Cu/AC.

with the copper loading. The morphology of the materials is analyzed using SEM and is shown in Figure 4. Interestingly, the morphology of the NMC-2 carbon support showed a uniform and spherically shaped mesoporous carbon structures, which are quite different from NMC-0 and NMC-7. This difference in the structure of NMCs is likely due to the difference in the precursors of polymers. The SEM image for 3Cu/AC showed even structures without any visible mesoporosity or channel like structures.

The TEM images of as-synthesized materials in Figure 5 shows uniform and highly ordered mesopores throughout the materials. The measured pore widths are in the range of 5-6 nm for NMC-7, NMC-2 and 8-10 nm for NMC-0, which agree well with the results from the N_2 physisorption analysis. The TEM image of 3Cu/AC in Figure 5(d) shows the particles with average size of 22.1 nm. Figure 5(a-c) shows the TEM images of 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/NMC-7. With the exception of a few large particles on the external surface of the catalysts, the images show a high dispersion of Cu particles distributed throughout the ordered mesoporous carbons. The size distribution based on the measurement of >200 Cu particles are shown in Figure S4. Most particles in 3Cu/NMC-7 are small with an average particle size of around 6.4 nm. The TEM image of 3Cu/NMC-0 shows both small and large nanoparticles with an average size of particles around 12.4 nm. The copper nanoparticles in 3Cu/NMC-2 has an average size of 11.5 nm. In general, the average size of the nanoparticles increases in the order 3Cu/NMC-7 < 3Cu/NMC-2 < 3Cu/NMC-0. The HAADF image of 3Cu/NMC-7 shown in Figure S5 confirms the confinement of uniformly distributed copper nanoparticles owing to the high nitrogen content. The TEM images for the other materials such as

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Figure 5. TEM Images of a) 3Cu/NMC-0, b) 3Cu/NMC-2, c) 3Cu/NMC-7 and d) 3Cu/AC.

Figure 6. EDX Element distribution of a) N in NMC-2 b) Cu in 3Cu/NMC-2 c) N in NMC-7 and d) Cu in 3Cu/NMC-7.

1Cu/NMC-2, 8Cu/NMC-0, 8Cu/NMC-2, 1Cu/NMC-7 and 8Cu/NMC-7 are shown in Figure S5.

The reducibility of the copper particles on 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/NMC-7 as compared to 3Cu/AC was investigated by H_2 -TPR, see Figure S6. The H_2 -TPR profile show differences in the shape, number and temperature range of the peaks for the three materials. The difference in the shape of the peaks indicates the presence of more than one type of copper species in the materials.^[32] Notably, the TPR profile of the materials showed peaks below 300 °C. This may be explained by the presence of small and well-dispersed copper nanoparticles that are easily reduced.^[32,33] In contrast, the high-temperature peak above 400 °C in TPR of 3Cu/AC indicates the presence of large copper oxide nanoparticles that are difficult to reduce.^[34]

Figure 6 shows the surface elemental composition of 3Cu/NMC-2 and 3Cu/NMC-7 as determined by EDX analysis. Figure 6(a) and 6(c) shows the N mapping in NMC-2 and NMC-7 respectively, where the N signals are evenly distributed on the surface of ordered mesoporous carbon. However, the intensity of N signal is relatively less in NMC-2 in comparison to NMC-7 and this can be attributed to the nitrogen loading in each sample. Figure 6(b) and 6(d) shows the Cu mapping in NMC-2 and NMC-7, respectively, where the intensity of the Cu photopeak is uniform for both 3Cu/NMC-2 and 3Cu/NMC-7.

Additionally, the surface composition of catalyst materials was conducted using XPS to analyze the and oxidation state of copper nanoparticles on the surface of the carbon support. Deconvolution of the N1s spectra shows the difference in nitrogen species on the different materials (NMC-2 and NMC-7) before and after adding Cu as shown in Figure 7.

The peaks are typically attributed to 4 different types of nitrogen corresponding to pyridinic-N (N1 398.2 eV), pyrrolic-N (N2 399.9 eV), quaternary-N (N3 400.7 eV) and pyridine N-oxide (N4 402.7 eV) for NMC-7^[20] Cu loading on the mesoporous carbon support (NMC-7) results in a significant change in the spectra, see Table S1. Figure 7(b and d) shows that both the N1 and N2 peaks shifted by 0.2 - 1 eV towards higher binding energy. This can be attributed to the strong interaction of Cu with nitrogen species.^[35,36] The interaction of Cu species with pyridinic-N results in decrease in the

Figure 7. XPS N1s spectra of a) NMC-2, b) NMC-7, c) 3Cu/NMC-2 and d) 3Cu/NMC-7.

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Figure 8. XPS Cu $2p_{3/2}$ spectra of a) 3Cu/AC, b) 3Cu/NMC-0, c) 3Cu/NMC-2 and d) 3Cu/NMC-7.

relative intensity of N2 over N3 after impregnating Cu over NMC-7. This further reinforces the strong interaction between copper and nitrogen in Cu loaded samples. The interaction of Cu with NMC-2 resulted in the small decrease in the N2 and N3 peaks. These factors could attribute to the effect of N-doping on Cu. [20,37]

Figure 8 shows the XPS analysis of the Cu $2p_{3/2}$ photopeaks of 3Cu/NMCs and 3Cu/AC. The materials 3Cu/NMC-2 and 3Cu/NMC-7 showed a narrow Cu⁺/CuO peaks in XPS and the intensity of Cu²⁺ satellite peak was less in both samples. However, the samples 3Cu/AC and 3Cu/NMC-0 showed broad and large Cu²⁺ satellite peak. The results show a strong interaction of Cu and N species in N-doped catalysts. Moreover, the Cu²⁺ satellite peak around 942 eV was negligibly small for 3Cu/NMC-7, which supports the interaction of Cu and nitrogen in 3Cu/NMC-7. [20,14,38] Additionally, Cu LMM spectra were analyzed, and the spectra are shown in Figure S7. 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/AC had broad peaks in the Cu⁺, Cu⁰ region. Unfortunately, the intensity of Cu LMM spectra were too weak to distinguish between Cu⁺ or Cu⁰. [39]

The surface content of C, N, O and Cu in 3Cu/NMC-0, 3Cu/NMC-2, 3Cu/NMC-7 and 3Cu/AC based on XPS are given in the Table 3. The data (C and N) are in good

Table 3. XPS Data for as-synthesized materials..

Catalyst	Carbon (%)	Oxygen (%)	Nitrogen (%)	Copper (%)
3Cu/AC	92.3	6.7	0	1.0
3Cu/NMC-0	82.4	16.4	0	1.2
3Cu/NMC-2	88.6	8.8	1.5	1.1
3Cu/NMC-7	87.8	5.3	6.8	0.1

Figure 9. Effect of temperature on the catalytic activity for 3Cu/AC, 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/NMC-7 using 10% ethanol as reactant feed

agreement with the expected composition from the mesoporous carbon precursors used in the synthesis. All materials showed characteristic peaks of copper on the surface of the impregnated catalysts. However, the results showed a lower surface concentration of Cu on NMC-7 confirming higher encapsulation of copper nanoparticles by mesoporous carbon support. XPS data for all as-synthesized catalysts are given in Table S2 and S3.

Catalytic activity test: The catalysts were tested for the dehydrogenation of bioethanol (10% ethanol + 90% water reaction feed) at a gas hourly space velocity, GHSV= 21250 h⁻¹. Figure 9 shows the yield of acetaldehyde against temperature for as-synthesized catalysts and 3Cu/AC. As shown in the figure, the commercial Cu catalyst 3Cu/AC was completely inactive and did not show any catalytic activity for the dehydrogenation reaction. We speculate that the lack of activity of 3Cu/AC was due to the fast oxidation of exposed copper sites or by steam-induced sintering of Cu nanoparticles. [40,41] The yield of acetaldehyde for all synthesized catalysts increased with the temperature. 3Cu/NMC-7 showed a significantly higher acetaldehyde yield than 3Cu/NMC-0 and 3Cu/NMC-2, which demonstrates the positive effect of nitrogen content and/or the small size of copper nanoparticles on ethanol conversion. To estimate the possible influence of pore diffusion on the reaction rate we used the Weisz-Prater criteria as shown in Table S4. Since the Weisz modulus was significantly below 1, we concluded that extent of internal diffusion limitation was negligible.

Figure S8 shows the catalytic activity results for all other catalysts, including 1Cu/NMC-2, 1Cu/NMC-7, 8Cu/NMC-0, 8Cu/NMC-2 and 8Cu/NMC-7. In general, the yield of acetaldehyde increased with the temperature and reaches up to 57% yield of acetaldehyde at 350 °C for 1Cu/NMC-7 and 48% yield of acetaldehyde for 1Cu/NMC-2. Above 99% selectivity towards acetaldehyde was observed for all catalysts irrespective of the N-content of the ordered mesoporous carbon support. Table S5 summarizes the conversion of ethanol for different catalysts at 350 °C. Furthermore, Figure S9 compares the catalytic activity of 3Cu/NMC-7 carbonized at 600, 700 and 800 °C, respectively. 3Cu/NMC-7 carbonized at 600 °C and 700 °C

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Figure 10. Stability test at 260 °C for as-synthesized catalysts with 10% ethanol feed

exhibited similar activity towards ethanol conversion, while the material carbonized at 800 °C showed less activity due to the decrease in nitrogen content. These results indicate that both the surface area and the nitrogen content has a significant effect on the catalytic activity. The catalytic activity was investigated using pure ethanol under similar GHSV and the results are shown in Figure S10. The as-synthesized catalysts showed identical catalytic performance as that of 10% ethanol whereas 3Cu/AC showed some ethanol conversion from 260 °C.

Figure 10 shows the stability of 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/NMC-7 tested at 260 °C for 800 minutes. All catalyst showed high selectivity above 99% throughout the reaction interval. The catalyst 3Cu/NMC-7 retained around 93% of its initial activity even after 800 minutes whereas the catalysts 3Cu/NMC-2 and 3Cu/NMC-0 retained 68% and 40% of the initial activity, respectively. The high stability of 3Cu/NMC-7 is possibly due to the small and highly dispersed copper nanoparticles combined with high nitrogen content present in the catalyst. 3Cu/NMC-7 also showed higher stability when tested at higher temperature (320 °C) as shown in Figure S11(a). The stability test is also conducted with pure ethanol at the same flowrate (GHSV = 21250 h⁻¹) using 3Cu/AC and 3Cu/NMC-7. Figure S11(b) shows the stability test of 3Cu/NMC-7 as compared to 3Cu/AC. The higher stability of 3Cu/NMC-7 strengthens the evidence for a strong stabilization effect of doped nitrogen against sintering of copper nanoparticles. Stability of the catalysts with 8 wt% Cu using 8Cu/NMC-7 and 8Cu/NMC-2 are also tested at 260 °C

Figure 11. Reusability tests of catalysts a) 3Cu/NMC-2 and b) 3Cu/NMC-0.

with the results shown in Figure S11(c). 8Cu/NMC-7 showed good stability and it retained nearly 80% of its initial activity after 800 minutes. In general, the loss of activity was less in the case of catalysts with high nitrogen content and can attribute to the strong Cu and support interaction.

The reusability of the catalysts was tested by regenerating the catalysts using an in-situ reduction at 450 °C for 2 hours under H₂. The regenerated catalysts were then subjected to the same catalytic test. Figure 11(a) and 11(b) show the re-usability of 3Cu/NMC-2 and 3Cu/NMC-0, respectively. The regenerated catalyst 3Cu/NMC-2 showed 95% and 84% of initial activity over fresh catalyst in cycle 2 and cycle 3. For comparison, 3Cu/NMC-0 showed acetaldehyde yields of 60% and 37% from its initial activity over fresh catalyst in cycle 2 and cycle 3, respectively. The reusability results for the catalyst 3Cu/NMC-7 are shown in Figure S11(d).

Figure 12 shows the TEM images of the spent catalysts analyzed after the stability tests. The TEM image of 3Cu/NMC-0 showed both small and big particles with an average particle size 15.4 nm. In contrast, the TEM images of 3Cu/NMC-7 with the highest content of N, showed well-dispersed nanoparticles and no significant change in the particle size distribution after the catalytic test, see Figure 13. This shows that the copper nanoparticles are effectively confined in the mesoporous carbon of 3Cu/NMC-7. The average size of the Cu nanoparticles in 3Cu/AC was increased from 22.1 nm to 34 nm after the stability test and shows higher migration of Cu nanoparticles in 3Cu/AC as compared to the as-synthesized catalysts. Figure S12 shows the particle size distribution of 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/AC after the stability test.

Figure 12. TEM Image after stability test for a) 3Cu/NMC-0, b) 3Cu/NMC-2, c) 3Cu/NMC-7 and d) 3Cu/AC.

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Figure 13. Particle size distribution histogram of 3Cu/NMC-7 before and after the catalytic activity test

Figure 14 shows the XRD pattern of the catalysts after the stability test. Compared to the XRD patterns of the fresh catalysts, the intensity of Cu(111) diffraction peak was increased. The intensity of Cu(111) peak increased in the order 3Cu/NMC-7 < 3Cu/NMC-2 $\approx$ 3Cu/AC < 3Cu/NMC-0. The results are a clear indication of the confinement of small nanoparticles in ordered mesoporous carbon combined with stabilizing effect of copper nanoparticles by nitrogen doping in 3Cu/NMC-7. This stabilization effect due to nitrogen doping is not found in 3Cu/NMC-0 resulting in the sintering of copper nanoparticles during the reaction, a well-known reason for deactivation of copper nanoparticles in dehydrogenation reaction of ethanol.^[42,43] The appearance of the typical diffraction peak of Cu₂O(111) further support that surface oxidation may contribute to the deactivation of the catalysts. In line with the previous results, the effect is most significant for the catalysts with no or low nitrogen content.

Figure 15 shows the Arrhenius plots for the catalysts with 3 wt% Cu loading. The apparent activation energies of catalysts are around 86.1, 81.6 and 81.2 kJ/mol for 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/NMC-7, respectively. This indicates that the N-doping has no effect on the rate-limiting step and can be related to the dispersion of the Cu nanoparticles. The lowering of the light-off temperature is expected to be caused by an increase in active sites, due to the higher Cu dispersion, which provide more active sites for

Figure 14. XRD patterns after stability test.

Figure 15. Arrhenius plot of reaction rate over temperature of as-synthesized catalyst.

the dehydrogenation to occur. At 260 °C, the site-time yield (STY) of the catalysts are 14.6, 39.1 and 175 mol_{acetaldehyde}/mol_{Cu}/h for 3Cu/NMC-0, 3Cu/NMC-2 and 3Cu/NMC-7, respectively. The catalyst 3Cu/NMC-7 was also tested at a high GHSV 26500 and 45450 h⁻¹ where STY increased to 202 and 265 mol_{acetaldehyde}/mol_{Cu}/h. To the best of our knowledge, catalytic activity of 3Cu/NMC-7 showed best STY of similar catalysts reported. Table S6 shows comparison on activity of catalysts in recently published literature.

In order to investigate the effect of nitrogen in the reaction mechanism, we studied the mechanism on the surface of catalysts by in-situ DRIFTS at temperatures between 50 to 350 °C. The in-situ DRIFTS studies were conducted on 3Cu/NMC-7 and 3Cu/NMC-2. The in-situ DRIFT spectra of 3Cu/NMC-7 and 3Cu/NMC-0 are given in Figure S13(a) and (b). The detailed explanation on major observations from the spectra are given the supporting info. With the spectra of both 3Cu/NMC-7 and 3Cu/NMC-0 showing similar behavior through the temperature range, we can confirm that dehydrogenation of ethanol to acetaldehyde follows similar reaction mechanism with ethoxy formation as an intermediate. Furthermore, nitrogen has no role in defining the mechanism of dehydrogenation reaction.

Conclusion

In this work, we report the synthesis of an efficient and highly selective catalyst for the conversion of bioethanol to acetaldehyde via selective dehydrogenation. The catalyst is comprised of Cu nanoparticles supported on N-doped ordered mesoporous carbon prepared by carbonization of a templated polymer by increasing the amount of N in the polymer precursors, we were able to increase the amount of N in the carbon support from 0 to 7%. The ordered mesoporous carbon with the highest amount of N resulted in the highest Cu loading and, consequently, the highest catalytic activity and stability. We contribute this effect to increased metal-support interactions. Under the given reaction condition, 3Cu/NMC-7 resulted in a high yield of

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acetaldehyde with a STY of 175 mol_{acetaldehyde}/mol_{Cu}/h, more than 99% selectivity. Furthermore, the N-doped carbon prevent deactivation by surface oxidation or steam induced sintering in the presence of water. In situ DRIFTS studies confirm that the formation of acetaldehyde occurs via an ethoxy intermediate independent but does not indicate that the N-doping activates the ethanol or change the rate-determining step.

Experimental section

Materials: All chemicals and materials are used as received from Sigma-Aldrich with no further purification. Pluronic® F-127 (M_n ~ 12 500), 3-aminophenol (3AMP, 98%), hexamethylenetetramine (HMTA, 99%), formaldehyde (FA, 37%), resorcinol (≥99.0%) ammonia (28% aqueous solution, ≥99.99%), sodium carbonate (≥99.0%), ethanol (EtOH >99.8%), copper on activated carbon (3 wt%, 3Cu/AC), copper nitrate hemipentahydrate (Cu(NO₃)₂ · 2.5H₂O, ≥99.99%).

Synthesis of NMC-0: F-127 (8.8 g) is dissolved in deionized water (208 mL) at room temperature followed by adding resorcinol (4.4 g) and formaldehyde 37% (8.85 mL) by stirring at room temperature. Na₂CO₃ (20 mg) is then added and stirred at 80 °C for 24 hours. The precipitate is collected by centrifugation and washed with deionized water three times. The reddish-brown product is dried at 80 °C overnight and then carbonized at 600 °C in argon atmosphere for 3 hours with a heating ramp of 1 °C/min.

Synthesis of NMC-2: F-127 (8.8 g) is dissolved in deionized water (208 mL) at room temperature followed by adding resorcinol (4.4 g) and hexamethylenetetramine (2.8 g) by stirring at room temperature. NH₃ solution 28% (8 mL) is then added and the mixture is stirred at 80 °C for 24 hours. The precipitate is collected by centrifugation and washed with deionized water three times. The reddish-brown product is dried at 80 °C overnight and then carbonized at 600 °C under argon atmosphere for 3 hours with a heating ramp of 1 °C/min.

Synthesis of NMC-7: The synthesis of NMC-7 was based on a modified version of the procedure reported by Guozhu Shen.^[25] F-127 (8.8 g) is dissolved in deionized water (208 mL) at room temperature followed by adding 3-aminophenol (4.4 g) and hexamethylenetetramine (2.8 g) by stirring at room temperature. NH₃ solution 28% (8 mL) is then added and the mixture is stirred at 80 °C for 24 hours. The precipitate is collected by centrifugation and washed with deionized water three times. The reddish-brown product is dried at 80 °C overnight and then carbonized at 600 °C under argon atmosphere for 3 hours with a heating ramp of 1 °C/min.

The same procedure is repeated to prepare two additional NMC-7 samples with carbonisation temperatures of 700 °C and 800 °C, respectively.

Synthesis of xCu/NMC-y: The carbon-supported catalysts are prepared by incipient wetness impregnation using Cu(NO₃)₂ as metal precursor and ethanol as solvent. The appropriate amount of Cu(NO₃)₂ · 2.5H₂O is mesoporous carbon support (0.485 g) followed by thorough mixing. The resulting material is reduced under a flow of pure H₂ at 450 °C for 2 hours with a heating ramp of 5 °C/min. The same procedure is used to prepare catalysts with 1, 3 and 8 wt% of

Cu. The catalysts are named xCu/NMC-y, where x represent the Cu loading and y represent the weight percentage of nitrogen in the mesoporous carbon support.

Catalytic activity test: The catalysts were tested in a fixed-bed quartz tubular reactor under atmospheric pressure. 50 mg of the catalyst (1Cu/NMC-7) without fractionation (approx. particle size < 100 μm) was mixed with fractionated quartz (300-355 μm) and loaded in the reactor. The catalyst was then reduced using 10% H₂ in N₂ gas (100 mL/min) for 90 minutes at 450 °C a heating ramp of 5 °C/min under atmospheric pressure. The gas was then switched to pure N₂ (50 mL/min) and the temperature was then lowered to 350 °C. An aqueous solution of 10% ethanol was introduced using a micro pump and the preheated gas mixture is then passed through the reactor with a gas hourly space velocity (GHSV) 21250 h⁻¹. The conversion and selectivity were quantified using an online GC equipped with a flame ionization detector (FID). Gas samples from the reaction outlet were collected and analyzed using GC-MS. The procedure was repeated with pure ethanol. Ethanol flow was adjusted using a syringe pump to get the GHSV similar to the experiment with 10% ethanol.

Characterization: X-ray powder diffraction (XRD) patterns are recorded using a Huber G670 powder diffractometer and Cu-Kα radiation (λ = 1.54056 nm). The diffraction patterns are recorded from 2θ = 5-100°. A Micrometrics 3Flex physisorption instrument is used to record the nitrogen adsorption-desorption isotherm at 77K. The total surface area is determined by the BET method, the total pore volume is determined from a single-point read at 0.95 p/p₀, the microporous volume is calculated from the t-plot and the pore-size distribution are calculated according to the BJH method. Prior to physisorption analysis, the samples are degassed at 200 °C in vacuum for overnight. Scanning electron microscopy (SEM) analysis is performed using a QUANTA FEG 400 SEM instrument and transmission electron microscopy (TEM) analysis is performed using a Tecnai T20 instrument operated at 200 kV. Prior to the analysis, the samples are directly dispersed on a lacey carbon grid. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis is performed on an aberration-corrected JEOL ARM300CF instrument operated at 300 kV. X-ray photoelectron spectroscopy (XPS) is carried out using an angle-resolved XPS instrument Thermo Scientific™ K-Alpha™ spectrometer. All XPS spectra were collected on reduced catalysts which were exposed to air during transfer sample preparation.

The Cu loading is determined by inductively coupled plasma optical emission spectroscopy using Thermo Scientific™ iCAP™ 7200 ICP-OES. Samples (20 mg) are first treated with 20 mL of aqua regia to dissolve the Cu and then diluted accordingly. The concentration is determined from a calibration line made from a commercial ICP standard. The elemental composition of the mesoporous N-doped carbon support is determined with a Thermo scientific FlashSmart™ Elemental Analyzer. The reduction temperature of the supported Cu nanoparticle are analyzed by temperature-programmed reduction (H₂-TPR) using a Micromeritics Autochem-II instrument. Samples are heated up to 500 °C at a ramp of 10 °C per minute in 5% H₂ in Ar gas flow (50 mL/min). The H₂ consumption is monitored using a thermal conductivity detector (TCD). A cold trap with dry ice is used to trap the water formed during the reduction with H₂. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is performed on a Thermo Nicolet 6700 FTIR using a reactor and Praying Mantis diffuse

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reflectance accessory from Harrick Scientific Products. Prior to the analysis, the catalysts are mixed with KBr. The catalyst is then reduced at a temperature of 450 °C for 2 hours followed by a collection of background IR spectra under a flow of N₂. After cooling to 50 °C the N₂ is bubbled through ethanol to introduce the reactant into the reactor. IR spectra are then collected in a temperature range between 50 – 300 °C. Spectra are recorded continuously every 30 seconds until saturation of ethanol on the surface of the catalysts. The flow of ethanol is stopped afterwards followed by passing N₂ on the catalyst surface. Spectra are recorded for every 30 seconds for around 20 to 30 minutes during this process. The same procedure is repeated for temperature 100, 200, 300 and 350 °C. Spectra of pure ethanol on KBr pellet is also recorded in order to differentiate between the DRIFTS peaks of gaseous ethanol and the ethanol on catalyst surface.

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Entry for the Table of Contents

Here, we investigate the catalytic dehydrogenation of bioethanol to acetaldehyde using Cu nanoparticles supported on different N-doped ordered mesoporous carbons. Our study shows that N-doping has a significant effect on the dispersion of the Cu nanoparticles and that the highest content of N results in the highest catalytic activity and stability. At 260 °C, the best catalyst results in >99% selectivity and a STY of 175 molacetaldehyde/molCu/h.

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