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Highly dispersed metal carbide over ZIF-derived pyridinic-N doped carbon for CO₂ enrichment and selective hydrogenation

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Abstract: CO₂ catalytic conversion to chemicals is a critical issue for energy and environmental. Among them, converting CO₂ to CO has been regarded as a significant foundation to generate a series of liquid fuels and chemicals in a large scale. In this work, M/ZIF-8-C (M= Ni, Fe, Co and Cu) with highly dispersed metal carbide was prepared for CO₂ selective hydrogenation. Under the same conditions of metal loadings, CO2 hydrogenation activity to CO follows the order: Ni/ZIF-8-C≈Fe/ZIF-8-C>Co/ZIF-8-C>Cu/ZIF-8-C. These catalysts are composed of carbide or metal supported on pyridinic N structure. ZIF-8-derived pyridinic nitrogen and carbide favor CO₂ adsorption while dispersed Ni or Fe carbide and metal species serve as an active site for CO₂ hydrogenation. Extraordinary catalytic performance of Ni supported catalyst results from high dispersion of metal and exposure of carbide. Based on highsensitivity low-energy ion scattering (HS-LEIS) and line scan results, density functional theory (DFT) was used to understand reaction mechanism of CO₂ selective hydrogenation over Ni/ZIF-8-C. The result presents that product CO derives mainly from the direct cleavage of C-O bond in CO₂* rather than decomposition of COOH*. CO* desorption energy on Ni/ZIF-8-C is lower than that for further hydrogenation and dissociation. Comparison Ni/ZIF-8-C with ZIF-8-C indicates that synergy effects of highly dispersed metal or carbide and weak CO adsorption result in high CO selectivity for CO2 hydrogenation.

Introduction

Efficient utility of carbon dioxide, as a cheap and renewable carbon resource, has become an important topic for the

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greenhouse effect and energy conversion through a thermal catalytic hydrogenation, photocatalysis or electrocatalysis process.^[1,2] Valuable chemicals from CO₂ conversion include formic acid,^[3] methanol,^[4] hydrocarbons^[5] and carbon monoxide.^[6,7] Since thermocatalytic CO₂ conversion via CO can produce a bunch of liquid fuels and chemicals massively through existing technologies, such as methanol and Fischer-Tropsch synthesis,^[8-11] CO₂ selective hydrogenation to CO has recently received great attentions.

At present, catalysts for this reaction mainly involve supported Rh, Pt, and Ru^[12-14] and Cu, Co, Ni.^[15-18] The base metal catalysts are favored due to a relatively low cost. For example, Gonçalves et al. reported that highly dispersed nickel supported on silica synthesized by magnetron sputtering deposition method shows high activity and selectivity for CO synthesis.^[11] Additionally, highly dispersed Cu on β -Mo₂C also demonstrated the superior activity for CO₂ hydrogenation to CO.^[16]

As we all known, heterogeneous catalytic reaction process involves diffusion, adsorption and surface reaction of reactants and desorption and diffusion of products. However, a large number of studies on CO₂ catalytic conversion have generally focused on designing and synthesizing active sites for CO₂ hydrogenation. By comparison, reactant adsorption/product desorption in heterogeneous catalytic process has been considered scarcely. Adsorption of reactants on the catalyst surface is a prerequisite to further catalytic reaction. Using the adsorbents, metal carbide or pyridinic-N doped carbon, which can capture and enrich reactants, is beneficial to the more occurrence of subsequent catalytic conversion. For hydrogenation, CO₂ enrichment on catalysts also can overcome its low solubility in aqueous solution to some extent when CO2 is converted.^[19] On the other hand, to obtain high yield, the generated product should be apt to desorb in time from the surface of catalysts to avoid further reactions. That is to say, desorption energy of CO* is relatively lower than that of other reactions,^[20] while in contrast, hydrogenation activity is moderate in this case. The d-band center shift tremendously influences the energy for dissociative adsorption of adsorbents.^[21] If the surface atoms undergo compressive strain force, the d-orbital overlap increases and d-band center drops. Thus, surface atom can weakly bind with adsorbents, even resulting in them release. To achieve compressive strain force between metals, certain dissimilar metal with the larger radii is required to introduce into parent metal. Based on these principles, designed catalyst for CO₂ hydrogenation to CO might be composed of dissimilar metal and alkaline component.

The catalyst performances in the reversible water gas shift (RWGS) reaction are tremendously affected by the particle size of metal. Large metallic particles or aggregates generally might decrease the selectivity of RWGS and contribute to produce

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more CH4. [12] Metal-organic frameworks (MOFs), constituted of the metal ions or clusters and organic ligands, [22, 23] provide the versatile and abundant choices to design and construct the nanostructures. It has been proved that MOFs are effective templates or precursors for the synthesis of porous transition metal materials. For adsorption, zeolitic imidazolate framework-8 (ZIF-8) treated by ammonia or ethylene diamine has showed high CO₂ adsorption capacity due to the more amounts of basicity.^[24-26] For catalytic hydrogenation, Hu et al. synthesized Fe₂O₃ supported ZIF-8 or MIL-53 (AI) for CO₂ hydrogenation to hydrocarbons.^[5] Maina et al. prepared the TiO₂ and Cu-TiO₂ doped ZIF-8 materials to efficiently photocatalyze CO2 conversion to methanol and CO.[27] In the meanwhile, these studies also confirm that base metal can be efficiently dispersed in MOF-derived catalysts from conventional preparation methods.[28]

In this work, trigged by CO₂ adsorption capacity and hydrogenation performance of MOF based material, we synthesized transitional metal (Fe, Co, Ni and Cu) supported alkaline ZIF-8 catalysts for CO₂ hydrogenation. Results show that Ni/ZIF-8-C shows high catalytic performance for CO2 hydrogenation to CO due to highly dispersion of metal and carbide. We mainly focus on the nature of high catalytic performance of Ni/ZIF-8-C. Study indicates that pyridinic nitrogen and metal carbide can capture and enrich CO₂ while at the same time the later can also serve as an active site for the CO₂ hydrogenation. Based on the characterizations, DFT calculation was conducted to understand reaction mechanism of CO₂ selective hydrogenation to CO over Ni₃ZnC_{0.7} of Ni/ZIF-8-C. Results showed that in comparison with CO* hydrogenation and dissociation, the lower desorption energy accounts for high CO selectivity. The synergistic effect of alkaline ZIF-8 carrier, transitional metal carbide dispersed and weak CO adsorption brings about the outstanding selectivity for CO₂ hydrogenation to CO. The successful design and synthesis of multifunctional catalysts are helpful to CO₂ catalytic conversion in a large scale.

Results and Discussion

Physiochemical characterizations

Figure S1 shows that XRD result of the as-obtained ZIF-8, which has the similar characteristic peaks to simulated pure phase.^[29] After calcination treatment, diffraction peaks for ZIF-8-C shift towards higher 20 values in comparison with ZIF-8, indicating that calcination at high temperature leads to ZIF-8 lattice shrinking under the conditions of maintaining the crystal structure. SEM (Figure S2) also presents that the morphology of the as-obtained ZIF-8-C through pyrolysis process inherits the structure of ZIF-8 to some extent. By comparison, there are numerous small particles distributed homogeneously on M/ZIF-8-C.

After impregnating the solution of base metal salt, all the asprepared samples demonstrate characteristic peaks of 31.7° , 34.4° , 36.2° relative to (100), (002), (101) of ZnO phase (JCPDF#89-0510)^[30] in Figure 1. Additionally, the characteristic peaks for Ni/ZIF-8-C at 42.8°, 49.8° and 73.1° are assigned to (111), (200) and (220) reflections of cubic Ni₃ZnC_{0.7} (JCPDF#28-0713),^[30] whereas Fe/ZIF-8-C and Co/ZIF-8-C display the diffraction peaks corresponding to (111) of Fe (JCPDF#06-0696), (031) of Fe₃C (JCPDF#35-0772), (111) and (200) facets of Co (JCPDF#15-0806) and (103) of Co₃C (JCPDF#26-0450), respectively. These data indicate that M/ZIF-8-C (M=Ni, Fe and Co) catalysts are composed of Ni₃ZnC_{0.7}, Fe and Fe₃C, Co and Co₃C, respectively, as well as ZnO crystal phase. In contrast, Cu/ZIF-8-C has only diffraction peaks ascribed to Cu (JCPDF#04-0836).



Figure 1. XRD patterns of M/ZIF-8-C catalysts.

Table 1 presents structure and composition of the supported samples. As given in Table 1, the base metal and Zn loadings are about 7.5 wt.% and 24.0 wt.% in all as-prepared M/ZIF-8-C catalysts, respectively, which means that all the catalysts possess the similar metal contents.

Table 1. Physiochemical characterization result of M/ZIF-8-C catalysts							
catalyst	Metal loading/%	Zn content/%	Particle size [a]/nm	C/N[b] /mole ratio			
Ni/ZIF-8-C	7.38	23.94	10.50	2.09			
Fe/ZIF-8-C	7.60	24.62	13.10	2.06			
Co/ZIF-8-C	6.85	25.31	17.70	2.16			
Cu/ZIF-8-C	7.61	24.15	19.80	2.02			

[a] The data are estimated by the Scherrer's equation from XRD results [b] C/N ratio comes from element analysis

To depict the alkaline properties on catalyst surfaces, CO₂-TPD of M/ZIF-8-C and ZIF-8-C catalysts were presented in Figure 2a. The peak around 110 °C originates from the weak alkaline site while that in the range from 450 °C to 750 °C, corresponds to the strong one.^[31] The ZIF-8-C possesses the highest peak of CO₂ desorption among all the samples. This was because alkaline sites are associated with the N–H species in the ZIF-8,^[24, 32] which may partially decompose due to catalysis of base metal in calcination process. Element analysis also

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shows that the molar ratio of C/N is about 2.1 in M/ZIF-8-C (Table 1), a little higher than the imidazole-derived carbon to nitrogen ratio 2. It is known that chemisorption and activation of reactants are prerequisite to catalytic reaction. The addition of ammonia in synthesis process contributes to the increment of the alkalinity of catalysts, rendering adsorption and conversion of reactant CO₂ easier. Moreover, with the addition of base metal, metal carbide, corresponding to desorption peak at 375–627 °C, ^[33] is formed dramatically accompanied by decreasing in the N-H species. Therefore, adsorption of CO₂ over M/ZIF-8-C partially derives from the existence of metal carbide. ^[34]

The N 1s XPS spectra of all the catalysts (Figure 3) can be deconvoluted into three peaks at 398.50, 399.08 and 400.99 eV, assigned to pyridinic, pyrollic and graphitic N species or N interacting with metal.^[35] In comparison with XPS spectra of N1s in ZIF-8-C, relative decreasing in pyridinic-N of M/ZIF-8-C leads to the lower alkalinity sites.^[24] This is consistent with CO₂-TPD results. XPS of Ni 2p in Figure S3 shows the coexistence of Ni⁰ and Ni²⁺ in Ni/ZIF-8-C.^[36]



Figure 2. (a) $\rm CO_2\text{-}TPD$ curves of ZIF-8-C and M/ZIF-8-C catalysts; (b) Raman spectrum of ZIF-8-C and M/ZIF-8-C catalysts.

The Raman spectrum was conducted to understand the existence of carbon and nitrogen (Figure 2b). The typical D bands at 1320 cm⁻¹ and G bands at 1570 cm⁻¹ on all the catalysts are associated with the sp3 defect sites and bond stretching of all sp2-bonded pairs, including C–C and N–C,^[35] respectively. The I_D/I_G of ZIF-8-C, Ni/ZIF-8-C, Fe/ZIF-8-C, Co/ZIF-8-C and Cu/ZIF-8-C are 0.823, 0.804, 0.793, 0.778 and 0.761, respectively. Compared with ZIF-8-C, the lower ratio of the peak intensity for M/ZIF-8-C is due to decreasing in defects from N doping and further graphitization in calcination process.



Figure 3. XPS spectra of ZIF-8-C and M/ZIF-8-C sample of N 1s.

High-resolution transition electron microscopy (HRTEM) microphotographs of Ni/ZIF-8-C (Figure 4) were used to further investigate the size and ingredient of nanocrystalline Ni₃ZnC_{0.7}. The histogram of the nanoparticles shows that the nanoparticle size is about 9.64 nm (Figure 4a). Line scan results show that the abundant elements of the nanoparticle are Ni and Zn (Figure 4b) and contents of them increase simultaneously. Additionally, there is consensus on the change of carbon and nitrogen contents regardless on the surface or surrounding of Ni₃ZnC_{0.7}. The interplanar spacing of 0.21 nm is corresponding to (111) lattice planes of Ni₃ZnC_{0.7} on Ni/ZIF-8-C (Figure 4c, d). Energy dispersive spectroscopy (EDS) element mapping data (Figure S4) for Ni/ZIF-8-C further demonstrate that loadings of Ni and Zn vary simultaneously as well as C, O and N element. These results confirm again the existence of Ni₃ZnC_{0.7} over Ni/ZIF-8-C, consistent with the XRD tests. Notably, Ni₃ZnC_{0.7} is not highly crystalline in TEM microphotographs though obvious XRD diffraction peaks are observed for Ni/ZIF-8-C. The more harsh

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calcination temperature (for example 650°C for 2h) was required to test the effect of the highly crystalline of Ni₃ZnC_{0.7} on catalytic performance. By comparison, catalytic performance of Ni/ZIF-8-C with the highly crystalline is the lower than Ni/ZIF-8-C in this work (Figure S5). This might be ascribed to not only agglomeration of particles and the formation of Ni metal phase, but also further decrement of surface area due to the loss of carbon and nitrogen element. In addition, uncalcined Ni/ZIF-8-C without Ni₃ZnC_{0.7} crystalline phase also has the lower catalytic results than Ni/ZIF-8-C (Figure S5). Therefore, appropriate crystalline benefits high dispersion of Ni₃ZnC_{0.7}.



Figure 4. (a) TEM image of Ni/ZIF-8-C, (b) TEM-EDS line scan on $Ni_3ZnC_{0.7}$ and (c, d) HRTEM images of Ni/ZIF-8-C.

To further clarify the catalyst structure, high-sensitivity lowenergy ion scattering (HS-LEIS) was conducted. LEIS only probes the outermost atomic layer.^[37] If there is only a carbon layer on metal particles, then no Ni and Zn signal will be observed. HS-LEIS analysis (Figure 5) shows that metal elements present along with carbon and nitrogen on the outer surface layer or below the surface layer 2.0 nm for Ni/ZIF-8-C. Combining the above analysis, we believe that Ni₃ZnC_{0.7} is supported rather than wrapped by N-doped carbon.

Catalytic performances

The activity and selectivity of M/ZIF-8-C toward hydrogenation of CO₂ were evaluated in the temperature range between 320 °C and 420 °C and under the conditions of CO₂/H₂ (1:4) at 101.32 KPa. For comparison, ZIF-8-C and ZnO/C were also used to catalyze CO₂ conversion (Figure 6). Over all the catalysts, CO₂ conversion generally increases with the increase of temperature, indicating that high temperature is favorable to conversion of CO₂. By comparison with metal supported catalysts, CO₂ conversion on individual ZIF-8-C or ZnO/C is negligible. This

result implies that it is necessary to the existence of base metals on the surface of catalysts. Among all supported catalysts, Ni/ZIF-8-C and Fe/ZIF-8-C show high activity towards CO2 hydrogenation to CO and CO₂ conversion are 43.81% and 43.82% at 420 °C accompanied with CO selectivity of 97.37% and 97.22%, respectively. Cu/ZIF-8-C shows the lower activity than other catalysts and CO₂ conversion is only 24.66% at 420 °C. The turnover frequencies (TOF) of CO2 about Ni/ZIF-8-C, Fe/ZIF-8-C, Co/ZIF-8-C and Cu/ZIF-8-C are 88.58 µmol*g_{Ni}⁻¹*s⁻¹ 84.48 μ mol*g_{Fe}⁻¹*s⁻¹, 60.60 μ mol*g_{Co}⁻¹*s⁻¹ and 47.48 μ mol*g_{Cu}⁻¹*s⁻¹ ¹*s⁻¹, respectively. To clarify the efficiency of ZIF-8-C based catalysts, further comparison with literatures were carried out in Table 2. Obviously, M/ZIF-8-C illustrates higher catalytic results than most of other work under studied reaction conditions. The long-run experiment shows that the catalytic performance of the Ni/ZIF-8-C catalyst remains stable with respect to both CO2 conversion and product selectivity in a stability test for 36 h (Figure 7). XRD result shows the diffraction intensity of the spent catalysts is slightly higher than the fresh ones (Figure S6). In addition, TG and DTG analysis of the ZIF-8-C and Ni/ZIF-8-C in nitrogen atmosphere were conducted to understand the stability of the MOFs (Figure S7). From Figure S7, the weight loss occurs mainly from 600 °C to 900 °C. In contrast, it is negligible in the range of 320 °C and 420 °C, at which CO₂ hydrogenation was evaluated.



Figure 5. HS-LEIS spectra (a) Ni/ZIF-8-C at 3 keV $^4\text{He}^{\star},$ (b) Ni/ZIF-8-C at 5 keV $^{20}\text{Ne}^{\star}.$

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Table 2. Comparison of CO_2 conversion and CO yield of M/ZIF-8-C with literatures for hydrogenation CO_2 to CO.							
No	Catalyst	Reaction conditions	Xco₂/ %	Y _{CO} /%	Ref.		
1	Au@UIO- 67	0.2 g, GHSV: 12000 mL h ⁻¹ g _{cat} ⁻¹ ; CO ₂ :H ₂ = 1:3, 2.0 MPa, 408 °C	30.2	28.6	38		
2	Ni/Ce-Zr-O	0.5 g, GHSV: 6000 mL h ⁻¹ g _{cat} -1 CO ₂ :H ₂ = 1:1, 1.0 Mpa, 550 °C	34.0	19.7	39		
3	NiO/CeO ₂	1.0 g, GHSV: 14400 mL h ⁻¹ g _{cat} ⁻¹ CO ₂ :H ₂ = 1:1, 1.0 Mpa, 450 °C	12.4	10.2	40		
4	Ni-IMP /nSiO ₂	12 mg, GHSV: 250000 mL h ⁻¹ g _{cat} ⁻¹ CO ₂ :H ₂ :Ar = 1:4:45, 1.0 Mpa, 420 °C	42.5	34.0	11		
5	BaCe _x Zr _{0.8} _{-x} Y _{0.16} Zn _{0.04} O ₃	0.5 g, GHSV: 2400 mL h ⁻¹ g _{cat} ⁻¹ CO ₂ :H ₂ = 1:1, 1.0 Mpa, 600 °C	36.3	34.8	41		
6	K-Pt /mullite	0.1 g, GHSV: 30000 mL $h^{-1} g_{cat}^{-1}$ CO ₂ :H ₂ :Ar = 45:45:10, 0.1 Mpa, 425 °C	20.9	20.7	42		
7	Pt/TiO ₂	0.5 g, GHSV: 6000 mL h ⁻¹ g _{cat} ⁻¹ CO ₂ :H ₂ :Ar = 45:45:10, 0.1 Mpa, 400 °C	21.0	20.8	12		
8	Ni/ZIF-8-C	0.2 g, GHSV: 15000 mL h ⁻¹ g _{cat} ⁻¹ ; CO ₂ :H ₂ = 1:4, 0.1 MPa; 420 °C	43.8	42.7	This work		
9	Fe/ZIF-8-C	0.2 g, GHSV: 15000 mL h ⁻¹ g _{cat} ⁻¹ ; CO ₂ :H ₂ = 1:4, 0.1 MPa; 420 °C	43.8	42.6	This work		

a 50 Ni/ZIF-8-C Fe/ZIF-8-C 40 Co/ZIF-8-C Cu/ZIF-8-C CO, conversion(%) ZIF-8-C 30 ZnO/C 20 10 0 320 340 360 380 400 420 Temperature(°C) b 40 100 Ni/ZIF-8-C 90 CO selectivity(%) CH, selectivity(%) Fe/ZIF-8-C Co/ZIF-8-C 80 Cu/ZIF-8-C 20 ZIF-8-C ZnO/C 70 10 60 0 50 380 420 320 340 360 400 Temperature(°C)

Figure 6. (a) CO₂ conversion and (b) CO, CH₄ selectivity of M/ZIF-8-C. Reaction conditions: 0.2 g of catalyst, 320 °C-420 °C, $CO_2/H_2 = 1:4$, GHSV =15000 mL/(g.h).

Ni is dispersed in the form of Ni₃ZnC_{0.7}, in which Ni has two types of valences, Ni⁰ and Ni²⁺. This implies that Ni in Ni₃ZnC_{0.7} is highly dispersed in the form of similar single atom in catalysts despite 9.64 nm particle size of Ni₃ZnC_{0.7}. In turn, base metal in Fe/ZIF-8-C and Co/ZIF-8-C reduced exsits in the form of individual carbide and metal crystal particle despite the smaller particle size of Fe/ZIF-8-C. Obviously, the disbenifit of this existence form brings about the relatively lower dispersion of active sites than Ni/ZIF-8-C. Moreover, the number of exposed carbide from CO₂-TPD results after reduction is also in accordance with the order: Ni/ZIF-8-C>Fe/ZIF-8-C>Co/ZIF-8-C>Cu/ZIF-8-C. Combining with catalytic performances, we believe that hydrogenation activity of Ni/ZIF-8-C and Fe/ZIF-8-C result from higher dispersion of metal species and the more exposure of carbide.



Figure 7. CO_2 conversion and CO and CH_4 selectivity of Ni/ZIF-8-C with timeon-stream. Reaction conditions: 0.2 g of catalyst, 380 °C, CO_2/H_2 = 1:4, GHSV =15000 mL/(g.h).

Reaction mechanism of CO₂ hydrogenation

It's generally accepted that CO2 methanation occurs over the traditional Ni supported catalysts.^[43, 44] However, a large amount of CO product was obtained for CO2 hydrogenation over Ni/ZIF-8-C. CO₂ hydrogenation to CO can proceed via the decomposition of carboxyl intermediate (COOH*) from CO2 hydrogenation into CO* and OH*. Alternatively, CO2* can dissociate into CO* and O* via the direct C-O bond cleavage pathway. The obtained CO* is consumed through three ways. It is either hydrogenated to COH* or CHO*, or desorbed into CO gas, or further dissociated to C* and O*. CO selectivity is primarily determined by the relative rate of these three processes. When the rate of CO* desorption is faster than the others, a large amount of CO product is generated for CO₂ hydrogenation. Conversely, when CO* is strongly bound, hydrogenation or dissociation likely occur than desorption.^{[20, 45} ^{46]} Thus, the catalyst is likely to show lower CO selectivity.



To understand the essence of high CO selectivity, DFT calculations were conducted for CO2 selective hydrogenation reactions over Ni₃ZnC_{0.7} supported N-modified carbon (Figure 8). Direct CO2* dissociation to CO* has lower activation energy than COOH* decomposition. Product CO mainly comes from the direct cleavage of C-O band in CO₂*. Activation energy of CO* hydrogenation to COH* or CHO* is 1.82 or 1.45 eV for direct hydrogenation and that of CO* dissociation to C* and O* is 2.68 eV, respectively, while that for desorption of CO* is 1.36 eV. By comparison, energy required for desorption CO* is lower than hydrogenation and decomposition, indicating that CO* is facile to desorb from the surface rather than further conversion. Better routes to yield CO are as follows: adsorbed CO2* firstly dissociates into CO* and O*, which is further hydrogenated via OH* to H_2O^* . After that, CO* releases from the surface of catalysts into gas phase CO. This accounts for high CO selectivity over Ni/ZIF-8-C. As the radius of Ni atom is smaller than Zn, with the Zn addition, the surface atoms undergo compressive strain force in Ni₃ZnC_{0.7} and the d-orbital overlap increases.^[21] This weakens the adsorption strength of CO* with Ni₃ZnC_{0.7}. In situ CO FTIR result also confirmed that the peak position of the linear-bonded CO over Ni/ZIF-8-C has higher wavenumber than the traditional CO adsorption, about 2100 cm ¹ (Figure S8). This result indicates that the CO-catalyst bond is elongated and the intensity of CO adsorption is relatively weak on Ni/ZIF-8-C.

Herein, the activation of the adsorbed CO₂ occurs on N-doped carbon or metal carbide along with H₂ activation over carbide species surrounded by N-doped carbon. Consequently, hydrogen activated by metal carbide reacts with dissociated oxygen atom from CO₂ to convert into H₂O^{*} and CO^{*}. Finally, generated CO^{*} desorbs from the surface of catalysts into CO in gas phase. Thus, high CO selectivity is obtained from CO₂ hydrogenation over Ni/ZIF-8-C.



Conclusions

Combining CO₂ adsorption properties of ZIF-8 and uniformly dispersed metal and carbide, M/ZIF-8-C was prepared from precursor solution of base metal impregnating calcined ZIF-8. Under the conditions of the similar metal loadings, Ni/ZIF-8-C and Fe/ZIF-8-C present higher catalytic activity for CO2 hydrogenation to CO than Co/ZIF-8-C and Cu/ZIF-8-C. Dispersed Ni or Fe species in catalysts catalyzes hydrogenation while pyridinic nitrogen and carbide interacts as an adsorbent for CO2 enrichment and activation. DFT calculation shows that generated CO is mainly from direct CO₂* dissociation. Since CO* generated is apt to desorb from the surface of Ni/ZIF-8-C in comparison with CO* further reactions, high CO selectivity is obtained. Comparison of catalytic performances over Ni/ZIF-8-C with ZIF-8-C in the absence of nickel shows that synergistic effect among dispersed metal carbide and weak CO adsorption accounts for high CO selectivity from CO₂ hydrogenation. These results will benefit to design and synthesize various catalysts involving CO₂ conversion and utility to chemicals, such as hydrocarbons and cyclic carbonate.

Experimental Section

Calculation Details

Density functional theory with empirical dispersion corrections (DFT-D) calculations was executed to evaluate reaction mechanism of CO₂ selective hydrogenation on the periodic Ni₃ZnC_{0.7}/C₅N₁ surface (see Calculation section in Supporting Information for detail). The specific calculation details were given in literature.^[47] For the surface structure, two atomic layers of Ni₃ZnC_{0.7} were cleaved at the 2D C₅N₁ plane. By the calculation of adsorption energy, Ni₃ZnC_{0.7}/C₅N₁ features are clarified. The

linear synchronous transit (LST) calculation was achieved according to literature. $^{\left[48\right] }$

Synthesis of ZIF-8 and ZIF-8-C

ZIF-8 was synthesized by the impregnation method according to the literature.^[29] Typically, 5.2520 g zinc acetate dihydrate was first dissolved in 24.0 mL deionized water and 3.2850 g 2-methyl-1H-Imidazole was dissolved in 48.5 mL ammonia solution (25 wt.%). Then, zinc acetate solution was added dropwise into 2-methyl-1H-Imidazole one. The as-obtained sample was vigorously mixed at room temperature for 4 h before centrifugation and wash with deionized water. Subsequently, the samples were dried at 65 °C in air overnight. The resulted sample is denoted as ZIF-8. Then it was calcined at 450 °C for 1 h under N₂ at a heating rate of 5 °C/min and 550 °C at a heating rate of 2 °C/min for another 1 h. The resulted sample is ZIF-8-C.

Preparation of M/ZIF-8-C and ZnO/C

A series of 10% M/ZIF-8-C catalysts were prepared by ethanol solution of Ni(acac)₂ (Fe(acac)₃, Co(acac)₃ or Cu(acac)₂) impregnating ZIF-8-C. Typically, 0.7224 g Ni(acac)₂ was dissolved in 150.0 mL ethanol to form a dark green solution at 60 °C. Subsequently, 1.5000 g ZIF-8-C was dissolved into the above solution under continuous agitation. After stirred for 16 h under air atmosphere, the products were collected by rotary evaporation at 60 °C. Finally, the obtained claybank solid, 10% Ni/ZIF-8-C precursor was dried at 60 °C in air overnight, after that, the sample was calcined at 450 °C for 1 h and 550 °C for another 1 h under inert atmosphere (N₂) to obtain Ni/ZIF-8-C. The ZnO/C catalyst was prepared through calcination the ZIF-8 at 450 °C for 1 h under air atmosphere.

Catalyst characterization

Analysis of metal element in the catalysts was performed on inductive couple plasma (ICP, Agilent ICP-MS 4500-300). Carbon and nitrogen element analysis was carried out with an elemental analyzer (Vario ELIII, Elementar). X-ray diffraction (XRD) patterns were recorded by a Rigaku Ultima IV diffractometer with Cu Ka radiation at 35 kV, 15 mA at a scan rate of 10°/min. Prior to the measurement, the sample was prereduced with H₂ (99.999%, purity) at 450 °C for 2 h and exposed in the 2 vol.% O_2/N_2 for 1 h. Scanning electron microscope (SEM) images of catalysts were acquired with a Hitachi S-4800 FE-SEM. High-resolution transition electron microscopy (HRTEM) images were collected using a TECNAI F30 (300 kV) instrument. Energy dispersive spectroscopy (EDS) line-scan profile result and elemental mapping were also obtained by using a TECNAI F30 electron microscope. X-ray photoelectron spectroscopy (XPS) tests were obtained by the PHI Quantum 2000 Scanning ESCA Microprobe equipment.

High sensitivity-low energy ion scattering (HS-LEIS) tests of the samples were conducted on an Ion-TOF Qtac100 lowenergy ions scattering analyzer with a 20 Ne⁺ beam energy of 5 keV and a 4 He⁺ beam energy of 3 keV. Prior to the test, the catalysts were reduced at 450 °C for 2 h with H₂. The carbon dioxide temperature-programmed desorption (CO₂-TPD) was conducted on a Micromeritics Autochem II 2920 instrument. Prior to the measurement, the sample was prereduced with 50 vol.% H₂/N₂ at 450 °C for 2 h. When the sample was cooled to 50 °C, the gas flow was switched to CO₂ (99.99%, purity) for adsorption. After flushed with argon, the sample was heated up for CO₂ desorption. Raman spectrum measurements were carried out using a Raman spectrometer (Model 2000, Renishaw, UK). Prior to the measurement, the sample was prereduced with H₂ (99.999%, purity) at 450 °C for 2 h and exposed in the 2 vol.% O₂/N₂ for 1 h. CO Fourier transform infrared spectroscopy (CO-FTIR) of the catalysts was in situ collected in a reactor cell placed in a Bruker Vertex 70 FTIR spectrometer.

Catalytic reactions

The CO₂ hydrogenation performances over M/ZIF-8-C catalysts were evaluated with a fixed-bed reactor under atmospheric pressure. Typically, 0.2 g catalyst was loaded into a quartz reactor (i.d.13 mm). Prior to the catalytic testing, the catalyst was pretreated at 450 °C for 2 h with H₂. In catalytic reaction process, the feed gas containing 20 vol.% CO₂, 80% vol.% H₂ was introduced with a flow rate of 50 mL/min. K-type thermocouples at the central axis and the outside of the reactor were tested and controlled the reaction temperature, respectively. The effluent gas products were analyzed by an online gas chromatograph (GC9010) with two columns, Porapak Q and Molecular Sieve 5Å and a thermal detector. The turnover frequency of CO₂ (TOF, defined as moles of CO₂ converted per g of M in the catalyst per second) was calculated on the basis of CO₂ conversion.

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Conflicts of interest

There are no conflicts to declare

Keywords: carbide • zeolitic imidazolate framework-8 • adsorption • CO₂ selective hydrogenation • DFT

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Title

Highly dispersed metal carbide over ZIF-derived pyridinic-N

doped carbon for CO₂ enrichment and selective hydrogenation



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