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Mild-temperature hydrogenation of carbonyls over Co-ZIF-9 derived Co-ZIF*x* nanoparticle catalyst



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ABSTRACT

Benzimidazole and metal cobalt salts were employed in the synthesis of Co-ZIF-9 by solvothermal crystallization. Highly active catalysts for selective hydrogenation of carbonyl compounds were developed. The optimal nanocatalyst Co-ZIF-350 manifested remarkable activity and selectivity for the hydrogenation of cyclohexanone under mild conditions. Catalytic conversion of cyclohexanone reached the highest over the catalyst of Co-ZIF-9-pyrolyzed at 350 °C for 2 h, in which the conversion of cyclohexanone was 100 % and the selectivity of cyclohexanol was > 99 % at 50 °C. A wide scope of ketones/aromatic aldehydes could be selectively reduced to the corresponding alcohols with high yields. Importantly, the nanocatalyst Co-ZIF-350 presented good tolerance of substrates with various functional groups under mild conditions.

1. Introduction

Catalytic reduction of carbonyls (ketones and aldehydes) is one of the most important and prevalent methods in the chemosynthesis of alcohols.[1,2] The alcohols produced from the hydrogenation reaction provide more convenient potential for the synthesis of amines, esters, acetals, acids etc., which are widely used in chemical industry and pharmaceutical applications.[3-10] Furthermore, ketone compounds are one of the most common unsaturated substrates, and the reduction of which will lead to corresponding alcohols which are important intermediates in chemical industry.[11,12] Previously, there were a lot of works to show that stoichiometric methods such as alkali hydrides (LiAlH₄) and borohydrides (NaBH₄, NaCNBH₃) were successfully used to reduce a variety of aldehydes and ketones.[13-16] In spite of their respective merits, but the hydrogenation processes produced much waste, accompanied by the dangers associated with the treatment of highly reactive hydride reagents.[17] In the last few decades, the scientific researches and most industrial hydrogenation catalysts have been chiefly focused on the use of precious metals.[18-20] However, the rarity, high cost and biotoxicity of precious metals limit the sustainability of catalytic systems.[21,22] Because of above unavoidable problems in noble metal catalysts, it is of great significance to develop

environmentally-friendly non-noble transition metal-catalyzed reactions.[23-25]

Recently, the catalytic use of MOFs materials has been attracting growing interests owing to low cost, easily availability and good catalytic activity.[26–29] For instance, well-defined Fe(II) catalyst catalyzed selective reduction of aldehydes attached with fifteen functional groups in the presence of ketone and other reducible functionalities. [30] Jorge reported that silica-supported copper nanoparticles was efficient for selective hydrogenation of α , β -unsaturated carbonyl compounds to produce the corresponding saturated esters, ketones, and aldehydes in the absence of additives.[31] Furthermore, Gong et al. utilized ZIFs (ZIF-67 derived nitrogen-doped carbon nanotubes) as high-performance selective hydrogenation (SH) catalytic agent to selectively hydrogenate ketone, carboxyl, aldehyde and nitro groups of biomass derived compounds to high-value-added fine chemicals.[32]

It is noteworthy that MOFs can provide adjustable coordination space and chemically-tailored inner surface of the cavity, which can support nano-metal particles as promising catalyst carriers, especially metal nanoparticles in heterogeneous catalysis.[33–41] As an important member of MOFs, ZIFs derivatives have been widely used in catalytic hydrogenation as active catalysts due to high specific surface area, excellent stability and high dispersion of metal active sites. Yang

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reported that red phosphorus was injected into ZIF material (ZIF-67) with high surface area, which was then calcined at high temperature to obtain nitrogen heterocarbon composite supported Co_2P , with excellent catalytic activity for selective hydrogenation of nitrobenzene to aniline. [42] Guo obtained Co-based porous carbon catalysts by carbonizing the zeolite imidazolium ester skeleton Co-ZIF-67 precursor. The prepared catalyst showed excellent catalytic performance for CO_2 methanation at low temperature.[43] Li reported the synthesis of palladium nanoparticles immobilized on ZIF-67-derived magnetic porous carbon, which was applied as an effective catalyst for semi-hydrogenation of phenylacetylene under mild conditions.[44]

Recently, our group prepared Co@CN catalysts derived from ZIF-9 (synthesized by rotary crystallizaion method) material to catalyze a relatively large amount of nitroarenes up to 100 % conversion at mild conditions.[45] In this paper, a series of Co-ZIF-9 materials with hexahedral structure were synthesized by static solvothermal method. The effects of different synthesis and post-pyrolysis conditions on the structure and activity of the composite in the hydrogenation of carbonyls were discussed. This will provide a feasible method for the synthesis of alcohol chemicals with high-added-value at mild conditions.

2. Experimental

2.1. Chemical reagents

 $Ni(NO_3)_2$ ·6H₂O, Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Fe(NO₃)₃·9H₂O, benzimidazole and sodium formate (HCOONa) were ordered from Aladdin Chemicals Co. Ltd.

2.2. Synthesis of Co-ZIF-9

Co-ZIF-9 was synthesized by static solvothermal crystallization method. Typically, 26.3 mmol sodium formate and 26.0 mmol benzimidazole were added into 20 g DMF solution under stirring. Next, 6.5 mmol of $Co(NO_3)_2$ ·6H₂O was added into such solution. Thereafter, another 50 g DMF was slowly added into the above solution while stirring for another 30 min. The mixture solution was transferred to an autoclave, sealed and crystallized at temperature of $100 \sim 180$ °C for $12 \sim 72$ h. Finally, the pressure autoclave was naturally cooled to room temperature. The precipitate was collected by filtration, washed several times with deionized water, and then further washed with 95 % ethanol at a 55 °C water bath, and then filtered. The recovered solid was dried in a vacuum chamber at 80 °C overnight to receive the Co-ZIF-9 material. Similarly, other metal-ZIF-9 materials were also synthesized by this method.

2.3. Synthesis of Co-ZIF-x catalysts

Appropriate amount of Co-ZIF-9 material was put into a crucible and put it into tube furnace for pyrolysis treatment. The reduction temperature was lifted to 250, 350, 450 or 550 °C at a rate of 5 °C/min, and maintained at this temperature for 2 h in hydrogen atmosphere. The furnace was then cooled down to room temperature in hydrogen. The obtained materials were named as Co-ZIF-250, Co-ZIF-350, Co-ZTF-450 and Co-ZIF-550, respectively.

2.4. Characterization of materials

Powder X-ray diffraction (XRD) measurement was carried out on a Bruker D8A25 diffractometer operating under conditions of *CuKa* radiation (λ is 1.54184 Å) at 40 kV and 40 mA. Fourier transform infrared (FTIR) spectra were analyzed at an OPUS Fourier transform infrared spectrophotometer with the range of 400-4000 cm⁻¹. Scanning electron images (SEM) were recorded on a JEOL (JSM6700 F) with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were collected under JEOL-135 2010 F Transmission Electron Microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were collected on a Perkin-Elmer PHI ESCA system. Thermal gravimetric analysis (TGA) in N₂ atmosphere was performed on a PerkinElmer thermal analyzer. Temperature-programmed reduction using H₂ (H₂-TPR) was carried out on the TP-5076 automatic gas sorption analyzer.

2.5. Catalytic hydrogenation reactions

Catalytic hydrogenation of carbonyl compounds was completed in a 50 mL stainless steel autoclave lined with polytetrafluoroethylene. In the typical process, 15.0 mg catalyst and 1.0 mmol substrate were dispersed in 5.0 mL ethanol and then sealed in the autoclave. The pressure reactor was purged 3 times with nitrogen in order to remove the internal air and then purged 3 times with hydrogen. Finally, the reaction device was stirred at a certain reaction temperature for several hours. The liquid mixture was separated by filtration and analyzed by gas chromatograph (GC).

3. Results and discussion

3.1. Characterization of Co-ZIF-x materials

In order to prepare high performance catalytic materials, we first optimized the synthesis conditions of Co-ZIF-9 precursor, including synthesis temperature and crystallization time. In order to prepare high catalytic activity catalyst, we first optimized the synthesis conditions of the Co-ZIF-9 precursor, including crystallization temperature and crystallization time. It can be observed from XRD patterns of Fig. 1 that the crystal structure of Co-ZIF-9 was not formed at 100 °C. When the crystallization temperature was raised to 120 °C, weakly characteristic diffraction peaks of Co-ZIF-9 were generated. At the crystallization temperature of 140 and 160 °C, the characteristic diffraction peak corresponding to $2\theta = 9.1^{\circ}$, 27.5° was gradually enhanced, meaning the successful synthesis and the intact crystal structure of Co-ZIF-9 material. At the synthesis temperature of 180 °C, the characteristic diffraction peak was weakened, which showed that higher temperature (> 160 °C) was not conducive to the crystallization of the material. Therefore, the optimal crystallization temperature of Co-ZIF-9



Fig. 1. XRD patterns of Co-ZIF-9 prepared at various crystallization temperatures.



Fig. 2. XRD patterns of Co-ZIF-x.

precursor was 160 °C. Fig. S1 discussed the effect of crystallization time on the crystal structure of Co-ZIF-9 material. It can be clearly seen that when the crystallization time was less than 24 h, there were no characteristic peaks of Co-ZIF-9. When the crystallization time was \geq 36 h,

observable diffraction peaks of Co-ZIF-9 emerged. The intensity of the characteristic diffraction peaks ($2\theta = 9.1^{\circ}$ and 27.5°) gradually increased with extended crystallization time.

Fig. 2 shows the XRD patterns of the Co-ZIF-x material obtained by pyrolysis of the Co-ZIF-9 precursor at different pyrolysis temperatures. When the pyrolysis temperature was 250 °C, the Co-ZIF-9 material was partially pyrolyzed. The part of organic skeleton structure was still retained, so that the characteristic diffraction peak of Co° was hardly seen. However, when the pyrolysis temperature was higher than 350 °C, the intensity of diffraction peak disappeared totally, three diffraction peaks shown at $2\theta = 44.2^{\circ}$, 51.6° and 75.8° , belong to (111), (200) and (220) diffractions of Co° metal (JCPDS 15-0806). With the increase of pyrolysis temperature, the XRD peak intensity of the Co phase was remarkably enhanced, indicating that well-crystallized Co particles were formed. The intensity of the peak was related to the uniformity of the dispersion; the more intense the diffraction peak was, the worse the dispersion of crystalline Co particles. Obviously, the sample Co-ZIF-350 obtained at 350 °C showed that Co° particles was more uniformly disperse.

IR spectra of Co-ZIF-9 and Co-ZIF-x samples are shown in Fig. S2. When controlled the pyrolysis temperature to 250 °C, the IR spectrum of the catalyst was the same as that of Co-ZIF-9 precursor, in which the stretching vibration band of the organic group in Co-ZIF-250 was maintained. However, as the pyrolysis temperature increased to 350 °C, in the IR spectrum of Co-ZIF-x catalyst the characteristic band of the organic group disappeared. The removal of the organic linker from Co-ZIF-9 was above 350 °C, consistent with the characterization results obtained from XRD patterns in Fig. 2.

SEM images of Co-ZIF-9 with different crystallization temperatures



Fig. 3. SEM images of Co-ZIF-x with different pyrolysis temperature: a: 250 °C, b: 350 °C, c: 450 °C, d: 550 °C; and Elemental mapping of Co-ZIF-350 (e-1~e-4).

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were shown in Fig. S3. It can be seen from the figure that all Co-ZIF-9 materials are square block crystals having a side length of 15–0 µm. As the crystallization temperature increased, the regular morphology of Co-ZIF-9 was gradually strengthened. At the temperature of lower than 140 °C, Co-ZIF-9 was not crystallized completely, but when the temperature was 160 °C, the crystallization was very complete. When the synthesis temperature was lifted to 180 °C, the ligand benzimidazole was easily decomposed to affect the crystallization time on the morphology of Co-ZIF-9 is depicted in Fig. S4. With the extension of time, the block morphology of Co-ZIF-9 material gradually formed. When the crystallization time was \geq 36 h, the Co-ZIF-9 material could be successfully synthesized. It is apparent that the optimal synthesis conditions for Co-ZIF-9 in static solvothermal synthesis were 160 °C and 48 h.

The effect of reduction temperature on the surface morphology (SEM) of the catalyst was shown in Fig. 3. When the reduction temperature was lower than 250 °C, the morphology of the sample did not change much. At the temperature of \geq 350 °C, the ZIF structure changed and the surface of the material began to become defective and rough. In order to further study the morphology and microstructure of the materials, TEM images were detected in Fig. 4. As the reduction temperature was \geq 350 °C, the Co-ZIF crystal structure collapsed to form a mixture of nanoparticles and carbon nanotubes, as shown by the XRD result in Fig. 2. When the pyrolysis temperature further increased to 450-550 °C, the amount of Co nanoparticles increased, also consistent with the diffraction peaks of some Co nanoparticles formed by Co-ZIF-*x* at high pyrolysis temperature (Fig. 2). According to statistical results, the average particle sizes of Co-ZIF-350, Co-ZIF-450 and Co-ZIF-550 were 9.4, 10.8 and 13.7 nm, respectively. As observed from the elemental mapping of Co-ZIF-350, there was a good spatial overlap of C, N and Co elements, showing homogeneous distribution of Co NPs on the sample rather than simple physical mixing.

Fig. 5 showed the XPS spectra of the catalysts prepared at different reduction temperatures. When the pyrolysis temperature was 250 °C, the crystal structure of Co-ZIF-9 was roughly preserved, and the cobalt elements were basically composed of Co^{2+} ions. As the pyrolysis temperature increased to \geq 350 °C, the N in the ZIF material was greatly reduced by hydrogen to NH₃. On the other hand, one part of Co^{2+} was reduced to Co° on the surface of the material, so that the total metal ratio of Co° was gradually increased, as confirmed in the corresponding XRD patterns (Fig. 2).

The N₂ sorption analysis and the pore size distribution of the representative sample Co-ZIF-350 is shown in Fig. 6. The adsorption and desorption behavior of the sample was a typical type IV isotherm. It has a hysteresis loop when the relative pressure range is $P/P^{\circ} = 0.4-0.9$, which showed that there were mesopores in the sample and the average pore size was 3.8 nm. This sample has a specific surface area of 136.3 m² g⁻¹ as calculated by the Brunauer-Emmett-Teller (BET) method, which is typical for Co@carbon based composites. Co-ZIF-350 material has a specific surface area of 136.3 m² g⁻¹ (calculated by Brunauer-Emmett-Teller (BET) method). Hysteresis loop belongs to H₁ type,

which is a mesoporous material with relatively narrow pore size distribution, also confirmed by SEM and TEM with uniformly spherical aggregate.

As shown in Fig. 7, the thermogravimetric analysis of Co-ZIF-9 and Co-ZIF-*x* materials was tested under air atmosphere. It can be seen from the figure that the weight loss between 100 and 300 °C was attributed to the loss of water. The collapse process of the Co-ZIF structure occurred in the range of 300–450 °C. In this process, the Co species and the organic ligands were oxidized to CoOx, CO₂ and NxOy; when the temperature was higher than 450 °C, the Co species was totally converted to Co₃O₄. After being thermally treated, the final percentage of Co₃O₄ from Co-ZIF-9 precursor, Co-ZIF-250, Co-ZIF-350, Co-ZIF-450, Co-ZIF-550 was 24.7, 29.1, 74.9, 84.3 or 94.5 %.

The reducibility of Co-ZIF-x materials and the interaction between Co and the support were further characterized by H₂-TPR analysis. The reducible ability of the catalytic material and the interaction strength of each component correspond to different reduction temperature position. As can be seen in Fig. 8, the TPR profile of the Co-ZIF-9 precursor shows three different signal peaks, attributable to the structural collapse of the Co-ZIF material and the transformation of the Co species to CoO and Co°. The Co-ZIF material was firstly pyrolyzed and carbonized to form CoO and hydrocarbons, and then CoO was further reduced by H₂ in a high temperature region to Co°. For Co-ZIF-250, the TPR curve was similar to that of Co-ZIF precursor, but the H₂ reduction temperature was relatively lower than that of Co-ZIF precursor. For the samples Co-ZIF-350, Co-ZIF-450 and Co-ZIF-550, the majority of the ligand moiety had been largely dissociated during the pyrolysis process, so that those merely showed the signal peak of CoO reduced to Co°. In addition, for the samples pyrolyzed at 350, 450, 550 °C, the reduction temperature of the ZIF-derived material gradually rose with increasing the pyrolysis temperature. As a result, if the dispersion of species was lowered, the reduction temperature was increased.

3.2. Catalytic performance

3.2.1. Effect of catalysts on the hydrogenation of cyclohexanone

Table 1 showed the results of the cyclohexanone hydrogenation with different catalysts. In the catalyst screening study, Co-ZIF precursor had no catalytic activity for cyclohexanone hydrogenation. In addition, cobalt powder, CN material (obtained by filtering, washing and drying Co-ZIF-350 treated with hydrochloric acid) and Co₃O₄ (Co-ZIF-350 treated with 400 °C air for 3 h) were used as comparative catalysts. It was found that under the same reaction conditions, the hydrogenation of cyclohexanone could hardly be catalyzed by Co powder and Co₃O₄, and the conversion of cyclohexanone was only 55.8% over CN material. At the same time, the catalytic properties of nitrogen-doped carbon-supported metals such as Ni, Cu, or Fe and related materials have also been studied. The conversion on Ni-ZIF-350, Fe-ZIF-350 or Cu-ZIF-350 was only 53.5 %, 1.4 % or < 1 % at 50 °C. In contrast, Co-ZIF-350 catalyst exhibited 100 % conversion of cyclohexanone and > 99 % selectivity of cyclohexanol at 50 °C. As the reaction temperature was increased to 70 °C, Ni-ZIF-350 and Cu-ZIF-350 could



Fig. 4. TEM images of Co-ZIF-x with different pyrolysis temperatures: a: 350 °C, b: 450 °C, c: 550 °C.



Fig. 5. XPS spectra of Co-ZIF-x catalysts.



Fig. 6. N_2 adsorption/desorption isotherms and the pore size distribution of Co-ZIF-350.



Fig. 7. TGA curves of Co-ZIF-9 and Co-ZIF-x.

obtain 95.8 % and 50.0 % conversion of cyclohexanone. When the reaction temperature was increased to 100 $^\circ$ C, the conversion of cyclohexanone was only 23.5 % over Fe-ZIF-350 catalyst. Moreover,



Fig. 8. H₂-TPR profiles of Co-ZIF-9 and Co-ZIF-x materials.

Table 1

Effect of different materials on the hydrogenation of cyclohexanor	materials on the hydrogenation of cyclohexa	lrogenation of cyclohex	e hy	on tl	materials	different	of	Effect
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Catalyst	Conversion (%)	Cyclohexanol selectivity (%)
Co-ZIF-9	0	-
Со	2	-
CN	55.8	> 99
Co ₃ O ₄	0	-
Co-ZIF-350	100	> 99
Ni-ZIF-350	53.5	> 99
Ni-ZIF-350 ^a	95.8	> 99
Cu-ZIF-350	1.4	-
Cu-ZIF-350 ^a	50.0	> 99
Fe-ZIF-350	< 1	-
Fe-ZIF-350 ^b	23.5	> 99

Reaction conditions: catalyst (15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa H₂, 50 °C, 4 h. $^{\rm a}$: 70 °C, $^{\rm b}$: 100 °C.

compared with other metal catalysts reported in the literature (Table S1),[46–51] the Co-ZIF-350 catalyst in this study exhibited an excellent conversion for carbonyls under much lower reaction temperature.

The catalytic activity of different Co-ZIF-350 materials was investigated by the hydrogenation of cyclohexanone with hydrogen. It

Table 2

Effect of different cobalt sources on the hydrogenation of cyclohexanone.

Catalyst	Cobalt source	Conversion (%)	Cyclohexanol selectivity (%)
Co-ZIF-350 Co-ZIF-350 Co-ZIF-350	$Co(NO_3)_2 \cdot 6H_2O$ $CoSO_4 \cdot 7H_2O$ $Co(CH_COO)_2 \cdot 4H_2O$	100 3.5	> 99 - > 99
Co-ZIF-350 Co-ZIF-350 Co-ZIF-350 10%Co(NH ₃) ₆ Cl ₃ /SiO ₂ ^a	$Co(Ch_{3}COO)_{2}^{4}H_{2}O$ $CoCl_{2}^{6}H_{2}O$ $Co(C_{5}H_{7}O_{2})_{3}$ $Co(NH)_{6}Cl_{3}$	88.8 100 92.5 50.2	> 99 > 99 > 99 > 99 > 99

Reaction conditions: catalyst (15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa $\rm H_2,$ 50 °C, 4 h.

^a 100 °C.

can be seen from Table 2 that the conversion of cyclohexanone was 100% as using cobalt nitrate and cobalt chloride as the cobalt source. As a comparison, the cobalt sulfate was used as the cobalt source to prepare Co-ZIF-350 material, which had poor catalytic activity with only 3.5% conversion of cyclohexanone. It may be attributed to the unique stability of cobalt sulfate, which maintained the original structure of Co-ZIF-9 throughout the reduction process, difficult for the reduction of Co^{2+} to Co° catalyzing the hydrogenation of cyclohexanone. When organic cobalt salts (such as cobalt acetate and cobalt III acetoacetate) were used, the conversion of cyclohexanone by Co-ZIF-350 was 88.8 % or 92.5 %, with > 99 % selectivity of cyclohexanol. In addition, SiO₂ supported Co(NH₃)₆Cl₃ was also used as the catalyst, the conversion of cyclohexanone was only 50.2%.

Table 3 shows the effect of different ligands. As-prepared Co-ZIF-350 by N-methylimidazole ligand showed very low conversion of cyclohexanone (2.9%), indicating that the 1 st nitrogen proton in imidazole was substituted by methyl is not an efficient catalyst for cyclohexanone hydrogenation. This may be due to the weak coordination ability of N-methylimidazole, resulting in low catalytic activity. The conversion of cyclohexanone catalyzed by Co-ZIF-350 materials synthesized with 2-methylbenzimidazole, 2-methylimidazole, imidazole or benzimidazole as ligands was 39.1, 51.4, 57.9 or 100 %. The selection of the ligand ratio was very important, and benzimidazole was the best ligand to synthesize Co-ZIF-9 derived catalyst.

Fig. 9 presents the effect of crystallization temperature of the precursor (Co-ZIF-9) on catalytic efficiency of the Co-ZIF-*x* catalysts. It can be seen that the hydrogenation activity of cyclohexanone increased

Table 3

Effect of different nitrogen sources on the hydrogenation of cyclohexanone.



Reaction conditions: catalyst (Co-ZIF-350, 15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa H_2 , 50 °C, 4 h.



Fig. 9. Effect of Co-ZIF-9 crystallization temperature on the hydrogenation of cyclohexanone. Reaction conditions: catalyst (Co-ZIF-350, 15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa H_2 , 50 °C, 4 h.

before 160 °C, and then decreased with the increase of crystallization temperature. In particular, the conversion of cyclohexanone increased from 67.8 % to 100 % when the temperature was increased from 100 to 160 °C. When the crystallization temperature of the precursor Co-ZIF-9 was further increased to 180 °C, the conversion of cyclohexanone decreased to 60.7 %. As shown in Fig. 10, the crystallization time of the Co-ZIF-9 precursor also affects the catalytic activity of the Co-ZIF-350 catalyst for the hydrogenation of cyclohexanone. When the crystallization time was extended from 12 h to 48 h, the conversion of cyclohexanone increase the crystallization time to 60 h and 72 h, the catalytic activity of the obtained catalytic material for the hydrogenation of cyclohexanone remained at 100 %. Comparing comprehensively, the optimal crystallization time of Co-ZIF-x catalyst precursor was 48 h.

Fig. 11 studies the effect of pyrolysis temperatures on the hydrogenation activity of the Co-ZIF-*x* catalyst. The blank reaction (without any catalyst) did not show any activity in this system. As can be seen from Fig. 11, the hydrogenation of cyclohexanone also has no activity when the pyrolysis temperature was 250 °C. Combining with XRD



Fig. 10. Effect of Co-ZIF-9 crystallization time on the hydrogenation of cyclohexanone. Reaction conditions: catalyst (Co-ZIF-350, 15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa H_2 , 50 °C, 4 h.



Fig. 11. Effect of Co-ZIF-9 pyrolysis temperatures on the hydrogenation of cyclohexanone. Reaction conditions: catalyst (Co-ZIF-x, 15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa H₂, 50 °C, 4 h.

patterns at different pyrolysis temperatures (Fig. 2), it can be seen that at the low pyrolysis temperature, the skeleton structure of Co-ZIF remained, so there was almost no Co° particles with catalytic activity were formed. It was quite clear that the catalysts prepared at suitable pyrolysis temperatures exhibited good catalytic activity. It can be seen that the Co-ZIF-350 exhibited the highest conversion of 100% and > 99 % selectivity to the target product cyclohexanol. With the pyrolysis temperature was continuously risen from 350 to 500 °C, the conversion of cyclohexanone gradually decreased from 100 to 85.0 %. These results indicated that the content and variation of N dopant has played important roles in the hydrogenation of cyclohexanone (Fig. 7).

3.2.2. Effect of reaction conditions on the hydrogenation of cyclohexanone The hydrogenation results showed that the change in solvent significantly affected the reaction efficiency and the reaction result was shown in Table 4. The effects of different alcohols were compared according to the entry 1–4. Among the solvents tested, ethanol was the optimal one, giving 100 % conversion of cyclohexanone and > 99 % selectivity of cyclohexanol. The conversion of cyclohexanone appeared in descending order of ethanol > methanol > isopropanol > octanol. According to the entry 5–7, when ethyl acetate, methyl acetate, 1,4epoxy hexacyclic and tetrahydrofuran were used as the reaction solvents, the conversion of cyclohexanone were only 13.6, 9.5, 10.5 and 6.7 %, respectively. Obviously, the hydrogenation of cyclohexanone should be more easily performed in polar solvents. The possible explanation was that the N-doped Co-ZIF-350 catalyst has a higher affinity with polar solvents, which leads to a uniform dispersion of the

Table 4

Effec	t	of solvents	on t	he	hydrogenation	of	cyclohexanone.

Entry	Solvent	Conversion (%)	Cyclohexanol selectivity (%)
1	Ethanol	100	> 99
2	Methanol	99.1	> 99
3	Isopropanol	69.7	> 99
4	1-Octanol	26.6	> 99
5	Ethyl acetate	13.6	> 99
6	Methyl acetate	9.5	> 99
7	1,4-Dioxane	10.5	> 99
8	Tetrahydrofuran	6.7	> 99
9	H ₂ O	90.7	> 99

Reaction conditions: catalyst (Co-ZIF-350, 15 mg), cyclohexanone (1.0 mmol), solvent (5.0 mL), 1.5 MPa H_2 , 50 °C, 4 h.

catalyst in ethanol so as to improve the catalyst exposure to the reactants, consequently increasing the catalytic performance. As a comparative study, when polar solvent H_2O was used as the reaction solvent (entry 9), the conversion of cyclohexanone was 90.7 %.

The effect of the catalyst amount on the hydrogenation of cyclohexanone was also compared. As shown in Fig. S5, the change trend of the catalyst hydrogenation activity was studied when the amount of the catalyst was 5.0, 10.0, 15.0 and 20.0 mg, respectively. It can be seen from the figure that the conversion of cyclohexanone increased gradually with the increased of catalyst amount. When using 5.0 and 10.0 mg catalyst, the conversion of cyclohexanone was 56.5% and 72.5 % respectively. The conversion of cyclohexanone can be completely converted to cyclohexanol when the amount of catalyst was increased to 15.0 and 20.0 mg. Hydrogen pressure was also one of the important reaction conditions affecting the catalytic activity (Fig. S6) and the observed conversion (100 %) at 1.5 MPa was more than 1.5 times higher than at 0.5 MPa (65.0 %). When the H_2 pressure was 1.0 MPa, the conversion of cyclohexanone was 93.6 %. Therefore, the hydrogenation of cyclohexanone over Co-ZIF-350 was more sensitive to catalyst amount and H₂ pressure.

The influence of reaction temperature on catalytic activity was investigated under 30–60 °C at 1.5 MPa H_2 pressure, as shown in Fig. 12. At low hydrogen pressure of 1.5 MPa, even though the temperature raise was slightly varied from 30 to 50 °C, the cyclohexanone conversion was greatly increased from 52.3 % at 30 $^\circ C$ to 100 % at 50 $^\circ C,$ meaning significant effect of reaction temperature on reaction effect over Co-ZIF-350 catalyst. When the reaction temperature was continuously increased from 50 to 60 °C, the conversion of cyclohexanone was basically kept 100 %. The conversion trend of cyclohexanone was 52.3 % at 30 $^\circ C$ and 72.9 % at 40 $^\circ C$, respectively, while the cyclohexanone could be completely conversion to cyclohexanol by increasing the reaction temperature to 50 °C. The reaction time also has a great influence on the catalytic hydrogenation of cyclohexanone, which was shown in Fig. S7. When the reaction time was extended from 1 h to 2 h, the conversion of cyclohexanone increased from 36.2% to 73.0%, and as the reaction time was continued to extend to 3 h and 4 h, the conversion of cyclohexanone continued to increase to 80.9 % and 100 %.

The recycling experiments of Co-ZIF-350 catalyst for the hydrogenation of cyclohexanone were conducted. As observed from Fig. S8, the decreased conversion of the substrate on the catalyst was much small with recycling, but the selectivity of cyclohexanol remained unchanged. Co-ZIF-350 still displayed 85.6 % of catalytic conversion at



Fig. 12. Effect of reaction temperature on the hydrogenation of cyclohexanone. Reaction conditions: catalyst (Co-ZIF-350, 15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa H_2 , 4 h.

Table 5

Entry	Reactant	Product	Conversion (%)	Selectivity (%)
1 ^a	°	ОН	100	> 99
2 ^c	° (он	79.6	> 99
3 ^c	~ \ o	ОН	86.2	> 99
4 ^a	0	ОН	31.5	он
				(17.9%)
	CH ₃	CH3		OH CH3
				(82.1%)
5 ^b	0	ОН	93.0	> 99
6 ^c	0	но	44.7	> 99
7 ^b		НО	86.0	> 99
8 ^c	OH OH	но	68.8	> 99
		ОН		
9 ^c		но	100	> 99
	OH	Un		
10 ^d	ОН	он	27.8	> 00
10			27.0	~ 33
	OCH3	OCH3		

(continued on next page)

Table 5 (continued)



Reaction conditions: catalyst (Co-ZIF-350, 15 mg), cyclohexanone (1.0 mmol), ethanol (5.0 mL), 1.5 MPa H₂, 4 h. ^a 50 °C, ^b 70 °C, ^c 100 °C, ^d 120 °C

the fourth recycle. When the catalyst was used by the fifth recycle, the reaction time of 8 h was required to receive 100 % conversion of cyclohexanone. This indicated that the catalyst was not deactivated at all during recycling. ICP-OES analysis of reaction solutions did not detect the leaching of any metal, indicating that the leaching was not the cause of the decreased activity. The most possible reason was that the organic compounds partially covered the surface of the catalyst during the reaction to suppress the catalytic activity.

3.2.3. Hydrogenation of other aldehydes and ketones

To illustrate the catalytic applicability of the prepared Co-ZIF-350 material to other ketone and aldehyde compounds, a series of ketones and aldehydes were selectively hydrogenated, as presented in Table 5. The experimental results showed that due to the structural differences of the carbonyl groups of different ketone compounds, the conversions of isopentanone and 3-pentanone were much lower than cyclohexanone (Entry 1-3). When the substrate was 3-methyl-2-cyclopenten-1-one, which contained α , β -unsaturated carbonyl compound, the conversion of 3-methyl-2-cyclopenten-1-one was only 31.5 %, and the selectivity of the hydrogenation products 3-methyl-2-cyclopenten-1-ol and 3-methyl cyclopentanol was 17.9 % and 82.1 %, respectively (Entry 4). For the hydrogenation of benzaldehyde compounds, the effects of different substituents on the hydrogenation activity of benzaldehyde were studied (Entry 5-10). The substrate conversion was listed in descending order: 2,4-dihydroxy benzaldehyde (100 %) > benzaldehyde (93.0 %) > m-hydroxy benzaldehyde (86.0 %) > p-hydroxy benzaldehyde $(68.8 \ \%) > p$ -methyl benzaldehyde $(44.7 \ \%) > 4$ -hydroxy-2-methoxy benzaldehyde (27.8 %). For benzoic acid (Entry 11), it did not show good catalytic activity, and the conversion was only 8.1 % at 120 °C.

4. Conclusions

Co-ZIF-350 catalyst was obtained by simple pyrolysis in hydrogen using Co-ZIF precursor synthesized by static solvothermal method. The catalyst exhibited excellent catalytic performance for the hydrogenation of aldehydes and ketones to the corresponding alcohols under mild conditions. Cyclohexanone can be completely converted into cyclohexanol within 4 h at 50 °C and 1.5 MPa H₂ pressure. High catalytic activity was attributed to the in-situ synthesis of Co nanoparticles on the surface of the catalyst, which was highly dispersive. Since a large amount of Co° particles are present in the catalyst, the material has strong magnetic properties. This characteristic of the catalyst makes it easy be separated from the reaction system during recovery.

Author contributions

All authors contributed to the writing of this manuscript and approved the final version of the manuscript.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111149.

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