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Articels

Effect of Different Morphologies Induced by Solvent on ZIF-67 Derived Co@NC for Catalytic Phenol Hydrogenation

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Abstract: The Co@NC catalysts with different morphologies were prepared by two step process, solvent control growth and pyrolysis method. The polyhedral Co@NC-67P-450 catalyst has a relatively high CoN_x content and exhibits excellent phenol hydrogenation activity (conversion 96.9%) at 160 °C, 3 MPa, which is higher than that of leaf shaped Co@NC-67L-450 catalyst (conversion 75.4%). We demonstrated Co_3O_4 was reduced to the Co^0 during the reaction. Moreover, CoN_x species contribute to the superior hydrogenation activity of phenol. The Co-based catalysts can be easily recovered through the magnetic separation and performed the high stability.

 Key words: metal organic frameworks; Co-based catalyst; morphology; phenol hydrogenation

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Cyclohexanol is the starting point of many current products such as the synthesis of Nylon 66, pharmaceuticals, plasticizers and surfactants^[1–2]. Industrially, the cyclohexanol production methods mainly include selective oxidation of cyclohexane^[3], hydration of cyclohexene^[4], and hydrogenation of phenol^[5]. Among these methods, hydrogenation of phenol to cyclohexanol is particularly attractive due to its high efficiency, high atom utilization, readily available raw materials from lignin, and green technology[^{6–9]}]. Generally, the noble metal (Pd^[10–11], Rh^[12], Pt^[13], Ru^[14–15]) catalysts present superior catalytic performances for the hydrogenation of phenol. However, the high cost and venture for supply limited their practical applications, so the development of non-noble metal catalysts suitable for catalytic phenol hydrogenation is an inevitable and beneficial research direction.

Recently, the non-noble metal Co-based catalysts have exhibited good activity and selectivity for cyclohexanol in phenol hydrogenation. For example, Wang *et al.*^[16] constructed $CoO_x@CN$ porous catalysts for phenol hydrogenation and performed cyclohexanol with a 98% yield. Li *et al.*^[17] reported the CoNi alloy encapsulated in N-doped carbon matrix was employed to catalyze the hydrogenation of phenol, in which exhibited >99.9% cyclohexanol conversion and selectivity. Li *et al.*^[18] prepared N-doped porous carbon supported Co catalysts, which could achieve full phenol conversion with 100% cyclohexanol selectivity. In sum, nitrogen-doped carbon material supported Co catalysts are promising phenol hydrogenation catalysts, which the doped nitrogen can stabilize Co nanoparticles and regulate the electronic property of catalyst, subsequently improving the dispersion and catalytic activity.

In addition, Hu *et al.*^[19] prepared Co/CeO₂ catalysts with different CeO₂ morphologies as support for the hydrogenation of phenol, which indicated the CeO₂ morphology and oxygen vacancies could influence the catalytic activity. Chen *et al.*^[20]reported hollow structures of Co@HCN catalysts contribute to the superior catalytic activity for selective hydrogenation of *o*-cresol. Yuan *et al.*^[21] revealed the effect of morphology, microstructure and surface property of Ni/carbon catalysts on the catalytic performance of phenol hydrogenation. Inspired by these successes, the metal-organic framework (MOF) derived CN materials have distinct properties including surface area, pore architecture, composition and microstructure^[22–23], and the MOF material also shows excellent performance in phenolic hydrogenation^[24–25], while the effect of different morphologies of MOF on catalytic hydrogenation activity of phenol has never been studied.

Herein, we have developed a facile solvent control method for growth of the Co-based ZIF with the flat leaf-shaped (ZIF-67L) and polyhedral (ZIF-67P) morphologies. More specifically, the Co-based ZIF with different morphologies were further pyrolyzed under the argon atmosphere at high temperature forming the Co@NC catalysts, and the catalytic phenol hydrogenation activities of Co@NC catalysts were investigated. As expected, the catalyst Co@NC-67P-450 has a relatively high CoN_x content and exhibits excellent phenol hydrogenation activity (conversion 96.9%, selectivity 99.9%, 160 °C, 3 MPa, and 8 h) which is higher than that of the catalyst Co@NC-67L-450 (conversion 75.4%, selectivity 99.9%). In

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addition, ammonia synthesis was used as the probe reaction, we confirmed that CoN_x species indeed existed in the Co@NC catalyst and played an important role in phenol hydrogenation.

1 Experimental section

1.1 Materials

Cobalt nitrate (Co(NO₃)₂·6H₂O) was obtained from Xilong Scientific Co., Ltd. 2-methylimidazole was purchased at Bidepharm. Anhydrous methanol was supplied by Rionlon Bohua (Tianjin) Pharmaceutical & Chemical Co., Ltd. Phenol purchased from Chengdu Kelong Chemical Co., Ltd. The resistivity of deionized water used in the experiment was 18.25 $M\Omega$ ·cm. The purity of the gases (H₂, N₂, NH₃) used in the experiment was 99.999%.

1.2 Co-based ZIF preparation

Polyhedral shape (ZIF-67P): 3.0 g $Co(NO_3)_2$ ·6H₂O and 6.0 g 2-methylimidazole were dissolved in 40 mL of anhydrous methanol solution, respectively. The two solutions were then mixed together and stirred for 2 h at room temperature. The obtained sample was treated after standing at room temperature for 24 h, centrifuged for 1 min at 10 000 r·min⁻¹, washed with methanol three times, and finally dried in a 60 °C drying oven for 12 h to obtain ZIF-67P.

Leaf shape (ZIF-67L): 0.3 g Co(NO₃)₂·6H₂O and 0.65 g 2-methylimidazole were dissolved in 20 mL of deionized water, respectively. The two solutions were then mixed together and stirred for 3 h at room temperature. After that, the obtained solution was centrifuged for 1 min at 10 000 r·min⁻¹, washed three times with deionized water, and the resulting product was dried in a 60 $^{\circ}$ C oven for 24 h to obtain ZIF-67L.

1.3 Catalyst preparation

The prepared ZIF-67P and ZIF-67L were calcined for 4 h in a tube furnace under an argon atmosphere at calcination temperatures of 400, 450, and 500 °C, respectively, the heating rate was 5 °C ·min⁻¹. After furnace calcination, the sample is taken out and naturally cooled to room temperature, which is the catalyst used in the experiment. The samples were donated as Co@NC-67P-*T* and Co@NC-67L-*T*, where *T* refers to the calcination temperature.

The preparation of Co@AC catalyst: the activated carbon treated with nitric acid was calcined for 4 h in a tube furnace under an argon atmosphere at a calcination temperature of 450 °C and a heating rate was 5 °C min⁻¹. Then 1.3 g Co(NO₃)₂·6H₂O was dissolved in an anhydrous methanol solution, the prepared activated carbon (0.5 g) was added, impregnated and stirred at room temperature for 24 h, and the obtained sample was centrifuged at 10 000 r·min⁻¹, washed with methanol for 3 times, and dried in an oven at 60 °C. After drying, the samples were roasted in a tube furnace under H₂ for 4 h at 450 °C and the heating rate was 5 °C min⁻¹. After calcination, the sample is naturally cooled to room temperature and taken out, denoted as Co@AC catalyst.

1.4 Catalyst activity evaluation

The catalyst activity was tested by phenol hydrogenation. The reaction was carried out in a 50 mL stainless steel highpressure reactor. 150 mg phenol was dissolved in 20 mL deionized water as reaction solution and 50 mg catalyst was added. After the reactor was purged with H_2 three times to remove air, fill the reactor with 3 MPa H_2 , and then stirred for 8 h at 140, 150, and 160 °C, respectively. After the reaction, the mixture is extracted with ethyl acetate. The content of the mixture was analysed and the product was identified by gas chromatography-mass spectrometry and gas chromatography. (Agilent Technologies 5975C and 7890A, SHIMADZU Nexis GC-2030).

The performance of the catalyst was tested by using ammonia synthesis as a probe reaction. The amount of catalyst is 0.2 g for the ammonia synthesis reaction. The reaction is carried out in a fixed-bed reactor where the catalyst is loaded into a stainless steel reaction tube (Φ 0.6 mm). After the catalyst is stabilized at different temperatures for 1 h (reaction conditions: 1 MPa, 60 mL·min⁻¹, and H₂/N₂=3), the experimental data is collected by chemical titration of H₂SO₄ at known concentrations (Congo red is the indicator).

1.5 Catalyst characterization

JEM-2010 transmission electron microscopy (TEM) was used to observe the morphology and size of the samples at an accelerator voltage of 200 kV. X-ray powder diffraction (XRD) (X'pert PANalytical, Dutch) was used to analyse the crystal structure of the sample, using Cu-Ka radiation ($\lambda = 0.154050$ nm), 2θ ranges were 5°~80°. The elemental composition of the sample was examined using an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi) and the electron binding energy scale of all spectra was calibrated using C 1s at 284.8 eV. The BET surface area (S_{BET}) and pore volume (V_{Pore}) of all the samples were determined using N₂ physisorption at -196.15 °C with a Micromeritics ASAP 2020 apparatus. Thermogravimetric (TG) analysis was performed by DTG-60H analyser (Shimadzu, Tokyo, Japan) at a heating rate of 10 °C min⁻¹. The FT-IR spectral profiles of the samples were captured on a NEXUS 670 FT-IR spectrometer using manual grinding of KBr pellets. The temperature programmed reduction of H₂ (H₂-TPR) and temperature programmed desorption of NH₃ (NH₃-TPD) were performed on the Tianjin First Right Company TP-5080 Meter with a TCD detector. For the H₂-TPR, the 50 mg sample was pretreated at 300 °C in He flow (27 mL·min⁻¹) for 1 h and then cooled to room temperature. Then, the test was conducted by subjecting the sample to heating in a H₂/He (H₂, 10%) mixture flow (30 mL·min⁻¹) at a constant heating rate 10 °C·min⁻¹, and linearly heating to 900 °C. For the TPD, 100 mg sample was heated to 300 °C in a He gas flow with a flow rate of 36 mL min⁻¹, held for 1 h and then cooled to room temperature. The He purged to a stable baseline and automatically switched to 10% NH₃/He mix gas with a flow rate of 40 mL \cdot min⁻¹. The program initiates at the starting temperature, with a heating rate of 10 $^{\circ}$ C min⁻¹, gradually increases the temperature up to 900 °C.

2 Results and discussion

2.1 Characterization of ZIF-67P and ZIF-67L samples

The fabrication process of Co@NC catalyst is shown in Scheme 1. By changing the solvent, the Co-based ZIF with polyhedral and leaf shape was obtained. The morphological characterization of the synthesized ZIF-67P and ZIF-67L materials were conducted by TEM analyses. Fig. 1(a–b) show the typical TEM images of ZIF-67P and ZIF-67L *via* solvent control growth process, clearly revealing that methanol control polyhedral ZIF-67P formed with a size distribution of 500~600 nm, while a flat leaf-shaped Co-based ZIF-67L with a size of $3\sim4 \mu m$ is obtained by deionized water as the solvent. The XRD patterns of ZIF-67P and ZIF-67P, the intensity of

ZIF-67L increases significantly at 15° -25°, suggesting that the flat leaf-shaped morphology of ZIF-67L leads to the increase of specific crystal faces. Moreover, more peaks presented in ZIF-67L than that in ZIF-67P, which could be reasoned to the residual 2-methylimidazole. The FTIR spectra of 2-methyl-imidazole, ZIF-67P and ZIF-67L can be seen in Fig. 1(d). Compared with the FTIR spectra of 2-methylimidazole, the new peak at 423 cm⁻¹ in ZIF-67P and ZIF-67L can be attributed to the Co—N stretching vibration, thus it formed the chemical bond to support the ZIF-67P structure^[26]. The peaks at 1 850 and 1 598 cm⁻¹ disappeared, as well as the peaks at 2 250~3 500 cm⁻¹, which can conclude the formation of ZIF structures. Interestingly, the ZIF-67L sample exhibits a broad adsorption band ranging from 2 500~3 700 cm⁻¹ which corresponds to a non-coordinating 2-methylimidazole N—H…N hydrogen bond

and the N—H group^[27], which is in good agreement with the XRD patterns of ZIF-67L containing the residual 2methylimidazole. Fig. 1(c) shows the thermal stability of ZIF-67P and ZIF-67L in N₂ atmosphere. It can be clearly observed that the pyrolysis process of ZIF-67P and ZIF-67L is divided into three stages. The first stage (below 260 °C) is mainly related to water loss due to adsorbed water and CH₃OH. The continuous mass loss that occurs in the second stage (260~ 500 °C) is due to the thermal decomposition and beginning of carbonization of the organic ligand 2-methylimidazole^[28], which is in accordance with the XRD (Fig.1(c)) and FTIR (Fig.1(d)) results. When the temperature reaches above 500 °C, the structure of ZIF began to severely damage. Therefore, the Co@NC catalysts can be obtained at 450 °C that retains parts of ZIF structure and exposes the Co-based functional group.



Scheme1 Synthesis of Co@NC-67P-450 and Co@NC-67L-450 catalysts



Fig.1 TEM images of (a) ZIF-67P and (b) ZIF-67L; (c) XRD patterns of ZIF-67P and ZIF-67L; (d) FTIR spectra of 2-methylimidazole, ZIF-67P and ZIF-67L; (e) TG curves of ZIF-67P and ZIF-67L

2.2 Characterization of Co@NC catalysts

The Co@NC-67P-*T* and Co@NC-67L-*T* catalysts were obtained from ZIF-67P and ZIF-67L pyrolyzing at different temperatures (T=400, 450, 500 °C) under argon flow in a tube furnace. Fig. 2 shows the typical TEM images of Co@NC-67P-*T* and Co@NC-67L-*T* catalysts. It can be noted the structure of

ZIF-67P and ZIF-67L were gradually destroyed with the increase of calcination temperature. Fig. 2(a–c) show the TEM images of the prepared Co@NC-67P-*T* catalysts retains parts of the polyhedral morphology of ZIF-67P. Compared with ZIF-67L, Co@NC-67L-*T* was decomposed into small pieces after high temperature calcination (Fig. 2(d–f).



Fig.2 TEM images of (a) Co@NC-67P-400; (b) Co@NC-67P-450; (c) Co@NC-67P-500; (d) Co@NC-67L-400, (e) Co@NC-67L-450 and (f) Co@NC-67L-500

Fig. 3 and Fig. 4 show the XRD patterns and FTIR spectra of Co@NC-67P-*T* and Co@NC-67L-*T* catalysts, respectively, which further revealed that the structure of Co-based ZIF-67P and ZIF-67L gradually cracks with the increase of calcination temperature. It can be seen that Co@NC-67P-400 and Co@NC-67L-400 calcined at 400 °C retained more ZIF structure, while Co@NC-67P-450 and Co@NC-67L-450 calcined at 450 °C still observe some characteristic peaks of ZIF, indicating that the ZIF framework had not been completely pyrolyzed. With the temperature further rising to 500 °C, the ZIF structure was destroyed, which was consistent with the TEM results. Moreover, the peak appearing at 44.3° can correspond to the (111) plane of Co⁰(JCPDS: 01-1254), reflecting the formation of metal Co after calcination at 500 °C.

Fig. 5(a–b) present the high-resolution TEM images of Co@NC-67P-450 and Co@NC-67L-450 samples. The lattice spacing of 0.24 and 0.46 nm can be attributed to (111) and (311) planes of Co₃O₄, respectively. The lattice spacing of 0.21 nm in Co@NC-67P-450 belongs to the Co (111) plane, which is consistent with the XRD (Fig. 3) results, indicating that Co and Co₃O₄ exist simultaneously after ZIF-67P calcination at 450 °C. The structural parameters of the catalyst such as porosity and specific surface area were investigated by N₂ adsorption experiment. The results are shown in Table 1, Co@NC-67P-450 mainly exists in the form of mesoporous pores with relatively small specific surface area and pore volume, while Co@NC-67L-450 is mainly composed of micropores with relatively large specific surface area and pore



Fig.3 XRD patterns of (a) Co@NC-67P-T and (b) Co@NC-67L-T (T=400, 450 and 500 °C)



Fig.4 FTIR spectra of (a) Co@NC-67P-T and (b) Co@NC-67L-T

volume. Fig. 5(c–d) show the distribution of elements for the Co@NC-67P-450 and Co@NC-67L-450 catalysts. It can be seen that after calcination at 450 $^{\circ}$ C, the elements C, N, O and Co in the catalyst are evenly distributed.

Furthermore, the surface chemical states of Co@NC-67P-450 and Co@NC-67L-450 catalysts have been explored by XPS (Fig. 6). Fig. 6(b) shows the deconvolution of the Co 2p regions of Co@NC-67P-450 and Co@NC-67L-450, which is



Fig.5 HRTEM image of (a) Co@NC-67P-450 and (b) Co@NC-67L-450; Elemental mapping images of (c) Co@NC-67P-450 and (d) Co@NC-67L-450

Co 2p

-0

Co

785

-0

:=O

C=0

530

780

775

Со-О (9.4%)

Co-O (26.2%)

528

770

O 1s

Table 1 Textural parameters of Co@NC-67P-450 and Co@NC 67L 450

	and Co@NC-07L-430					
Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{Pore}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$D_{\rm Pore}/{\rm nm}$			
Co@NC-67P-450	56.6	0.042	6.80			
Co@NC-67L-450	242.7	0.790	0.43			



Fig.6 XPS spectra of Co@NC-67P-450 and Co@NC-67L-450: (a) survey spectra; (b) Co 2p; (c) N 1s and (d) O 1s

eV) and C-OH (533.3 eV), respectively (Fig. 6(d))^[35-36]. The relative contents of different Co species are shown in Table 2. It can be noted that the amount of Co-N_x in Co@NC-67P-450 (47.2%) was higher than that in Co@NC-67L-450 (33.4%). On the other hand, the amount of Co-O in Co@NC-67P-450 (22.7%) was lower than that of Co@NC-67L-450 (37.5%). In the spectrum of N 1s, the Co– N_x amount in Co@NC-67P-450 catalyst is 33.1%, which is higher than that of Co@NC-67L-450 (31.9%), which is consistent with the result of Co 2p.

H₂-TPR was used to explore the reduction behaviour of the catalysts (Fig. 7). Obviously, the reduction peak of Co_3O_4 was began at 350 °C, which is similar with the reduction peak in Co@NC-67L-450 catalyst. It can be rationally concluded Co₃O₄ was formed during the calcination process at 450 °C, which is consistent with the TEM results (Fig. 5).

Table 2 The relative contents (%, atom fraction) of different Co species

Sample	$Co-N_x$	Со—О
Co@NC-67P-450	47.2	22.7
Co@NC-67L-450	33.4	37.5

2.3 Phenol hydrogenation

The hydrogenation of phenol reaction was carried out to evaluate the catalytic activity of Co@NC-67P-450 and Co@NC-

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consisted of Co-O (780.1 eV), Co-N_x (783.3 eV), and satellite

peaks $(786.6 \text{ eV})^{[29-30]}$. Fig. 6(c) shows the N 1s spectra of the two catalysts, and the presence of pyridinic N, pyrrolic N, and graphitic N can be well observed at 398.5, 400.2, and 401.2 eV^[31-33]. According to previous studies, the peak appearing at 399.1 eV is $Co-N_x^{[34]}$. The O 1s has a broad spectral peak,



67L-450 catalysts. From Fig. 8(a), it is clearly observed that the selectivity of cyclohexanol was above 99.9%, the conversion of phenol increases with the increase of temperature (140~160 °C). Furthermore, the catalytic activity of Co@NC-67P-450 (conversion 96.9%, selectivity 99.9%) at 160 °C, 3 Mpa, which is higher than that of Co@NC-67L-450 catalyst (conversion 75.4%, selectivity 99.9%). This may be due to the amount of Co-N_x (47.2%) in Co@NC-67P-450 is higher than that in Co@NC-67L-450 (33.4%). Previously, Wang et al.^[15] explored the hydrogenation of phenol on the CoO_x@CN catalysts, and reported that the Co₃O₄ played the role in the adsorption and activation of phenol and Co⁰ was responsible for hydrogen adsorption and dissociation. However, the amount of Co-O (9.4%) in Co@NC-67P-450 is lower than that in Co@NC-67L-450 (26.2%), so CoN_x species plays an important role in the adsorption and activation of phenol. Then, the Co@NC-67P-

450 catalyst performed the high stability in recycling experiments (Fig. 8(b)). The conversion of phenol decreased only 1% in the fifth cycle. Meanwhile, the TEM results of the used catalysts show that the Co species were uniform dispersion and Co-based catalysts can be easily recovered through the magnetic separation (Fig.9). Table 3 compares the performance of Co@NC-67P-450 and previously reported catalysts for the hydrogenation of phenol to cyclohexanol. It can be found that Co@NC-67P-450 has higher phenol conversion and cyclohexanol selectivity under similar conditions.

To deeply gain insight into the effect of different morphologies on catalytic hydrogenation of phenol. XPS was employed to investigate the surface composition of the used Co@NC-67P-450 and Co@NC-67L-450 catalysts after the reaction (Fig. 10(a-c)). It can be clearly seen that the peaks of Co–O (780.1 eV, Co 2p) and Co–O (529.9 eV, O 1s) dis-





Fig.9 TEM images of used catalysts: (a) Co@NC-67P-450; (b) Co@NC-67L-450 and (c) catalysts magnetic separation

Catalyst	<i>T</i> /℃	p/MPa	<i>t</i> /h	Conv./%	Sel./%	Ref.
Co@NC-67P-450	160	3.0	8	96.9	>99.9	This work
Pd/SiO ₂	230	5.0	4	54.2	25.4	[37]
Pd/NaY	230	5.0	4	78.2	92.3	[37]
Ni ₃ Co ₁ @C/ZrO ₂	200	2.0	4	96.3	91.1	[38]
CoO _x @CN-800	150	3.0	16	98.0	>99.9	[16]
Ni-ZSM-24	150	3.0	2	94.1	50.6	[39]
Co/NC	120	2.0	3	81.3	>99.9	[18]
1Co-1Ni@NC-600	100	0.8	12	84.4	>99.9	[17]

appeared, which indicated that Co_3O_4 was reduced to the Co^0 during the reaction. Fig. 10(d) shows the XRD patterns of the used Co@NC-67P-450 and Co@NC-67L-450 catalysts. The peak at 44.3° was corresponding to the (111) plane of Co^0 (JCPDS: 01-1254), which reflects the formation of metal Co during the reaction. Combined with the reported works^[15,18], the results confirmed that the metal Co nanoparticles were responsible for hydrogen adsorption and dissociation and further reaction for the adsorption and activation of phenol. Besides, the larger CoN_x species content performed higher catalytic activity. The rich electron N can stabilize Co and regulate the electronic property of Co, and which also can form the hydrogen bond with -OH in phenol. Thus, the CoN_x species and Co^0 contribute to the superior catalytic hydrogenation activity of phenol.

Generally, CoN_x species were the high active sites for

activating N₂ and H₂ molecules for ammonia synthesis. The catalytic activity of CoN_r species were also confirmed by the ammonia synthesis as a probe reaction. Fig. 11(a) shows the ammonia synthesis activity of Co@NC-67P-450, Co@NC-67L-450, and Co/AC catalysts under conditions of 1 MPa and 340~400 °C. It can be observed that no ammonia synthesis activity of Co/AC catalyst at 400 °C and 1 MPa, while Co@NC-67P-450 (424.3 μ mol h^{-1} g⁻¹) and Co@NC-67L-450 (856.3 μ mol h⁻¹ g⁻¹) performed the high activity at 340 °C and 1 MPa. Moreover, the ammonia synthesis activity of Co@NC-67L-450 was 6 497.2 μ mol h⁻¹ g⁻¹ at 400 °C and 1 MPa, which was 1.8 times higher than Co@NC-67P-450 (3 614.1 μ mol·h⁻¹·g⁻¹). These results indicate that CoN_r species can promote the ammonia synthesis reaction. Fig. 11(b) shows the NH₃-TPD of the Co@NC-67P-450 and Co@NC-67L-450 catalysts to investigate the acidic sites and NH₃ desorption property. For



Fig.10 The high-resolution XPS spectra for (a) Co 2*p*; (b) N 1*s* and (c) O 1*s*; (d) XRD patterns of used Co@NC-67P-450 and used Co@NC-67L-450



Fig.11 (a) NH₃ synthesis rate at 340~400 °C, 1 MPa over Co@NC-67P-450, Co@NC-67L-450 and NH₃ synthesis rate at 400 °C, 1 MPa over Co@AC; (b) NH₃-TPD profiles of Co@NC-67P-450 and Co@NC-67L-450

Co@NC-67P-450 catalysts, the NH₃-desorbed temperature was 625 $^{\circ}$ C, which was higher than those in Co@NC-67L-450 catalysts (462, 580, and 617 $^{\circ}$ C). The results indicated the lower NH₃-desorption energy can enhance the ammonia synthesis activity.

On the basis of the above results, the structure-activity relationship between the catalysts and the hydrogenation of phenol reaction could be ascribed to the following reasons: firstly, different morphologies of catalysts have varied surface structures, pores, and composition (CoN_x, Co^0, Co_3O_4) , and acidic sites. Moreover, the CoN_x species contribute to the superior hydrogenation activity of phenol. Finally, the Co-based catalysts can be easily recovered through magnetic separation and perform high stability in recycling experiments.

3 Conclusions

In summary, different morphologies of Co@NC catalysts were prepared by two step process, solvent control growth and pyrolyzed under the argon atmosphere. The polyhedral Co@NC-67P-450 catalyst has a relatively high CoN_x species content and exhibits excellent phenol hydrogenation activity (conversion 96.9%, selectivity 99.9%) at 160 °C, 3 MPa, and 8 h, which is higher than that of leaf shaped Co@NC-67L-450 catalyst (conversion 75.4%, selectivity 99.9%). Additionally, Co₃O₄ was reduced to the Co⁰ during the reaction. The Cobased catalysts can be easily recovered through magnetic separation and perform high stability in recycling experiments. This study provides an efficient strategy for constructing the non-noble metal phenol hydrogenation catalysts.

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溶剂诱导法制备不同形貌 ZIF-67 衍生 Co@NC 催化剂 对苯酚加氢活性的影响

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摘要:通过溶剂控制生长和氩气气氛热解两步法制备了不同形貌的 Co@NC 催化剂,得到了具有多面体形貌的 Co@NC-67P-450 和具有叶片状的 Co@NC-67L-450. 以苯酚加氢为研究对象评价了两个催化剂的性能,在 160 ℃, 3 MPa 的条件下,环己醇的选择性均在 99.9% 以上, Co@NC-67P-450 催化剂的苯酚转化率为 96.9%,高于 Co@NC-67L-450 催化剂的 75.4%. 在反应过程中, Co₃O₄ 被还原为 Co⁰, Co@NC-67P-450 的 CoN_x 含量为 47.2%,高于 Co@NC-67L-450 (33.4%),这些共同促进了其苯酚加氢活性. 同时以氨合成为探针反应,研究了 CoN_x 对 N₂ 和 H₂ 的 催化活性,进一步证实了其对苯酚加氢活性的促进作用. 通过磁分离可以回收钴基催化剂,并表现出较高的稳定性. **关键词:** 金属有机骨架; 钴基催化剂; 形貌; 苯酚加氢