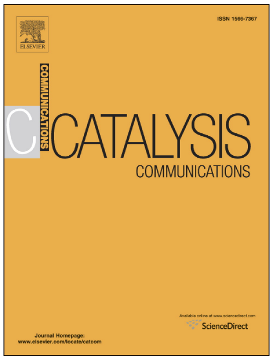

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Highly selective hydrogenation of α, β-unsaturated carbonyl compounds over supported Co nanoparticles

Pengbo Jiang, Xinlin Li, Wenbin Gao, Xiang Wang, Yu Tang, Kai Lan, Bin Wang and Rong Li*

State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China. E-mail: liyirong@lzu.edu.cn; Fax: +86-931-891-2582; Tel: +86-18919803060.

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Abstract

A nitrogen-doped porous carbon materials (CPNs) with supported Co nanoparticles (Co@CPNs) with lamellar structure, high surface area and excellent magnetic properties was synthesized successfully by one-pot method. The Co@CPNs exhibited an excellent catalytic activity with 99% conversion and selectivity for hydrogenation of furfural (FAL) to furfuryl alcohol (FOL) under the pressure of H_2. In addition, the Co@CPNs were further investigated in the kinetic study and selective hydrogenation of the other α, β unsaturated carbonyl compounds. The study of the Co@CPNs indicated that it was suitable for selective hydrogenation of the α, β unsaturated carbonyl compounds in the industry.

Keywords: Furfural, Furfuryl alcohol, Kinetic study, Selective hydrogenation, Liquid phase

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Introduction

Furfuryl alcohol (FOL) is an important intermediate for the production of lysine, ascorbic, drugs, and various lubricants, which also deserves attention as a potential platform for biofuels to take place of the fossil fuels [1-3]. The industrial method of producing FOL is hydrogenation of furfural (FAL), which can be obtained from the lignocellulosic biomass by catalytic dehydration [4], by the catalysts of copper chromate [5]. However, many factors including partial size, reaction temperature and pressure of H_2 influence the activity and selectivity of catalysts [6, 7]. Therefore, accomplishing chemical selectivity is considerably challenging for hydrogenation of all C=O and C=C unsaturated bonds of furfural, which may respectively lead to tetrahydrofurfural or tetrahydrofurfuryl alcohol. In addition, the poisonous Cr_2O_3 is a serious contaminant, which promotes the investigators to develop other metals to take the place of Cr. Recently, abundant of supported bimetallic (Cu-Ni [8], Pd-Fe [9]), precious metal (Ru [10], and Pd [11]) or metallic oxide (Co_3O_4 [12]) catalysts were reported for the gas phase, liquid phase hydrogenation with H_2 or transfer hydrogenation [13]. Nevertheless, most synthesis methods of the catalysts are complicated and the use of noble metals can increase the expenditure. Hence, it’s essential that project and compound of efficient catalysts with high selectivity, activity and low cost.

Co, a cheap and high activity non-noble metal, has been loaded on SBA-15 [14], TiO_2 [15] and carbonaceous materials [16], which were studied in selective hydrogenation of FAL. It is found that the Co is low active at low temperature and low selective at high temperature. Hence, Co based catalysts with excellent activity and selectivity are still necessary. And the Nitrogen-doped carbon materials have advantages of high surface area, facile and have involved broad investigation as catalysts carriers during the past several years.

In this work, Co nanoparticles were supported on nitrogen-doped porous carbon materials (CPNs) by one-pot method, and characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), transmission electron microscopy (TEM) etc. This study affords the encouraging potential application of Co@CPNs catalysts in the selective hydrogenation reactions. Compared with noble metal catalysts, such as Au/Al_2O_3 [17], Pt/MgO [18], Co@CPNs possesses non-poisonous peculiarity, simple synthesis method and low price. Co/CPNs also exhibits superiority on conversion and selectivity (both 99%) compared with the non-noble metal catalysts $Fe\text{-}Cu/\gamma Al_2O_3$ catalyst with 93% furfural conversion and 98% selectivity to furfuryl alcohol [19] and Fe-promoted Cu/SiO_2 maintains 95% conversion and 87 % selectivity to FOL [20].

2. Experimental Section

2.1. Reagents and chemicals

All reagents and chemicals were of analytical grade and used as received without any further purification. Cobalt (Ⅱ) nitrate hexhydrate ($Co(NO_3)_2{\cdot}6H_2O$, 99.0%) was purchased from Shanghai Zhongqin Chemical Reagents Co., Ltd. Sodium chloride (NaCl, 99.5%) was purchased from Tianjin Guangfu Chemical Reagents Co., Ltd.

Melamine ($C_3N_3(NH_2)_3$) was purchased from Sinopharm Chemical Reagents Co., Ltd. Chitosan was purchased from Reagents Co., Ltd.

2.2. Synthesis of the catalysts

1.5 g Chitosan, 1.5 g Melamine, 1.0 g $Co(NO_3)_2\cdot 6H_2O$, and 4.0 g NaCl were thoroughly mixed, and the resulting mixture were transferred into a porcelain boat and heated up to 500 ℃ in 220 min, then it was kept at 500 ℃ for 60 min. Then, the mixture was heated up to desired temperature at a rate of 3.75 ℃/min and was hold for 60 min under the nitrogen atmosphere. After the temperature cooled down to room temperature, the mixture was washed by 200 mL deionized water in the ultrasonic irradiation to promote the dissolve of NaCl and in the Fig. 2c were not found the elements of Cl and Na, this phenomenon provide the NaCl was remove clearly. Finally, the mixture were filtrated and dried at 60 ℃ for 12 h and got the Co@CPNs catalysts. The schematic caption of the synthesis of catalysts were shown in Fig. 1.

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Fig. 1 the schematic caption of the synthetize catalyst.

3. Results and discussion

3.1. Characterizations of the catalysts

The ingredient and morphology of the catalysts are displayed in Fig. S2 with TEM and SEM. Fig. S2a presents that the Co nanoparticles were well-proportioned dispersed on the CNPs. Fig. S2b show that the average sizes of Co nanoparticles is about 31.2 nm. Fig.2c was the EDX of the catalysts, which shows that the catalysts have the elements of C, N, O and Co. HR-TEM (Fig. S2d) shows that the lattice distance is 0.209 nm, which can be assigned to the (111) planes of metallic Co. Fig. S2e is the result of mapping zone and the results are presented in the Fig. S2f. In Fig. S2f, the green zone is the mapping of cobalt, and the other two yellow and red zones are the N and C, respectively. It is obvious that the zone of elements of C, N were mostly overlap, and the element of Co is inserted into the other two elements. And from the Fig. S1, It could be obverted that the cobalt was observed with a thin layer of carbon and the thickness of the carbon is about 1.89 nm [21].

The patterns of XRD were displayed in Fig. S3a, which could provide the composition of catalysts. The two peaks of 2θ =26.0° and 44.0° were corresponding to (002) and (101) planes of carbon (JCPDS 75-1621) [22]. In addition, It can be found that the (101) peak of carbon is the same as the (111) peak of cobalt. The peaks located at 2θ= 44.0°, 51.5°, and 75.8° were corresponding to the Co lattice planes of (111), (200) and (220) (JCPDS 1-1255) [23]. Therefore, the cobalt existed in the Co@CPNs-1.5-1.5-4 with state of Co^0, which fitted in with the result of TEM.

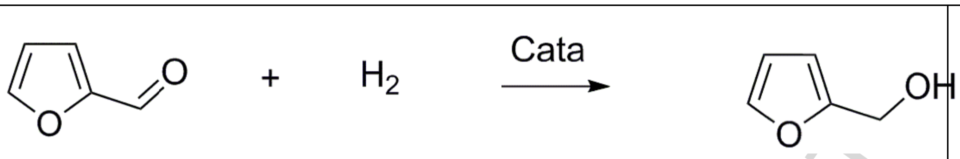
The XPS were displayed in the Fig. S3b-f, which provided the chemical elements valence states and molar fraction of Co (7.83%), C (74.63%), N (1.58%), and O (15.96%) on the surface of the catalysts, and all the binding energys from the XPS analysis were calibrated by using the C1s peak at 284.6 eV. The Fig. S3b shows the wide survey spectrum of the Co@CPNs, and the peaks at the binding energies of 285.2 eV, 399.8 eV, 531.3 eV and 780.3 eV were attributed to the C 1s, N 1s, O 1s, and Co 2p species, respectively [24]. From the high-resolusion spectrum it can be observed that the C 1s (Fig. S3c) peak components with binding energys at 286.6 eV, 285.0 eV and 284.3 eV were related to the C-O, C-C, and C-N, respectively [25, 26]. The N 1s spectrum (Fig. S3d) was deconvoluted into two peaks that corresponding to the following functional groups: 401.1 eV for C-N and 399.1 eV for C=N [27, 28]. There were three signals observed of O 1s (Fig

. S3e) (532.8 eV for C-O-C, 531.4 eV for Co-O and 530.1 eV for C-O)[29, 30]. Co 2p (Fig. 3f) was spilt into Co $2p_{3/2}$ at 778.3 eV and Co $2p_{1/2}$ at 793.2 eV, these two peaks stand for metal of cobalt and the results was corresponded to the results of the XRD [31]. The binding energys of oxidised Co of $2p_{3/2}$ was located at 781.7 eV and the $2p_{1/2}$ was located at 803.6 eV [32, 33]. There are two reasons of having peaks of oxidised cobalt, one was that the suffice of cobalts have a little oxidation when the catalysts were exposured to air and the other was that the oxygen in the chitosan have a reaction with the cobalt at high tempeture. However, from the image of XRD, there were not the peaks of cobaltous oxide, this phenomenon may be caused by the lattice of oxidised cobalt was amorphous and these species were not detected by XRD.

3.2 Performance of catalysts

The performance of catalysts were tested by selective hydrogenation of FAL to FOL(Table 1). All the types of the catalysts were tested at 3 MPa of H_2, 453 k for 2.5 h, and the iPrOH as solvent. Starting to stirring when the temperature reached to 453 k. From the Table 1, It could see that the catalyst perform the highest activity when the mass of chitosan and melamine were both 1.5 g, the mass of NaCl was 4.0 g, and the temperature of calcination was 1073 k. From the Table 1, the mass of NaCl influence the surface area of the catalysts was very obviously and the influence of the reaction activity was also distinct. It was deduced that the NaCl was influencing the surface area of the catalysts, which can increase the exposure of the center of activity of catalysts.

Table 1 the selective hydrogenation of the FAL with the different catalysts [a].

 					
Entry	Catalyst	Conversion (%)	Selectivity (%)	Yield (%)	TOF h^{-1}
1	Co@CPNs1.5-1.5-0	75	95	71	14.5
2	Co@CPNs1.5-1.5-2	81	98	79	15.6
3	Co@CPNs1.5-1.5-4	99	99	98	19.3
4	Co@CPNs1.5-1.5-6	53	94	50	10.3
5	Co@CPNs1.0-2.0-4	52	98	51	9.0
6	Co@CPNs2.0-1.0-4	35	99	34	8.8
7	Co@CPNs1.5-1.5-4[b]	78	98	76	15.1
8	Co@CPNs1.5-1.5-4[c]	70	96	67	13.5
9	CPNs	0	0	0	0
10	Co@C	31	97	30	10.9

(a) reaction conditions: furfural (4 mmol), catalyst (20 mg), isopropanol (20 mL), 3 MPa H_2, 453 k, reaction time 2.5 h. Conversion and selective were determined by GC-MS (b) the highest calcination temperature is 1173 k, (c) the highest calcination temperature is 973 k, and the mass content of cobalt of entry 1-4, 5, 6 and10 are around 20.4%, 22.8%, 15.5% and 11.2%, respectively.

It also tested the activity of catalysts (Table 1 Entry 3) in different solvent and the results were shown in Table 2. From the results, it can be got that the catalysts have a good activity when the solvent have hydroxyl and high polarity. When the solvent was the water there have a low conversion, this may be the substrate could not dissolve in the water and the substrate could not exposure adequately with H_2.When the solvent was methyl alcohol, the catalysts behaved high activity, however, the selective was not very well, the reaction produced too much byproducts The main reaction of the generation of byproducts were that the methyl alcohol and FAL have an aldol condensation reaction and the mechanism was shown in Fig. S7 [34]. Considering the rate of reaction and the yield of objective product, the iPrOH was chose as the final solvent. We also test the final solvent with GC-MS, there was no acetone founded, it could dope out that the hydrogen donors was H_2 but not the iPrOH.

Table 2 Effect of solvents on the selective hydrogenation of furfural using Co@CPNs-1.5-1.5-4[a].

Entry	solvent	Conversion (%)	Selective (%)	Yield (%)	polarity
1	water	5	99	4.9	10.2
2	Methyl alcohol	99	85	84.2	6.6
3	Ethyl alcohol	98	80	78.4	4.3
4	n-hexane	85	90	76.6	0.06
5	cyclohexane	21	99	20.7	0.1
6	1,4-dioxane	16	95	15.2	4.8

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7	toluene	15	99	14.8	2.4
8	n-butyl alcohol	85	90	76.5	3.7
9	ethyl acetate	21	99	20.7	4.3
10	isopropanol	99	99	98	4.3

(a) reaction conditions: furfural 4 mmol, Co@CPNs-1.5-1.5-4 20 mg, solvent 20 mL, 3 MPa H_2, 453 k, 2.5 h. Conversion and selective were determined by GC-MS.

From the Table 3, it could see that at high temperature the catalysts have a well activity and the best reaction temperature was 453 k. At the lower temperature, the higher yield can be get through the increase the reaction time (entry 2 and 4). From the entry 7-9, we found that the conversion will increase with the increase the pressure of H_2 and when the pressure was 3MPa, the conversion achieve the highest.

Table 3 Effect of temperature on the selective hydrogenation of furfural using Co@CPNs-1.5-1.5-4[a].

Entry	T (k)	P (MPa)	Conversion (%)	Selective (%)	Yield (%)
1	423	3.0	24	99	23.8
2[b]	423	3.0	54	99	53.5
3	433	3.0	53	99	52.5
4[b]	433	3.0	68	99	67.3
5	443	3.0	70	98	68.6
6	453	3.0	99	99	98.1
7	463	3.0	99	95	94.0

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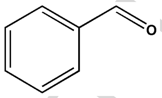
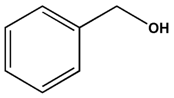
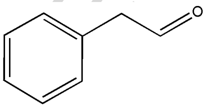
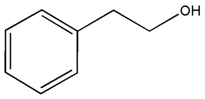
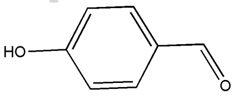
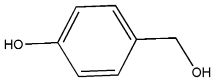
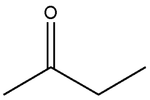
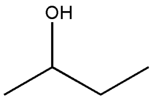
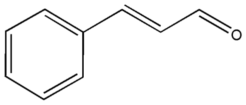
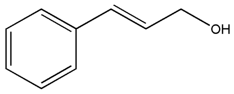
8	453	2.5	78	99	77.2
9	453	2.0	61	99	60.4
10	453	1.5	46	99	45.5

(a) reaction conditions: furfural (4 mmol), Co@CPNs-1.5-1.5-4 (20 mg), isopropanol (20 mL), reaction time 2.5 h. Conversion and selective were determined by GC-MS.(b) the reaction time was 5 h.

Finally, the selective hydrogenation of various α, β-unsaturated carbonyl or ketone were also tested with the catalysts, and the results were shown in the Table 4. From the table 4 we can see that the catalysts also behave high activity and selectivity with other compounds except the acid, this may be the carboxyl was too stable.

Table 4 Selective hydrogenation of various α, β-unsaturated carbonyl or ketone [a].

Entry	Substrate	Product (%)	Conversion (%)	Selective (%)
1			98	92
2[b]			99	99
3			99	95
4			99	99
5[c]			99	80

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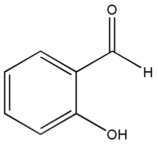
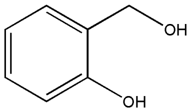
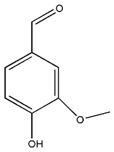
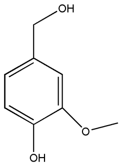
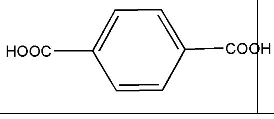
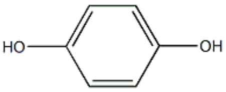
6			99	90
7			95	80
8			30	90

(a) reaction conditions: substrate (5 mmol), Co@CPNs-1.5-1.5-4 (20 mg), isopropanol (20 mL), 3 MPa H_2, 453 k, reaction time 2.5 h. (b)the reaction time is 1 h, (c)the reaction time is 0.6 h Conversion and selective were determined by GC-MS.

So as to test the ability of the circulation of catalysts, selective hydrogen of FAL was performed at 453 k, 3 MPa of H_2 for 2.5 h. The used catalysts were washed by iPrOH for five times for the next cycle, and the results were shown in Table 5. After four times cycling, the activity and the selectivity of the catalysts were not changed apparently, this results suggested that the cycling ability of catalysts were favorable. We also analyzed the catalysts after the recycle by ICP and the mass content of cobalt was 17.29%, which was less about 3% than the fresh catalysts. The loss of the cobalt in the reaction may result the decline of the conversion.

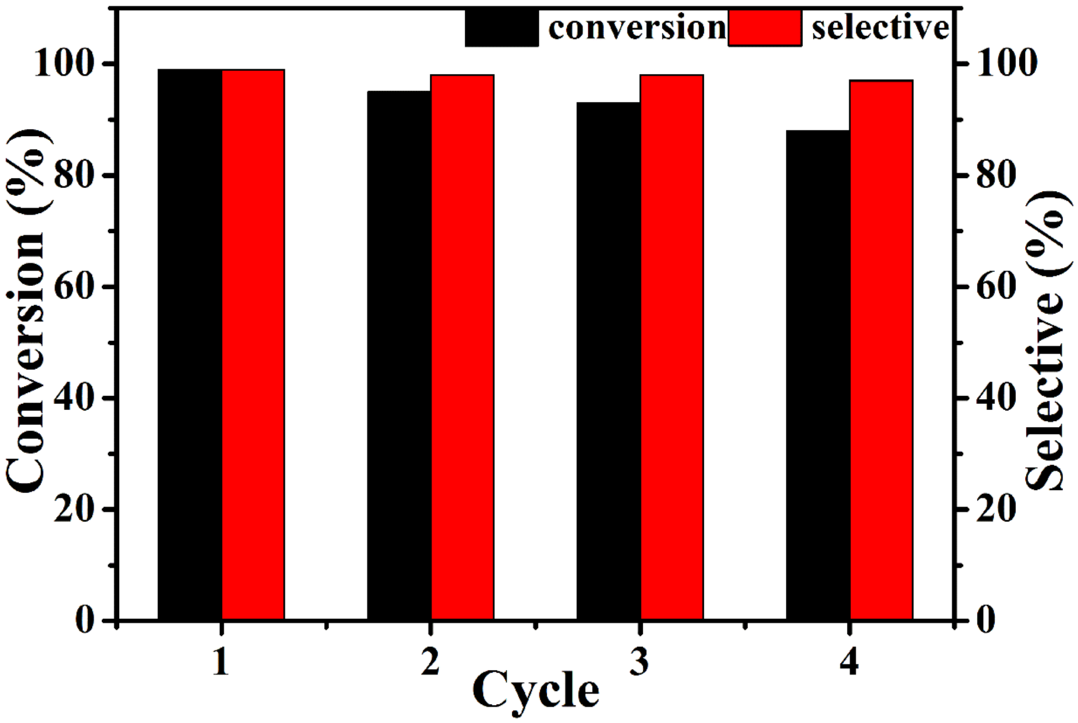


Table 5 The recycles ability of the Co@CPNs-1.5-1.5-4.

4. Conclusion

In this study, Co nanoparticles were supported on nitrogen-doped carbon porous materials (CPNs) by single pot method and utilized to selective hydrogenation of the FAL to FOL. After the screening of the reaction condition, satisfactory conversion and selectivity were obtained. Co@CPNs-1.5-1.5-4 exhibited best catalysts activity among all types of the catalysts, which performs the high activity, conversion (99%) and selectivity (99%) of FAL to FOL. Avoiding the noble metal shortcoming of the high cost and the non-noble metal weakness of low catalytic activity. This study demonstrated the high catalytic activity Co@CPNs-1.5-1.5-4 were prepared in the selective hydrogenation of FAL to FOL.

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Highlights

- The catalysts Co@CPNs were easily prepared.
- The catalysts are very cheap and can be separated by the external magnetism.
- Kinetic study of the hydrogenation of the Furfural to Furfuryl alcohol.

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