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Article

High-efficiency oxidative esterification of furfural to methylfuroate with a non-precious metal Co-N-C/MgO catalyst



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ABSTRACT

From both fundamental and practical perspectives, the production of chemicals from biomass resources using high-efficiency non-precious metal catalysts is important. However, many processes require addition of stoichiometric or excess quantities of base, which leads to high energy consumption, leaching problems, and side reactions. In this study, we investigated the high-efficiency oxidative esterification of furfural to methylfuroate by molecular oxygen with a Co-N-C/MgO catalyst. The catalyst was prepared by direct pyrolysis of a cobalt(II) phenanthroline complex on MgO at 800 °C under N₂ atmosphere. From furfural, 93.0% conversion and 98.5% selectivity toward methylfuroate were achieved under 0.5 MPa O₂ with reaction at 100 °C for 12 h without a basic additive. The conversion and selectivity were much higher than those obtained with cobalt catalysts produced by pyrolysis of a cobalt(II) phenanthroline complex on activated carbon or typical basic supports, including NaX, NaY, and CaO. X-ray photoelectron spectroscopy, X-ray diffraction, transmission electron microscopy, and experimental results revealed that the high efficiency of Co-N-C/MgO for production of methylfuroate was closely related to the cobalt-nitrogen-doped carbon species and its catalytic ability in hydrogen abstraction. In contrast, Co-N-C(HCl) that synthesized by removing MgO with HCl from Co-N-C/MgO, as the catalyst produced mainly an acetal as a condensation product, and chloride ions had a negative effect on the oxidative esterification. Although the catalytic performance of the cobalt-nitrogen-doped carbon species was greatly affected by HCl treatment, it could be recovered to a great extent by addition of MgO. Moreover, changes in the oxygen pressure hardly affected the oxidative esterification of furfural with Co-N-C/MgO. This study not only provides an effective approach to prepare methylfuroate, but also for designing high-performance non-precious metal catalysts for the oxidative esterification of biomass-derived compounds.

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1. Introduction

The non-precious metal approach for production of chemi-

cals from biomass resources is attracting immense research interest globally and is very important from the perspectives of green chemistry and sustainable development [1–6]. For

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large-scale biomass conversions, precious metal catalysts and basic additives are generally used to achieve high performance. A typical case is the oxidative esterification of furfural, which is derived from lignocellulosic biomass and recognized as a promising renewable resource [7–11], to produce methylfuroate. It is an attractive route because of the applications of methylfuroate as an anti-explosive additive in petrol and an anti-tumor drug. In most cases, homogeneous bases are added to promote the reaction and facilitate the abstraction of active hydrogen. For example, Au/Fe_xO_y-hydroxyapatite catalyst affords a 92% yield of methylfuroate with addition of K₂CO₃ after reaction at 140 °C for 4 h [12]. Christensen et al. [11] reported that addition of CH₃ONa remarkably improved the catalytic performance of Au/TiO₂ in the oxidative esterification of furfural. Recently, Co_xO_y-N@C showed high potential in catalysis, and gave a 95% yield of methylfuroate from furfural and methanol with addition of K₂CO₃ [13]. However, base additives lead to high energy consumption, leaching problems, and side reactions. In future, it is necessary to develop an inexpensive and environmentally friendly catalyst that provides efficient oxidative esterification of furfural without the requirement for a basic additive.

Metal-containing N-doped carbon catalysts can be used as an alternative to precious metal catalysts, and are inexpensive and show unique properties in electrocatalysis [14–16] and organic reactions [17–20]. To date, various cobalt-nitrogen-doped carbon catalysts have been synthesized by pyrolysis of nitrogen-rich metal complexes or mixtures of metal salts and N-containing ligands on supports under an inert atmosphere. Research has focused on the structures and factors influencing the catalytic activity. There is evidence that a single Co atom bonded to N atoms within graphitic sheets can act as an active center in aerobic oxidative cross-coupling and hydrogenative coupling reactions [21,22]. Basic additives, such as LiOH or NaOH, are indispensable for Co-N-C catalysts in these reactions, and it is not known if Co-N-C catalysts can achieve high efficiency without the assistance of basic additives.

Previous studies performed in our laboratory showed that the basic support Mg(OH)₂ remarkably increased the performance of gold catalyst in oxidative conversions [23]. Further research indicated that pyridinic N-doped carbon species might behave as Lewis bases and greatly promoted the catalysis of Co_x-N/C to achieve high efficiency for the oxidative esterification of diformylfuran in a neutral medium [24]. These findings suggested that cobalt-nitrogen-doped carbon supported on basic carrier could realize high efficiency oxidation of furfural without the requirement for a basic additive. In the present study, a Co-N-C/MgO catalyst was synthesized and used for production of high yields of methylfuroate under mild conditions without any basic additives. This method could be used for the development of high-performance non-precious metal catalysts for oxidative esterification conversions of biomass and biomass-derived compounds.

2. Experimental

2.1. Materials

All reagents and chemicals used were of analytical grade unless otherwise specified. Furfural, MgO, ethanol, activated carbon, and 1,10-phenanthroline were obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). Methanol was obtained from Kermel Chemical Reagent Development Center (Tianjin, China). Cobalt acetate tetrahydrate was from Sinopharm Chemical Reagent Co. Ltd. NaX and NaY were from Nanhua Catalyst Co. Ltd (Tianjin, China). CaO was from Damao Chemical Reagent Factory (Tianjin, China).

2.2. Catalyst preparation

The Co-N-C/MgO catalyst was synthesized according to a reported method with some modifications [18]. 1,10-Phenanthroline (182 mg, 1.0 mmol) and cobalt acetate tetrahydrate (125.8 mg, 0.5 mmol) were dissolved in 50 mL of ethanol and stirred for 30 min at room temperature. Then, 692.2 mg of MgO was added to the solution, and the mixture was stirred for 4 h at 60 °C. The ethanol was removed under vacuum and the mixture was cooled to room temperature. The sample was then dried at 80 °C for 12 h. Then, the sample was placed in an oven, which was heated to 800 °C at 25 °C min⁻¹ and maintained at this temperature for 2 h under a nitrogen atmosphere. For comparison, cobalt-based catalysts were prepared by a similar method using activated carbon and typical basic supports (NaX, NaY, and CaO). The resulting samples were denoted as CoO_x-N/C, CoNC/NaX, CoNC/NaY, and CoNC/CaO.

2.3. Catalyst characterization

The samples were analyzed by X-ray powder diffraction (XRD) on a Rigaku D/Max 2500/PC powder diffractometer with Cu K_α radiation (λ = 0.15418 nm) at 40 kV and 200 mA at a scanning rate of 5° min⁻¹. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2000EX electron microscope with samples deposited on a carbon polymer supported copper grid. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250Xi using a Mg K_α (1253.6 eV) radiation source and a chamber pressure lower than 5 × 10⁻⁸ Pa. Inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin Elmer ICP-OES 7300DV was used to determine the cobalt content. A carbon/sulfur analyzer (EMIA-8100, HORIBA) and oxygen/nitrogen/hydrogen analyzer (EMGA-930, HORIBA) were used to determine the carbon and nitrogen contents, respectively.

2.4. Oxidative esterification of furfural

Oxidative esterification of furfural was performed in a 10-mL Teflon lined stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge, and automatic temperature control apparatus. Typically, 0.5 mmol of furfural, 80 mg of Co-N-C/MgO (3.9% mass fraction, 0.05 mmol of Co), and 5 mL of methanol were loaded into the autoclave. The autoclave was purged with oxygen and then pressurized to the required value.

During the reaction, the pressure was maintained by supplying oxygen. After the reaction was completed, the autoclave was cooled to room temperature. The liquid reaction mixture was analyzed on an Agilent gas chromatograph (GC7890D) equipped with a flame ionization detector (FID) and Agilent GC/MS 6890-5973. The conversion and selectivity toward methylfuroate were evaluated by the internal standard method using *n*-dodecane as the internal standard.

3. Results and discussion

3.1. Catalyst characterization

First, the Co-N-C/MgO catalyst was analyzed by XRD in the range 5°–80°. The Co-N-C/MgO only displayed diffraction peaks for MgO (Fig. 1(e)), and no cobalt nanoparticles were observed on the surface of the MgO in the TEM image (Fig. 1(b)). After acid treatment and microwave digestion, the Co-N-C/MgO was analyzed by ICP-OES. The results confirmed the formation of cobalt, nitrogen, and carbon after pyrolysis under N₂. The cobalt was highly dispersed on the catalyst surface, and cobalt-nitrogen-doped carbon species formed. To verify this, the Co-N-C/MgO was treated with 2 mol L⁻¹ HCl to remove MgO, which was confirmed by the disappearance of its characteristic peaks in the XRD pattern (Fig. 1(f)). Additionally, a diffraction peak appeared at 26°, indicating that the carbon formed (carbon mass fraction = 71.8% by ICP). In contrast to

Co-N-C/MgO, the TEM image (Fig. 1(c)) of self-supported Co-N-C(HCl) showed obvious MgO-shaped cavities, which would have been occupied by MgO before the acid treatment. Moreover, the ICP-OES results showed that the Co-N-C(HCl) contained cobalt and nitrogen. These observations were consistent with previous reports that the moderate interaction of MgO with Co species may be beneficial for generation of cobalt-nitrogen-doped carbon species by pyrolysis of a cobalt(II) phenanthroline complex on MgO [22].

XPS was used to characterize the N and Co. The N 1s spectrum of Co-N-C/MgO displayed three peaks at 399.0, 400.8, and 402.0–403.2 eV, which could be assigned to pyridinic N bonded to cobalt, graphitic N, and pyridine N-oxide, respectively (Fig. 2) [21,25]. Meanwhile, in agreement with the N 1s spectrum and XRD pattern, the binding energy of the Co 2p_{3/2} peak at 780.5 eV and its satellite peak corresponded to Co(II), which may be coordinated with N atoms in the carbon species [26,27]. These results revealed that cobalt-nitrogen-doped carbon species and carbon were formed by pyrolysis of a cobalt(II) phenanthroline complex on MgO at 800 °C under a N₂ atmosphere, which agrees with previous research [15,21,22,28].

3.2. Catalytic performance

The catalytic performance of Co-N-C/MgO, CoO_x-N/C, CoNC/NaX, CoNC/NaY, and CoNC/CaO was compared.

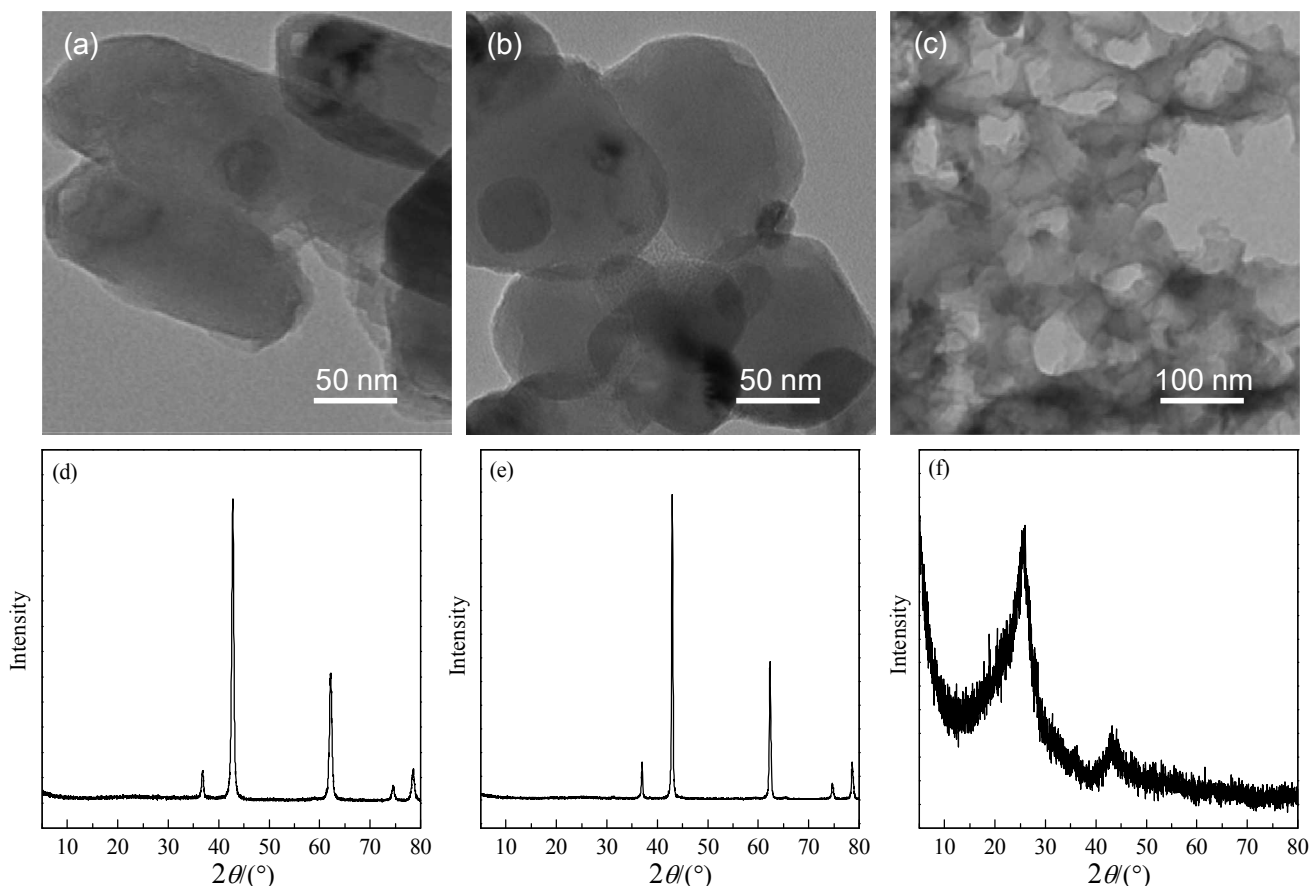


Fig. 1. TEM images of MgO (a), Co-N-C/MgO (b), and Co-N-C(HCl) (c); XRD patterns of MgO (d), Co-N-C/MgO (e), and Co-N-C(HCl) (f).

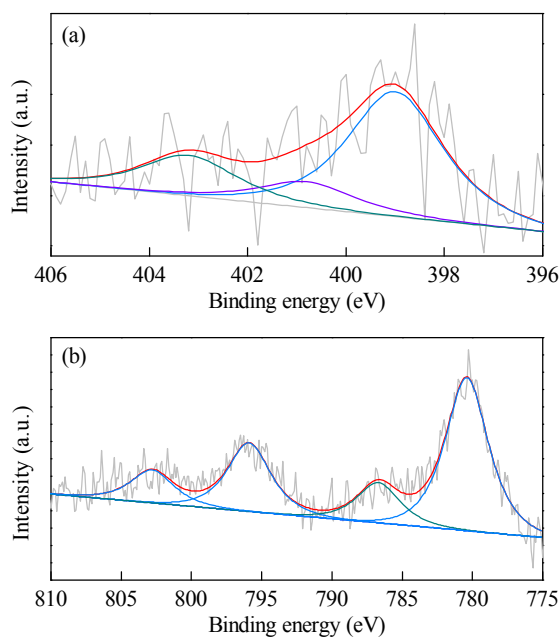


Fig. 2. XPS spectra of the N 1s (a) and Co 2p_{3/2} (b) electron regions of Co-N-C/MgO.

Exploratory experiments were performed in methanol in a 10-mL autoclave reactor (Fig. 3). Co-N-C/MgO exhibited excellent performance in the oxidative esterification of furfural without a basic additive, where it gave 89.3% conversion of furfural to methylfuroate with 90.1% selectivity at 100 °C for 6 h. When the reaction time was increased to 12 h, a satisfactory result (93.0% conversion with 98.5% selectivity toward methylfuroate) was obtained. In previous studies, cobalt oxide-nitrogen/catalyst (CoO_x-N/C) gave a good yield for methylfuroate produced by oxidative esterification of furfural with K₂CO₃ as an additive [13,26]. Here, CoO_x-N/C only gave a

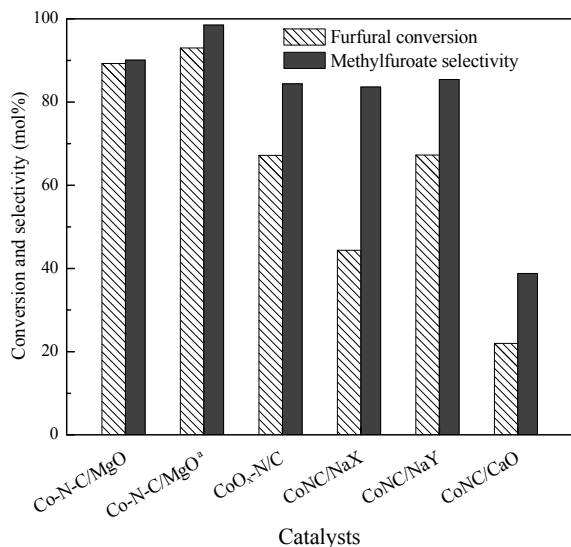


Fig. 3. Catalytic performance of various Co-based catalysts in the oxidative esterification of furfural. Reaction conditions: 0.5 mmol furfural, 80 mg catalyst, 5 mL methanol, 100 °C, 0.5 MPa O₂, and 6 h or *12 h.

67.2% conversion of furfural and 84.4% selectivity toward methylfuroate without addition of a base. By contrast, the Co-based catalysts with the typical basic zeolites NaX and NaY as supports exhibited moderate catalytic activity with 83.6% and 85.4% selectivity toward methylfuroate, respectively. CoNC/CaO only achieved 22.0% conversion and 38.8% selectivity toward methylfuroate. The choice of support obviously affected both the catalytic activity and selectivity. As demonstrated by XRD, TEM, XPS, and previous reports, the use of MgO as a support gave good distribution and formation of cobalt-nitrogen-doped carbon species, which may be closely related to the remarkable catalytic activity of Co-N-C/MgO.

Considering that hydrogen abstraction is a key step in the oxidative esterification of an aldehyde with an alcohol, we compared the catalytic performance of Co-N-C/MgO with other Co-based catalysts in the dehydrogenative esterification of furfural with methanol under N₂ (Table 1). The choice of support was critical for the selectivity to the dehydrogenative esterification product, which was consistent with the results for oxidative esterification. As expected, in the presence of Co-N-C/MgO, the reaction of furfural with methanol at 100 °C mainly converted the aldehyde into ester. Co-N-C/MgO exhibited the highest selectivity toward methylfuroate, whereas CoO_x-N/C, CoNC/NaX, CoNC/NaY, and CoNC/CaO were not efficient for the generation of methylfuroate. These results imply that the excellent performance of Co-N-C/MgO could be attributed to its good catalytic ability in hydrogen abstraction.

To further investigate the catalytic performance of the cobalt-nitrogen-carbon species, Co-N-C(HCl) (0.05 mmol of Co) was synthesized by removing MgO with HCl, and used as a catalyst in the oxidative esterification of furfural in methanol under 0.5 MPa O₂ at 100 °C for 5 h. Interestingly, in the absence of MgO, the majority of furfural was converted to the acetal (2-(dimethoxymethyl)furan, 81.0% conversion), and no methylfuroate was detected by GC analysis. To obtain more information, MgO was introduced (molar ratio of MgO/Co = 34.8) to the Co-N-C(HCl). The GC/MS chromatograms obtained before and after addition of MgO were distinct (Fig. 4). MgO dramatically increased the selectivity toward the ester, with the selectivity toward methylfuroate increasing from not detected to 84.4% (Table 2, entry 2). This showed the catalytic performance of the cobalt-nitrogen-doped carbon species was greatly affected by HCl treatment, but could be recovered to a great extent by addition of MgO. The condensation of furfural with methanol to acetal and the oxidative esterification of furfural to methylfuroate are competitive pathways, with the

Table 1
Dehydrogenative esterification of furfural with methanol.

Entry	Catalyst	Conversion (mol%)	Selectivity ^a (mol%)
1	Co-N-C/MgO	11.2	81.2
2	CoO _x -N/C	16.6	43.7
3	CoNC/NaX	12.9	55.8
4	CoNC/NaY	18.4	43.0
5	CoNC/CaO	12.3	35.7

Reaction conditions: 0.5 mmol furfural, 80 mg catalyst, 5 mL methanol, 100 °C, 0.1 MPa N₂ (initial pressure before heating), and 12 h.

^aSelectivity toward methylfuroate.

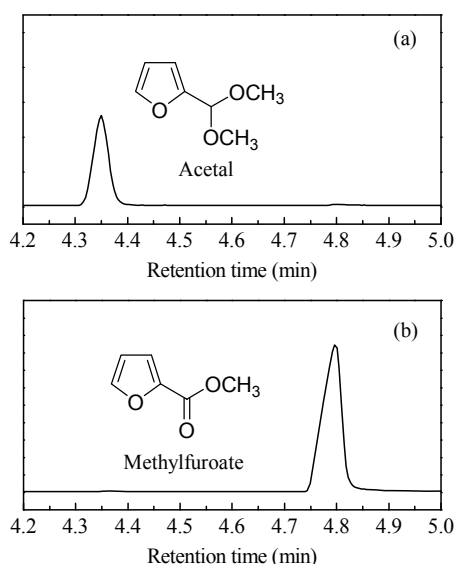


Fig. 4. Typical GC/MS chromatograms for (a) condensation and (b) oxidative esterification of furfural with methanol. Reaction conditions: 0.5 mmol furfural, 5 mL methanol, 100 °C, 0.5 MPa O₂, 5 h; (a) 58.9 mg Co-N-C(HCl), (b) 58.9 mg Co-N-C(HCl) and 70 mg MgO.

dominant process determining the main product. These differences indicated that the -CHO groups were mainly converted via the competing condensation pathway with Co-N-C(HCl), or via the oxidative esterification pathway with Co-N-C(HCl) and MgO. Other research has shown that specific anions, including Cl⁻, greatly affect the catalyst performance of M-N-C catalyst because they might coordinate with the active metal center [29]. In our case, although the MgO could be removed from the Co-N-C/MgO by washing with HCl, residual Cl⁻ may affect the metal center and lead to an obvious loss of catalytic activity for the oxidative esterification.

Two experiments were carried out to confirm the negative role of Cl⁻. When NaCl (0.5 mmol) was introduced to the reaction with the Co-N-C/MgO catalyst, the conversion decreased from 93.0% to 56.3% and the selectivity toward methylfuroate decreased slightly (Table 2, entry 3). If Co-N-C/MgO was pretreated with NaCl solution, thoroughly washed with water, and then calcined at 800 °C, both the conversion and selectivity decreased obviously (Table 2, entry 4). These changes confirmed that Cl⁻ ions had a negative effect on the oxidative esterification reaction. Therefore, we believe

Table 2

Catalytic performance of various Co-based catalysts in the oxidative esterification of furfural.

Entry	Catalyst	Co content (wt%)	Additive	Conversion (mol%)	Selectivity ^a (mol%)
1	Co-N-C(HCl)	5.3	—	81.0	n.d.
2	Co-N-C(HCl)	5.3	MgO	90.0	84.4
3	Co-N-C/MgO ^b	3.9	NaCl	56.3	88.4
4	Co-N-C/MgO(NaCl) ^b	—	—	64.4	67.5
5	CoO _x -N/C ^c	3.9	K ₂ CO ₃	92.6	95.0
6	Co-N-C/MgO ^c	3.9	K ₂ CO ₃	99.6	95.2

Reaction conditions: 0.5 mmol furfural, Co-based catalyst (0.05 mmol Co), 5 mL methanol, 100 °C, 0.5 MPa O₂, 5 h, ^b 12 h or ^c 6 h.

^aSelectivity to methylfuroate.

that using MgO as a support or additive allows for high catalytic efficiency of the cobalt-nitrogen-doped carbon catalyst and greatly reduces the negative effects of Cl⁻. In addition, preliminary studies indicated that the use of basic additives such as K₂CO₃ could increase the catalytic activity and selectivity in oxidation and oxidative esterification reactions by promoting the elimination of active hydrogen. Thus, Co-N-C/MgO was compared with the representative Co-based catalyst CoO_x-N/C in the oxidative esterification of furfural in methanol with the addition of 0.1 mmol of K₂CO₃. Both catalysts achieved excellent results. Using CoO_x-N/C, the conversion increased from 67.2% to 92.6% and the selectivity toward methylfuroate increased from 84.4% to 95.0%. Meanwhile, Co-N-C/MgO gave 99.6% conversion with 95.2% selectivity toward methylfuroate. Therefore, the effect of MgO is similar to that of K₂CO₃, which implies that MgO may play a similar role to a base like K₂CO₃ in this reaction.

Next, the reaction conditions for the oxidative esterification of furfural with Co-N-C/MgO catalyst were optimized. The catalytic performance of Co-N-C/MgO was investigated at 100 °C for 6 h with oxygen pressures of 0.3, 0.5, 0.7, and 1.0 MPa (Table 3, entries 1–3 and Fig. 3). The oxygen pressure had a negligible effect on the oxidative esterification of furfural with Co-N-C/MgO in this pressure range. Considering the conversion of furfural may reach or be close to maximum values at 6 h, we shortened the reaction time to 1.5 h to further investigate the effect of the oxygen pressure. As expected, even at moderate conversion, there was also no apparent change in the conversion or selectivity toward methylfuroate with changes in the oxygen pressure. Additionally, the influence of temperature was examined at 60, 80, 100, and 120 °C (Table 3, entries 8–10 and Fig. 3). The conversion of furfural gradually increased as the reaction temperature increased, and 100 °C and 120 °C were the optimum temperatures for this reaction.

Recycling of the Co-N-C/MgO catalyst was investigated by evaluating the catalytic activity in repeat use for the oxidation esterification of furfural at 100 °C under 0.5 MPa O₂. The Co-N-C/MgO catalyst retained its activity for at least four recycling runs. In the fourth cycle, the catalyst gave 84.7% conversion of furfural and 87.5% selectivity toward

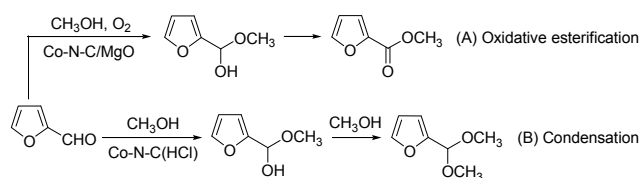
Table 3

The influence of pressure and temperature on oxidative esterification of furfural to methylfuroate.

Entry	Pressure (MPa)	Temperature (°C)	Time (h)	Conversion (mol%)	Selectivity ^a (mol%)
1	0.3	100	6	89.0	87.3
2	0.7	100	6	89.7	90.7
3	1.0	100	6	89.2	90.9
4	0.3	100	1.5	53.5	89.6
5	0.5	100	1.5	54.5	91.5
6	0.7	100	1.5	49.0	91.2
7	1.0	100	1.5	51.3	89.3
8	0.5	60	6	72.5	91.5
9	0.5	80	6	87.9	91.3
10	0.5	120	6	91.4	90.0

Reaction conditions: 0.5 mmol furfural, 80 mg Co-N-C/MgO, 5 mL methanol.

^aSelectivity to methylfuroate.



Scheme 1. Oxidative esterification and condensation of furfural with methanol.

methylfuroate. These results show that the Co-N-C/MgO catalyst is stable and can be reused in the oxidation of furfural to methylfuroate.

The oxidative esterification of furfural involves oxidative esterification and condensation of –CHO with –OH (Scheme 1). In methanol, furfural is converted into the intermediate hemiacetal, and subsequently undergoes dehydrogenation to form the target product methylfuroate. A competitive reaction of hemiacetal condensation with methanol can occur to generate the side product acetal in the presence of specific catalytic sites or in the blank reaction (without any catalyst or additive). In our case, with Co-N-C/MgO as the catalyst, the main product was methylfuroate. This suggests that the dehydrogenation of hemiacetal to methylfuroate is dominant. By contrast, with Co-N-C(HCl) as the catalyst, the main reaction was the condensation of –CHO with –OH generating the acetal as the main product. To exclude the possibility of producing methylfuroate via esterification of the hydroxyl and carboxyl groups, an oxidative esterification experiment using furancarboxylic acid as the starting substrate was performed in the presence of Co-N-C/MgO under the same conditions. No methylfuroate was detected in the GC chromatogram (data not shown). This clearly proved that the oxidative esterification did not proceed along the esterification pathway. The details for the mechanism of the Co-N-C/MgO catalyst are being clarified in further investigations.

4. Conclusions

A non-precious metal catalyst of cobalt-nitrogen-doped carbon supported on MgO was prepared via impregnation and pyrolysis of a cobalt(II) phenanthroline complex on MgO at 800

°C in N₂. Investigation of various supports (MgO, activated carbon, NaX, NaY, and CaO) showed the choice of support greatly affected the catalytic activity and selectivity toward the target ester product. The Co-N-C/MgO catalyst exhibited excellent performance for the oxidative esterification of furfural to methylfuroate (93.0% conversion and 98.5% selectivity) without the requirement for a basic additive under 0.5 MPa O₂ at 100 °C for 12 h. However, use of Co-N-C(HCl) as the catalyst produced mainly an acetal as a condensation product. Chloride ions had a negative effect on the oxidative esterification. The inclusion of MgO as a support increases the catalytic efficiency of the cobalt-nitrogen-doped carbon species, and as additive greatly reduces the negative effect of Cl[–]. Additionally, the oxygen pressure (0.3–1.0 MPa) has a negligible effect on the oxidative esterification of furfural with Co-N-C/MgO. This knowledge could be used to develop non-precious metal catalysts for the oxidative esterification of biomass-derived compounds.

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Graphical Abstract

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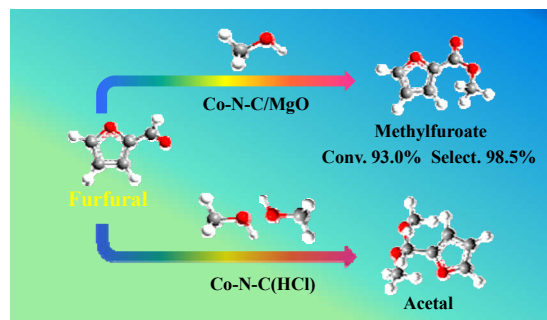
High-efficiency oxidative esterification of furfural to methylfuroate with a non-precious metal Co-N-C/MgO catalyst

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The non-precious metal catalyst Co-N-C/MgO showed high efficiency in the oxidative esterification of furfural to methylfuroate (93.0% conversion and 98.5% selectivity). The reaction with the catalyst Co-N-C(HCl) proceeded via a condensation pathway with acetal as the dominant product.



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非贵金属Co-N-C/MgO高效催化糠醛氧化酯化制糠酸甲酯

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摘要: 设计开发绿色、可持续的生物质资源高效转化制化学品催化过程具有重要的科学与应用研究价值。生物质基平台分子糠醛在分子氧存在下与甲醇发生氧化酯化, 提供了一条糠酸甲酯的“非石油基”合成新路线。该反应采用贵金属/非贵金属催化体系, 目前通常需要引入K₂CO₃或CH₃ONa等碱性添加剂, 以提高催化氧化酯化反应活性和选择性; 但是存在活性组分流失、生成副产物及污染环境等问题, 阻碍了其进一步应用。探索高性能非贵金属催化剂, 实现无碱条件下糠醛高效氧化酯化, 对于提高该生物质路线竞争力与推动工业化进程具有重要意义。

本文利用浸渍法将1,10-邻菲罗啉合钴(II)负载到碱性载体氧化镁上, 在氮气气氛下800 °C热解, 制备了非贵金属Co-N-C/MgO催化剂。在糠醛氧化酯化制糠酸甲酯反应中, Co-N-C/MgO催化剂表现出优异的性能, 在0.5 MPa O₂, 100 °C条件下反应12 h, 糠醛转化率达到93.0%, 糠酸甲酯选择性达到98.5%, 远超过相同方法制备的其他载体(活性炭、NaX、NaY和CaO)负载的钴基催化剂, 实现了无碱性添加剂条件下糠醛高效氧化酯化制糠酸甲酯。X射线光电子能谱、X射线衍射、透射电镜、元素分析以及对比实验结果表明, Co-N-C/MgO催化剂上可能存在含钴的氮掺杂碳物种; 该催化剂在糠醛氧化酯化中的高性能与其脱氢能力密切相关。并且在0.3–1.0 MPa氧气压力范围内, Co-N-C/MgO催化糠醛氧化酯化过程基本不受压力变化影响。

糠醛与甲醇的氧化酯化反应和缩合反应为两个竞争路径, 反应路径决定了反应的主要产物。我们使用盐酸处理Co-N-C/MgO催化剂, 脱除MgO载体, 制备了Co-N-C(HCl)催化剂。当使用该催化剂时, 糠醛与甲醇主要发生缩合反应, 得到缩醛产物2-(二甲氧基甲基)呋喃。如果在Co-N-C(HCl)催化反应体系中引入MgO添加剂, 则主要发生糠醛氧化酯化反应, 主产物为糠酸甲酯。为了验证Cl⁻是否对反应产生影响, 使用NaCl溶液对Co-N-C/MgO进行浸渍、清洗处理, 或直接使用NaCl为添加剂; 在这两种情况下, 糠醛转化率与糠酸甲酯选择性均下降, 表明Cl⁻对糠醛氧化酯化反应具有负面作用。根据实验结果, 阴离子(Cl⁻)可能与Co(II)中心发生配位, 从而影响了金属活性中心的催化性能。Co-N-C(HCl)加入氧化镁, 使得糠醛主要遵循氧化酯化路径进行转化, 降低Cl⁻对Co-N-C(HCl)催化活性中心的影响。以上研究可为生物质基醛类化合物氧化酯化转化过程以及高性能非贵金属催化剂的设计开发提供有益参考。

关键词: 催化; 钴-氮-碳; 糠醛; 糠酸甲酯; 氧化镁; 氧化酯化

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