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Original article

Selective conversion of furfural to cyclopentanol over cobalt catalysts in one step

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Graphical abstract



A series of cobalt catalysts with different supports were prepared for the selective conversion of biomass-derived furfural to cyclopentanol in one step. The best CPL yield was 82 mol% at 160 °C, 2 MPa H₂, 4 h when cobalt was supported on tetragonal zirconia that can be obtained by doping La_2O_3 .

ABSTRACT A series of cobalt catalysts with different supports were prepared for the selective conversion of biomass-derived furfural to cyclopentanol (CPL) in one step. The best CPL yield was 82 mol% at 160 °C, 2 MPa H_2 , 4 h when cobalt was supported on ZrO₂-La₂O₃. The supports were characterized by X-ray diffraction (XRD) and temperature-programmed desorption of ammonia (NH₃-TPD). The XRD results indicated that the more stable t-ZrO₂ formed by doping La₂O₃. The amount of acid sites of the catalyst increased, too. The influences of parameters such as reaction temperature, hydrogen pressure, and reaction time on the catalytic activity were also investigated. The polymer formed during the reaction may cause the deactivation of the Co/ZrO₂-La₂O₃ catalyst. This work provides a possibility to prepare the stable t-ZrO₂ and apply with cobalt metal for biomass valorization.

Keywords: Furfural Cobalt Cyclopentanol Hydrogenation Tetragonal Zirconia

1. Introduction

Biomass is the most attractive alternative feedstock of fossil resource to produce fuels and bulk chemicals since it is a widely available carbon source [1]. Furfural is an important biomass platform chemical that can be produced by acid-catalyzed dehydration from pentose [2-6]. In addition, it can also be prepared from hexose via isomerization step to form a ketose prior to the retro-aldol reactions [7-9]. Basically, furfural can be converted into many useful chemicals such as furan, furfuryl alcohol (FAL), tetrahydrofurfuryl alcohol (THFAL), 2-methylfuran, pentanediol, levulinic acid, *etc.* [11]. As a new route, furfural could be transformed into cyclopentanol (CPL) which is used for the production of fragrance chemicals and pharmaceuticals. Traditionally, CPL was obtained from an extra hydrogenation process of cyclopentanone (CPO) which was prepared by the pyrolysis of adipic acid or its derivatives and the oxidation of cyclopentene [12-14]. Therefore, the direct synthesis of CPL form biomass-derived furfural by rearrangement is meaningful, which could reduce the social dependence on fossil resource. However, there were only a few related researches. The possible reason is that it is hard to fulfill the hydrogenation of CPO to CPL without the saturation of furan ring to side-product THFAL.

As another rearrangement product, CPO has been studied widely. In 2012, Hronec *et al.* proposed the method to produce CPO from lignocellulose-derived furfural in the presence of metal catalysts and water [15]. The best yield of CPO was 76.5 mol% over 5% Pt/C catalyst and water was an essential part in the ring rearrangement. Then, they found the support had an influence on the product distribution [16]. A 44.7% CPO yield was obtained over the 1% Pt/Al₂O₃ while the main product was furfuryl alcohol over 1% Pt/MgO at 160 °C, 8 MPa H₂, 30 min. Other noble metal catalysts such as Ru/MIL-101 [17], Pd-Cu₂O/C [18], Au/TiO₂-A [19] and Ru/CNTs [20] were also reported and the CPO yield was more than 91%. Considering the high price and low reserves of noble metals, many non-noble metals had also been investigated, especially Cu and Ni. NiCu-50/SBA-15 [21], Cu-Ni-Al [22] and CuNi@C [23] were synthesized and exhibited good catalytic activity for the conversion of furfural into CPO. Our group developed CuZnAl catalyst for the conversion of furfural to CPO and achieved a 62% of CPO yield at 150 °C and 4 MPa H₂ [24]. Among these catalysts, CPO is the main rearrangement product instead of CPL, which means an additional hydrogenation process is necessary.

The reaction mechanism was proposed by Hronec *et al.* and shown in Scheme 1 [16,25]. After the hydrogenation of furfuryl, furfuryl alcohol was obtained and converted by different pathways: rearrangement, polymerization and over-hydrogenation, which were competitive reactions. Through the rearrangement pathway, furfuryl alcohol was protonated by hydrogen ions and cationic intermediate was formed. Subsequently, it opened the ring by interacting with water, the furan ring was rearranged to 4-hydroxy-2-cycloentenone (4-HCP). It is an unstable intermediate and can be found in the spontaneous hydrolysis of furfuryl alcohol under N₂ atmosphere without any catalyst [16]. Thus 4-HCP was hardly detected in the reaction system. Then 4-HCP was dehydrated to 2-cyclopentenone on Lewis acid sates. These two intermediates are high reactivity and the conversion was fast in the catalytic system [17]. 2-cyclopentenone underwent further hydrogenation to CPO and CPL. Polymerization and over-hydrogenation should be avoided. Therefore, the catalytic metals should be able to hydrogenate furfural and 2-cyclopentenone but not saturate the furan ring to THFAL. The weak Lewis acid support can contribute to dehydration [26].

It is a challenge to catalyze furfural into CPL directly. Therefore, it will be significant to develop new catalytic systems, especially catalysts with high activity to fulfill the conversion of CPL in one step without THFAL. Xiao's group reported the CPL was obtained as the main product over some non-noble metal catalysts. The yield of CPL was 83.6% at 140 °C, 5 MPa H₂ over 30% Ni/CNTs [27]. High loading of Ni was required to obtain CPL. CuMgAl [28] and CuZnAl [29] were highly active and the yield of CPL was 93.4% at 140 °C, 4 MPa H₂, 10 h and 84% at 150 °C, 4 MPa H₂, 10 h, respectively. Except for the high H₂ pressure and long reaction time, these catalysts agglomerated during the recycling. Li *et al.* used Cu-Co catalysts to convert furfural into CPL under mild H₂ pressure and short reaction time (2 MPa H₂, 1 h). The CPL yield was 67 mol% at 170 °C [30]. Besides molecular H₂, methanol can also be used as hydrogen donor [31].

According to previous reported [32,33], Co is a promising hydrogenation metal. In this study, we prepared several supported cobalt catalysts for the selective conversion of furfural to CPL in one step under mild conditions. The supports were the typical weak Lewis acid materials. Except for TiO₂ and Al₂O₃, we also studied ZrO₂ and changed its phase by doping La₂O₃ and characterized by X-ray diffraction (XRD) and temperature-programmed desorption of ammonia (NH₃-TPD). The influences of various reaction conditions including reaction temperature, hydrogen pressure and reaction time on the catalytic activity were also investigated. The deactivation of the Co/ZrO₂-La₂O₃ catalyst was also studied.

2. Results and discussion

2.1. Effect of different supports on the hydrogenation of furfural

Based on the previous reports [15], the rearrangement of furfuryl alcohol to form CPL or CPO occurred only in aqueous-phase. Thus, water was employed as the solvent in the following reactions. Table 1 showed the results of furfural conversion in water by using different cobalt catalysts. The supports include Al₂O₃, TiO₂, ZrO₂ and ZrO₂-La₂O₃. After the reaction, the main products were CPL, CPO and THFAL. CPL and CPO were the rearrangement products. THFAL came from over-hydrogenation of furfuryl alcohol. Furfural and furfuryl alcohol could be converted to oligomeric and polymeric compounds by heat [34,35] or acid sites [36] when they were accumulated in the reaction system. The loss of carbon was related to polymerization. As showed in Table 1, furfural could be converted to polymer with a 24% carbon loss. The polymerization product was hardly detected, so we count the loss of carbon as its ratio. When Co/Al₂O₃ was used as catalyst, the by-product THFAL was 17 mol%. Most of furfuryl alcohol was polymerized on the acid support, which was consistent with the previous reports [15,37,38]. It indicated that rearrangement reaction was hindered by the polymerization and over-hydrogenation. As for Co/TiO₂, because the cobalt particles were encapsulated in the TiO₂ in the effect of SMSI [39], the polymer formed by heat could block the some caves resulting in the partial loss of hydrogenation activity. Hence, the yield of CPO was higher than CPL. When Co was supported on ZrO₂, the polymerization reduced and the main product of CPL increased to 49 mol%. Changing the temperature to 160 °C, the yield of THFAL reduced to 2 mol%, which showed high temperature contributed to the rearrangement by increasing the concentration of hydrogen ions which was related to temperature. The catalytic activity increased and product distribution tended to be CPL. Therefore, the furfuryl alcohol underwent the rearrangement reaction instead of over-hydrogenation and polymerization. After doping La2O3, the catalytic activity raised and CPO was further hydrogenation into CPL. The 82 mol% yield of CPL was obtained at 160 °C, 2 MPa, 4 h over Co/ZrO₂-La₂O₃.

The reason of high catalytic activity with the addition of La₂O₃ was studied by XRD and NH₃-TPD. All Zr-based supports were characterized by XRD patterns to study the crystal morphology. As showed in Fig. 1, the diffraction peaks of ZrO₂ could be indexed to two different phases: the diffraction peaks at 24.3°, 28.1°, 31.3°, 34.6°, 41.2° and 50.1° were monoclinic zirconia (m-ZrO₂) while 30.3°, 35.2°, 50.6°, 60.0° and 62.23° were tetragonal zirconia (t-ZrO₂). The mixture phases were existed in ZrO₂. However, after adding some La, the diffraction peaks of m-ZrO₂ were disappeared. Only the diffraction peaks of t-ZrO₂ were observed without La species appeared. The shift of diffraction peaks in ZrO₂-La₂O₃ to lower angle suggested that La had been doped into ZrO₂ lattice and increased the interplanar spacing. Thus, t-ZrO₂ can be obtained from the mixture phase of t-ZrO₂ and m-ZrO₂ by doping La₂O₃, which may be the main reason for the good performance. After impregnation and calcination, Co/ZrO₂-La₂O₃ was synthesized and the t-ZrO₂ phase did not change compared with ZrO₂-La₂O₃. There was not the diffraction peak contributed by metallic Co, which demonstrated that Co species were highly dispersed on the surface of supports. Then, Co/ZrO₂-La₂O₃ was investigated at different conditions.

The acidic properties of the synthesized supports were investigated by NH₃-TPD. The results were shown in Fig. 2. The acid sites can be classified as weak acid sites (<200 °C), medium acid sites (200-400 °C) and strong acid sites (>400 °C) depending on NH₃ desorption temperatures [40]. The sample showed a desorption peak at about 120 °C, which meant the existence of weak acid sites. It was obvious that the peaks increased after doping of La₂O₃. This could be explained that the amount of acid sites in t-ZrO₂ was more than that in m-ZrO₂, which was consistent with previous reports [41]. This phenomenon indicated the dispersion of La species in ZrO₂ lattice was important for the increase of the acidity which may contributed to the conversion of furfural to CPL

2.2. Effect of reaction conditions on the conversion of furfural to CPL

The yields of furfural at different temperature catalyzed by Co/ZrO₂-La₂O₃ were illustrated in Fig 3a. The volcanic type curve of CPL could be recognized. The results showed that temperature had an influence on the product distribution during the hydrogenation process. In the investigated temperature range, the yield of CPL reached the maximum at 160 °C. Some CPO and furfural alcohol were remained at 150 °C. Lower temperature limited both the hydrogenation activity of the catalyst and the dissociation constant of water [42]. When the temperature was at 170 °C or higher, the polymerization was dominant. Based on the previous studies, furfuryl alcohol could polymerize [43]. It occurred at α -position and β -position of furan ring in the reaction system [36]. The polymer could attach on the surface of the catalyst and impair the activity. Therefore, 160 °C was optimal temperature for the rearrangement and hydrogenation. This moderate temperature not only produced enough hydrogen ions but also minimized the polymerization of furfural and furfuryl alcohol by heat.

The hydrogen pressure was one of the important factors affecting the final products. The initial hydrogen pressure was studied for the hydrogenation of furfural by Co/ZrO₂-La₂O₃. Fig. 3b showed the results of furfural hydrogenation carried out on different hydrogen pressure. When the initial pressure was 1 MPa, the main product was CPO. When the initial pressure raised to 2 MPa, CPO was hydrogenated to CPL. The yield of CPL improved obviously when the initial pressure raised from 1 MPa to 2 MPa, which was similar to the Ni/CNTs [27]. Thus, the low pressure was suitable for producing CPO while the high pressure can increase the selectivity to CPL. A further increase in hydrogen pressure showed no improvement in selectivity, but a slight slip for CPL. A part of furfuryl alcohol was over-hydrogenated and 6 mol% THFAL was obtained when the pressure was up to 4 MPa. Therefore, the higher pressure could lead to a high selectivity to THFAL, which was the product of over-hydrogenation of furfuryl alcohol during the competing reaction with rearrangement. Therefore, 2 MPa was the optimal pressure for the high selectivity for CPL.

The kinetics curves could reflect the reaction pathway clearly. The Fig. 3c exhibited the product distribution for the conversion of furfural at different reaction time. The zero time was the moment that the reaction temperature reached 160 °C. Firstly, furfural was fast hydrogenated into furfuryl alcohol and then CPO began to accumulation by rearrangement. With the extension of time, CPL was obtained by the hydrogenation of CPO. The carbon balance was decreased significantly at the beginning since furfuryl alcohol polymerized partly to the compounds having conjugated diene structures with 5 to 30 furanic moieties [44]. It increased a little owing to the decomposition reaction according to the former report [45]. When the polymer formed, it would deposit on the surface of the catalyst, which could block the active sites for hydrogenation and decrease the catalytic activity [46].

2.3. The study of deactivation

A series of experiments were designed over $Co/ZrO_2-La_2O_3$ to study the deactivation in Table 2. When the reaction was preform at 80 °C for 2 h, the conversion was 95% without carbon loss. There wasn't polymer. The products were furfuryl alcohol and THFAL. The rearrangement didn't occur duo to lower concentration of hydrogen ions. After the recycle, the catalyst activity didn't change. Then, when the reaction was carried out at 160 °C, reaction time was set at 1 h to show the difference obviously. The conversion was 100% and the main product was CPL with a 42 mol% yield. There was 24% carbon loss which was caused by polymerization. However, after the reuse of catalysts, the main product was CPO without further hydrogenation and the conversion reduced to 92%. When CPO was the substrate, the conversion was 65% without polymerization under the same conditions. The catalytic activity was almost unchanged after the recycle, indicating the structure of the catalyst was intact. Therefore, the polymer could be the reason for the decrease the catalytic activity and the inhibition of the polymer formation should improve over the supported Co catalysts

3. Conclusion

In summary, cobalt catalysts loading on different supports were synthesized and applied in the hydrogenation of furfural into CPL in one step. Among the different supports, t-ZrO₂ obtained by doping La₂O₃ was high-efficient for the conversion of furfural into CPL after loading cobalt metal. Under the optimized conditions (160 °C, 2 MPa H₂ pressure and 4 h), the yield of CPL could reach up to 82 mol%. The change of phase in ZrO₂ was proved by XRD and the increase of acidity was demonstrate by NH₃-TPD that could improve the catalytic activity. Further studies to control the polymer formation during the reaction are currently undergoing.

4. Experiment

4.1. Chemicals materials

Furfural was purified by vacuum distillation and stored at -15°C. Furfuryl alcohol was not purified. Furfural (AR, >99%) Furfuryl alcohol (AR, >99%), tetrahydrofurfuryl alcohol (AR, >97%), cyclopentanone (AR, >97%), cyclopentanol (AR, >97%), Co(NO₃)₂·6H₂O (AR, >99%), La(NO₃)₃·6H₂O (AR, >44%), ZrOCl₂·8H₂O (AR, >99%), (NH₄)₂Ce(NO₃)₆ (AR, >99%) and CTAB (AR, >99%) were from Sinopharm Chemical Reagent Co., Ltd. Al₂O₃ was purchased from Aladdin Chemical Reagent Co., Ltd. TiO₂ was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd.

4.2. Catalyst preparation

 ZrO_2 was synthesized by co-precipitation/hydrothermal crystallization with a modification. Typically, a certain amount of hexadecyltrimethylammonium bromide (CTAB) was dissolved in deionized water at 60 °C with agitation. Zirconium oxychloride solution was added to give a clear homogeneous solution. The mixed solution contains Zr, CTAB and H₂O with molar ratio of 1:0.5:100, respectively. After 0.5 h, 1 mol/L sodium hydroxide solution was prepared and added dropwise under vigorous stirring to a constant pH of 9. Then, the mixture was aged at 90 °C for 10 h and followed by filtration and washing with deionized water and ethanol. Finally, the precipitate was dried at 105 °C overnight and then calcined in air at 550 °C for 4 h.

 ZrO_2 -La₂O₃ was synthesized by adding zirconium oxychloride solution and lanthanum solution to the clear homogeneous solution. The mixed solution contains Zr, La, CTAB and H₂O with a molar ratio of 1:0.2:0.5:100, respectively. After that, the process was same as that for preparing ZrO₂.

The Co based catalysts were prepared by impregnation method. Al_2O_3 and TiO_2 were calcined in air at 750 °C for 4 h to remove the impurities. The support (0.5 g) was dispersed in acetone (45 mg) with stirring at 45 °C. Cobalt nitrate (0.246 mg) was dissolved in 5 ml acetone and then added drop by drop to the above solution. After stirring for 24 h, acetone was removed by rotary evaporation. The catalyst was dried at 105 °C overnight and calcined at 300 °C for 2 h to remove the nitrates with a heating rate of 1 °C/min. Finally, the catalyst was calcined at 600 °C for 2 h at a rate of 1 °C/min again. The calcined catalysts were reduced in a H₂ atmosphere at 600 °C for 2 h with a heating rate of 1 °C/min before reaction. All the loadings were 8.8 wt% for the Co based catalysts according to ICP-AES.

Catalytic hydrogenation of furfural was carried out in a 25 ml stainless steel autoclave equipped with a magnetic stirrer. Typically, a mixture of furfural (1 mmol), catalyst (50 mg) and water (10 ml) were put into the reactor and purged with H_2 for several times. The reactor was pressured with H_2 to 2 MPa. Then the autoclave was heated to the desired temperature for 4 h. After reaction, the reactor was cooled to ambient temperature. The liquid products were extracted by ethyl acetate and then analyzed by a gas chromatograph (GC, Kexiao 1690) with a HP-INNOMAX capillary column (30 m×0.25 mm×0.25 µm) and GC-MS (Agilent 7890A). The GC

detecting conditions were as follows: nitrogen was the carrier gas; injection port temperature was 280 °C; detector (FID) temperature was 280 °C. Column temperature heated from 40 °C to 250 °C with a heating rate of 10 °C/min. The *n*-hexanol was used as internal standard to quantify the products.

4.3. Characterization methods

X-ray diffraction (XRD) was conducted on an X-ray diffractometer (TTR-III, Rigaku Corp, Japan) using Cu K α radiation (λ = 1.54056 Å). The data were recorded over 2 θ ranges of 20-70°.

Temperature-programmed desorption was carried out in a home-built reactor system coupled to a gas chromatograph. All the gas flow was set to 40 mL/min. Temperature-programmed desorption of ammonia (NH_3 -TPD) was employed to determine the total acidity of the catalysts. Prior to absorption of ammonia, 80 mg catalyst sample was heated at 500 °C for 1 h under Ar flow and then cooled to 80 °C followed by saturating with pure NH_3 for 1 h. Then after flushing with Ar for 1 h, the NH_3 -TPD was performed from 80 to 650 °C with a heating rate of 10 °C/min. Desorbed ammonia was monitored by an on-line gas chromatograph equipped with a thermal conductivity detector (TCD).

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Fig. 1. XRD patterns of (a) ZrO₂, (b) ZrO₂-La₂O₃ and (c) Co/ZrO₂-La₂O₃.



Fig.2. NH₃-TPD profiles of (a) ZrO₂, (b) ZrO₂-La₂O₃.



Fig. 3. Catalytic performance of Co/ZrO₂-La₂O₃ at different temperature (a), hydrogen pressure (b), reaction time (c).



Scheme 1. The reaction mechanism for the conversion of furfural into CPL

Table 1	Hydrogenation	of furfural	with various	cobalt cataly	sts.
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Entry	Catalyst	Temperature (°C)	Conversion (%)	Yield (mol%)	Carbon			
				CPL	CPO	FAL	THFAL	Balance (%)
1	-	150	24	0	0	0	0	76
2	Co/Al ₂ O ₃	150	100	32	1	0	17	50
3	Co/TiO ₂	150	100	21	36	8	5	70
4	Co/ZrO ₂	150	100	49	2	0	8	61
5	Co/ZrO ₂	160	100	68	14	0	2	84
6	Co/ZrO ₂ -La ₂ O ₃	160	100	82	4	0	2	88

Reaction condition: Furfural (1 mmol), catalyst (50 mg), 2 MPa H_2 , H_2O (10 mL), 4 h.

Table 2 Hydrogenation of furfural and CPO at different conditions over Co/ZrO₂-La₂O₃

Entry S	Carls at an ta	Temperature	Time Pressure		Conversion	Yield (mol%)				Carbon
	Substrate	(°C)	(h)	(MPa)	(%)	CPL	CPO	FAL	THFAL	balance (%)
1	Furfural	80	2	2	95	0	0	94	1	100
2 a	Furfural	80	2	2	95	0	0	94	1	100
3	Furfural	160	1	2	100	42	26	4	4	76
4 ^a	Furfural	160	1	2	92	2	56	14	0	80
5	CPO	160	1	2	65	65	35 ^b	0	0	100
6 ^a	CPO	160	1	2	64	64	36 ^b	0	0	100

^a Recycle experiment.

^b The yield of CPO means the unreacted CPO.