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Selective Conversion of Furfural to Cyclopentanone or Cyclopentanol Using Co-Ni Catalyst in Water

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Abstract: Co-Ni catalysts, prepared by a typical wetness impregnation method, can selectively convert furfural (FFA) to cyclopentanone (CPO) or cyclopentanol (CPL) in water, respectively. The catalytic performance depends strongly on the support. It is also strongly influenced by the Co-Ni loadings of the catalyst. The 10%Co-10%Ni/TiO_2 catalyst showed the highest selectivity toward CPO (53.3%) with almost complete FFA conversion, and the main product was CPL (45.4%) over 20%Co/TiO_2 at the optimized conditions (150 °C, 4 MPa H_2, 4 h). The surface morphology, surface area, composition and reducibility properties of these catalysts were fully characterized by XRD, H_2-TPR, ICP-AES and SEM. The factors that influenced the activity of catalysts were also investigated in detail. Additionally, the stability of catalyst for the hydrogenative rearrangement of FFA was studied.

Keywords: furfural; Co-Ni catalyst; cyclopentanone; cyclopentanol; hydrogenation

1. Introduction

The development and utilization of renewable sources for chemical and energy production are significant replacements for fossil-based chemical and fuel production [1,2]. Among the biomass-derived chemicals, furfural (FFA) derived from hemicellulose is viewed as an important platform molecule and used as a raw material for the synthesis of important industrial chemicals which are employed in plastic, agrochemicals and pharmaceutical. Meanwhile, furfural can be applied to resin production or as an extracting agent of aromatic compounds of lubricants. Furfural can be converted into higher added-value products such as furfuryl alcohol (FA), tetrahydrofurfurylalcohol (THFA), 2-methylfuran (MF), cyclopentanone (CPO) and cyclopentanol (CPL) through hydrogenation, rearrangement and resinification [3,4]. CPO or CPL, containing five-membered alicyclic rings, can be utilised as starting materials for the synthesis of medicines, pharmaceuticals, fungicides, fragrance chemicals, and so on [5,6]. The traditional method for production of CPO or CPL is mainly by catalytic cyclization of 1,6-hexanediol or adipic esters [7–9] with yields of 53% and 22%, respectively.

The selective hydrogenation rearrangement of furfural in aqueous solution provides an alternative route for the production of CPO and CPL from renewable resources instead of from nonrenewable petroleum. Supported precious metal catalysts (such as Au, Ru, Rh and Pt) [10–14] have been extensively investigated in this reaction due to their good hydrogenation performance, approaching 100%, which are practically hindered because of high cost and limited resource. In recent years, many non-noble catalysts were all reported as being active catalysts in the hydrogenation of FFA. Over NiCu-50/SBA-15 [15,16] catalysts, the nearly complete conversion of furfural was achieved with 62% selectivity of CPO and 3% of CPL. 99.3% conversion of furfural and a 96.9% yield of cyclopentanone could be produced with CuNi@C [17]. Using Co/ZrO_2-La_2O_3 [18] could catalyze furfural completely and obtain CPO and CPL with yields of 4% and 82%, respectively. Some researchers studied the Cu–Co-OG-500 catalysts with a yield of 67% of CPO and a yield of 68% CPL [19]. Unfortunately, these catalysts often promoted unsaturated C=C in the furan ring hydrogenation. Catalytic furfural-to-CPO transformation in a highly selective, efficient, robust and scalable manner still remains a pending challenge. Therefore, as an effective alternative, Ni-based catalysts are a good choice for the selective conversion of FFA to CPO or CPL due to their high efficiency for C=O polarization and poor activity for furan ring hydrogenation. However, Ni catalysts often promote excessive C=O hydrogenation, resulting in a low selectivity to CPO. It was reported that Co-based catalysts had a good hydrogenation and ring closing ability in the synthesis of five-membered rings [19]. On the other hand, Co could stabilize the Ni–Co structure, and so it is more attractive to use inexpensive Ni–Co catalysts rather than other supported metal catalysts. TiO_2 affords mild water-compatible Lewis acid sites, which can facilitate the rearrangement of five-substituted furan derivatives.

In this work, a series of TiO_2 supported Ni–Co catalysts were prepared and tested for the production of CPO or CPL from furfural by selective hydrogenation rearrangement. These samples were characterized to study the relationship between the structure and their catalytic performance. The influence of reaction conditions, including temperature, H_2 pressure and reaction time, on the catalytic performance was also discussed. Moreover, experiments of catalyst recycling were also performed.

2. Results and Discussion

2.1. Catalyst Characterization Studies

2.1.1. XRD

The phase structure of the reduced samples was analyzed using X-ray diffraction. The XRD patterns for Ni/TiO_2, CoNi/TiO_2, and Co/TiO_2 after reduction are shown in Figure 1. The phase attributed to anatase-TiO_2 with the characteristic diffraction peaks at 2θ of 25.3°, 37.9°, 47.9°, 54.1°, 54.8° and 62.8° [20] is observed in all samples with different Ni-Co content. It is found that there is hardly any difference in TiO_2 structure among these four catalysts after reduction, and no phase transfer of TiO_2 is observed. XRD patterns of reduced Ni/TiO_2 catalyst show peaks at 2θ of 45.5°, 51.9° and 76.4°, respectively corresponding to lattice plane (111), (200) and (220) of metallic nickel (JCPDS 04-0850) [21,22]. One obvious diffraction line at 2θ of 44.2° attributed to crystalline Co is observed for the Co/TiO_2 sample [23], indicating that only metallic Ni or Co presented on the surface of Ni/TiO_2 or Co/TiO_2 after reduction with H_2, which can also be verified by XPS results (Figure S1 in the Supporting Information). It can be clearly seen from patterns b and c that only one peak is observed for all of the Co–Ni/TiO_2 catalysts. This reveals that a homogeneous CoNi alloy is formed after reduction for the bimetallic catalysts [24–26]. All diffraction peaks of these catalysts are sharp and intense, indicating their highly crystalline nature.

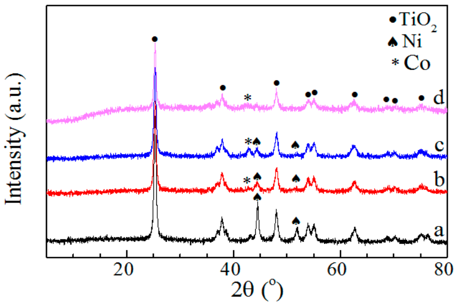

Figure 1. XRD patterns of (a) 20%Ni-TiO_2; (b) 10%Co-10%Ni-TiO_2; (c) 10%Co-10%Ni-TiO_2-A; and (d) 20%Co-TiO_2 after reduction.

2.1.2. H_2-TPR

H_2-TPR studies were carried out to elucidate the impact of active phase (Ni and or Co) composition or support (TiO_2) on the redox properties of different catalysts [27]. The TPR profile of the Ni/TiO_2 sample (curve a, Figure 2) shows mainly one reduction peak from around 300 to 475 °C, which can be assigned to the reduction of amorphous NiO to Ni^0 [26]. The Co/TiO_2 sample (curve d) presents two reduction peaks in the range of 200~600 °C, one around 330 °C, corresponding to the reduction of Co_3O_4 to CoO and the other at ca. 465 °C are attributed to the complete reduction of CoO to metallic Co [20]. For the bimetallic catalysts, the peaks are observed to start at a lower temperature of 245 °C and end at 510 °C. The TPR profile of 10%Co-10%Ni-TiO_2 sample (curve b) shows two sharp peaks at 270 °C and 428 °C, assigned to the reduction of NiO and $NiCo_2O_4$, respectively. For the 10%Co-10%Ni-TiO_2-A sample (c), two reduction peaks are also observed, one centred at 282 °C and the latter centred at 438 °C, both shifted to higher temperature in comparison with 10%Co-10%Ni-TiO_2, which may be partly ascribed to the strong metal support interaction after addition of NaOH. The above results clearly indicate that the Co-Ni alloy is formed in the bimetallic samples at higher temperatures compared with those of Co^0 and Ni^0 formation in monometallic samples.

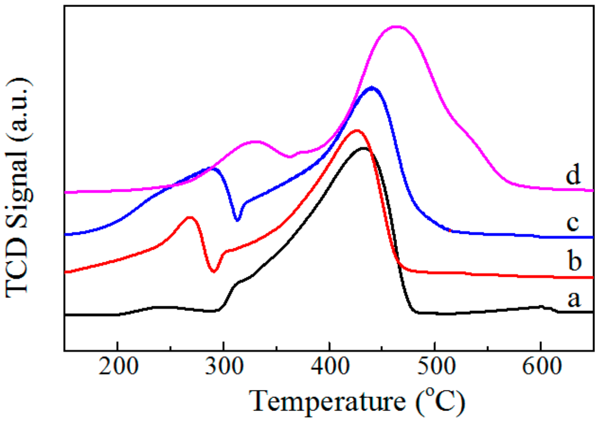

Figure 2. H_2-TPR profiles of catalysts: (a) 20%Ni-TiO_2, (b) 10%Co-10%Ni-TiO_2, (c) 10%Co-10%Ni-TiO_2-A, (d) 20%Co-TiO_2.

2.1.3. SEM

Figure 3 shows the SEM images of 20%Ni-TiO_2, 10%Co-10%Ni-TiO_2, 10%Co-10%Ni-TiO_2-A and 20%Co-TiO_2. Both 20%Ni-TiO_2 (Figure 3a) and 20%Co-TiO_2 (Figure 3d) consist of solid microspheres with a relatively smooth surface, with diameters in the range of several tens to hundreds of nanometers. As showed in Figure 3b,c, the surface morphology of the catalysts 10%Ni-10%Co-TiO_2 and 10%Ni-10%Co-TiO_2-A are similar to those of 20%Ni-TiO_2 and 20%Co-TiO_2 samples, showing that the crystal structure is stable. However, the size of the microspheres of Co–Ni-codoped TiO_2 samples increases obviously, in good agreement with XRD results. This could be ascribed to Co^{2+} or Ni^{2+} ions partial substitution of Ti^{4+} ions or doping into the lattice structures of TiO_2 by occupying the octahedral site to form a solid solution.

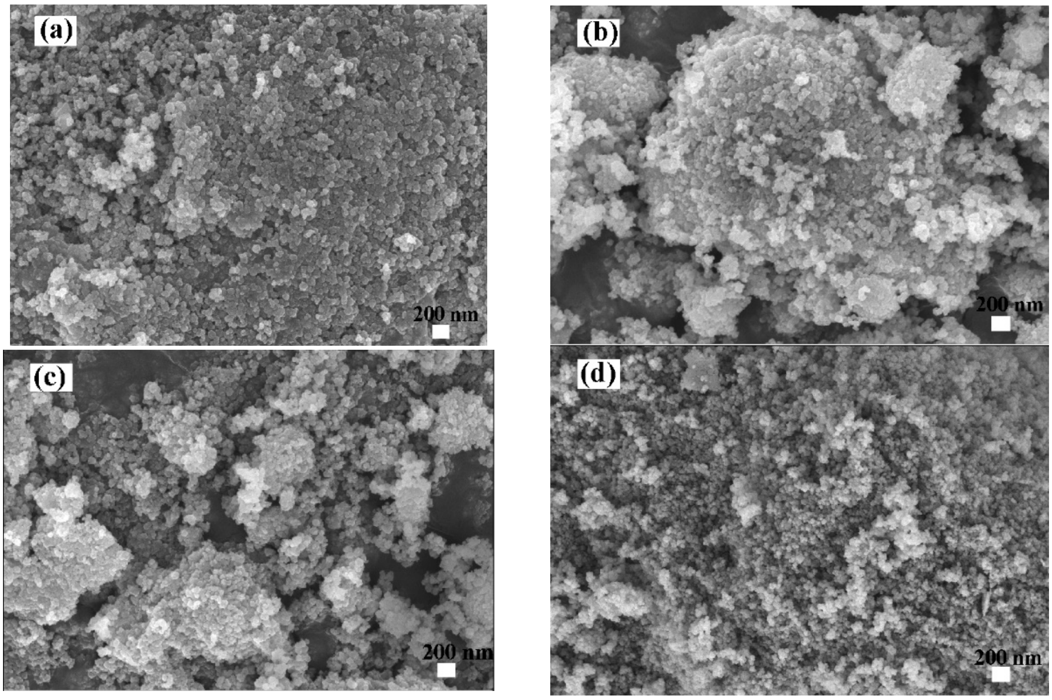

Figure 3. SEM micrograph for the catalysts: (**a**) 20%Ni/TiO_2; (**b**) 10%Ni-10%Co/TiO_2; (**c**) 10%Ni-10%Co/TiO_2-A and (**d**) 20%Co/TiO_2 in different views.

2.2. Screening of Catalysts for the Conversion of Furfural

The catalytic hydrogenation of FFA in water over nickel and cobalt-based catalysts was carried out under 150 °C and 4 MPa H_2. Table 1 shows the catalytic results obtained over a series of supported Ni-Co catalysts for the selective conversion of furfural to CPO or CPL in aqueous solution. On these investigated catalysts, CPO, CPL, FA, THFA, 1,2-pentanediol (1,2-PeD) and 1,5-pentanediol (1,5-PeD) were formed as the major products. Other products mainly included little 2-cyclopentenone, butanol, 2-pentanol and some unidentified compounds possibly from the resinification of furfural or furfural alcohol at higher concentration, which was identified by GC and GC-MS analysis (Figures S2 and S3 in Supporting Information).

Table 1. Results of furfural conversion over supported catalysts.

Catalyst	**Conv. (%)**	**Product Selectivity (%)**					
		CPO	**CPL**	**FA**	**THFA**	**1,2-PeD**	**1,5-PeD**
5%Ni-15%Co/H-ZSM5	59	14	23	1.7	2.4	0.4	0
5%Ni-15%Co/HPO	63	18	3	6.1	4.6	0	0
5%Ni-15%Co/γ-Al_2O_3	89	6.7	33	13	24	0	0
5%Ni-15%Co/ZrO_2	84	15	3	21	0	0.9	0
5%Ni-15%Co/TiO_2	100	42.1	11.5	13.2	0.4	3.4	1.4

FFA: furfural; CPO: cyclopentanone; CPL: cyclopentanol; FA: furfuryl alcohol; THFA: tetrahydrofurfurylalcohol; PeD: pentanediol. HPO: hollow titanium silicalite zeolite provided by Research Institute of Petroleum Processing (RIPP), SINOPEC. Reaction conditions: FFA (5.2 mmol), catalyst (0.3 g), water (10 mL), 150 °C, 4 MPa H_2, 4 h.

Only 18% selectivity of CPO and CPL was obtained when the hydrogenation of furfural catalyzed by 5%Ni-15%Co/ZrO_2 in water at 140 °C (Table 1, entry 4). The byproducts were mainly FA. The 5%Ni-15%Co/H-ZSM5 and 5%Ni-15%Co/HPO catalysts gave the combined CPO and CPL selectivity of 37% and 21%, respectively. When 5%Ni-15%Co/γ-Al_2O_3 was used, the selectivity to CPO and CPL increased to 39.7%. As for 5%Ni-15%Co/TiO_2 catalyst, a conversion of 100% was obtained at the reaction time of 4 h. Meanwhile, the selectivity of CPO and CPL reached 53.6%. These results demonstrate that TiO_2 is an effective support for the Ni-Co catalyst in the selective conversion of furfural.

Thus, a series of Co-Ni catalysts with different Co/Ni contents were prepared and their catalytic activities were tested for the production of CPO or CPL from FFA. The results of hydrogenation of furfural over various catalysts were listed in Table 2. No CPO or CPL were detected when TiO_2 was used as catalyst, indicating that TiO_2 itself was nearly inactive in this reaction (Table 2, entry 1). TiO_2-supported Co or Ni catalysts displayed better activity but only 1.0% selectivity of CPO for 20%Co/TiO_2 and 12.2% selectivity of CPO for 20%Ni/TiO_2. Correspondingly, the selectivity of CPL could reach up to 45.4% and 39.4%, respectively (entries 2 and 6). Compared to 20%Co/TiO_2 or 20%Ni/TiO_2 catalysts, 80.4% FFA conversion and 42.1% CPO selectivity was achieved over 5%Ni-15%Co/TiO_2 (entry 3). As Ni content increased, the CPO selectivity was improved, with the biggest value of 53.3% over 10%Ni-10%Co/TiO_2 catalyst at a FFA conversion of 100% (entry 4), and then dropped as the Ni loading continued to increase. The selectivity of CPO dropped to 49.6%, for catalyst 15%Ni-5%Co/TiO_2 (entry 5) under the same reaction conditions. This reveals that Ni-Co and TiO_2 collaboratively catalyze this reaction. Clearly, the Ni/Co ratio of the catalysts had a strong influence on reaction activity and product distribution for furfural conversion. 10%Co-10%Ni/TiO_2-A catalyst (entry 7) showed different product distribution compared to the other six catalysts and a THFA yield of 71.1% (instead of CPO observed on the base-free catalysts) was obtained with 100% FFA conversion. These results indicated that hydrogenation rather than rearrangement of furan ring was favored on a basic support.

Table 2. Product distribution for the hydrogenation rearrangement of FFA over different catalysts.

Entry	Catalyst	Conv. (%)	Product Selectivity (%)						
			CPO	CPL	FA	THFA	1,2-PeD	1,5-PeD	Others
1	TiO_2	23.5	0	0	0.36	0.68	0	0	98.9
2	20%Co/TiO_2 [a]	100	1.0	45.4	10.6	2.7	0.4	0.6	39.3
3	5%Ni-15%Co/TiO_2 [a]	100	42.1	11.5	13.2	0.4	3.4	1.4	28
4	10%Ni-10% Co/TiO_2 [a]	100	53.3	16.3	1.6	2.3	5.3	2.2	19
5	15%Ni-5%Co/TiO_2 [a]	100	49.6	15.2	1.2	1.7	4.3	1.8	26.2
6	20%Ni/TiO_2 [a]	100	12.2	39.4	0.5	4.5	2	0	41.4
7	10%Co-10%Ni/TiO_2-A [b]	100	0	0.2	0.3	71.1	0.3	0.5	27.6

Conditions: FFA (5.2 mmol), catalyst (0.3 g), water (10 mL), 150 °C, a = 4 MPa H_2, b = 2 MPa H_2, 4 h. Products mainly including CPO, CPL, FA, THFA, 1,2-PeD and 1,5-PeD.

2.3. Optimization of Reaction Parameters

FFA hydrogenation rearrangement reactions were carried out in the temperature range from 110 to 170 °C (Figure 4). It was found that the reaction temperature had a significant influence on FFA conversion and the yield of main products. Above 70% FFA conversion was obtained with FA yield of 51.2%, even at the low temperature of 110 °C, indicating that 10%Co-10%Ni-TiO_2 catalyst had better catalytic activity for FFA conversion. As the reaction temperature increased from 110 to 140 °C, the formation of CPO increased from 6.9 to 22.1% and the FFA conversion almost remained the same (about 77%). The reason may be that the H^+ ions were produced from water dissociation at higher temperature, which played a key role in the protonation of FA, which was a key step in the rearrangement of FFA [19]. The yield of CPO continued to increase along with the rising temperature, especially from 140 to 160 °C. At temperatures of 150 °C, 16.3% of CPL was obtained by excessive hydrogenation, suggesting that CPO underwent further hydrogenation to CPL. Product distribution showed that the yield towards CPO was reduced to 28.4% at 170 °C, while the total yield for CPL, FA and THFA products decreased to 3.7%. At a temperature higher than 170 °C, the formation of oligomers was strongly enhanced, resulting in a sharp decline of product selectivity.

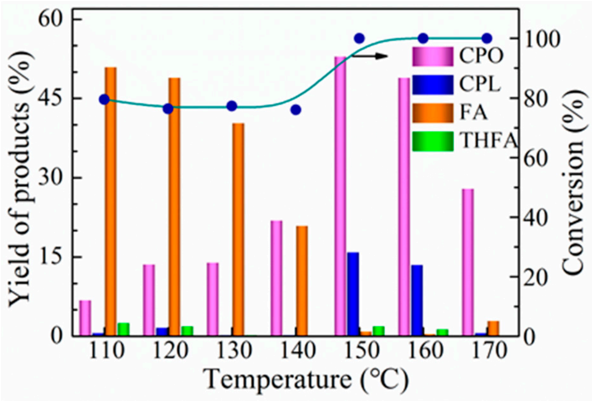

Figure 4. Conversion of furfural over 10%Co-10%Ni-TiO_2 at different temperatures. Reaction conditions: FFA (0.5 g), catalyst (0.3 g), water (15 mL), 4 MPa H_2, 4 h (●: conversion).

As shown in Figure 5, FFA conversion and CPO yield increased with H_2 pressure. 53.3% selectivity of CPO was gained with completed conversion of furfural at 4 MPa H_2, and then dropped with the continuously increasing H_2 pressure. The selectivity of CPL increased from 16.3% to 18.2% with the increase of the pressure from 4 to 5 MPa, demonstrating that higher H_2 pressure could promote further hydrogenation of unsaturated CPO as well as the further degradation of FFA.

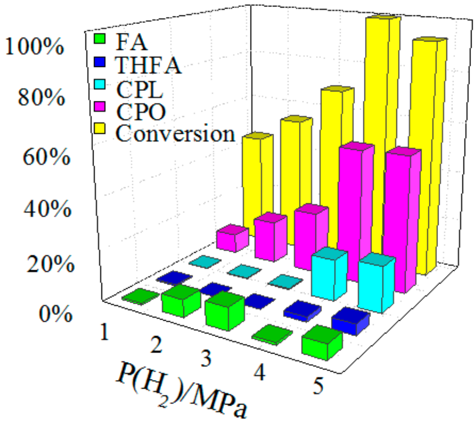

Figure 5. Conversion of furfural over 10%Co-10%Ni-TiO_2 at different H_2 pressure. Reaction conditions: FFA (0.5 g), catalyst (0.3 g), water (15 mL), 150 °C, 4 h.

The product distribution over 10%Co-10%Ni-TiO_2 catalyst in reaction time range of 1~6 h was determined and presented in Figure 6. It could be seen that FA was the main product in the first 1 h and decreased with time, indicating that FA as an intermediate was first formed during FFA hydrogenation. As the reaction proceeded, both FFA conversion and CPO yield gradually increased, suggesting that further rearrangement of FA to CPO occurred possibly via the catalysis reaction by H^+ ions. FFA converted completely over 10%Co-10%Ni-TiO_2 after 4 h, 15% CPL and 45% CPO were acquired. Further increasing the reaction time to 5 h, the yield of CPO kept constant and the main by-products was 14% CPL, 7% FA and 2.3% THFA. It was worth noting that the catalytic activity did not improve with further increasing reaction time to 6 h.

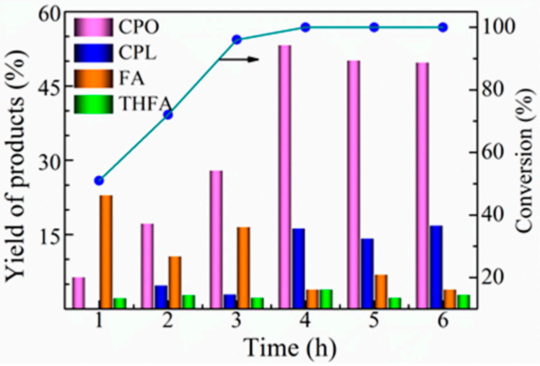

Figure 6. Effect of reaction time on FFA conversion and product selectivity over 10%Co-10%Ni-TiO_2. Reaction conditions: FFA (0.5 g), catalyst (0.3 g), water (15 mL), 150 °C, 4 MPa H_2 (•: conversion).

2.4. Catalyst Recycling

Testing the stability of the 10%Co-10%Ni-TiO_2 catalyst, recycling experiments were performed in five repeated runs. After reaction, the catalyst was collected with centrifugation. Then, the spent catalyst was fully washed with ethanol and subsequently with water for three times each to remove the adsorbed products after each run. After being dried under 70 °C, the catalyst was reused in a subsequent run. As shown in Figure 7, FFA conversion (100% in the first two cycles versus 94% in the third cycle) and the total selectivity of CPO and CPL (64.5~69.6%) almost remained constant over 10%Co-10%Ni-TiO_2 in the first three runs. The conversion of FFA decreased to 85% for the fifth run, and the combined yields of CPO and CPL decreased to 50% in the case of cycle 5. It was shown that the activity of the catalyst decreased to some extent. A series of tests were also carried out to determine the key factors leading to the slight activity loss of the catalyst. There was no significant change in the XRD patterns between fresh and reused 10%Co-10%Ni-TiO_2 catalyst (Figure S4, Supporting Information). Morphology of 10%Co-10%Ni-TiO_2 was also not changed after the reaction (Figure S5, Supporting Information). Ni content decreased from 10 to 8.98 wt % after being recycled five times, which indicated that the metal leaching existed in the reaction (Table S1 of the Supporting Information). The solution was also collected after the fifth cycles with the 10%Co-10%Ni-TiO_2 catalyst and the Ni and Co content in the solution were 0.165 and 0.012 g/L, respectively. Thus, the partial loss of Ni from 10%Co-10%Ni-TiO_2 materials might be the main reason for the slight loss of the reaction activity, which may be due to relatively weaker interaction between Ni and the support TiO_2.

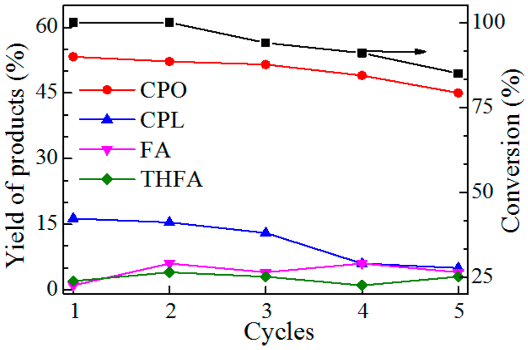

Figure 7. Reuse of the 10%Co-10%Ni-TiO_2 catalyst in FFA hydrogenation. Reaction conditions: FFA (5 mmol), catalyst (0.3 g), water (15 mL), 150 °C, 4 MPa H_2, 4 h (■: conversion).

3. Experimental Section

3.1. Catalyst Materials and Preparation

Furfural (>99.0%, AR), furfuryl alcohol (>99.0%, AR), tetrahydrofurfuryl alcohol (>99.0%, AR), cyclopentanol (>97%, CP) and cyclopentanone (>97%, CP) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, H-ZSM-5, γAl_2O_3, ZrO_2, HPO, TiO_2 were purchased from Macklin Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received without further purification.

Co-Ni catalysts with different supports and mass percentages of cobalt and nickel were prepared by a typical wetness impregnation method [28]. Typically, a certain proportion of $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in 10 mL of deionized water under magnetic stirring at 80 °C. Then 4 g supports (H-ZSM-5, γ-Al_2O_3, ZrO_2, HPO or TiO_2) were added and the mixture was stirred for 2 h. Subsequently, the solid was calcined at 350 °C for 4 h (heating ramp was 5 °C min^{-1}) after drying for 24 h at 110 °C. The obtained samples were then reduced in a H_2 atmosphere at 350 °C for 4 h. The obtained Co-Ni catalysts were denoted as x%Co-y%Ni/supports (x, y refer to Co and Ni loading, respectively, supports means H-ZSM-5, γ-Al_2O_3, ZrO_2, HPO or TiO_2). 10%Co-10%Ni/TiO_2-A was prepared with the same procedure as 10%Co-10%Ni/TiO_2, except that the mixture pH was adjusted to 7.0 by NaOH (2.5 M) after adding TiO_2.

3.2. Characterization of Catalysts

Powder X-ray diffraction (XRD) patterns of different catalysts were obtained with a Bruker D8 Advance X-ray diffractometer (Bruker, Ettlingen, Germany) using Cu Kα irradiation (λ = 1.54056 Å) over 2θ ranges from 10 to 80°. The temperature-programmed reduction (H_2-TPR) study was performed by Auto Chem. II 2920 Instrument (Mircromeritics, Norcross, GA, USA). Scanning electron microscopy (SEM) (Hitachi S-4800, Tokyo, Japan) analysis was conducted on a Hitachi S-4800 electron microscope working at 200 kV. ICP analyses were carried out on a Thermo IRIS Intrepid II XSP atomic emission spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) to determine the chemical composition of catalysts and metal leaching during reactions. The products were identified using a gas chromatograph coupled with a mass spectrometer (GC-MS, Agilent, 7890 A, Santa Clara, CA, USA).

3.3. Typical Procedure for Catalytic Conversion of Furfural

The catalytic conversion of furfural was performed in a 50 mL stainless autoclave equipped with a magnetic stirrer, a pressure gauge and automatic electric heating sleeve. Following the loading of the autoclave with 0.5 g of furfural, 0.3 g of catalyst and 15 mL of deionized water, the reactor was sealed and purged with H_2 three times to exclude air. Then, the hydrogen pressure was raised to a certain value and the reaction was conducted at a series of temperatures (110 to 170 °C) for a certain reaction time (1 to 6 h) with the stirring speed of 600 rpm. After reaction, the resultant product mixtures were analyzed by gas chromatography (GC, Agilent, 7890A, Santa Clara, CA, USA). The products were identified by a 7890A (Agilent) gas chromatography coupled with a 5975C mass spectrometer detector. FFA conversion, product yield and selectivity and carbon balance were defined as follows:

$$\text{Conversion of FFA } (\%) = \left(1 - \frac{\text{moles of FFA after reaction}}{\text{moles of FFA introduced}}\right) \times 100\%$$

$$\text{Yield of product } (\%) = \left(\frac{\text{moles of each product}}{\text{moles of FFA introduced}}\right) \times 100\%$$

$$\text{Selectivity of product } (\%) = \left(\frac{\text{moles of each product}}{\text{moles of FFA converted}}\right) \times 100\%$$

$$\text{Carbon balance } (\%) = \left(\frac{\text{moles of products}}{\text{mole of FFA converted}}\right) \times 100\%$$

4. Conclusions

In summary, a Co/Ni catalytic system was developed for the selective conversion of FFA to CPO or CPL in aqueous solution. The product selectivity could be easily modulated by support and mass ratio of Co/Ni as well as the pH of the impregnation solution. Complete conversion of FFA with a selectivity to CPO higher than 53.3% was achieved and showed some activity decrease after being recycled five times over bimetallic 10%Co-10%Ni/TiO_2 catalyst under 150 °C and 4 MPa H_2. The relatively poor hydrothermal stability of the 10%Co-10%Ni/TiO_2 was partially responsible for the decrease in the repeated runs. 10%Co-10%Ni/TiO_2-A catalyst was favored for transformation of FFA to THFA with a high yield of >71% under the same reaction conditions. Further research is underway to improve the selectivity and stability of current catalysts and to achieve the rational design of catalysts for the direct conversion of carbohydrates to the desired CPO and CPL products.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/5/193/s1, Table S1. The compositions of 10%Co-10%Ni-TiO_2 catalysts; Figure S1. XPS spectras and the deconvoluted configurations for (a) 20%Ni/TiO_2, (b,c) 10%Ni-10%Co/TiO_2, (d,e) 10%Ni-10%Co/TiO_2-A and (f) 20%Co/TiO_2 catalysts; Figure S2. Representative GC spectrum of furfural hydrogenation in water over. 10%Ni-10%Co/TiO_2; Figure S3. The qualitative results for liquid products from furfural hydrogenation by GC-MS; Figure S4. XRD patterns of fresh (a) and used (b) 10%Co-10%Ni-TiO_2 catalyst; Figure S5. SEM micrograph for the fresh (a) and used (b) 10%Co-10%Ni-TiO_2 catalyst.

Author Contributions: X.G., Y.L. and Y.S. conceived and designed the experiments; Y.L. performed the experiments; X.M. and X.C. analyzed the data; D.L. contributed reagents/materials/analysis tools; Y.L. and X.G. wrote the paper.

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Conflicts of Interest: The authors declare no conflicts of interest.

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