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Effective synthesis of 5-amino-1-pentanol by reductive amination of biomass-derived 2-hydroxytetrahydropyran over supported Ni catalysts

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ABSTRACT

A highly efficient and green process was developed for the synthesis of useful 5-amino-1-pentanol (5-AP) from biomass-derived dihydropyran by coupling the in situ generation of 5-hydroxypentanal (5-HP, via the ring-opening tautomerization of 2-hydroxytetrahydropyran (2-HTHP)) and its reductive amination over supported Ni catalysts. The catalytic performances of the supported Ni catalysts on different oxides including SiO₂, TiO₂, ZrO₂, γ-Al₂O₃, and MgO as well as several commercial hydrogenation catalysts were investigated. The Ni/ZrO₂ catalyst presented the highest 5-AP yield. The characterization results of the oxide-supported Ni catalysts showed that the Ni/ZrO₂ catalyst possessed high reducibility and a high surface acid density, which lead to the enhanced activity and selectivity of the catalyst. The effect of reaction parameters on the catalytic performance of the Ni/ZrO₂ catalyst was studied, and a high 5-AP yield of 90.8% was achieved in the reductive amination of 2-HTHP aqueous solution under mild conditions of 80 °C and 2 MPa H₂. The stability of the Ni/ZrO₂ catalyst was studied using a continuous flow reactor, and only a slight decrease in the 5-AP yield was observed after a 90-h time-on-stream. Additionally, the reaction pathways for the reductive amination of 2-HTHP to synthesize 5-AP were proposed.

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1. Introduction

Nitrogen-containing compounds, particularly primary amines, are among the most important intermediates in the chemical industry with wide applications in the synthesis of polymers, pharmaceuticals, agrochemicals, dyes, and surfactants [1–3]. Nowadays, the general commercial routes for primary amine synthesis are the direct amination of alkyl halides

or epoxides with ammonia, and the hydrogenation of nitriles or amides [2,4]. These processes generally suffer from high cost due to the lack of organic feedstocks with special functional group(s) or the generation of large amounts of waste. Therefore, much attention has been paid to the development of new catalytic processes for the efficient and sustainable production of primary amines [2,4–9].

Due to the readily available alcohols from not only the coal

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and petroleum industry but also renewable biomass, the direct amination of alcohols has been developed for the production of primary amines in recent years [2,4,10–12]. The direct amination of alcohols is widely considered to be proceeded by the borrowing hydrogen mechanism (BH, Scheme 1), and water is generated as the main byproduct [2,4,10–13]. Nonetheless, this process generally requires high reaction temperatures in the range of 150–250 °C, owing to the dehydrogenation of C–OH over metal catalysts usually occurred at a high temperature (Scheme 1, Step 1) [2]. Such a high temperature favors the generation of many byproducts, e.g., secondary and tertiary amines, and other nitrogen-containing heterocyclic compounds [2]. Differently, the direct reductive amination of aldehydes or ketones with ammonia does not require the dehydrogenation of C–OH. Thus, this provides an attractive approach to the synthesis of primary amines with high selectivity at temperatures ≤ 120 °C [2,3,9].

It is known that carbonyl intermediates are usually generated during the preparation of alcohols (including diols) by transforming renewable lignocellulose and its derived platform molecules [9,14–16]. Therefore, the coupling of the formation of renewable aldehydes or ketones and their reductive amination may shed light on the sustainable synthesis of amines with high efficiency [2,8,9,14]. For instance, Zhang and coworkers [9] recently reported the first example of the direct conversion of cellulose into highly useful ethanolamines by a two-step approach: cellulose conversion to glycolaldehyde, followed by reductive amination. Ethanolamine with 10% yield was obtained from cellulose over a Ru/ZrO₂ catalyst at a low temperature of 75 °C, and a high (93%) ethanolamine yield could be achieved using glycolaldehyde as a reactant. Sels et al. [8] reported a new process for the efficient synthesis of short amines from carbohydrates by reductive aminolysis of the short carbonyl intermediates from the enzymatic retro-aldol C–C bond scission of the sugar molecule. Valuable bio-based amines with yields of up to 87% were attained in one step at a temperature below 132 °C.

In this work, we report on the efficient synthesis of 5-amino-1-pentanol (5-AP), an important amino alcohol that can be used in the synthesis of anti-inflammatory drugs and anticancer drugs, from biomass-derived dihydropyran by coupling the in situ generation of 5-hydroxypentanal (5-HP) and its reductive amination over supported Ni catalysts under mild conditions (Scheme 2, Route B). 5-HP is a ring-opened tauto-

Scheme 1. Direct amination of alcohols with ammonia by the borrowing hydrogen mechanism.

Scheme 2. Synthesis of 5-AP from biomass-derived 1,5-pentanediol (Route A) and dihydropyran (Route B, large black arrow).

mer of 2-hydroxytetrahydropyran (2-HTHP), and the equilibrium composition of 5-HP at room temperature (25 °C) is about 2.4% [17]. The ring-opening tautomerization is an endothermic reaction; consequently, the transformation of 2-HTHP to 5-HP increased with increasing temperature [17]. The compound, 2-HTHP, can be readily synthesized by the autocatalytic hydration of biomass-derived dihydropyran with a yield of up to 92% [18]. In comparison with the production of 5-AP from 1,5-PD by its reaction with concentrated hydrogen chloride, followed by amination with ammonia (Scheme 2, Route A) [19], the synthesis of 5-AP from dihydropyran (Scheme 2, Route B) is not only more efficient but also much cleaner (almost no waste generation). Moreover, a higher 5-AP total yield of ~82% could be obtained by this new route in contrast to the 66% yield by the 1,5-PD route. The catalytic performances of the supported Ni catalysts on different oxides including SiO₂, TiO₂, ZrO₂, γ -Al₂O₃, and MgO were investigated and compared with a serial of commercial hydrogenation catalysts, including CuCr₂O₄, Raney Ni, and carbon-supported noble metals of Ru, Pd, Pt, and Rh. Ni/ZrO₂ was found to present the highest 5-AP yield among the catalysts investigated, and the high performance of this catalyst was discussed based on the characterization results of the oxide supported Ni catalysts. In addition, the reaction parameters including the reaction temperature, H₂ pressure, time, and 2-HTHP to NH₃ molar ratio were examined, and possible reaction pathways for the synthesis of 5-AP from 2-HTHP were proposed.

2. Experimental

2.1. Materials

The SiO₂ support, Al₂O₃ support, MgO support, Ru/C (5.0 wt%, reduced, 50% water wet), Pt/C (10.0 wt%, reduced, 50% water wet), Pd/C (10.0 wt%, reduced, 50% water wet), 1,5-pentanediol (98%), and dihydropyran (99%) were purchased from Alfa Aesar. The TiO₂ support and ZrO₂ support were obtained from Xuan Cheng Jing Rui New Material Co., Ltd. The Rh/C (5 wt%) catalyst was purchased from Innochem (Beijing) Technology Co., Ltd. The reagents, 1,2-pentanediol (98%) and 5-amino-1-pentanol (95%), were obtained from Aladdin Chemical Reagent Co. Ltd. The compound, 2-hydroxytetrahydropyran (90%), was purchased from ACROS. H₂ (99.999%) and He (99.999%) were obtained from the Lanzhou Lanmei Cryogenic Products Co., Ltd., China. A 10 vol% NH₃ in nitrogen solution was purchased from Shangdong Tianhai Co., Ltd. The aqueous solution of 2-HTHP with 21.8 wt% (90.8% yield) was synthesized by the autocatalytic hydra-

tion of the dihydropyran method [18]. The hydration reaction was carried out in a 2 L autoclave equipped with a mechanical stirrer. After adding 100 g of dihydropyran and 400 g of DI water, the autoclave was sealed and pressured with nitrogen to 2 MPa. Thereafter, the autoclave was heated to 100 °C for 1 h. All other chemical reagents were of analytical grade and were used without further purification.

2.2. Catalyst preparation

Oxide supports supported Ni catalysts with 15 wt% Ni were prepared by a wetness co-impregnation method [20]. Typically, a calculated amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water and ethylene glycol at a molar ratio of Ni: EG = 1: 1, and subsequently impregnated onto the oxide supports with stirring at room temperature for 2 h. Thereafter, the obtained samples were dried at 110 °C for 12 h and calcined at 450 °C for 2 h in a nitrogen atmosphere. The obtained calcined samples were denoted as Ni/SiO₂, Ni/Al₂O₃, Ni/MgO, Ni/TiO₂, and Ni/ZrO₂ according to the supports used.

2.3. Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface area and average pore diameter of the supported Ni catalysts were determined using a TriStar II 3020 (Micromeritics) surface area and porosity analyzer. Prior to the measurement, the samples were pretreated in a nitrogen flow at 300 °C for 4 h. A transmission electron microscope (TEM, TF20, operated at 200 kV) was used to observe the shape and size of the Ni particles of the catalysts, and the catalysts were reduced at 450 °C for 3 h before being dispersed on the copper mesh for testing. The particle size dispersion of the Ni particles was statistically obtained from the TEM micrograph by counting more than 200 particles. The X-ray powder diffraction (XRD) patterns of the samples were obtained on a Rigaku D/MAX-2400 diffractometer in reflection mode (Cu K_α radiation) at a scanning rate of 10° s⁻¹ in the 2 θ range of 10°–90°. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB250xi spectrometer with a monochromatized Al K_α source ($h\nu$ = 1486.6 eV) at a constant analyzer pass energy of 20 eV. All binding energies were calibrated with the C 1s (284.6 eV) as an internal standard. The reduced catalysts were treated in a flow of 1% O₂ in a nitrogen atmosphere for 2 h at room temperature before carrying out the XRD and XPS measurements.

H₂ temperature-programmed reduction (H₂-TPR) measurements were conducted on a Quantachrome automated chemisorption analyzer (ChemBET pulsar TPR/TPD) to analyze the reducibility of the catalysts. In a typical process, 40 mg of the calcined catalyst sample was placed in a quartz tube reactor and subsequently flushed with high purity He at 200 °C for 1 h to remove water and other contaminants. After cooling to room temperature, a gas mixture containing 10 vol% H₂ in Ar was passed through the sample at a total flow rate of 30 mL min⁻¹. The H₂ consumption was recorded by a thermal conductivity detector (TCD), while the temperature was increased to 800 °C at a ramping rate of 10 °C min⁻¹.

NH₃ temperature-programmed desorption (NH₃-TPD) measurements were carried out with a Huasi DAS-7200 automatic chemical adsorption instrument to analyze the acidity of the catalysts. Prior to the measurements, the calcined sample (0.20 g) was reduced with 5% H₂/95% Ar (30 mL min⁻¹) at 450 °C for 2 h. After reduction, the sample was cooled to 100 °C, and then 10% NH₃/90% N₂ was supplied into the reactor at 30 mL min⁻¹ for 1 h. After NH₃ adsorption, the system was purged with He (30 mL min⁻¹) for 1 h, after which the temperature was increased from 50 to 800 °C at a rate of 10 °C min⁻¹. The NH₃ desorption was monitored by a TCD.

2.4. Catalytic test and product analysis

The discontinuous 2-HTHP reductive amination reaction was carried out in a 100 mL stainless steel autoclave reactor at a stirring speed of 800 rpm. Prior to the reaction, the calcined Ni catalysts were reduced at 450 °C in pure H₂ at a flow rate of 80 mL min⁻¹ for 3 h. In a typical experiment, 15 g of the 21.8 wt% 2-HTHP aqueous solution together with 15 g of the 25 wt% concentrated ammonia solution was added into the reactor. The reduced catalyst, which was sealed in a H₂ atmosphere, was quickly tipped into the reaction solution to avoid oxidation. After flushing the tightly sealed reactor with H₂ 3 times, the reactor was initially pressurized with H₂ to 2.0 MPa, and then heated to 80 °C, a temperature that was maintained during the reaction.

The stability of the selected catalyst was studied using a continuous flow reactor (length: 36 cm, and inner diameter: 0.9 cm) at 80 °C and 3 MPa H₂. The calcined catalyst (2.0 g) with sizes of 20–40 meshes was embedded with quartz powders (20–40 meshes) in both sides of the catalyst bed. The catalyst was prereduced at 450 °C in pure H₂ at atmospheric pressure and a flow rate of 80 mL min⁻¹ for 3 h. After cooling to the reaction temperature, the reactor was pressured to 3 MPa with H₂; afterward, a well-mixed solution of 21.8 wt% 2-HTHP aqueous solution and 25 wt% concentrated ammonia at a weight ratio of 1:1 was pumped into the reactor at a speed of 9 g h⁻¹. The H₂ to 2-HTHP molar ratio was 30. Liquid samples were collected from a stainless-steel gas-liquid separator every 5 to 10 h.

The reactant and liquid products were analyzed using a gas chromatograph (Agilent 7890A GC) equipped with an HP-5MS capillary column (50 m × 0.32 mm × 2.0 μm). The temperatures of the injector and detector were 250 and 280 °C, respectively. The temperature program was conducted as follows: initial temperature and time = 110 °C and 6 min; final temperature and time = 260 °C and 10 min; heating rate = 15 °C min⁻¹. The products were also identified on a GC-MS instrument (Agilent 7890A/5975C) equipped with an HP-5MS column. The detected liquid products were 5-amino-1-pentanol (5-AP), 1,5-pentanediol (1,5-PD), 5-imino-1-pentanol (5-IP), and 5-[(5-hydroxypentyl)imino]-1-pentanol (5-HPIP). The product 1,2-pentanediol (1,2-PD) was used as an internal standard for quantitative analysis. Due to the unavailability of the standards for 5-IP and 5-HPIP, their GC response factors were assumed to be identical and twice that of 5-AP, respectively. The conversion and product selectivity were calculated as follows:

Table 1

Textural properties of Ni catalysts supported on different oxides.

Catalyst	A_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	D_{pore}^b (nm)	Ni ⁰ crystallite size ^c (nm)	Ni ⁰ particle size ^d (nm)	Acid amount ^e (mmol g^{-1})	Acid density ^f ($\mu\text{mol m}^{-2}$)
Ni/MgO	171.4	10.7	—	4.5	<0.01	<0.01
Ni/SiO ₂	78.5	11.0	6.3	3.7	0.15	1.91
Ni/TiO ₂	82.4	11.9	10.4	10.0	0.27	3.28
Ni/Al ₂ O ₃	202.4	9.7	—	4.1	0.44	2.17
Ni/ZrO ₂	29.1	22.9	11.0	12.6	0.12	4.24

^a Surface area calculated by the BET method. ^b Desorption average pore diameter calculated by the BJH method. ^c Calculated by the Scherrer equation through the Ni (111) diffraction peak. ^d Measured from TEM images. ^e Amount of the surface acidic site determined by NH₃-TPD. ^f Density of the surface acidic site estimated from the surface area of the catalysts and NH₃-TPD results.

$$\text{Conversion (\%)} = \frac{\text{mol of 2-HTHP charged} - \text{mol of 2-HTHP left}}{\text{mol of 2-HTHP charged}} \times 100.$$

$$\text{Selectivity (\%)} = \frac{\text{mol of product} \times \text{C atoms in product}}{(\text{mol of 2-HTHP charged} - \text{mol of 2-HTHP left}) \times \text{C atoms in 2-HTHP}} \times 100.$$

3. Results and discussion

3.1. Characterization of catalysts

The textural properties of the Ni catalysts supported on different oxides are listed in Table 1. The BET surface area of the calcined catalyst samples varied from 29.1 to 202.4 $\text{m}^2 \text{g}^{-1}$, decreasing in the order of Ni/Al₂O₃ > Ni/MgO > Ni/TiO₂ > Ni/SiO₂ > Ni/ZrO₂. This difference could be ascribed to the intrinsic difference of the supports and the dispersion of Ni in the catalysts. The average pore diameters of the catalyst samples were all in the mesopore range of 9.7–22.9 nm.

Fig. 1 shows the XRD patterns of the Ni catalysts supported on different oxides after calcination and reduction. For the calcined samples (Fig. 1(a)), no noticeable diffraction peaks of NiO could be observed in Ni/Al₂O₃ and Ni/MgO, indicating that the NiO particles were very small or highly dispersed in these samples. The diffraction peaks of NiO with different intensities appeared in Ni/TiO₂, Ni/ZrO₂, and Ni/SiO₂. After reduction at 450 °C for 3 h, the diffraction peaks of NiO disappeared, meanwhile

the characteristic diffraction peaks of Ni⁰ appeared in the Ni/ZrO₂ and Ni/TiO₂ catalysts (Fig. 2(b)), indicating the reduction of NiO to Ni⁰. There were no diffraction peaks of Ni⁰ in the Ni/Al₂O₃ and Ni/MgO catalysts, and only a broad diffraction peak at around $2\theta = 44.4^\circ$ attributed to Ni⁰, was observed in Ni/SiO₂, revealing the high dispersion of Ni⁰ in these catalysts. The Ni⁰ crystallite sizes of the Ni catalysts supported on SiO₂, TiO₂, and ZrO₂ were calculated to be 6.3–11.0 nm by the Scherrer equation (Table 1).

Fig. 2 displays the TEM images and particle size distributions of the Ni catalysts supported on different oxides. As can be seen, quasi-circular Ni particles with a mean particle size smaller than 5 nm were well dispersed in Ni/MgO, Ni/SiO₂, and Ni/Al₂O₃. Differently, many relatively large particles were observed in the Ni/TiO₂ and Ni/ZrO₂ catalysts, and it is slightly difficult to discriminate the Ni particles from the oxide support. Based on the HRTEM analysis, some Ni⁰ nanoparticles were identified (Fig. S1). The average particle sizes of Ni in Ni/TiO₂ and Ni/ZrO₂ were around 10.0 and 12.6 nm. The particle sizes obtained from the TEM measurements coincided with the results calculated well from the XRD patterns with the exception of Ni/SiO₂. The larger Ni⁰ crystallite size obtained from XRD for Ni/SiO₂ as compared with that from TEM was probably due to the bimodal size distribution of the Ni⁰ particles [21,22].

Fig. 1. XRD patterns of the Ni catalysts supported on different oxides. (A) After calcination; (B) After reduction.

Fig. 2. TEM images and particles size dispersion of different Ni catalysts. (a) Ni/MgO; (b) Ni/SiO₂; (c) Ni/TiO₂; (d) Ni/Al₂O₃; (e) Ni/ZrO₂.

Fig. 3 displays the H₂-TPR profiles of the Ni catalysts supported on different oxides. As can be seen, the calcined samples generally presented three hydrogenation consumption peaks with the low-temperature peaks appearing at temperatures below 379 °C, and the high-temperature peaks appearing at temperatures above 419 °C. Both of the calcined Ni/ZrO₂ and Ni/TiO₂ samples showed reduction peaks below 470 °C, while

the other three samples showed high-temperature peaks at temperatures above 528 °C with that of Ni/MgO appearing at temperatures above 700 °C. This indicated that the reducible Ni species in Ni/ZrO₂ and Ni/TiO₂ appeared at a lower temperature, while those in Ni/MgO appeared at a much higher temperature. Generally, NiO with small particle sizes or low interaction with the support could be reduced at low temperatures, while Ni²⁺ with strong metal-support interaction was reduced at relatively high temperatures [23,24]. Accordingly, the three reduction peaks from low to high temperature for the catalysts samples are probably associated with the reduction of small NiO particle sizes with low metal-support interactions, bulk NiO with larger sizes, and Ni²⁺ with relatively strong metal-support interactions, respectively. Evidently, the majority of the Ni species in the calcined Ni/Al₂O₃ and Ni/MgO are highly dispersed Ni particles in strong interaction with the support, while a large amount of bulk NiO was present in the calcined Ni/ZrO₂ and Ni/SiO₂. These findings are in agreement with the above XRD and TEM characterizations. The amount of H₂ consumption for the catalysts decreased in the order of Ni/Al₂O₃ > Ni/ZrO₂ > Ni/SiO₂ > Ni/TiO₂ > Ni/MgO, roughly reflecting the amount of Ni²⁺ species that could be reduced to Ni⁰, which may affect the catalytic performance of the catalysts.

It has been reported that the surface acidity of the catalyst could promote the condensation of carbonyl groups and NH₃ or amino groups to form imine intermediates [9,25]. NH₃-TPD was carried out to determine the surface acidity of the different oxide-supported Ni catalysts. As shown in Fig. 4, the acid properties of the Ni catalysts were different from each other. Almost no noticeable NH₃ desorption peak could be seen for Ni/MgO, indicating the rather low acidity of this catalyst. Two or three NH₃ desorption peaks were observed in the range of 200–420 °C for the other four catalysts with those of the Ni/Al₂O₃ being extremely high. The acid amount of the catalysts decreased in the order of Ni/Al₂O₃ > Ni/TiO₂ > Ni/SiO₂ > Ni/ZrO₂ > Ni/MgO. The densities of the acidic sites of the catalysts (Table 1) show that the Ni/ZrO₂ catalyst exhibited the highest acidic site density among the five catalysts investigated.

Fig. 3. H₂-TPR profiles of different oxide-supported Ni catalysts.

Fig. 4. NH_3 -TPD patterns of different oxide-supported Ni catalysts.

3.2. Catalytic performance

3.2.1. Catalytic performance of different catalysts in the reductive amination of 2-HTHP

Table 2 shows the catalytic performance of different catalysts in the reductive amination of 2-HTHP at 80 °C and 2 MPa H_2 . As can be seen, the conversion of 2-HTHP in all tests was considerably high (>92%), indicating the high reactivity of 2-HTHP, which is in line with the previous studies by Brentzel et al. on the direct hydrogenation of 2-HTHP and its dimmers to produce 1,5-PD [17]. The conversion of 2-HTHP reached 100% even in the absence of a catalyst, while the amination product of 5-IP was the main detected product with a 29.5% selectivity (entry 1). The generation of the dimmers of 2-HTHP [17] and some other undetected byproducts might account for the low

Table 2

Catalytic performance of different catalysts toward the amination of the 2-HTHP aqueous solution prepared from dihydropyran ^a.

$ \begin{array}{c} \text{2-HTHP} + \text{NH}_3 \cdot \text{H}_2 \rightarrow \text{5-AP} + \text{1,5-PD} + \text{5-IP} + \text{5-HPIP} \\ \text{+ other products} \end{array} $							
Entry	Catalyst	Conversion (%)	Selectivity (%)				
			5-AP	1,5-PD	5-IP	5-HPIP	Others ^e
1	No Catalyst	100	0	0	29.5	0	70.5
2	Ni/MgO ^b	97.9	6.5	1.1	17.8	15.3	59.2
3	Ni/SiO ₂ ^b	99.0	21.0	1.2	11.9	19.3	46.6
4	Ni/TiO ₂ ^b	100	43.0	1.7	3.6	6.9	44.8
5	Ni/Al ₂ O ₃ ^b	100	80.7	2.9	0	0	16.4
6	Ni/ZrO ₂ ^b	100	84.7	2.4	0	0	12.9
7	Raney Ni ^c	100	62.5	7.8	0	0	29.7
8	CuCr ₂ O ₄ ^c	92.7	0	0	45.5	2.0	52.5
9	Ru/C ^c	100	41.7	9.9	0	1.0	47.4
10	Pd/C ^c	100	9.2	0	0	0	90.8
11	Pt/C ^c	100	6.1	11.1	0	0	82.8
12	Rh/C ^d	100	55.7	2.8	0.5	0	41.0

^a Reaction conditions: 15 g of 21.8% 2-HTHP aqueous solution, 15 g of 25 wt% ammonia, 2 MPa H_2 , 80 °C, 1 h. ^b 0.33 g. ^c 0.5 g. ^d 0.25 g.

^e Including the dimmers of 2-HTHP and some undetected byproducts.

carbon balance. The selectivity of the supported Ni catalysts toward 5-AP differs greatly depending on the supports, which increased in the order of Ni/MgO < Ni/SiO₂ < Ni/TiO₂ < Ni/Al₂O₃ < Ni/ZrO₂, with the Ni/ZrO₂ catalyst exhibiting the highest selectivity of 84.7% (entries 2–6). All the supported Ni catalysts showed low selectivity toward 1,5-PD (<3%), the by-product from the direct hydrogenation of 5-HP (the ring-opened tautomer of 2-HTHP) [17,21]. The selectivity of the oxide-supported Ni catalysts toward 5-IP and 5-HPIP generally decreased in the opposite trend to that of 5-AP, and almost no 5-IP and 5-HPIP could be detected over the Ni/Al₂O₃ and Ni/ZrO₂ catalysts with a high 5-AP selectivity (>80%).

For comparison, the catalytic performances of a variety of commercial hydrogenation catalysts including Raney Ni, CuCr₂O₄, and the carbon-supported noble metals of Ru, Pd, Pt, and Rh (entries 7–12). Only Raney Ni and Rh/C showed moderate selectivity (~60%) toward 5-AP, while others exhibited considerably low selectivity (<42%) toward 5-AP. Evidently, the above findings indicate that Ni/ZrO₂ is a promising catalyst for this reaction. The high performance of the Ni catalysts in the 2-HTHP reductive amination is in line with previous studies, which reported that the Ni catalysts exhibit high activity in the reductive amination of carbonyl-containing compounds [8,26,27] and the amination of alcohols by the BH mechanism [12,28].

3.2.2. Effect of reaction parameters on the reductive amination of 2-HTHP over the Ni/ZrO₂ catalyst

Conventionally, the reductive amination of aldehydes or ketones involves several consequent reactions, including the condensation of the C=O group with ammonia or amino groups to form an imine or enamine intermediate, and the subsequent hydrogenation of the imine or enamine group to generate amine [2]. There are also many competitive reactions to generate byproducts, including the direct hydrogenation of the C=O group to form an alcohol, or the overalkylation reactions toward the di- and tri-alkylamine groups [2]. Therefore, the efficient synthesis of amines from aldehydes or ketones highly depends on the reaction parameters, besides the catalysts. To improve the reaction activity and also elucidate the reaction mechanism and pathways, the effects of the reaction parameters including temperature, H_2 pressure, NH_3 to 2-HTHP molar ratio, and time on the reductive amination of 2-HTHP over the Ni/ZrO₂ catalyst were investigated.

Fig. 5 shows the effect of the reaction temperature on the catalytic conversion and selectivity of Ni/ZrO₂ at 2 MPa H_2 . In the temperature range of 50–90 °C, the reaction temperature had a slight influence on the 2-HTHP conversion, but it influenced the product selectivity noticeably. The conversion of 2-HTHP could reach 98.9% even at a low temperature 50 °C and then increased to 100% with further increasing temperature to 60 °C, indicating the high reactivity of 2-HTHP as mentioned above. The selectivity of 5-AP increased sharply from 38.5% at 50 °C to a maximum of 84.7% at 80 °C, and then dropped slightly to 84.4% at 90 °C. The selectivity toward 1,5-PD decreased gradually from 3.4% at 50 °C to 1.8% at 90 °C. Meanwhile, the selectivity toward 5-IP and 5-HPIP declined

Fig. 5. Effect of the reaction temperature on the catalytic conversion and selectivity of Ni/ZrO₂. Reaction conditions: 15 g of 21.8% 2-HTHP aqueous solution, 15 g of 25 wt% ammonia, 0.33 g of catalyst, 2 MPa H₂, 1 h.

drastically from 11.4% and 26.2% at 50 °C to 0 at temperatures ≥ 70 °C, respectively, indicating that a high temperature favors the quick transformation of these products to the target product, 5-AP. The formation of more byproducts at a relatively high temperature of 90 °C accounts for the slight decrease in the 5-AP selectivity. Therefore, the above findings indicate that the high yield of 5-AP ($> 84\%$) could be achieved in the reductive amination of 2-HTHP at a temperature of 80 °C.

Fig. 6 shows the influence of H₂ pressure on the catalytic conversion and selectivity of the 2-HTHP reductive amination. When there was no H₂ charged in the reactor, a high 2-HTHP conversion of 95.7% was obtained, while no 5-AP was generated, and the main detected product was 5-IP with 24.7% selectivity, indicating that 2-HTHP could be converted to 5-IP without H₂ via the amination reaction. The 2-HTHP conversion increased to 100% when the H₂ pressure increased to 0.5 MPa and above. The 5-AP selectivity increased significantly to 79.1% at 0.5 MPa, peaked at 2 MPa H₂ with an 84.7% selectivity, and then slightly decreased to 83.1% at 4 MPa. The selectivity of 5-IP dropped to 0 when the H₂ pressure was ≥ 0.5 MPa, showing the high reactivity of such a product under H₂ atmos-

Fig. 6. Effect of H₂ pressure on the catalytic conversion and selectivity of Ni/ZrO₂ at 80 °C. Reaction conditions: 15 g of 21.8% 2-HTHP aqueous solution, 15 g of 25 wt% ammonia, 0.33 g of catalyst 1 h.

phere. The 1,5-PD selectivity increased gradually from 0.7% to 3.4% with increasing the H₂ pressure from 0.5 to 4 MPa, indicating that a high H₂ pressure also favors the direct hydrogenation of 2-HTHP to 1,5-PD.

Fig. 7 displays the effect of the NH₃/2-HTHP molar ratio on the catalytic conversion and selectivity of Ni/ZrO₂ at 80 °C and 2 MPa H₂. The 2-HTHP conversion was maintained at 100% irrespective of the NH₃ to 2-HTHP molar ratio, while the selectivity toward 5-AP increased sharply from 63.2% to 90.8% with the increase in the NH₃/2-HTHP molar ratio from 2:1 to 12:1. This indicates that the high NH₃ to 2-HTHP molar ratio favors the conversion of 2-HTHP to the target 5-AP product. Meanwhile, the selectivity toward 1,5-PD gradually decreased from 6.8% to 1.4%, and almost no 5-IP and 5-HPIP were detected. Obviously, the direct hydrogenation of 2-HTHP to 1,5-PD is a competitive reaction against the reductive amination of 2-HTHP. It has been reported that increasing the amount of NH₃ could inhibit the formation of secondary amine [26,29]. Thus, the generation of a large amount of di-1-pentanolamine byproduct is probably the main reason for the low selectivity toward 5-AP at a low NH₃ to 2-HTHP molar ratio.

Fig. 8 shows the catalytic conversion and selectivity of Ni/ZrO₂ in the 2-HTHP reductive amination as a function of the reaction time. The 2-HTHP conversion reached 96.4% when the reaction temperature rose to 80 °C (reaction time recorded as 0 min) and then increased to 100% at the reaction time of 10 min. This result confirmed the high reactivity of 2-HTHP. A small amount of 5-AP with 9.6% selectivity was detected when the reaction temperature approached 80 °C, and 5-IP and 5-HPIP were the major products with 31.8 and 33.6% selectivities, respectively. The selectivity of 5-AP sharply increased to 84.3% at 60 min, and then gradually increased to 87.8% as the time increased to 360 min. In the meantime, the selectivities toward 5-IP and 5-HPIP quickly decreased to 0 after the 60 min reaction. The increase in the 5-AP selectivity at the expense of 5-IP and 5-HPIP demonstrated that 5-IP and 5-HPIP might be the intermediates for the formation of 5-AP. The selectivity toward 1,5-PD was maintained at a low level in the range of

Fig. 7. Effect of the NH₃/2-HTHP molar ratio on the catalytic conversion and selectivity of Ni/ZrO₂. Reaction conditions: the amounts of 90% 2-HTHP, 25 wt% ammonia and DI water were varied to attain the desired NH₃ to 2-HTHP molar ratio, 0.33 g of catalyst, 80 °C, 1 h.

Fig. 8. Effect of the reaction time on the catalytic conversion and selectivity of Ni/ZrO₂. Reaction conditions: 15 g 21.8% 2-HTHP aqueous solution, 15 g 25% concentrated ammonia, 0.33 g catalyst, 2 MPa H₂, 80 °C

0.7–1.8% with increasing the reaction time to 360 min. This indicates that it might be a stable byproduct, which could not be converted to other products under the reaction conditions.

3.2.3. Reaction stability of the Ni/ZrO₂ catalyst in the 2-HTHP reductive amination

The stability of the selected Ni/ZrO₂ catalyst was investigated using a continuous flow reactor, and the result is shown in Fig. 9. As can be seen, the conversion of 2-HTHP was maintained at 100% during the 90 h time-on-stream. The selectivity toward 5-AP was maintained at ~83% during the initial 22 h and slowly decreased to ~67% after a 90-h time-on-stream. Almost no 5-IP and 5-HPIP were formed during the initial 22 h; their selectivities gradually increased to 3.8% and 11.2%, respectively, after a 36-h reaction, and then remained nearly unchanged. The selectivity of 1,5-PD was maintained around 1.1% during the 90-h time-on-stream.

The slow decrease in the 5-AP selectivity during the time-on-stream indicates the gradual deactivation of the cata-

Fig. 9. Reduction amination of 2-HTHP with Ni/ZrO₂ in a continuous flow reactor. Reductive amination of 2-HTHP with Ni/ZrO₂ in a continuous flow reactor. Reaction conditions: mixed solution of 21.8 wt% 2-HTHP aqueous solution and 25 wt% concentrated ammonia at a weight ratio of 1:1, 80 °C, 3 MPa H₂, WHSV of 2-HTHP = 0.5 h⁻¹, and H₂/2-HTHP molar ratio = 30.

lyst, and the deactivation rate is calculated to be ~19% after 90 h. To elucidate the possible reasons for the deactivation of the catalyst, the used catalyst after the 90-h reaction was characterized by TEM, XRD, and TG. No appreciable sintering of active particles can be observed in the TEM image of the used catalyst (Fig. S2). The XRD result (Fig. S3) showed no noticeable change in the catalyst structure after the reaction, and the Ni⁰ crystallite size slightly increased to 15.3 nm. In addition, no remarkable weight loss due to the desorption/decomposition of coke was observed from the TG profile (Fig. S4). These findings excluded the Ni particles sintering and coke formation as the major reasons for the deactivation. ICP analysis of the collected reaction product showed a noticeable Ni leaching of 4.3 μg/g, which would be one of the reasons for the deactivation. Note that the surface oxidation of the active Ni⁰, caused by the dissolved oxygen in the reactant, may also considerably result in the deactivation of the catalyst. However, no firm conclusion could be drawn on this because the oxidation of the used catalyst during the preparation of the sample for XPS measurement (Fig. S5) cannot be excluded.

3.3. Reaction pathways and Structure-activity relationship

Based on the reaction parameter studies, we propose the reaction pathway for the synthesis of 5-AP and the byproducts as shown in Scheme 3. Firstly, 2-HTHP is equilibrated with its ring-opened tautomer (5-HP) [17], which is then rapidly condensed with NH₃ to form the reactive imine intermediate (5-IP). Imines are reported to be the key intermediates in the amination of both alcohols and carbonyl compounds for the synthesis of primary amines [2,11,26,30–32]. The 5-IP intermediate is readily hydrogenated to the target 5-AP product over metallic active sites in the presence of sufficient H₂. The terminal amino group in 5-AP could condense with the C=O group in 5-HP to generate the secondary imine (5-HPIP). Note that 5-AP could also react with 5-IP to generate the intermediate, 5-HPIP, by the release of one NH₃ molecule, which is similar to the generation of N-benzylidenebenzylamine from benzylamine and phenylmethanimine [26]. The 5-HPIP intermediate can be further transformed to 5-AP in the presence of excess NH₃ and H₂. The hydrogenation of 5-HP and 5-HPIP in the presence of H₂ and active metal can produce the 1,5-PD and di-1-pentanolamine byproducts, respectively.

As can be seen from Scheme 3, high NH₃ to 2-HTHP molar ratios favor the synthesis of the target product (5-AP) by promoting not only the condensation of the in situ generated 5-HP

Scheme 3. Proposed reaction pathway for the synthesis of 5-AP and the main byproducts.

with ammonia but also the transformation of the 5-HPIP intermediate into 5-AP, as exactly indicated in Fig. 7. H₂ is indispensable for the reductive amination of 2-HTHP as one H₂ molecule was consumed in the reduction of 5-IP to 5-AP. The direct hydrogenation of 5-HP to 1,5-PD and hydrogenation of 5-HPIP to di-1-pentanolamine are competitive reactions against the hydrogenation of 5-IP to 5-AP; consequently, a moderate H₂ pressure in the range of 2–3 MPa is beneficial for the production of 5-AP, while a high H₂ pressure (e.g., >3 MPa, Fig. 6) results in relatively high byproduct yields of 1,5-PD and di-1-pentanolamine.

Because 5-HP could readily react with NH₃ to form 5-IP (Table 2, entry 1, Fig. 8), the hydrogenation of 5-IP to 5-AP is proposed to be the rate-determining step. A recent study by Zhang et al. [33] also indicated that the hydrogenation of imines was the rate-determining step involved in the one-pot reductive amination of carbonyl compounds with nitro compounds. Evidently, the hydrogenation activity of the metal catalysts played a key role in obtaining a high 5-AP yield. The hydrogenation activity of metal catalysts depends on the intrinsic property of the metal, as shown in Table 2, and on the number of active metal sites that is available. In our cases, a high 5-AP yield (>80%) was attained over supported Ni catalysts, particularly over Ni/ZrO₂, under mild conditions of 80 °C and 2 MPa H₂ (Table 2). Considering that Ni/ZrO₂ had a relatively large H₂ consumption (Fig. 3), the high reducibility of this catalyst may contribute to the relatively high 5-AP yield as more Ni²⁺ species could be reduced to active Ni⁰ prior to the reductive amination reaction. It has been reported that the condensation of carbonyl groups and NH₃ or amino groups to form imine intermediates could be enhanced by the acidity of the catalyst [9,25]. The relatively large acidic site density of the Ni/ZrO₂ catalyst (Table 1) may also contribute to its relatively high performance in the synthesis of 5-AP from 2-HTHP.

4. Conclusions

We reported an efficient method for the synthesis of useful 5-amino-1-pentanol (5-AP) from biomass-derived dihydropyran by coupling the in situ generation of 5-hydroxypentanal (5-HP) and its reductive amination over supported Ni catalysts. The Ni/ZrO₂ catalyst was found to exhibit the highest 5-AP yield among several oxide supports, including SiO₂, TiO₂, ZrO₂, γ-Al₂O₃, and MgO loaded Ni catalysts, as well as a series of commercial hydrogenation catalysts, including CuCr₂O₄, Raney Ni, and the carbon-supported noble metals of Ru, Pd, Pt, and Rh. A 90.8% yield of 5-AP was obtained in a batch reactor over Ni/ZrO₂ catalyst in the reductive amination of 2-HTHP under mild conditions of 80 °C and 2 MPa H₂. The catalyst also presented an 83% 5-AP yield from 2-HTHP solution in a continuous flow reactor, and maintained 81% of its activity after a 90-h time-on-stream. The characterization results showed that the Ni/ZrO₂ catalyst exhibited high reducibility and a high surface acid density, which are suggested to account for its relatively high activity and selectivity.

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Graphical Abstract

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Effective synthesis of 5-amino-1-pentanol by reductive amination of biomass-derived 2-hydroxytetrahydropyran over supported Ni catalysts

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5-amino-1-pentanol was synthesized efficiently from biomass-derived dihydropyran by coupling the in situ generation of 5-hydroxypentanal and its reductive amination over supported Ni catalysts under mild reaction conditions.

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负载型Ni催化剂高效催化2-羟基四氢吡喃还原胺化制备5-氨基-1-戊醇

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摘要: 伯胺等含氮化合物是最重要的化工中间体之一, 被广泛应用于聚合物、医药、农药、染料和表面活性剂等产品的生产。当前, 商业化伯胺主要通过卤代烃或环氧化物直接胺化以及腈类或酰胺类化合物加氢制备, 这些过程受具有特定官能团的有机原料短缺以及产生较多废物等问题的限制, 导致其生产成本较高。因此, 高效可持续生产伯胺化合物路径的开发得到了广泛关注。醛和酮类化合物直接与氨还原胺化反应所需温度一般较低($\leq 120^\circ\text{C}$), 为伯胺的高选择性合成提供了一个重要途径。基于此, 本文利用2-羟基四氢吡喃能够原位转化为其互变异构体5-羟基戊醛, 而5-羟基戊醛中醛基具有较高还原胺化活性的特征, 发展了一种以生物糠醛衍生二氢吡喃为原料, 通过先水合得到2-羟基四氢吡喃再在温和条件下还原胺化合成5-氨基-1-戊醇的新方法。5-氨基-1-戊醇是一种分子中同时含有羟基和氨基的重要双官能团化合物, 广泛用于医药和农药合成, 也常被用作有机合成砌块, 目前其主要用途是合成具有很高药用价值的生物碱Manzamine A。5-氨基-1-戊醇的一条传统合成路线是以石化基1,5-戊二醇经浓盐酸进行单氯取代制备5-氯戊醇中间体, 该中间体经分离后再与氨气反应制得5-氨基-1-戊醇的方法。该方法原料成本高, 产生大量废弃物, 且只取得中等目标产物收率(66.6%)。

本文重点研究了不同氧化物载体包括 SiO_2 , TiO_2 , $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 和 MgO 负载Ni催化剂的2-羟基四氢吡喃还原胺化性能, 并对比考察了 CuCr_2O_4 , 雷尼Ni, Ru/C, Pd/C, Pt/C和Rh/C等商业加氢催化剂的性能。研究发现, ZrO_2 负载Ni催化剂的活性高于其他氧化物载体负载Ni催化剂的活性, 也明显优于所对比的系列商业加氢催化剂。系列物理化学表征结果显示, Ni/ ZrO_2 催化剂同时表现出较高的还原性和表面酸密度, 这可能是该催化剂表现出最高5-氨基-1-戊醇收率的原因。以Ni/ ZrO_2 为催

化剂, 于80 °C, 2 MPa H₂条件下在间歇式反应器中催化2-羟基四氢吡喃水溶液还原胺化可取得90.8%的5-氨基-1-戊醇收率. 通过固定床反应器研究了Ni/ZrO₂催化剂稳定性, 发现5-氨基-1-戊醇初始收率可达83%, 反应90 h活性缓慢下降至初活性的81%. Ni流失和表面氧化可能是催化剂的失活的主要原因. 通过对反应温度、H₂压力、2-羟基四氢吡喃/NH₃摩尔比等因素对反应活性调变规律的探究, 推测2-羟基四氢吡喃催化还原胺化制备5-氨基-1-戊醇反应机理如下: 首先, 受化学平衡作用, 2-羟基四氢吡喃逐渐转化为其互变异构体5-羟基戊醛; 然后, 5-羟基戊醛中醛基迅速与NH₃反应生成亚胺中间体; 最后, 亚胺中间体在金属催化剂上加氢得到5-氨基-1-戊醇.

关键词: Ni催化剂; 还原胺化; 二氢吡喃; 5-氨基-1-戊醇; 构效关系

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