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Introduction

Amine compounds are important chemical raw materials and synthetic intermediates, widely used in the synthesis of polymers, pharmaceuticals, pesticides, food-additives, surfactants, etc.¹⁻³ Currently, most of the industrially related aliphatic and aromatic amines as well as amino alcohols were produced from traditional fossil resources.^{2,4} From a green and sustainable chemical perspective, the production of bio-amines from renewable biomass is considered as an appealing approach to not only reduce the reliance on increasingly scarce fossil resources, but also make good use of the oxygen-containing functional groups in biomass.^{2,5,6} To date, amines are mainly produced through the reduction and ammonolysis processes,⁷ and the reductive amination of carbonyl compounds is one of the most attractive synthesis routes.8-11 The synthesis of amines via the reductive amination of carbonyl compounds only needs to selectively convert the oxygencontaining groups into nitrogen-containing groups, and water is the main by-product. Therefore, there is a strong incentive to develop sustainable amines from bio-based carbonyl compounds.

Reductive amination of bio-based 2-hydroxytetrahydropyran to 5-Amino-1-pentanol over nano-Ni–Al₂O₃ catalysts†

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The synthesis of useful amines from bio-based carbonyl compounds is highly desired owing to their mild reaction conditions and green sustainability. The reductive amination of bio-furfural-derived 2-hydroxytetrahydropyran (**2-HTHP**) to high-value-added 5-Amino-1-pentanol (**5-AP**) was carried out over efficient Ni–Al₂O₃ catalysts prepared by a co-precipitation method. Among the Ni–Al₂O₃ catalysts with different Ni loadings (0–100 wt%) tested, the 50Ni–Al₂O₃ catalyst exhibited the highest **5-AP** yield of 91.3% under mild conditions of 60 °C and 2 MPa H₂. This catalyst also presented good stability during a 150 h time-on-stream without appreciable deactivation. Characterization results showed that the 50Ni–Al₂O₃ catalyst exhibited small Ni⁰ nanoparticles (5.5 nm), a high reduction degree (up to 95%), and a large amount of strong Lewis acid sites. The cooperative catalysis of the strong Lewis acid sites and highly dispersed metallic Ni sites is suggested to play an important role in achieving high efficiency in **2-HTHP** reductive amination.

The major challenge in the reductive amination of carbonyl compounds to produce amines, particularly primary amines, is the control of selectivity because it usually suffers from competitive side reactions such as over-alkylation, carbonyl hydrogenation and cyclization.^{4,12,13} In view of these side reactions, selecting a suitable catalytic system is therefore key to achieve high selectivity for the desired amines. Up to now, there are just a few reports on the synthesis of primary amines from biobased carbonyl compounds, and these studies mainly focused on the application of noble metal heterogeneous catalysts thanks to their high catalytic activity and selectivity as well as easy separation and recovery.^{4,6,9,14,15} For example, Chatterjee et al.¹⁶ used Rh, Ru, Pt and Pd-based catalysts for the reductive amination of furfural to furfurylamine and a high selectivity of 92% to the target furfurylamine was obtained over the Rh-Al₂O₃ catalyst within 2 h at 80 °C. Taken the extremely high price of noble metals into consideration, it is more promising to use supported base metals, such as nickel^{11,12,17-19} and cobalt^{3,20} for the reductive amination of bio-based carbonyl compounds.

5-Amino-1-pentanol (5-AP) is an important pharmaceutical intermediate that can be used in the synthesis of anti-inflammatory and anti-cancer drugs, especially as a starting material for the synthesis of alkaloid manzamine. With an increasing demand for manzamine and only very expensive test doses currently available on the market, it is of great significance to find a cheap and large-scale preparation method for 5-AP synthesis and promote its application.²¹ Recently, our group reported an

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efficient and clean method for the synthesis of useful 5-AP through reductive amination of bio-furfural-derived 2-hydroxytetrahydropyran (2-HTHP) over supported Ni catalysts (Route B, Scheme 1) 22,23 in contrast to the chlorination and ammoniation of 1.5-PD (Route A, Scheme 1).²¹ The Ni-Mg₃AlO_r catalysts derived from hydrotalcite precursors by co-precipitation with proper Ni loadings were found to be more active and stable than the supported Ni-ZrO₂ catalyst prepared by impregnation.^{22,23} Nonetheless, obvious deactivation of the Ni-Mg₃AlO_x catalyst was seen after 90 h of time-on-stream. Nano-Ni-Al2O3 based catalysts have been reported to present high activity and good stability in not only reductive amination of aldehydes and ketones,11,18 but also direct amination of alcohols.²⁴⁻²⁶ In this work, a series of nano-Ni-Al₂O₃ catalysts with Ni loadings from 0 to 100 wt% were synthesized by co-precipitation and were investigated in the reductive amination of 2-HTHP to 5-AP under mild conditions with aqueous NH₃. The 50Ni-Al₂O₃ catalyst with \sim 50 wt% Ni was found to present the highest 5-AP yield (91.3%) and remarkable stability during a 150 h time-onstream reaction. The good performance of such a catalyst was discussed based on comparative characterization of the Ni-Al₂O₃ catalysts with different Ni loadings.

Results and discussion

Catalyst characterization

Fig. 1 shows the XRD patterns of the calcined NiO-Al₂O₃ samples and reduced Ni-Al₂O₃ catalyst samples with different Ni loadings. As can be seen from Fig. 1A, the diffraction peaks at approximately $2\theta = 31.9^{\circ}$, 37.6° , 39.5° , 45.9° , 60.9° and 67.0° observed in the pattern of Al₂O₃ support could be assigned to the (220), (311), (222), (400), (511) and (440) crystal planes of γ -Al₂O₃ (JCPDS Card No. 10-0425), respectively. However, no diffraction peaks related to Al₂O₃ were observed after doping nickel, indicating that Al₂O₃ was in the X-ray amorphous state in all NiO-Al₂O₃ samples.²⁷ For the calcined 10NiO-Al₂O₃ and 30NiO-Al₂O₃ samples, the diffraction peaks at $2\theta = 37.0^{\circ}$, 45.0° and 65.5° could be assigned to the (311), (400), and (440) crystal planes of the NiAl₂O₄ spinel (JCPDS Card No. 78-0552), indicating that the majority of NiO in these samples were inserted into the crystal lattices of Al₂O₃ support forming a NiAl₂O₄ spinel,²⁸ as will be supported by the XPS characterization shown below. With increasing nickel contents up to and above 50 wt%, the diffraction



Fig. 1 XRD patterns of (A) calcined NiO–Al_2O_3 samples and (B) reduced Ni–Al_2O_3 catalysts with different Ni loadings.

peaks shifted and appeared at $2\theta = 37.2^{\circ}$, 43.3° , 62.9° , and 75.4° , corresponding to the (111), (200), (220), and (311) crystal planes of NiO (JCPDS Card No. 71-1179).

After reduction in pure H₂ at 650 °C for 3 h, the disappearance of the NiO phase in all samples indicated that NiO has been reduced to metallic Ni (Fig. 1B), as supported by the appearance of diffraction peaks at $2\theta = 44.9^\circ$, 51.8° , and 76.4° corresponding to the (111), (200), and (220) crystal planes of Ni⁰ (JCPDS Card No. 70-1849). In contrast, obvious diffraction peaks of $NiAl_2O_4$ could still be observed for the 10Ni-Al2O3 and 30Ni-Al2O3 catalysts, implying that NiAl₂O₄ is more difficult to be reduced, which is in line with previous studies.²⁹⁻³¹ The crystallite sizes of Ni in the reduced Ni-Al2O3 catalysts decreased gradually from 9.8 nm to 5.3 nm with increasing Ni contents from 10 to 50 wt%, and then increased significantly from 5.5 nm for 70Ni-Al₂O₃ to 48.1 nm for pure Ni (Table 1). The smaller Ni crystallite sizes obtained over the Ni-Al2O3 catalysts with 50-70 wt% Ni loadings may be related to the formation of a hydrotalcite-like precursor in the dried samples (Fig. S1, ESI[†]), since their M²⁺/M³⁺ values are relatively close to the ideal 2-3.25,32 The catalysts from hydrotalcite-like precursors have been demonstrated to possess high metallic dispersion and high particle stability against

Table 1 Ni loadings and textural properties of Ni-Al₂O₃ catalyst samples with different Ni contents

Catalyst	Ni content ^a (wt%)	BET surface area ^b $(m^2 g^{-1})$	Average pore diameter ^c (nm)	Ni ⁰ crystallite size ^d (nm)	Ni ⁰ particle size ^e (nm)	Reduction degree ^f (%)
10Ni-Al ₂ O ₃	8.9	169.8	11.2	9.8	11.9	57.9
30Ni-Al ₂ O ₃	24.1	163.4	11.3	6.2	6.8	67.8
50Ni-Al ₂ O ₃	40.2	154.9	10.4	5.3	5.5	95.2
70Ni-Al ₂ O ₃	60.2	147.1	16.1	5.5	5.8	95.6
90Ni-Al ₂ O ₃	79.0	52.7	19.1	13.9	15.1	99.2
Pure Ni	100	1.5	14.5	48.1	_	100
Al_2O_3	0	145.9	8.4	—	_	_

^{*a*} Obtained from AAS analysis. ^{*b*} Calculated by the BET method. ^{*c*} BJH desorption average pore diameter. ^{*d*} Calculated from the Scherrer equation through the Ni(200) diffraction peak. ^{*e*} Measured from the TEM micrograph. ^{*f*} Calculated from H₂-TPR.

sintering under extreme conditions even for nickel contents up to 75 wt%. $^{27,33-35}$

Fig. 2 displays the XPS spectra of the Ni $2p_{3/2}$ of the calcined NiO–Al₂O₃ and reduced Ni–Al₂O₃ catalyst samples with different Ni loadings. For the calcined NiO–Al₂O₃ sample (Fig. 2A), the intense and broad Ni $2p_{3/2}$ main photoelectron peaks above 854 eV along with the presence of a characteristic shake-up satellite peak around 861.3–862.3 eV indicates that the nickel



Fig. 2 XPS spectra for the Ni $2p_{3/2}$ core level of calcined NiO-Al₂O₃ samples (A) and reduced Ni-Al₂O₃ catalysts (B) with different Ni contents.

oxidation state is +2 in all samples.^{36–39} However, the band shapes and binding energies vary with Ni contents. For 10NiO-Al₂O₃ and 30NiO-Al2O3 samples, the main Ni 2p3/2 peak appeared at 856.3 eV could be ascribed to the presence of $NiAl_2O_4$,³⁸ indicating that the majority of the Ni²⁺ species exist in the form of NiAl₂O₄. Comparatively, there is an asymmetric Ni²⁺ overlapping peak at a lower binding energy of around 854.1-854.7 eV in Ni-rich samples with Ni loadings of 50–90 wt%, which was close to that of the pure NiO (approximately 854 eV),^{39,40} indicating that Ni²⁺ species mainly exist as NiO with different metal-support interactions.41,42 An obvious shoulder peak at a binding energy of 855.8-856.4 eV is attributed to the multiplet splitting interaction of NiO. In addition, the NiO peak shifted from 854.7 to 854.1 eV with the increase of Ni loadings from 50 to 90 wt%, indicating that the interaction between NiO and Al₂O₃ was weakened to some extent due to the agglomeration of NiO particles. The color change of the calcined NiO-Al₂O₃ samples (as shown in Fig. S2, ESI⁺) also supported the change in composition. After reduction at 650 °C for 3 h, as shown in Fig. 2B, the Ni $2p_{3/2}$ peak that appeared at 852.6 eV could be attributed to Ni⁰ and the intensity of this peak increased along with Ni contents, which indicated that Ni²⁺ species in Ni-rich samples were more easily reduced.⁴¹ This finding could also be further confirmed by the H2-TPR of the calcined NiO-Al2O3 samples (Fig. 4).

Table 1 presents the textural properties of Ni–Al₂O₃ catalyst samples with different Ni loadings. The Ni contents in the Ni– Al₂O₃ catalyst measured by AAS were slightly lower than the nominal Ni loadings. The BET surface areas of the Ni–Al₂O₃ catalysts declined monotonically from 169.8 to 52.7 m² g⁻¹ with increasing Ni loadings from 10 to 90 wt%, likely due to a decrease in the amount of Al₂O₃ support, which had a surface area as high as 145.9 m² g⁻¹. The much lower surface area of 90Ni–Al₂O₃ might also be ascribed to the agglomeration of a larger amount of Ni particles, as revealed by the much lower surface area of pure Ni, which is 1.5 m² g⁻¹. The average pore diameters of all samples were located within the range of 8.4– 19.1 nm (Table 1 and Fig. S3, ESI†), indicating the existence of a mesoporous structure, which would be beneficial for the diffusion of the reactants and the generated products.⁴³

The TEM images and particle size distributions of the reduced $Ni-Al_2O_3$ catalysts with Ni loadings of 10–90 wt% are shown in Fig. 3. As can be seen from the TEM micrographs, most of the nickel species showed spherical shapes with the



Fig. 3 TEM images and particle size distributions of reduced Ni $-Al_2O_3$ catalysts with different Ni contents: (A) 10Ni $-Al_2O_3$, (B) 30Ni $-Al_2O_3$, (C) 50Ni $-Al_2O_3$, (D) 70Ni $-Al_2O_3$ and (E) 90Ni $-Al_2O_3$.

particles in catalysts containing 30–70 wt% Ni distributed more uniformly. The mean particle sizes of Ni nanoparticles calculated from TEM decreased from 11.9 to 5.5 nm upon increasing the Ni loading from 10 to 50 wt%, and then clearly increased to 14.8 nm for the 90Ni–Al₂O₃ catalyst. Obviously, the TEM findings agreed well with the results of XRD analysis (Table 1). The representative HAADF-STEM and EDX mapping of Ni–Al₂O₃ catalysts (Fig. S4, ESI†) also revealed a highly homogeneous Ni elemental distribution in 50Ni–Al₂O₃, which may be attributed to a strong metal– support interaction between Ni and Al₂O₃ support. However, a further increase in Ni loading leads to the agglomeration of Ni nanoparticles in 90Ni–Al₂O₃.



Fig. 4 $\,$ H_2-TPR profiles of the calcined NiO–Al_2O_3 samples with different Ni contents.

H2-TPR was performed on calcined NiO-Al2O3 samples with different Ni contents to study the surface Ni species, metalsupport interaction and reducibility. As shown in Fig. 4, the temperature of the main reduction peak of the samples generally shifted to a lower temperature with an increase of Ni contents. It has been reported that NiO with a low interaction with the support could be reduced at low temperatures, while Ni²⁺ species with a strong metal-support interaction were reduced at higher temperatures.^{44,45} According to XRD (Fig. 1) and XPS (Fig. 2) characterization studies, the main reduction peak of 10 NiO-Al₂O₃ that appeared at 765 °C could be ascribed to the reduction of the NiAl₂O₄ spinel, and the two reduction peaks of 30NiO-Al₂O₃ at 685 and 802 °C might be related to the reduction of NiO and NiAl₂O₄, respectively.⁴⁶ A similar reduction peak observed for 50NiO-Al2O3 and 70NiO-Al2O3 samples might be related to dispersed NiO with a strong interaction with the Al₂O₃ support. A broad reduction peak that appeared at 468 °C for the 90Ni-Al2O3 sample indicated the weak interaction between NiO and Al₂O₃, which might be due to the agglomeration of NiO on the support.46-49 Pure NiO showed a main reduction peak at 360 °C and a small shoulder peak at 513 °C, which were likely attributed to the reduction of bulk NiO with smaller and larger domains, respectively.⁵⁰ Furthermore, the reduction degree of the calcined samples, which to some extent reflects the availability of active metal sites, was also obtained by H₂-TPR. As shown in Table 1, the reduction degree of the samples increased sharply from 57.9% for 10NiO-Al₂O₃ to 95.2% for 50NiO-Al2O3, and then increased slightly to 99.2% for 90NiO-Al₂O₃.

It has been reported that the acid sites of the catalyst could activate the C=O group of the aldehydes/ketones, and thus promote the imine formation by the condensation of carbonyl groups with NH_3 .^{6,51,52} NH_3 -TPD was carried out on Ni-Al₂O₃ catalysts to study their surface acidity. As shown in Fig. 5, Al₂O₃ support showed an NH_3 desorption peak at around 128 °C, while the NH_3 desorption peak shifted to a high temperature after the incorporation of Ni. One major NH_3 desorption peak





Fig. 5 $\,$ NH_3-TPD patterns of the reduced Ni–Al_2O_3 catalysts with different Ni loadings.

at 186 °C was observed for the 10Ni-Al₂O₃ catalyst, and two or three NH₃ desorption peaks could be seen in the range of 190-440 °C upon increasing the Ni loading up to and above 30 wt% for the Ni-Al₂O₃ catalysts. In comparison with 50Ni-Al₂O₃ and 70Ni-Al₂O₃ catalysts, the NH₃ desorption peaks for 90Ni-Al₂O₃ substantially weakened, revealing that the former two catalysts presented larger amounts of acid sites than the latter. In contrast, almost no NH₃ desorption peaks could be detected for pure Ni. It has been reported that the NH₃ desorption peaks at around 200 °C, 300-350 °C and above 400 °C are associated with weak, medium-strong and strong acid sites, respectively.^{6,53} Accordingly, mainly the weak or medium-strong acid sites were present on the surface of the Ni-Al₂O₃ catalysts with Ni loadings below 50 wt%, and the Ni-rich catalysts (50-90 wt% loadings) additionally showed strong acid sites, while pure Ni showed almost no acid sites. The reduction degrees compiled in Table 1 imply that a small amount of Ni^{δ +} (Ni²⁺ > Ni^{δ +} > Ni⁰) may still exist even in 90Ni-Al2O3 reduced at 650 °C, which may be formed by the partial reduction of Ni²⁺ species with a strong metal-support interaction.54 Although the insufficiently reduced low valent metal sites were often reported to present Lewis acid sites,^{6,55} the reduction of the dispersed metal oxide phase to the metallic state was also found to contribute to the profoundly increased Lewis acidity of the catalyst.⁵⁶ Pyridine-FTIR shown in Fig. S5 (ESI[†]) confirmed the presence of Lewis acid sites on the 50Ni-Al₂O₃ catalyst. Therefore, it is likely that the strong Lewis acid sites of the reduced catalysts with Ni loadings of 50-90 wt% were enhanced by the presence of a large amount of dispersed Ni⁰.

Catalytic performance

Table 2 shows the catalytic performance of Ni–Al₂O₃ catalysts with Ni loadings from 0 to 100 wt% on the reductive amination of **2-HTHP** at 60 °C and 2 MPa H₂. The reactant **2-HTHP** was very reactive in the presence of NH₃ and the conversion reached 93% even without any catalyst (entry 1). 5-Imino-1-pentanol (**5-IP**) and THP-oxypentanimine (**THPOPI**) were obtained as the

Table 2 The catalytic performance of Ni–Al₂O₃ catalysts with different Ni contents toward the reductive amination of **2-HTHP**^a

$\begin{array}{c} HO \underbrace{1,5-PD}_{1,5-PD} \xrightarrow{OH} \underbrace{+H_2}_{+} \underbrace{0}_{2-HTHP} HO \underbrace{+H_2}_{+} \underbrace{DPA}_{+} \xrightarrow{OH}_{+H_2} \\ HO \underbrace{+NH_3}_{+} \underbrace{+H_2}_{+} \underbrace{+H_2}_{+} \underbrace{+H_2}_{+} \underbrace{HO} \underbrace{+H_2}_{5-HPIP} \xrightarrow{OH}_{+} \underbrace{+H_2}_{+} \underbrace{HO} \underbrace{+H_2}_{-} \underbrace{+H_2}_{+} \underbrace{HO} \underbrace{+H_2}_{-} \underbrace{+H_2}_{+} \underbrace{+H_2}_{+} \underbrace{+HO} \underbrace{+H_2}_{-} \underbrace{+HO} \underbrace{+H_2}_{-} \underbrace{+HO} \underbrace{+H_2}_{+} \underbrace{+HO} +$												
Conversion Selectivity (%)												
Entry	Catalyst	(%)	5-AP	1,5-PD	5-IP	тнрорі	5-HPIP	DPA				
1	No catalyst	93.1	0	0	50.5	31.3	0	0				
2	$Al_2O_3^b$	94.3	0	0	69.1	22.5	0	0				
3	$10Ni-Al_2O_3^c$	98.6	32.4	1.5	20.9	0	33.7	1.9				
4	$30Ni-Al_2O_3^{c}$	100	35.9	1.5	14.7	0	33.9	2.1				
5	50Ni-Al ₂ O ₃ ^c	100	84.6	2.3	0.6	0	2.4	2				
6	70Ni-Al ₂ O ₃ ^c	100	81.0	2.7	1.2	0	4.9	5.1				
7	$90Ni-Al_2O_3^c$	100	63.2	2.8	5.5	0	19.2	2.4				
8	Pure Ni ^c	95.4	0.5	0	65.5	0	5.4	0				

 a Reaction conditions: 15 g of 21.3 wt% **2-HTHP** aqueous solution, 15 g of 25 wt% aqueous ammonia, 60 °C, 2 MPa H₂, 1 h. b 0.1 g. c 0.05 g active Ni.

main products in the absence of a catalyst with selectivities of 50.5% and 31.3%, respectively. The 5-IP imine product was formed by the dehydration condensation of 5-HP with NH₃, while THPOPI was likely generated by the condensation of 5-IP with 2-HTHP.²² It seems that NH_3 promoted the ring-opening tautomerization of 2-HTHP to form the active 5-HP and then the in situ formed 5-HP intermediate condensed with ammonia to form imine intermediates. As expected, no hydrogenation products including the target 5-AP product were detected in the absence of a catalyst. Similar results were obtained when the Al_2O_3 support was solely used as a catalyst (entry 2). In the presence of Ni-Al₂O₃ catalysts, the conversion of 2-HTHP increased to 100% on 30Ni-Al2O3 and remained constant until pure Ni was used as a catalyst and the target product 5-AP was obtained (entries 3-8). The product selectivity of the Ni-Al₂O₃ catalysts largely depended on Ni loadings. The selectivity to the target 5-AP product increased rapidly to a maximum of 84.6% on 50Ni-Al₂O₃ and then dropped to 0.5% on pure Ni. The selectivity to 5-IP showed an opposite trend, which declined to a minimum of 0.6% and then increased to 65.5% over pure Ni, revealing that 5-IP is a primary imine intermediate for the target 5-AP. The selectivity to THPOPI dropped to 0 in the presence of an Ni-Al₂O₃ catalyst, inferring its rather high reactivity. The increase of 5-AP selectivity at the expense of the selectivity of 5-[(5-hydroxypentyl)imino]-1-pentanol (5-HPIP) for the Ni-Al₂O₃ catalysts with Ni loadings from 10 to 90 wt% (entries 3–7) suggested that it is a secondary imine that could be further transformed into the target 5-AP product. In the presence of NH₃, all the Ni-Al₂O₃ catalysts showed very low selectivity (<2.8%) to 1,5-PD, which is a direct hydrogenation product of 2-HTHP through the 5-HP intermediate.^{23,57} In addition, a small amount of di-1-pentanolamine (DPA) produced by 5-HPIP hydrogenation was also detected (<5.1%). The low selectivity to the direct hydrogenation by-products 1,5-PD and DPA for Ni-Al2O3 catalysts, especially those with Ni loadings around 50-70 wt%, accounts for their high selectivity to the target 5-AP product.

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Obviously, the above findings indicated that the Ni-Al₂O₃ catalysts with 50-70 wt% Ni loadings presented much better performance in the synthesis of 5-AP from the clean reductive amination of bio-2-HTHP. It has been suggested that the Lewis acid sites promotes the formation of imine by activating the C=O group of the aldehydes/ketones via the electron lone pair in oxygen, while the metal sites are responsible for the hydrogenation of imine to amine.^{6,45} Although 2-HTHP could readily react with NH₃ through 5-HP to form imine intermediates of 5-IP and THPOPI (Table 2, entry 1),²² the promotion effect of the strong Lewis acid sites on the surface of the 50Ni-Al₂O₃ and 70Ni-Al₂O₃ catalysts could not be excluded at present. In addition, because the hydrogenation of the imine intermediates over metallic sites is likely a rate-determining step for the reductive amination of aldehydes/ketones,^{17,22} the presence of a large amount of small Ni⁰ particles (Table 1, Fig. 1 and 3) would contribute to the high activity of these catalysts. Due to its outstanding performance, the 50Ni-Al₂O₃ catalyst was chosen for further studies.

Fig. 6 shows the effect of reaction parameters such as temperature, H_2 pressure, reaction time, and catalyst amount

on the reductive amination of 2-HTHP over the 50Ni-Al₂O₃ catalyst. These reaction parameters had a weak effect on 2-HTHP conversion, all of which were above 93% owing to its high reactivity,^{22,23,57} while significantly influencing the product selectivity. The conversion of 2-HTHP reached 100% even at a low temperature of 40 °C (Fig. 6(a)). At such a low temperature, the selectivity of the target 5-AP was only 28.6% and large amounts of imine products of 5-IP and 5-HPIP were detected with selectivities of 17.8% and 46.0%, respectively. The 5-AP selectivity increased sharply with increasing temperature and reached a maximum of 88.0% at 70 °C, which then slightly decreased to 84.6% upon further increasing the temperature to 80 °C. The selectivities to 5-IP and 5-HPIP decreased rapidly with increasing temperature and almost disappeared at temperatures up to 70 °C and above. The selectivity of 1,5-PD decreased gradually from 3.2% to 1.1% with an increase of temperature, implying that high temperature is more favorable for the reductive amination of 2-HTHP rather than its direct hydrogenation. The formation of large amounts of DPA and other undetected sideproducts at a higher temperature of 80 °C may account for a slight decrease of 5-AP selectivity at such a temperature. Therefore, an



Fig. 6 Effects of the reaction parameters on the reductive amination of **2-HTHP** over the $50Ni-Al_2O_3$ catalyst: (a) temperature, (b) H_2 pressure, (c) reaction time, and (d) catalyst amount. Reaction conditions: 15 g of 21.3% **2-HTHP** aqueous solution; 15 g of 25 wt% aqueous ammonia; (a) 0.1 g of $50Ni-Al_2O_3$ catalyst, 2 MPa H_2 , 1 h; (b) 0.1 g of $50Ni-Al_2O_3$ catalyst, 60 °C, 1 h; (c) 0.1g of $50Ni-Al_2O_3$ catalyst, 60 °C, 2 MPa H_2 ; and (d) 60 °C, 2 MPa H_2 , 1 h.

appropriate reaction temperature of \sim 70 °C is selected for the efficient synthesis of 5-AP.

The changes in conversion and product selectivity with H₂ pressure from 0 MPa to 4 MPa are shown in Fig. 6(b). In the absence of H₂, the conversion of 2-HTHP was 93.1%, and the main products were 5-IP and THPOPI with selectivities of 69.2% and 22.5%, respectively. The presence of 1 MPa and above H₂ resulted in the full conversion of 2-HTHP and the generation of hydrogenation products of 5-AP, 1,5-PD and DPA. The selectivity of 5-AP increased sharply from 58.4% at 1 MPa H₂ to 87.5% at 3 MPa H₂ and almost leveled off at 4 MPa H₂. The selectivities of 1,5-PD and DPA increased linearly from 1.1% and 1.4% at 1 MPa H_2 to 3.4% and 7.5% at 4 MPa H_2 , respectively. With an increase of H₂ pressure, 5-IP and 5-HPIP were quickly converted to 5-AP or DPA and completely disappeared at 3 MPa H₂. These results suggested that increasing the H₂ pressure promoted the increase of both the reductive amination and hydrogenation products, which in line with previous studies.^{22,23} Clearly, an appropriate H₂ pressure (2 MPa) is reasonable for the efficient production of the target 5-AP.

Fig. 6(c) shows the product distribution as a function of the reaction time from 0 min to 4 h. Due to its high reactivity, full conversion of 2-HTHP was achieved even upon increasing the temperature up to 60 °C. In addition, a small amount of 5-AP (17.1%) was detected during the increasing temperature process and large amounts of imine intermediates of 5-IP and 5-HPIP with selectivities of 30.2% and 42.3% were also detected, respectively. As the reaction went on, the selectivity of 5-AP significantly increased to 84.6% within 1 h, and then slowly rose up to 90.6% with the reaction time further extending to 4 h. The imine intermediates of 5-IP and 5-HPIP were considerably high at the beginning but then disappeared completely within 2 h following the increase of 5-AP. On the other hand, the DPA selectivity slightly increased from 0 to 4.0% within 4 h. These findings suggest that the 5-IP and 5-HPIP intermediates were more favorably converted to 5-AP in the presence of sufficient ammonia and H₂ than to DPA. 1,5-PD was detected with a low selectivity of \sim 2.0% and remained almost constant during the process, probably as a result of the very fast competitive reaction of the condensation of 2-HTHP and NH₃.

Fig. 6(d) shows the influence of catalyst amounts from 0.05 g to 0.4 g. 2-HTHP could be fully converted with the presence of even 0.05 g of catalyst. The selectivity to 5-AP increased sharply from 48.3% to a maximum of 91.3% with increasing catalyst amounts from 0.05 g to 0.2 g, and then decreased slowly to 88.3% with further increasing the catalyst amounts to 0.4 g. Simultaneously, the selectivities to other hydrogenation products of 1,5-PD and DPA also gradually increased from 2.5% and 2.7% to 4.1% and 7.7% upon increasing the catalyst amounts from 0.05 g to 0.4 g, respectively. The selectivities of 5-IP and 5-HPIP decreased sharply with increasing catalyst amounts and both disappeared at catalyst amounts up to 0.2 g. These results indicate that appropriate active Ni sites played a crucial role in the reductive amination of 2-HTHP to generate the target 5-AP with high selectivity. In addition, the Ni-Al₂O₃ catalyst was also active for the reductive amination of other biomass-derived



Fig. 7 Reductive amination of **2-HTHP** with NH₃ over the 50Ni–Al₂O₃ catalyst in a continuous flow reactor. Reaction conditions: a mixed solution of 21.3 wt% **2-HTHP** aqueous solution and 25 wt% concentrated ammonia at a weight ratio of 1:1, 60 °C, 2 MPa H₂, weight hourly space velocity (WHSV) of **2-HTHP** = 0.5 h⁻¹, and H₂/**2-HTHP** molar ratio = 30.

aldehydes and ketones to form the corresponding primary amines with high yields of 88–99% (Table S1, ESI⁺).

The stability of the 50Ni–Al₂O₃ catalyst on the reductive amination of **2-HTHP** was investigated *via* a fixed-bed flow reactor and the result is shown in Fig. 7. To our delight, this catalyst presented very good stability during a 150 h time-onstream. The **2-HTHP** conversion maintained 100% during the whole process, which is in line with our previous study using the 30Ni–Mg₃AlO_x catalyst²² due to the high reactivity of **2-HTHP**. The yield of **5-AP** maintained at ~86% and no appreciable decline in **5-AP** yield could be seen during the 150 h time-on-stream. In contrast, obvious deactivation was observed for the Ni–ZrO₂ catalyst after 22 h of reaction²³ and for the 30Ni–Mg₃AlO_x catalyst after 90 h of reaction²² under similar conditions, revealing the remarkable stability of the 50Ni–Al₂O₃ catalyst in the reductive amination of **2-HTHP**.

For a better understanding of the stability of the catalyst, the used 50Ni-Al₂O₃ catalyst after the 150 h time-on-stream was characterized by XRD, XPS and TEM. XRD results (Fig. S6, ESI[†]) showed that there were almost no perceptible changes for the diffraction peak of the Ni crystals as compared with the freshly reduced one, and the Ni crystallite size of the used catalyst just slightly enlarged from 5.5 nm to 7.0 nm, showing the good stability of the catalyst against sintering during the reaction. Such a finding was also confirmed by TEM characterization (Fig. 8), as Ni particles were still well dispersed on the support with a mean particle size of 6.7 nm. The good resistance to the sintering of the catalyst might be attributed to the strong interaction between the Ni²⁺ species and the Al₂O₃ support,⁵⁸ as revealed by the H2-TPR characterization shown in Fig. 4. Our previous studies^{22,23} showed that surface oxidation of active Ni⁰ might be another important reason along with sintering that accounted for the deactivation of Ni catalysts in 2-HTHP reductive amination. XPS characterization of the used 50Ni-Al₂O₃ catalyst (Fig. S6, ESI[†]) showed the presence of an obvious Ni⁰



Fig. 8 TEM image of the used 50Ni–Al $_2O_3$ catalyst after the 150 h time-on-stream.

peak similar to the freshly reduced and passivated catalyst. Such a finding infers that the 50Ni–Al₂O₃ catalyst also presents good resistance to surface oxidation, contributing to the remarkably enhanced reaction stability of the catalyst.

Experimental section

Materials

 $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3 and NaOH were purchased from West Long Science Co., Ltd. 1,2-Pentanediol (98%) was purchased from Maclean Biochemical Technology Co., Ltd. 5-Amino-1-pentanol (95%) was purchased from Aladdin Chemical Reagent Co. Ltd. All of the reagents were of analytical grade and were used without further purification.

An aqueous solution of 21.3 wt% **2-HTHP** was obtained by the autocatalytic hydration of dihydropyran.⁵⁹ The reaction was performed in a 2 L autoclave equipped with mechanical stirring. After adding 100 g of dihydropyran and 400 g of deionized water, the autoclave was sealed and flushed 3 times with N₂, and then pressurized to 2 MPa. The reaction was carried out at 100 °C for 1 h.

Catalyst preparation

The Ni–Al₂O₃ catalysts with Ni loadings from 0 to 100 wt% were prepared by the co-precipitation method. The specific preparation process was described below. A mixed salt solution of Ni(NO₃)₂·6H₂O (0.1 M) and Al(NO₃)₃·9H₂O, and a mixed alkali solution of NaOH (5 M) and Na₂CO₃ (1 M) were added dropwise concurrently into a three-necked flask under vigorous stirring. The pH of the solution was maintained as 10 \pm 0.1. After that, the precipitate was aged at 80 °C for 24 h, and then filtered and washed with deionized water until the pH was ~7. The obtained solid was dried at 110 °C overnight and calcined in a muffle furnace at 700 °C for 4 h. The calcined sample was reduced in flowing H₂ at 650 °C for 3 h to obtain active *x*Ni– Al₂O₃ catalysts with different Ni contents, where *x* represents the theoretical mass fraction of active Ni in the catalyst. For comparison, the calcined samples were denoted as *x*NiO–Al₂O₃.

Catalyst characterization

The Ni contents in the Ni–Al $_2O_3$ catalysts were detected using a fluorescence spectrometer (AAS, Analytik Jena ContrAA 700),

the samples were dissolved using a mixture of HCl and HNO₃ before the measurements. The BET surface area and average pore diameter of the calcined samples were measured by using a TriStar II 3020 (Micromeritics) surface area and porosity analyzer. Prior to the measurements, the samples were degassed in N₂ flow at 300 °C for 4 h to remove adsorbed water and impurities.

The X-ray powder diffraction (XRD) patterns of the samples were obtained on a Rigaku D/MAX-2400 diffractometer operating at 40 kV and 30 mA, using Ni-filtered Cu K α radiation with a scanning angle (2 θ) from 10° to 80° at a scan rate of 5° min⁻¹. The mean crystallite size of Ni is calculated using the Scherer equation. X-ray photoelectron spectra (XPS) were performed on an ESCALAB250xi spectrometer, using a monochromatized Al K α X-ray radiation source with a pass energy of 20 eV. All binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon with an uncertainty of 0.2 eV.

The transmission electron microscopy (TEM) images of the catalysts were obtained on a JEM2010 electron microscope operating at 200 kV and the pre-reduced catalyst was suspended in ethanol by sonication and deposited on the copper mesh for TEM inspection. The particle size distribution of Ni particles was statistically obtained from the TEM micrographs by counting at least 200 particles. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) mapping measurements were obtained using an FEI Talos $200 \times$ transmission electron microscope (USA) operated at an acceleration voltage of 200 kV.

 H_2 temperature-programmed reduction (H_2 -TPR) measurements were carried out on a Quantachrome automated chemisorption analyzer (ChemBET pulsar TPR/TPD). The calcined sample containing around 10 mg of Ni was charged into a quartz reactor and pretreated at 200 °C for 1 h under He flow. After cooling to room temperature, it was heated to 900 °C at a heating rate of 10 °C min⁻¹ under 10% H_2 -N₂ flow (30 mL min⁻¹). H_2 consumption was collected using a thermal conductivity detector (TCD). For determining the reduction degree of the catalyst, the same amount of calcined sample was pre-reduced at 650 °C for 2 h under 10% H_2 -N₂ flow (30 mL min⁻¹). After cooling to below 50 °C, the obtained reduced sample was subjected to another H_2 -TPR to obtain the calcined sample upon increasing the temperature to 900 °C, and the reduction degree was calculated as follows:⁶⁰

NH₃ temperature programmed desorption (NH₃-TPD) measurements were performed on a Huasi DAS-7200 automatic chemical adsorption instrument. The samples (200 mg) were firstly reduced at 650 °C for 3 h under 5% H₂–Ar flow (30 mL min⁻¹). Then, the sample was cooled to 100 °C followed by adsorbing NH₃ for 1 h under 10% NH₃–N₂ flow (30 mL min⁻¹). After purging the system with He (30 mL min⁻¹) for 1 h, the system was heated to 600 °C at a ramp rate of 10 °C min⁻¹ under He flow, and the desorption of NH₃ was detected by TCD. Pyridine Fourier transform infrared (py-IR) spectra were recorded on a Tensor 27 Fourier Infrared Spectrometer produced by Bruker.

Reduction Degree (%) = $\frac{\text{TPR peak area of calcined sample} - \text{TPR peak area of reduced sample}}{-}$

TPR peak area of calcined sample

After pretreating at 400 $^{\circ}$ C under 10⁻³ Pa for 1 h, the spectrum of the sample disk was collected as a blank experiment. Pyridine adsorption was carried out at room temperature, and the following desorption steps were performed at 30 $^{\circ}$ C, 100 $^{\circ}$ C and 150 $^{\circ}$ C for 30 min, respectively. The spectrum of each sample was acquired after cooling the sample.

Catalytic tests

The catalyst activity test was performed in a 100 mL stainless steel autoclave reactor at a stirring speed of 800 rpm. Prior to the reaction, the calcined NiO–Al₂O₃ samples were reduced at 650 $^{\circ}$ C in pure H₂ for 3 h to obtain the active catalysts. In a

with different Ni contents from 0 to 100 wt% prepared by co-precipitation. The selectivity to the desired product **5-AP** strongly depended on Ni loadings and the highest **5-AP** selectivity of 91.3% at full conversion was achieved over the 50Ni–Al₂O₃ catalyst under mild conditions of 60 °C and 2 MPa H₂. This catalyst also exhibited good stability during a 150 h time-onstream without appreciable deactivation. The outstanding performance of the 50Ni–Al₂O₃ catalyst could be ascribed to the highly dispersed Ni⁰ particles with strong interaction with the support and good resistance to surface oxidation during the reaction. The important findings of this work would be helpful for developing

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

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

typical experiment, 15 g of 21.3 wt% **2-HTHP** aqueous solution was firstly added into the reactor, and then the reduced active catalyst containing 0.05 g of Ni was loaded into the reactor in a glove box filled with Ar, followed by the addition of 15 g of 25% aqueous ammonia. After flushing the reactor 3 times with H_2 , it was pressurized to 2 MPa H_2 , then heated to 60 °C, and remained stable during the reaction.

The catalyst stability test was performed in a tubular fixed bed flow reactor (length 36 cm, inner diameter 0.9 cm) at 60 °C and 2 MPa H₂. 1.0 g of the prepared sample (40-60 mesh) was charged into the flow reactor, and the catalyst was pre-reduced under the flow of pure H₂ (40 mL min⁻¹) at 650 °C for 3 h. After cooling to the reaction temperature, the reactor was pressurized to 2 MPa with H₂, and then a solution mixed with 21.3 wt % 2-HTHP aqueous solution and 25 wt % aqueous ammonia at a mass ratio of 1:1 was pumped into the flow reactor at a flowing rate of around 5 g h^{-1} . Next, the reaction effluents was collected from a stainless steel gas-liquid separator every 5 to 10 h. The reaction products were identified using a GC-MS system (Agilent 7890A/ 5975C) and the detected products included 5-amino-1-pentanol (5-AP), 1,5-pentanediol (1,5-PD), THP-oxypentanimine (THPOPI), 5-imino-1-pentanol (5-IP), 5-[(5-hydroxypentyl) imino]-1-pentanol (5-HPIP), and di-1-pentanolamine (DPA). The quantification of the product was performed on an Agilent 7890A GC system equipped with an HP-5 capillary column, using 1,2-pentanediol (1,2-PD) as the internal standard. Due to the unavailability of the standards for 5-IP, 5-HPIP, THPOPI and DPA, the GC response factors of 5-IP and the other three products were assumed to be the same and twice as 5-AP, respectively. The conversion and product selectivity were calculated as follows: The carbon balance of the analysis was generally greater than 90%.

Conclusions

In summary, the reductive amination of bio-furfural-derived **2-HTHP** to value-added **5-AP** was studied over Ni–Al₂O₃ catalysts

novel base-metal catalysts for the synthesis of useful amines by reduction amination of carbonyl compounds.

Conflicts of interest

There are no conflicts to declare.

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