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ARTICLE TYPE

Direct Synthesis of 2-Ethylhexanol via *n*-Butanal Aldol Condensation-Hydrogenation Reaction Integration over Ni/Ce-Al_2O_3 Bifunctional Catalyst

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Direct synthesis of 2-ethylhexanol from *n*-butanal via the reaction integration of *n*-butanal self-condensation with 2-ethyl-2-hexenal hydrogenation is of a crucial interest for industrial production of 2-ethylhexanol. Furthermore, as an important and versatile chemical, *n*-butanol can be produced simultaneously by the reaction integration. In the present work, several bifunctional catalysts based on γ-Al_2O_3 were prepared by impregnation method and were characterized by means of H_2-TPR, XRD, TEM and H_2-TPD, and their catalytic performance for direct synthesis of 2-ethylhexanol from *n*-butanal was investigated. The results showed that Co/Al_2O_3 had a low activity for hydrogenation and Cu/Al_2O_3 had a high selectivity for the hydrogenation of C=O group while Ru/Al_2O_3 catalyst only favored the hydrogenation of *n*-butanal to *n*-butanol. Among them, Ni/Al_2O_3 catalyst showed the best catalytic performance and the yield of 2-ethylhexanol was the highest (49.4%). Ce-modified Ni/Al_2O_3 enhanced the competitiveness of aldol condensation versus hydrogenation of *n*-butanal and improved the selectivity of 2-ethylhexanol; the yield of 2-ethylhexanol rose to 57.8%. Then the influence of preparation conditions on the catalytic performance of Ni/Ce-Al_2O_3 was investigated and the suitable preparation conditions were obtained as follows: Ni loading = 10%, calcined at 550 °C for 5 h, and reduced at 570 °C for 4 h. The effect of reaction conditions on the integration reaction catalyzed by Ni/Ce-Al_2O_3 was investigated and the suitable reaction conditions were obtained as follows: weight percentage of Ni/Ce-Al_2O_3 = 15%, reaction temperature = 170 °C, reaction pressure = 4.0 MPa and reaction time = 8 h. Under the above reaction conditions, the yield of 2-ethylhexanol attained 66.9% and that of *n*-butanol was 18.9%. In addition, the components existing in the integration reaction system were identified by GC-MS analysis, and the main by-products were *n*-butyl butyrate, 2-ethylhexyl butyrate, *n*-butyric acid, etc. By the analysis of the reaction system, a reaction network for the direct synthesis of 2-ethylhexanol from *n*-butanal was proposed. Finally, the evaluation on the reusability of Ni/Ce-Al_2O_3 showed that the recovered Ni/Ce-Al_2O_3 catalyst lost its catalytic activity for the hydrogenation of C=O group. The main reason for deactivation was that Ni species were covered by the flaky boehmite γ-AlO(OH) formed from the hydration of γ-Al_2O_3 in the reaction process.

Introduction

2-Ethylhexanol (2EHO), an important organic chemical, is used as chemical intermediates and alternative fuels. For example, its carboxylic acid esters such as dioctyl terephthalate (DOTP), dioctyl phthalate (DOP) and dioctyl adipate (DOA) are widely used as plasticizers, especially in polyvinylchloride manufacture. Other uses of 2EHO include the production of intermediates for acrylic surface coatings, diesel fuel and lube oil additives and surfactants [1]. The industrial production of 2EHO comprises three reaction steps: propylene hydroformylation to *n*-butanal, *n*-butanal self-condensation to 2-ethyl-2-hexenal (2E2H), and 2E2H hydrogenation to 2EHO. At present, the industrial technology for the manufacture of 2E2H utilizing an aqueous caustic alkali as catalyst possesses many disadvantages: firstly, the selectivity of 2E2H is sensitively affected by the concentration of the aqueous alkali; secondly, the liquid alkali is strongly corrosive to the equipment; finally, the volume of emission of alkali wastewater is large and a lot of liquid acid is usually required for neutralization [2, 3]. The hydrogenation of 2E2H is composed of the processes of crude hydrogenation and refined hydrogenation catalyzed by the supported Cu or Ni catalysts [4]. The self-condensation of *n*-butanal is a typical aldol condensation reaction, which can be catalyzed by an acid, a base or an acid-base bifunctional catalyst. In

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order to overcome the existing shortcomings of the present industrial process, most researchers have focused on solid base catalysts including alkaline earth metal oxides and supported alkali catalysts [5-8] due to their characteristics such as high activity, high selectivity, and easy separation. However, they are sensitive to air and water and show poor stability, hindering their industrial application. In comparison, solid acid catalysts were widely used in industrial processes [9-11] due to their excellent catalytic activity and selectivity and good stability. Unfortunately very few studies on *n*-butanal self-condensation catalyzed by a solid acid catalyst have been published in the literature [12, 13]. Therefore, it is significant to develop a solid acid catalyst with an industrial application prospect.

Direct synthesis of 2EHO by the reaction integration of *n*-butanal self-condensation and 2E2H hydrogenation can eliminate the separation and purification operation between the two steps, simplifying the steps of operation, shortening the total operation period and saving energy. Therefore, the study on the integration reaction process has important academic and application values. At present, several reports on the other aldol condensation-hydrogenation reaction process integration have been published [14-19], but there is no relevant research on the integration of *n*-butanal self-condensation and 2E2H hydrogenation to 2EHO. However, the integration of *n*-butanal self-condensation and 2E2H selective hydrogenation to 2-ethylhexanal (2EH) has been studied by some researchers. Kelly et al. [5, 20] studied the reaction integration of *n*-butanal self-condensation and the C=C double bond selective hydrogenation of 2E2H to 2EH catalyzed by $Pd/Na/SiO_2$ in a fixed bed microreactor. The conversion of *n*-butanal was 42% and the selectivity of 2EH was 94.9% at 350 °C. Besides, a dual bed system containing *n*-butanal self-condensation reaction catalyzed by Na/SiO_2 in the first bed and the hydrogenation of 2E2H catalyzed by Cu/Zn in the second bed was investigated to produce a mixture of *n*-butanol (BO) and 2EHO starting from *n*-butanal feed. The highest conversion of *n*-butanal was 31.8% but only about 23.3% of the products was 2EHO while the rest was BO, indicating that the catalytic performance of Na/SiO_2 for aldol condensation was poor and the unreacted *n*-butanal was hydrogenated to form BO in the second bed. Strictly speaking, two separate reactions (not a reaction integration) took place in series in the dual bed system. Ko et al. [21] prepared several noble metal-solid base bifunctional catalysts and conducted the synthesis of 2EH from the reaction integration of *n*-butanal self-condensation and the selective hydrogenation of the C=C double bond of 2E2H in a fixed-bed reactor. The yield of 2EH was 59% under the optimum reaction conditions. Moreover, Sharma et al. [22] prepared a multi-functional catalyst by impregnation/intercalation of inorganic metal complex $HRu(CO)(PPh_3)_3$ on a solid base hydrotalcite to catalyze the synthesis of C_8 aldol derivatives from propylene and synthesis gas in a single-pot liquid reaction. This reaction process comprised two steps: the hydroformylation of propylene and synthesis gas was conducted at 60 °C for 3 h in toluene solvent, and then the aldol condensation and hydrogenation proceeded at 150 °C or 250 °C for 9 h after the synthesis gas was replaced by hydrogen. The $HRu(CO)(PPh_3)_3$ had catalytic activity not only for the hydroformylation reaction but also for the hydrogenation reactions of the aldol condensation product 2E2H, the hydroformylation product *n*-butanal and the feedstock propylene. Therefore, the composition of this reaction system was very complicated and its separation was very difficult.

Since 2EHO is the fully hydrogenated product of 2E2H, the hydrogenation catalyst is required for a complete hydrogenation of both the C=C and C=O double bonds. In this sense, the catalyst would inevitably catalyze the hydrogenation of *n*-butanal to BO. Therefore, there exist two rival parallel reactions, *n*-butanal hydrogenation and aldol condensation reactions, in this reaction process integration. Compared with *n*-butanal hydrogenation reaction, *n*-butanal aldol condensation reaction is more difficult to take place thermodynamically. Therefore the enhancement of the competitiveness of *n*-butanal aldol condensation is the key to realize the direct synthesis of 2EHO by the reaction process integration. Additionally, since BO is a versatile chemical, two important chemicals can be produced simultaneously by the reaction process integration.

In this paper, several metal-solid acid bifunctional catalysts were prepared by impregnation method using γ-Al_2O_3 as support which had excellent catalytic performance for *n*-butanal self-condensation. They were characterized by means of H_2-TPR, XRD, TEM and H_2-TPD and their catalytic performance for direct synthesis of 2-ethylhexanol from *n*-butanal was investigated. By the analysis of the reaction system, a reaction network was proposed. In addition, the reason for the deactivation of this bifunctional catalyst was discussed.

Experimental

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Materials and reagents

n-Butanal (AR, Tianjin Damao Chemical Reagent Factory, China), pseudo-boehmite (Tech, Aluminum Inc of Shandong Luzhong Industrial Trade Company, China), cobalt nitrate (AR, Tianjin Guangfu Fine Chemical Research Institute, China), nickel nitrate (AR, Tianjin Fengchuan Chemical Reagent Science and Technology Co. Ltd., China), ruthenium chloride (AR, Alfa Aesar (Tianjin) Chemical Co. Ltd., China), cerium nitrate and cupric nitrate (AR, Sinopharm Chemical Reagent Co. Ltd., China). All materials were used as received.

Preparation of catalysts

γ-Al_2O_3 was prepared by calcinating pseudo-boehmite at 500 °C for 4 h in air atmosphere and the metal-solid acid bifunctional catalysts were prepared by impregnation procedure. Taking Ni/Ce-Al_2O_3 as an example, Ce-Al_2O_3 was prepared by impregnating γ-Al_2O_3 with an aqueous solution of cerium nitrate, followed by aging at room temperature for 24 h, drying at 110 °C for 8 h and calcinating at 550 °C for 4 h. Finally, the bifunctional catalyst Ni/Ce-Al_2O_3 was prepared by impregnating Ce-Al_2O_3 with an aqueous solution of nickel nitrate, followed by aging at room temperature for 24 h, drying at 110 °C for 8 h and calcinating at 550 °C for 5 h, reducing at 570 °C for 4 h in H_2 atmosphere (20 vol.% in N_2). After the temperature of the reduction furnace fell to 250 °C, a flow of normal nitrogen gas was introduced until the furnace cooled to room temperature.

Characterization of catalysts

Temperature-programmed reduction (H_2-TPR) tests were carried out on a Micromeritics Auto Chem II-2920 apparatus. All samples (0.1 g) were pretreated in a flow of Ar (50 mL • min^{-1}) at room temperature for 5 min. Then the flowing gas was switched to H_2 (10 vol.% in Ar, 50 mL • min^{-1}) and the sample was heated to 1000 °C in a ramp of 10 °C • min^{-1}. The H_2 consumption was monitored by a thermal conductivity detector (TCD).

X-ray diffraction patterns (XRD) were recorded with a Rigaku D/MAX-2500 diffractometer using Cu Kα radiation source at 100 mA and 40 kV. The scan range covered from 10° to 90° at a rate of 4 ° • min^{-1}.

Temperature-programmed desorption of hydrogen (H_2-TPD) tests were performed on a Micromeritics Auto Chem II-2920 apparatus. All samples (0.1 g) were pretreated in a flow of He (50 mL • min^{-1}) at 570 °C for 60 min. After cooled to 50 °C in the He flow, the flowing gas was switched to H_2 (10 vol.% in He) until the amount of H_2 in effluent stream was constant. Excess of physically adsorbed H_2 was removed by allowing the sample to remain in He flow until no significant amount of H_2 could be detected. Finally the sample was heated to 950 °C in a ramp of 10 °C • min^{-1}. The amount of H_2 desorbed was monitored by a TCD.

Transmission electron microscopy (TEM) study was carried out in a FEI Tecnai G2 F20 instrument operating at an accelerating voltage of 200 kV. Samples were ultrasonically dispersed in ethanol, and a couple of drops of the suspension were deposited on a standard 3 mm copper grid covered with a holey carbon film.

Direct synthesis of 2EHO from n-butanal

40 mL (32 g) of *n*-butanal and 4.8 g of bifunctional catalyst (e.g. Ni/Ce-Al_2O_3) were placed in a 100 mL stainless steel autoclave. After purged with dry hydrogen, the mixture was heated and the integration reaction was carried out at 180 °C for 10 h under the pressure of 4.0 MPa. After the completion of reaction, the reaction system was cooled to room temperature. The gas was released and the liquid was separated by vacuum filter and then quantitatively analyzed by a gas chromatograph.

Product analysis

A qualitative analysis of the product was conducted on a GC-MS (Thermo Finnigan TRACE DSQ). EI ionization source was used in the mass spectrometry with the ion source temperature of 200 °C. The mass spectrum was recorded in the range of 40 - 500 amu. The temperature of both the vaporizing chamber and the transmission line was controlled at 250 °C. A BPX5 capillary column was used for separation of components and the column temperature was controlled according to the following program: initial temperature of 40 °C and then heated to 250 °C in a ramp of 10 °C·min^{-1} and held for 2 min.

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A quantitative analysis of the product was carried out using a SP-2100 gas chromatograph (Beijing Beifen-Ruili Analytical Instrument Co., Ltd). The product mixture was separated in a KB-1 capillary column whose temperature was controlled according to the following program: initial temperature of 80 °C and held for 3 min, heated to 160 °C in a ramp of 10 °C·min^{-1} and held for 2 min, then heated to 200 °C in a ramp of 10 °C·min^{-1} and held for 6 min. Nitrogen was used as a carrier gas and its flow rate was 30 mL·min^{-1}. The components were analyzed quantitatively in a flame ionization detector (FID) by internal standard method using cyclohexanol as the internal standard.

Results and discussion

Screening of catalysts

Several metal-solid acid bifunctional catalysts were prepared by impregnation method using γ-Al_2O_3 as support and their catalytic performance was evaluated under conditions of reaction temperature of 180 °C, pressure of 4.0 MPa and weight percentage of catalyst = 15%. The results are listed in Table 1. In these four metal-solid acid bifunctional catalysts, Co/Al_2O_3 had the highest selectivity to C_8 products (2E2H and its hydrogenated products 2EH and 2EHO), but it showed hardly any activity for hydrogenation. As a result, a small amount of BO was formed while no 2EHO was found. Ni/Al_2O, Ru/Al_2O_3 and Cu/Al_2O_3 had good catalytic activity; the conversion of *n*-butanal was 100% and the main products were the corresponding saturated alcohols. Among the three catalysts, Ni/Al_2O_3 had the highest catalytic activity for the aldol condensation and the selectivity to C_8 products was the highest. Cu/Al_2O_3 has the lowest catalytic activity for the aldol condensation, and the selectivity of C_8 products was only 14.3%. Contrary to the above activity order, the catalytic activity of Ni/Al_2O_3 for the hydrogenation of *n*-butanal was the lowest. However, Cu/Al_2O_3 showed the highest catalytic activity for the hydrogenation of *n*-butanal, resulting to the lowest selectivity ratio of 2EHO/BO. The results indicate that different metal-solid acid bifunctional catalysts exerted different competitiveness of the aldol condensation versus the hydrogenation reaction of *n*-butanal. When the integration reaction was catalyzed by Cu/Al_2O_3, the products contained a small amount of 2-ethyl-2-hexenol and a large amount of BO (the selectivity ratio of 2EHO/BO = 0.23), indicating that the supported Cu species had high catalytic activity for the hydrogenation of C=O group [23, 24]. When Ni/Al_2O_3 was used as the catalyst, the yield of 2EHO was the highest, 49.4%, and the selectivity ratio of 2EHO/BO was also the highest, 1.25. Therefore, Ni species was used as the active component for the hydrogenation reaction in the bifunctional catalyst.

Table 1 Screening of catalyst for direct synthesis of 2EHO from *n*-butanal

Catalysts	X_{BA}/%	Yield/%			Selectivity/%	
		2E2H	BO	2EHO	2E2H+2EHO	2EHO/BO
Ni/Al_2O_3	100	/	39.6	49.4	49.4	1.25
Ru/Al_2O_3	100		58.1	22.8	22.8	0.39
Cu/Al_2O_3^{a}	100	/	63.5	14.3	14.3	0.23
Co/Al_2O_3	91.3	80.0	1.8	/	87.6	/

Preparation conditions: the loading of Ru was 2 wt.% and the loadings of other metals were 10 wt.%.
Reaction conditions: temperature=180 ℃, pressure=4.0 MPa, time=10 h, weight percentage of catalyst= 15%.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.
a: a small amount of 2-ethyl-2-hexenol formed.

In our previous study, it was found that addition of Ce (loading of CeO_2 was 5 wt.%) could improve the catalytic performance of γ-Al_2O_3 for the aldol condensation reaction of *n*-butanal; the conversion of *n*-butanal increased to 93.8% from 87.5% and the yield of 2E2H increased to 83.1% from 76.6% [25]. Therefore, Ce was introduced into Ni/Al_2O_3 by impregnation in the present study and the result showed that the catalytic selectivity of Ni/Ce-Al_2O_3 was improved significantly for the integration process; the selectivity of 2EHO increased to 57.8% from 49.4%. As a result, the selectivity ratio of 2EHO/BO was up to 2.07,

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indicating that the competitiveness of the aldol condensation versus the hydrogenation reaction of *n*-butanal was enhanced. The reason for the improved catalytic performance of Ce modified Ni/Al_2O_3 was due to the following two points: ① Ce species on the surface of γ-Al_2O_3 would affect the catalytic activity for hydrogenation and the rate of hydrogenation reaction would decline, reducing the competitiveness of the hydrogenation of *n*-butanal in the two rival parallel reactions. Meanwhile the hydrogenation still could proceed under the investigated reaction conditions and the aldol product 2E2H could be fully hydrogenated to 2EHO. ② The base amount of catalyst is an important factor affecting the selectivity of 2E2H because the selectivity of 2E2H is higher along with the increase of base amount [26, 27]. Ce-Al_2O_3 not only has more base amount than γ-Al_2O_3 but also Ce has a specific 4f electronic structure which is beneficial to polarization of C=O group and promotes the formation of enol structure, thus the aldol condensation of *n*-butanal is favored. Therefore, Ce-Al_2O_3 had higher catalytic activity for aldol condensation reaction, improved the catalytic activity of Ni/Al_2O_3 for aldol condensation reaction directly, enhancing the competitiveness of the aldol condensation versus the hydrogenation reaction of *n*-butanal.

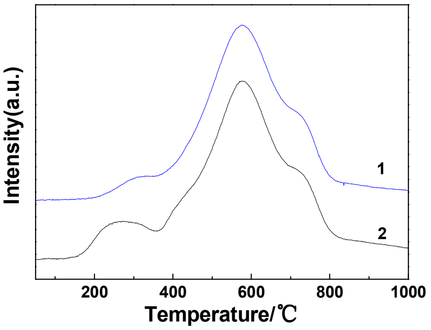

Fig. 1 H_2-TPR profile of Ni/Al_2O_3 and Ni/Ce-Al_2O_3 before reduced
1-Ni/Al_2O_3，2-Ni/Ce-Al_2O_3

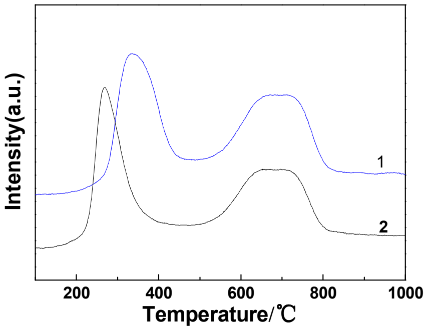

Fig. 2 H_2-TPR profiles of Ni/Al_2O_3 and Ni/Ce-Al_2O_3 after reduced
1-Ni/Al_2O_3，2-Ni/Ce-Al_2O_3

Fig. 1 shows H_2-TPR profiles of Ni/Al_2O_3 and Ni/Ce-Al_2O_3 before reduced. Both of the Ni/Al_2O_3 and Ni/Ce-Al_2O_3 catalysts had three reduction peaks which were representative of three different types of NiO species. According to the literatures [28,29], the reduction peak at 200 ~ 400 °C is attributed to the “free” NiO species, the reduction peak at 570 °C is ascribed to the NiO species interacting weakly with the support γ- Al_2O_3 and the reduction peak at 720 °C is assigned to the “fixed” NiO species interacting strongly with the support γ-Al_2O_3. The addition of Ce had no effect on the high-temperature reduction peak while the peak top temperature decreased and the peak area increased for the low-temperature reduction peak. It indicated that the addition of Ce could increase the reduction amount of the “free” NiO species and decrease the difficulty in reduction. Liu et al. [30] considered that the promotion of Ce on the reduction of NiO owed to the adsorption of Ce for hydrogen and the hydrogen adsorbed on the surface of CeO_2 could spill over to the surface of the surrounding NiO species, improving the reduction of NiO species. According to the analysis above, the addition of Ce improved the hydrogenation activity of the Ni/Al_2O_3 catalyst, which was opposite to the experimental results that the competitiveness of the aldol condensation versus the hydrogenation of *n*-butanal was enhanced. Considering the fact that Ni is oxidized easily, the H_2-TPR measurements of the reduced Ni/Al_2O_3 and Ni/Ce-Al_2O_3 catalysts were conducted. The H_2-TPR profiles are shown in Fig. 2 and the measurement data are listed in Table 2.

From Table 2 we found that these two catalysts could also consume a large amount of hydrogen, indicating that there were a large amount of unreduced NiO species in the catalysts after reduced. The “free” NiO species corresponding to the low-temperature reduction peak should have been reduced at 570 °C for 4 h in H_2 (20 vol.% in N_2) atmosphere. Compared with Fig. 1, the low-temperature peak area and top temperature increased while the reduction peak at 570 °C decreased and reduction peak at 720 °C was almost unchanged in Fig. 2. It indicated that the “fixed” NiO species could not be reduced under the reduction conditions while the amount of the “free” NiO species increased during the reduction process. The reason may be that the dispersed NiO species interacting weakly with γ- Al_2O_3 support which had been reduced to Ni in the furnace would be reoxidized by a small amount of oxygen in the normal nitrogen atmosphere during the cooling process, causing the increase of the amount of the “free” NiO species. It can be seen from Table 2 that the reduced catalysts had three reduction peaks. Even though the addition of Ce could not change the high temperature reduction peak, the top temperature and the area of the low temperature reduction peak decreased. It suggested that the addition of Ce decreased the amount of the “free” NiO species which could be *in-situ* reduced in the integration reaction process. The decrease in the amount of the “free” NiO species could inhibit the hydrogenation of *n*-butanal and would not affect the catalytic activity for aldol condensation reaction, enhancing the competitiveness of the aldol condensation versus the hydrogenation reaction of *n*-butanal. Therefore, the Ni/Ce-Al_2O_3 catalyst was chosen as the catalyst for direct synthesis of 2EHO from *n*-butanal for investigating the effect of preparation conditions.

Table 2 Reduction properties of the Ni/ Al_2O_3 and Ni/Ce-Al_2O_3 catalysts

Catalysts	Reduction peak at lower temperature		Reduction peaks at higher temperature			Total H_2 uptake /μmol·g^{-1}
	Top temperature/ °C	H_2 uptake /μmol·g^{-1}	Top temperature of peak 1/ °C	Top temperature of peak 2/ °C	H_2 uptake /μmol·g^{-1}	
Ni/Al_2O_3	337.2	592.7	653.1	724.1	572.0	1164.7
Ni/Ce-Al_2O_3	268.4	532.4	642.5	724.2	560.4	1092.8

Effect of preparation conditions

Effect of calcination temperature

Table 3 shows the effect of calcination temperature on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst. When the calcination temperature was lower than 600 °C, the Ni/Ce-Al_2O_3 catalyst had a better catalytic hydrogenation activity; the conversion of *n*-butanal was 100% and the reaction products were the corresponding saturated alcohols. With the increase of calcination temperature, the selectivity of C_8 products (2E2H, 2EH and 2EHO) rose while the yield of BO dropped, suggesting that the competitiveness of the aldol condensation versus the hydrogenation of *n*-butanal was enhanced. The yield of 2EHO increased firstly and achieved its maximum at a calcination temperature of 550 °C and then declined sharply. The selectivity ratio of 2EHO/BO could reach 2.33 and the yield of 2EHO was the highest, 60.8%, at the calcination temperature of 550 °C. When the calcination temperature was 600 °C, a large amount of the “fixed” NiO species was formed in the Ni/Ce-Al_2O_3 catalyst [31], decaying the catalytic hydrogenation activity. The main products were 2E2H and 2EH while 2EHO was formed just in a small amount, indicating that the catalytic hydrogenation activity of the Ni/Ce-Al_2O_3 catalyst decreased and furthermore the hydrogenation selectivity for C=C double bond was higher than C=O double bond. Therefore, the suitable calcination temperature was 550 °C.

The Ni/Ce-Al_2O_3 catalysts prepared at different calcination temperatures were characterized by H_2-TPR (the profiles are shown in Supporting Fig. S1). All the catalysts calcinated at different temperatures had three reduction peaks: a low-temperature reduction peak (< 400 °C) and two high-temperature reduction peaks (> 600 °C) which were overlapped with each other and corresponded to two types of NiO species interacting with the support. The “free” NiO species corresponding to the low-temperature reduction peak could be *in-situ* reduced under the reaction conditons while the NiO species interacting with the support in response to the two high-temperature reduction peaks could not. The TPR measurement data are listed in Table 4. With the increase of calcination temperature, the peak top temperature rose and the hydrogen consumption dropped for the low-temperature reduction peak while the peak top temperature of the high-temperature reduction peak 1 rose and that of the high-temperature reduction peak 2 kept unchanged but the total consumption of hydrogen increased. It indicated that the higher calcination temperature improved the interaction between the NiO species and the support γ-Al_2O_3 and the amount of the NiO species which could not be *in-situ* reduced increased gradually. The decrease of the “free” NiO species lowered the hydrogenation catalytic activity of the Ni/Ce-Al_2O_3 catalyst and enhanced the competitiveness of the aldol condensation versus the hydrogenation of *n*-butanal. It

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can be seen from Table 3 that the selectivity ratio of 2EHO/BO would rise firstly with the increase of calcination temperature and then dropped when the calcination temperature rose up to 600 °C. The reason might be that too small amount of the "free" NiO species led to the lower hydrogenation catalytic activity; not only the hydrogenation of *n*-butanal was restrained, but also 2E2H could not be hydrogenated fully to 2EHO.

Table 3 Effect of calcination temperature on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst

Calcination temperature / °C	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
450	100	/	43.7	/	44.2	44.2	1.01
500	100	/	27.9	/	57.8	57.8	2.07
550	100	/	26.1	/	60.8	60.8	2.33
600	93.1	36.7	1.6	33.0	1.6	76.6	1.0

Preparation conditions: the loading of Ni was 10 wt.%, m(Ni): m(CeO_2)=2: 1, calcination time=5 h, reduction temperature=570 °C, reduction time=4 h.

Reaction conditions: temperature=180 °C, pressure=4.0 MPa, time=10 h, weight percentage of Ni/Ce-Al_2O_3=15%.

X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

Table 4 Effect of calcination temperature on the reduction property of the Ni/Ce-Al_2O_3 catalyst

Calcination temperature / °C	Reduction peak at lower temperature		Reduction peaks at higher temperature			Total H_2 uptake /μmol·g^{-1}
	Top temperature / °C	H_2 uptake /μmol·g^{-1}	Top temperature of peak 1/ °C	Top temperature of peak 2/ °C	H_2 uptake /μmol·g^{-1}	
450	259.9	688.5	636.2	724.2	353.6	1042.1
500	268.4	532.4	642.5	724.2	560.4	1092.8
550	274.6	431.8	659.0	724.2	794.4	1226.2
600	275.7	347.3	689.3	724.2	1143.0	1490.3

Effect of calcination time

The effect of calcination time on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst was studied and the results are shown in Table 5. It was found that the Ni/Ce-Al_2O_3 catalyst calcinated at different time showed high catalytic performance; the conversion of *n*-butanal was 100% and the main products were BO and 2EHO. With the prolonging of calcination time, the yield of BO dropped firstly and then rose while the yield of 2EHO changed just the opposite. The selectivity ratio of 2EHO/BO could reach 2.71 and the yield of 2EHO was the highest, 62.9%, at the calcination time of 5 h. Therefore, the suitable calcination time was 5 h.

Compared with the calcination temperature, the calcination time had smaller effect on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst and the selectivity ratio of 2EHO/BO changed slightly. The Ni/Ce-Al_2O_3 catalyst calcinated at different time were characterized by H_2-TPR (see Supporting Fig. S2) and the measurement data are listed in Table 6. With the prolonging of calcination time, the hydrogen consumption of the high-temperature reduction peaks increased while the hydrogen consumption of the low-temperature reduction peak decreased, indicating that the amount of the "fixed" NiO species increased and that of the "free" NiO species decreased. The low catalytic activity for the hydrogenation is beneficial to the enhancement of the competitiveness of the aldol condensation versus the hydrogenation of *n*-butanal,

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leading to the promotion in the selectivity of 2EHO. Although the amount of the "free" NiO species decreased at the calcination time of 6 h, the yield of BO rose and the yield of 2EHO dropped, possibly due to the decline of the catalytic activity for the aldol condensation.

Table 5 Effect of calcination time on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst

Calcination time / h	X_{BA}/%	Yield/%		Selectivity/%	
		BO	2EHO	2EHO	2EHO/BO
3	100	32.1	54.6	54.6	1.70
4	100	26.1	60.8	60.8	2.33
5	100	23.2	62.9	62.9	2.71
6	100	26.4	60.6	60.6	2.30

Preparation conditions: the loading of Ni was 10 wt.%, m(Ni): m(CeO_2)=2: 1, calcination temperature of 550 °C, reduction temperature of 570 °C, reduction time of 4 h.
Reaction conditions: temperature=180 °C, pressure=4.0 MPa, time=10 h, weight percentage of Ni/Ce-Al_2O_3=15%.
X: conversion. BA: *n*-butanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

Table 6 Effect of calcination time on the reduction property of the Ni/Ce-Al_2O_3 catalyst

Calcination time / h	Reduction peak at lower temperature		Reduction peaks at higher temperature			Total H_2 uptake /μmol·g^{-1}
	Top temperature / °C	H_2 uptake /μmol·g^{-1}	Top temperature of peak 1/ °C	Top temperature of peak 2/ °C	H_2 uptake /μmol·g^{-1}	
3	269.3	482.7	644.2	724.2	715.9	1198.6
4	274.6	431.8	659.0	724.2	794.4	1226.2
5	274.8	388.8	659.3	724.2	834.4	1233.2
6	283.3	383.5	660.2	724.2	838.2	1221.7

Effect of reduction temperature

The reduction temperature directly affected the catalytic hydrogenation activity of the Ni/Ce-Al_2O_3 catalyst. Table 7 shows that the effect of reduction temperature on the catalytic activity of the Ni/Ce-Al_2O_3 catalyst calcinated at 550 °C for 5 h. With the increase of reduction temperature, the yield of BO increased and the selectivity of C_8 products decreased, indicating that the competitiveness of the aldol condensation versus the hydrogenation of *n*-butanal declined. When the reduction temperature was 520 °C, the selectivity of C_8 products was the highest, indicating that the catalytic activity for the aldol condensation reaction was the highest. However, 2E2H could not be hydrogenated fully due to the low catalytic hydrogenation activity of the catalyst and the main products were 2E2H and 2EH. When the reduction temperature was 620 °C, the products were mainly the saturated alcohols but the selectivity ratio of 2EHO/BO was low. The yield of 2EHO was highest, 62.9%, at the reduction temperature of 570 °C. Therefore, the suitable reduction temperature was 570 °C.

The Ni/Ce-Al_2O_3 catalysts prepared at different reduction temperature were characterized by H_2-TPR (the profiles are shown in Supporting Fig. S3) and the measurement data are listed in Table 8. With the increase of reduction temperature, the peak top temperature decreased and the peak area increased for the low-temperature reduction peak while the peak top temperature rose and the peak area decreased for the high-temperature reduction peaks, suggesting that the increased "free" NiO species came from the transformation of the NiO species interacting with γ-Al_2O_3 support. With the increase of reduction temperature, the amount of the NiO species interacting

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with the support γ-Al_2O_3 which was reduced to metal Ni species was enlarged. Since metal Ni species was easily oxidized back to the "free" NiO species during the cooling period after the reduction process, the amount of the "free" NiO species increased with the reduction temperature. Thus higher reduction temperature (620 °C) increased the amount of the "free" NiO species, improved the catalytic activity for hydrogenation reaction and lowered the competitiveness of the aldol condensation versus the hydrogenation of *n*-butanal. As a result, the selectivity of C_8 products declined. A lower amount of the "free" NiO species in the catalyst reduced at 520 °C resulted in a lower catalytic activity for hydrogenation, causing an incomplete hydrogenation of 2E2H to 2EH.

Table 7 Effect of reduction temperature on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst

Reduction temperature/℃	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
520	93.2	26.4	2.5	53.7	3.0	89.2	1.20
570	100	/	23.2	/	62.9	62.9	2.71
620	100	/	41.8	/	40.0	40.0	0.96

The loading of Ni was 10 wt.%, m(Ni): m(CeO_2)=2: 1, calcination temperature of 550℃, calcination time of 5 h, reduction time of 4 h.

Reaction conditions: Temperature=180 ℃, Pressure=4.0 MPa, time=10 h, weight percentage of Ni/Ce-Al_2O_3=15%.

X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol;

Table 8 Effect of reduction temperature on the reduction property of the Ni/Ce-Al_2O_3 catalyst

Reduction temperature /℃	Reduction peak at lower temperature		Reduction peak at higher temperature				Total H_2 uptake /μmol·g^{-1}
	Top temperature /℃	H_2 uptake /μmol·g^{-1}	Top temperature of peak 1/℃	Top temperature of peak 2/℃	Top temperature of peak 3/℃	H_2 uptake /μmol·g^{-1}	
520	292.9	262.6	/	606.2	722.8	1057.6	1320.2
570	274.8	388.8	/	659.3	724.2	834.4	1233.2
620	278.6	488.4	504.6	598.7	725.7	511.2	999.6

Effect of reduction time

The effect of reduction time on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst was studied and the results are shown in Table 9. With the prolonging of reduction time, the yield of BO increased and the selectivity of C_8 products dropped gradually while the yield of 2EHO rose firstly and then declined. It indicated that prolonging reduction time lowered the competitiveness of the aldol condensation versus the hydrogenation of *n*-butanal. When the reduction time was 3 h, the catalyst had the highest catalytic activity for aldol condensation reaction but its catalytic activity for hydrogenation reaction was the lowest. Most of the aldol products 2E2H would be hydrogenated only to form 2EH and the amount of 2EHO was very small. When the reduction time was longer than 3 h, the Ni/Ce-Al_2O_3 catalyst showed high catalytic activity for hydrogenation reaction and the products were the saturated alcohols. When the reduction time was 4 h, the selectivity ratio of 2EHO/BO was highest and the yield of 2EHO could reach the maximum of 62.9%. Therefore, the suitable reduction time was 4 h.

The Ni/Ce-Al_2O_3 catalysts reduced at different time were characterized by H_2-TPR (see Supporting Fig. S4) and the measurement data are listed in Table 10. With the prolonging of reduction time, the area of the low-temperature reduction peak increased and that of the high-temperature reduction peaks decreased roughly. When the reduction time was 3 h, the amount of the "free" NiO species was too small and the catalytic hydrogenation activity of the Ni/Ce-Al_2O_3 catalyst was low, causing that the aldol products 2E2H could not be hydrogenated fully. With the prolonging of reduction time, the amount of the "free" NiO species became larger and the catalytic activity for hydrogenation

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reaction was improved. The high catalytic activity for hydrogenation reaction enhanced the competitiveness of the hydrogenation of *n*-butanal, unfavourable for the formation of target product 2EHO. When the reduction time was 4 h, the amount of the "free" NiO species which could be *in-situ* reduced was moderate and appropriate; both of the catalytic activities for the aldol condensation and the hydrogenation reactions were preferable and the selectivity ratio of 2EHO/BO was the highest. Therefore, the suitable reduction time was 4 h.

Table 9 Effect of reduction time on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst

Reduction time / h	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
3	97.7	2.0	4.5	73.0	1.1	77.9	0.24
4	100	/	23.2	/	62.9	62.9	2.71
5	100	/	29.0	/	56.4	57.4	1.97
6	100	/	37.4	/	48.1	48.1	1.29

Preparation conditions: the loading of Ni was 10 wt.%, m(Ni): m(CeO_2)=2: 1, calcination temperature of 550 °C, calcination time of 5 h, reduction temperature of 570 °C.
Reaction conditions: temperature=180 °C, pressure=4.0 MPa, time=10 h, weight percentage of Ni/Ce-Al_2O_3=15%.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

Table 10 Effect of reduction time on reduction property of the Ni/Ce-Al_2O_3 catalyst

Reduction time / h	Reduction peak at lower temperature		Reduction peaks at higher temperature				Total H_2 uptake /μmol·g^{-1}
	Top temperature / °C	H_2 uptake /μmol·g^{-1}	Top temperature of peak 1/ °C	Top temperature of peak 2/ °C	Top temperature of peak 3/ °C	H_2 uptake /μmol·g^{-1}	
3	284.1	380.5	506.3	634.2	723.9	1050.7	1431.2
4	267.4	388.8	/	659.3	724.2	834.4	1233.2
5	268.2	418.9	/	654.7	724.1	691.1	1110.0
6	260.4	430.0	/	672.2	724.4	763.9	1193.9

Effect of Ni loading

The loading amount of Ni had great effect on the catalytic activity for hydrogenation reaction and then on the competitiveness of the aldol condensation versus the hydrogenation reaction of *n*-butanal, and finally affected the selectivity of 2EHO. A high loading amount of Ni could improve the catalytic activity for hydrogenation reaction, enhancing the competitiveness of *n*-butanal hydrogenation versus its aldol condensation reaction, decreasing the selectivity of 2EHO. A low loading amount of Ni would decay the catalytic activity for hydrogenation reaction, causing that the 2E2H could not be hydrogenated fully to 2EHO. Therefore, a high or low loading amount of Ni would decrease the yield of 2EHO. Table 11 shows the effect of the loading amount of Ni on the catalytic performance of the Ni/Ce-Al_2O_3 catalyst. With the increase of Ni loading, the yield of BO rose and the selectivity of C_8 products dropped, indicating that the competitiveness of the hydrogenation of *n*-butanal was enhanced. When the loading amount of Ni was 5%, the Ni/Ce-Al_2O_3 catalyst had low catalytic activity for hydrogenation reaction and the main products were 2E2H and 2EH. When the loading amount of Ni was 15%, the Ni/Ce-Al_2O_3 catalyst had high catalytic activity for the hydrogenation reaction of *n*-butanal and the main product was BO. When the loading amount of Ni was 10%, the selectivity ratio of 2EHO/BO was the highest, 2.71, and the yield of 2EHO was also the highest. Therefore, the suitable loading amount of Ni was 10%.

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Table 11 Effect of Ni loading on the catalytic performance of Ni/Ce-Al_2O_3

Loading of Ni /%	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
5	91.7	27.3	2.3	54.6	0.2	89.5	0.09
10	100	/	23.2	/	62.9	62.9	2.71
15	100	/	47.2	/	30.7	30.7	0.65

Preparation conditions: calcination temperature of 550 ℃, calcination time of 5 h, reduction temperature of 570 ℃, reduction time of 4 h.
Reaction conditions: temperature=180 ℃, pressure=4.0 MPa, time=10 h, weight percentage of Ni/Ce-Al_2O_3=15%.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

On the basis of the above experiments, the suitable preparation conditions were obtained as follows: the loading amount of Ni of 10%, calcinations temperature of 550 °C, calcination time of 5 h, reduction temperature of 570 °C and reduction time of 4 h.

Effect of reaction conditions

The effect of reaction conditions on *n*-butanal aldol condensation-hydrogenation integration reaction was investigated using the Ni/Ce-Al_2O_3 catalyst prepared under the suitable conditions.

Effect of catalyst dosage

The effect of the Ni/Ce-Al_2O_3 catalyst dosage on *n*-butanal aldol condensation-hydrogenation integration reaction was investigated and the results are listed in Table 12. It was found that increasing the amount of Ni/Ce-Al_2O_3 could improve the two parallel reactions of the aldol condensation and the hydrogenation of *n*-butanal simultaneously. The conversion of *n*-butanal rose to 100% from 90.1% when the weight percentage of Ni/Ce-Al_2O_3 increased from 10% to 15%. When the weight percentage of Ni/Ce-Al_2O_3 was 10%, the catalytic activity for hydrogenation reaction was low, especially for the C=O group; the yields of the saturated alcohols (BO and 2EHO) were lower. It suggested that the main reactions in this point were the aldol condensation of *n*-butanal and the hydrogenation reaction of C=C double bond. The yields of the saturated alcohols (BO and 2EHO) increased along with increasing the amount of Ni/Ce-Al_2O_3, suggesting that the catalytic activity for hydrogenation reaction were improved. It meant that the hydrogenation reactions of the C=O and C=C double bonds would not proceed completely until a certain amount of active sites for hydrogenation was supplied. When the weight percentage of Ni/Ce-Al_2O_3 was over 15%, the yields of BO and 2EHO kept almost the same. It indicated that the catalyst dosage higher than 15% would not change the competitiveness between the aldol condensation and the hydrogenation of *n*-butanal. So the two reaction rates remained unchanged. Therefore, the suitable weight percentage of Ni/Ce-Al_2O_3 was 15%.

Table 12 Effect of Ni/Ce-Al_2O_3 dosage on the integration reaction

Weight percentage of Ni/Ce-Al_2O_3 /%	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
10	90.1	28.3	2.1	48.9	1.6	85.7	0.76
15	100	/	18.2	/	65.5	65.5	3.60
20	100	/	18.2	/	63.4	63.4	3.48

Reaction conditions: temperature=180 ℃, pressure=4.0 MPa, time=10 h.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

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Effect of reaction temperature

Table 13 shows the effect of reaction temperature on *n*-butanal aldol condensation-hydrogenation integration reaction. When the reaction temperature was 160 °C, the self-condensation of *n*-butanal mainly occurred and the C_8 products (2E2H and 2EH) were mainly formed while the yields of BO and 2EHO were very low. When the reaction temperature increased over 170 °C, the conversion of *n*-butanal reached 100% and the competitiveness between the aldol condensation and the hydrogenation of *n*-butanal changed little. The Ni/Ce-Al_2O_3 catalyst did not have the catalytic activity for the hydrogenation of C=O group at 160 °C. With the increase of reaction temperature, both the C=C and C=O double bonds could be hydrogenated and BO and 2EHO were formed. It can be seen that the yields of BO and 2EHO were almost unchanged at the reaction temperature higher than 170 °C. Therefore, the suitable reaction temperature was 170 °C.

Table 13 Effect of reaction temperature on the integration reaction

Reaction temperature / °C	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
160	90.1	48.3	2.7	31.2	2.0	88.5	0.74
170	100	/	16.7	/	68.5	68.5	4.10
180	100	/	18.2	/	65.5	65.5	3.60
190	100	/	18.1	/	67.8	67.8	3.75

Reaction conditions: pressure=4.0 MPa, time=10 h, weight percentage of Ni/Ce-Al_2O_3=15%.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

Table 14 Effect of reaction pressure on the integration reaction

Reaction pressure / MPa	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
3.0	100	/	17.8	1.2	66.2	67.4	3.72
3.5	100	/	17.4	/	65.1	65.1	3.74
4.0	100	/	16.7	/	68.5	68.5	4.10
4.5	100	/	27.7	/	32.5	32.5	1.17

Reaction conditions: temperature=170 °C, time=10 h, weight percentage of Ni/Ce-Al_2O_3=15%.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

Effect of reaction pressure

The effect of reaction pressure on *n*-butanal aldol condensation-hydrogenation integration reaction was studied and the results are listed in Table 14. It can be seen that the reaction pressure affected the hydrogenation reaction significantly. When the reaction pressure was 3.0 MPa, the reaction rate of hydrogenation was low and there were a certain amount of 2EH left after the completion of reaction. With the increase of reaction pressure, the catalytic activity for hydrogenation of the C=O and C=C double bonds was improved obviously; both the C=O and C=C double bonds were fully hydrogenated. When the reaction pressure was 4.5 MPa, the hydrogenation reaction rate was considerably high and the 2EHO generated would undergo some other side-reactions to the by-products of *n*-butyl butyrate and 2-ethylhexyl butyrate, causing the decrease of the yield of 2EHO. Therefore, the suitable reaction pressure was 4.0 MPa.

Effect of reaction time

Table 15 indicates the effect of reaction time on *n*-butanal aldol condensation-hydrogenation integration reaction. When the reaction time was shorter than 8 h, there existed a small amount of 2EH left after the completion of reaction, indicating that the hydrogenation reaction was not accomplished thoroughly. When the reaction time was 8 h, the yields of BO and 2EHO were 18.9% and 66.9%, and the disappearance of 2EH suggested that the hydrogenation reaction proceeded completely. With a further prolonging of reaction time, BO would undergo a side-reaction with *n*-butyric acid to form the by-product of *n*-butyl butyrate, resulting in the decrease of yield of BO. However, the yield of 2EHO changed a little. Therefore, the suitable reaction time was 8 h.

Table 15 Effect of reaction time on the integration reaction

Reaction time / h	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
7	100	/	18.1	2.0	65.7	67.7	3.63
8	100	/	18.9	/	66.9	66.9	3.54
9	100	/	18.2	/	67.1	67.1	3.67
10	100	/	16.7	/	68.5	68.5	4.10

Reaction conditions: temperature=170 °C, pressure=4.0 MPa, weight percentage of Ni/Ce-Al_2O_3= 15%.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

Analysis of reaction system

The products of the reaction integration of *n*-butanal aldol condensation and 2E2H hydrogenation catalyzed by Ni/Ce-Al_2O_3 were identified by GC-MS. Besides the target product 2EHO, many by-products were found such as BO, butyl butyrate, 2-ethylhexyl butyrate, *n*-butyric acid, 4-heptanone, *n*-heptane, 2-ethyl-1,3-hexanediol, *n*-butyl ether, *n*-butyl 2-ethylhexyl ether, 4-heptanol, 5-ethyl-2,4-dipropyl-1,3-dioxane and so on. There might be several kinds of side-reactions involving the Tishchenko, hydrogenation, esterification, dehydration and ketonization in the integration reaction system. According to the study of Tsuji et al. [32], butyl butyrate could be produced from the Tishchenko reaction of *n*-butanal. Keen [33] studied one-step synthesis of ethyl acetate from ethanol and proposed that ethyl acetate was produced by the dehydrogenation of hemiacetal. Since there existed a large amount of hydrogen in the present integration reaction system, it is difficult for dehydrogenation reaction to take place. Therefore butyl butyrate must be produced from the Tishchenko reaction of *n*-butanal. Furthermore, the intermediate, 2-ethyl-3-hydroxyhexanal, might transform to 2-ethyl-3-hydroxyhexyl butyrate with *n*-butanal in the same way. Shen et al. [34] and Glinski et al. [35] thought that the 4-heptanone might be produced by the ketonization reaction of butyl butyrate and then the C_7 alkenes were formed after the hydrogenation-dehydration of 4-heptanone. So we proposed that: (1) butyl butyrate was ketonized to form 4-heptanone, (2) 4-heptanone was hydrogenated to 4-heptanol, (3) 4-heptanol was dehydrated to form 3-heptylene and (4) 3-heptylene was hydrogenated to *n*-heptane. Shen also proposed that 2E2H could undergo hydrogenation/dehydration to 3-methylheptane. Zhang et al. [36] found that Raney nickel could catalyze the Cannizzaro reaction of aldehydes to corresponding alcohols and carboxylic acids. So we proposed that (1) *n*-butanal proceeded the Cannizzaro reaction to form BO and *n*-butyric acid and (2) 2EH transformed to 2EHO and 2-ethylhexnoic acid via the Cannizzaro reaction. As we all know, esters could be hydrolyzed to form alcohol and carboxylic acid. However, 2-ethylhexanoate was not detected in the products. So 2-ethylhexnoic acid in the products must be produced from the Cannizzaro reaction of 2EH. Two molecules of BO could be dehydrated intermolecularly to form *n*-butyl ether while BO could be dehydrated with 2EHO to *n*-butyl 2-ethylhexyl ether in the same way. The intermediate, 2-ethyl-3-hydroxyhexanal, also could be hydrogenated to form 2-ethyl-1,3-hexanediol and then the by-product 5-ethyl-2,4-dipropyl-1,3-dioxane was generated by the acetalization of 2-ethyl-1,3-hexanediol with *n*-butanal [3]. In addition, there existed several kinds of alcohols and carboxylic acids in the reaction system and some esterification reactions catalyzed by acidic catalyst could occur, e.g. the esterification of *n*-butyric acid with 2EHO to 2-ethylhexyl butyrate.

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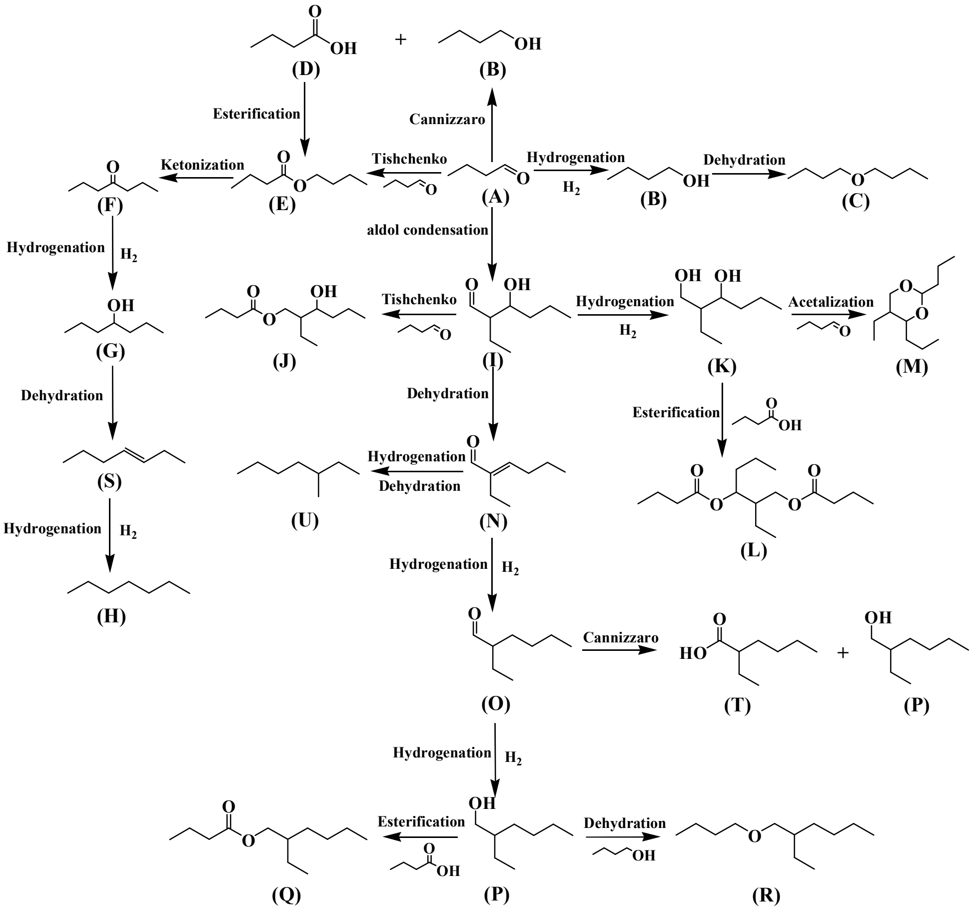

Scheme 1 Reaction network of *n*-butanal aldol condensation-hydrogenation to 2EHO catalyzed by Ni/Ce-Al_2O_3 catalyst

Therefore, based on the results of the product analysis and discussion above, a possible reaction network for direct synthesis of 2EHO from *n*-butanal catalyzed by the Ni/Ce-Al_2O_3 catalyst was proposed as shown in Scheme 1. Since there is an active α-H in a *n*-butanal molecule, a majority of *n*-butanal undertakes aldol condensation to 2-ethyl-3-hydroxyhexanal (I) followed by a dehydration reaction to an α,β-unsaturated aldehyde 2E2H (N). Paralleled with the aldol condensation reaction, a minority of *n*-butanal is hydrogenated directly to form BO (B). BO can be dehydrated intermolecularly to form *n*-butyl ether (C). In addition, *n*-butanal may transform to *n*-butyric acid (D) and BO by the Cannizzaro reaction. BO can also react with *n*-butyric acid by esterification reaction to butyl butyrate (E) which may also be produced by the Tishchenko self-esterification of *n*-butanal. The ketonization of butyl butyrate forms 4-heptanone (F), followed by a hydrogenation reaction to 4-heptanol (G). 4-Heptanol is dehydrated and hydrogenated to *n*-heptane (H). The intermediate, 2-ethyl-3-hydroxyhexanal, can react with another *n*-butanal molecule to 2-ethyl-3-hydroxyhexyl butyrate (J) by the Tishchenko reaction. 2-Ethyl-3-hydroxyhexanal may also be hydrogenated to 2-ethyl-1,3-hexanediol (K), followed in two routes: reacting with *n*-butyric acid to 2-ethyl-1-propyl-1,3-propyleneglycol dibutyrate (L) by esterification, or reacting with another *n*-butanal molecule to 5-ethyl-2,4-dipropyl-1,3-dioxane (M) by acetalization. 2E2H may undergo hydrogenation/dehydration to 3-methylheptane (U). Because of the higher hydrogenation selectivity for C=C double bond than C=O, the C=C double bond of 2E2H is selectively hydrogenated to 2EH (O). 2EH can be fully hydrogenated to 2EHO (P) or transform to 2EHO and 2-ethylhexanoic acid (T) by the Cannizzaro reaction. 2EHO may react with *n*-butyric acid by esterification

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reaction to 2-ethylhexyl butyrate (Q) or be dehydrated intermolecularly with BO to *n*-butyl 2-ethylhexyl ether (R).

Reusability of Ni/Ce-Al_2O_3

After the completion of the reaction, the Ni/Ce-Al_2O_3 catalyst was separated from the reaction system by filtration and then treated in two methods: ① being washed three times with absolute alcohol and dried at 110 °C for 8 h to removed the remaining organic products; ② being washed three times with absolute alcohol, dried at 110 °C for 8 h to removed the remaining organic products, calcined at 550 °C for 5 h and then reduced at 570 °C for 4 h in H_2 (20 vol.% in N_2) atmosphere. The recovered and treated Ni/Ce-Al_2O_3 catalysts were separately used in the integration reaction and the results are listed in Table 16. It can be seen that the catalytic performance of the recovered Ni/Ce-Al_2O_3 catalyst treated in both methods ① and ② declined obviously and could not be regenerated by calcination and reduction. *n*-Butanal could not be converted completely and the aldol product 2E2H also could not be hydrogenated fully. The main product was 2EH and the yields of BO and 2EHO were very low. It suggested that the recovered Ni/Ce-Al_2O_3 catalyst could catalyze the aldol condensation of *n*-butanal while the catalytic performance for hydrogenation was declined, especially for the C=O group.

Table 16 Reusability of Ni/Ce-Al_2O_3

Ni/Ce-Al_2O_3	X_{BA}/%	Yield/%				Selectivity/%	
		2E2H	BO	2EH	2EHO	2E2H+2EH+2EHO	2EHO/BO
fresh	100	/	18.9	/	66.9	66.9	3.54
Recovered and treated using method ①	94.1	12.9	4.9	57.6	3.3	73.8	0.67
Recovered and treated using method ②	93.2	12.6	3.2	57.9	2.5	73.0	0.78

Reaction conditions: temperature=170 °C, pressure=4.0 MPa, time= 8 h, weight percentage of Ni/Ce-Al_2O_3=15%.
X: conversion. BA: *n*-butanal; 2E2H: 2-ethyl-2-hexenal; 2EH: 2-ethylhexanal; BO: *n*-butanol; 2EHO: 2-ethylhexanol.

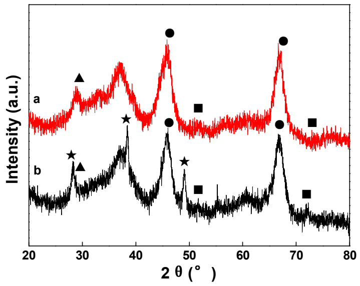
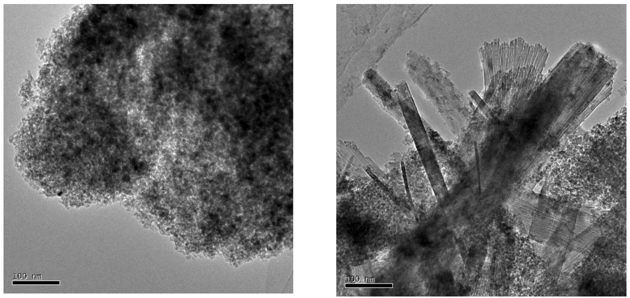


Fig. 3 XRD patterns of the Ni/Ce-Al_2O_3 catalyst before and after reaction
a: fresh b: recovered
▲: CeO_2, ■: Ni , ●: Al_2O_3, ★: AlO(OH),



(a) (b)

Fig. 4 TEM images of the fresh and the deactivated Ni/Ce-Al_2O_3 catalysts
a: fresh b: recovered ①

The XRD patterns of the fresh and the recovered Ni/Ce-Al_2O_3 catalyst treated by method ① are shown in Fig. 3. It can be seen that both of the fresh and the recovered Ni/Ce-Al_2O_3 catalyst showed γ-Al_2O_3 (2θ = 37.5°, 45.7° and 66.7°) and metal Ni (2θ = 44.6°, 51.9° and 76.1°) diffraction peaks. In addition, the recovered Ni/Ce-Al_2O_3 catalyst showed γ-AlO(OH) diffraction peaks (2θ = 28.2°, 38.4° and 49.2°), indicating that γ-Al_2O_3 support was hydrated with the by-product water from the aldol condensation to form boehmite γ-AlO(OH). The TEM images of the fresh and the recovered Ni/Ce-Al_2O_3 catalyst are shown in Fig. 4. It can be seen that the fresh Ni/Ce-Al_2O_3 catalyst had the typical structure of γ-Al_2O_3 particle and the Ni species and CeO_2 were distributed uniformly on the surface of γ-Al_2O_3. However, a new hydration structure was observed in the recovered Ni/Ce-Al_2O_3 catalyst. Furthermore the aggregation of Ni particles might occur. The atomic percentage of the hydration structure on the new surface was determined; O: Al=63:36 is between 1:2 of γ-AlO(OH) and 2:3 of γ-Al_2O_3. Therefore, the new surface hydrate structure is the mixture of γ-AlO(OH) and γ-Al_2O_3.

In order to determine the distribution of metal Ni on the surface of the Ni/Ce-Al_2O_3 catalyst, the fresh and the recovered Ni/Ce-Al_2O_3 catalyst were characterized by H_2-TPD (the profiles are showed in Supporting Fig. S5). The H_2-TPD profiles could be roughly divided into two regions: low-temperature region (< 250 °C) and high-temperature region (> 250 °C). The low temperature desorption peak may be assigned to the desorption of the weakly adsorbed hydrogen species in a dissociated state while the high temperature desorption peaks are due to the desorption of the strongly chemisorbed hydrogen in a dissociated state [37]. The main desorption peaks of the fresh and the recovered Ni/Ce-Al_2O_3 were high temperature desorption peaks. The measurement data of H_2-TPD are listed in Table 17. As compared with the fresh Ni/Ce-Al_2O_3 catalyst, the top temperatures of the desorption peaks increased but the hydrogen desorption capacities decreased in the recovered one. A higher desorption peak top temperature suggested a stronger adsorption on the metal-support interface caused by the aggregation of Ni species. These H_2-TPD peaks were due to the dissociated hydrogen species anchoring on the free Ni particles. The smaller H_2-TPD peak area of the recovered Ni/Ce-Al_2O_3 catalyst suggested that the amount of bare metal Ni species on the surface decreased. Li et al.[38] studied the deactivation of Ni/Al_2O_3 catalyst in the liquid phase hydrogenation of crude 1,4-butanediol aqueous solution and found that the Al_2O_3 support transformed into boehmite γ-AlO(OH) during the reaction process. Therefore, we think that the hydration of γ-Al_2O_3 support was the main reason for the deactivation of the Ni/Ce-Al_2O_3 catalyst. The new structure of γ-AlO(OH) would cover up parts of Ni species on the surface, hindering the contact of hydrogen with Ni species. The decreasing amount of effective Ni on the surface led to the lower catalytic activity of hydrogenation, which could not be recovered even though the γ-AlO(OH) was transformed to γ-Al_2O_3 after calcination and reduction processes. In order to validate that some Ni species were covered on the surface, the recovered Ni/Ce-Al_2O_3 was impregnated by a nickel nitrate aqueous solution, dried at 110 °C for 8 h and then calcinated at 550 °C for 4 h and finally reduced at 570 °C for 4 h. The as-prepared Ni/Ce-Al_2O_3 was used in the integration reaction and the result showed that BO and 2EHO were formed again. It further proved that the decreasing amount of Ni species on the surface of the Ni/Ce-Al_2O_3 caused by the hydration of γ-Al_2O_3 support was the main reason for the deactivation of the Ni/Ce-Al_2O_3 catalyst. The deactivation may be eliminated by the surface modification of the support γ-Al_2O_3 by SiO_2 or other substances to restrain the hydration in the aldol reaction.

Table 17 H_2 chemisorption capability of the fresh and the recovered Ni/Ce-Al_2O_3 catalysts

Ni/Ce-Al_2O_3	peak at lower temperature		peaks at higher temperature			Total H_2 capacity /μmol·g^{-}
	Top temperature / °C	H_2 capacity /μmol·g^{-1}	Top temperature 1 / °C	Top temperature 2 / °C	H_2 capacity /μmol·g^{-1}	
fresh	96.2	2.05	505.4	699.0	496.30	496.35
Recovered and treated using method ①	110.8	2.49	521.6	725.9	277.78	280.27
Recovered and treated using method ②	145.2	10.26	556.0	745.1	398.52	408.78

Conclusions

The direct synthesis of 2-ethylhexanol from *n*-butanal via the reaction integration of *n*-butanal self-condensation with 2-ethyl-2-hexenal hydrogenation were realized using metal-solid acid bifunctional catalysts. Among the four kinds of metal-solid acid bifunctional catalysts, Co/Al_2O_3 had a low selectivity for

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hydrogenation and Cu/Al_2O_3 had a high selectivity for C=O hydrogenation while Ru/Al_2O_3 catalyst only favored the hydrogenation of *n*-butanal to *n*-butanol. Ni/Al_2O_3 catalyst showed the best catalytic performance. The addition of Ce into Ni/Al_2O_3 enhanced the competitiveness of *n*-butanal aldol condensation to its hydrogenation and improved the selectivity of 2-ethylhexanol; the yield of 2-ethylhexanol rose to 57.8%. The suitable preparation conditions were obtained as follows: Ni loading = 10%, calcined at 550 °C for 5 h, and reduced at 570 °C for 4 h in 20% H_2 in N_2 gas mixture. Under the suitable reaction conditions of weight percentage of $Ni/Ce-Al_2O_3$ = 15%, reaction temperature = 170 °C, reaction pressure = 4.0 MPa and reaction time = 8 h, the conversion of *n*-butanal was 100%, the yield of 2-ethylhexanol was 66.9% and the yield of *n*-butanol was 18.9%. The components existing in the reaction mixture were identified by GC-MS analysis and the main by-products such as *n*-butyl butyrate, 2-ethylhexyl butyrate, *n*-butyric acid were detected. Then a reaction network for the direct synthesis of 2-ethylhexanol from *n*-butanal was proposed. Finally, the evaluation on the reusability of the $Ni/Ce-Al_2O_3$ catalyst showed that the recovered $Ni/Ce-Al_2O_3$ catalyst lost its catalytic activity for the hydrogenation of C=O group. The main reason was that the Ni species were covered by the flaky boehmite γ-AlO(OH) formed from the hydration of γ-Al_2O_3 support during the reaction process. The deactivation may be eliminated by surface modification of γ-Al_2O_3 with SiO_2 or other substances.

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Appendix A. Supplementary material

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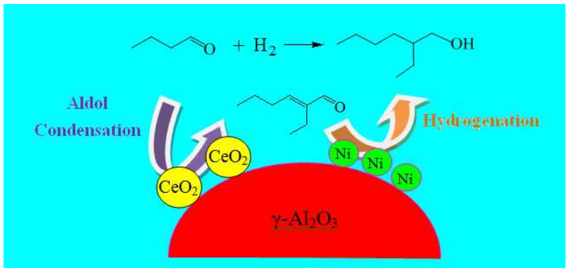

A reaction integration of aldol condensation-hydrogenation for the direct synthesis of 2-ethylhexanol from *n*-butanal was realized.