

Article

A One-Pot Hydrothermal Preparation of High Loading Ni/La₂O₃ Catalyst for Efficient Hydrogenation of Cinnamaldehyde

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Abstract: It is a challenging task for selective hydrogenation of cinnamaldehyde (CAL) to hydrocinnamaldehyde (HCAL) without additional by-product formation. In this work, a La₂O₃ supported high Ni content nanoparticle catalyst was prepared for CAL selective hydrogenation. Meanwhile, Co-La₂O₃ catalysts were used as a reference catalyst. XRD, TEM, STEM-HAADF, XPS, and H₂-TPR measurements were used to investigate the physicochemical properties of Ni-La₂O₃ catalysts. The experimental results confirmed that the CAL conversion and HCAL selectivity were effectively promoted with the increase of Ni loading amounts. At a Ni/La molar ratio of four, a high HCAL selectivity of 87.4% was obtained at a CAL conversion of 88.1% under mild reaction conditions. The catalyst was recycled five times without activity loss. Combined with various characterizations, it could be inferred that the good hydrogen adsorption and dissociation capacity of Ni and the presence of a certain amount of oxygen vacancies on the La₂O₃ support have a positive effect on the improvement of HCAL selectivity. This work provided an effective path to design transition-metal-based supported oxide catalyst for the cinnamaldehyde hydrogenation to hydrocinnamaldehyde.

Keywords: Ni/La₂O₃; cinnamaldehyde; catalytic hydrogenation; hydrocinnamaldehyde



Citation: Yan, H.; Ren, Y.; Zhang, R.; Chang, F.; Wei, Q.; Xu, J. A One-Pot Hydrothermal Preparation of High Loading Ni/La₂O₃ Catalyst for Efficient Hydrogenation of Cinnamaldehyde. *Catalysts* **2023**, *13*, 298. <https://doi.org/10.3390/catal13020298>

Academic Editor: Tian-Sheng Zhao

Received: 21 December 2022

Revised: 24 January 2023

Accepted: 26 January 2023

Published: 28 January 2023



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1. Introduction

α , β -unsaturated aldehydes containing C=C and C=O bonds are important raw materials and intermediates in organic synthesis and the chemical industry [1]. Moreover, the hydrogenation products of such aldehydes have high application values in fragrance, pharmaceutical, and fine chemical industries [2]. For example, cinnamaldehyde, which is one of the α , β -unsaturated aldehydes families, has two hydrogenation products, namely, the cinnamyl alcohol (COL) from the C=O group hydrogenation and the hydrocinnamaldehyde (HCAL) from the C=C group hydrogenation. These two products can be used in the formulation of fragrance and cosmetic flavors [3], and in the development of novel anti-AIDS (Acquired Immune Deficiency Syndrome) drugs [4]. Currently, the main route for the production of HCAL is based on the hydrolysis method of toluene chlorination, in which the benzylidene chloride is generated by side chain methyl dichloro reaction of toluene and then hydrolyzed in acid or alkaline to form HCAL. Despite the high yield of this method, the waste stream (acidic) is difficult to be handled, meanwhile, the HCl produced tends to corrode the reaction equipment. In contrast, adopting hydrogenation of CAL to prepare HCAL could be effective to avoid the production of corrosive by-products or wastes. Therefore, the study of selective hydrogenation of cinnamaldehyde is of important significance. For cinnamaldehyde hydrogenation, the C=C bond, due to its lower energy at 615 kJ/mol, is more likely to be thermodynamically hydrogenated to HCAL as compared to that of the C=O bond with a relatively high energy at 715 kJ/mol [5]. Although the C=C bond is more easily hydrogenated, achieving a high selectivity in target products

(HCAL or COL) undoubtedly encounters some difficulties. Consequently, more studies of catalysts have been devoted to the selective hydrogenation of cinnamaldehyde.

In the hydrogenation reaction, noble metals usually present excellent catalytic activities [6–8]. Moreover, some studies were also focused on metal introduction, aiming to improve COL selectivity. The alloy catalyst prepared by some synthetic methods is an effective measure for the hydrogenation reaction of cinnamaldehyde. For example, a Pt-Co bimetallic nanocatalyst [9] was used for the hydrogenation of cinnamaldehyde, and the result exhibited an excellent COL selectivity of 89.3%, which was mainly ascribed to the preferential adsorption of the C=O group over the synergistic effect between Pt nanoparticles and an amorphous Co-Aspartic acid polymer. Furthermore, Zhang and his co-workers [10] prepared an Al₂O₃-supported Pt-Fe bimetallic catalyst and obtained 96.6% CAL conversion and 77.2% COL selectivity, respectively. Based on the results, the introduction of Fe could change the electronic and surface properties of the active Pt sites. Another way to obtain high selectivity is to design catalysts with specific structures, which may improve metal dispersion and limit the adsorption of the functional groups of substrate molecules. Han et al. [11] reported a highly dispersed Pd nanocatalyst confined in ZSM-5 zeolite crystals using a “secondary growth” synthesis strategy. The results showed that under the confining effect of the zeolite structure, the selectivity of HCAL was 73.3% over Pd@SG-ZSM-5. Furthermore, catalysts with a core-shell structure were also employed for the hydrogenation reaction of cinnamaldehyde. Zhang [12] et al. reported a kind of Pt nanocatalyst encapsulated in a hollow-flower-like Zr-MOFs double shell micro-reactor, which maintained high stability and improved the selectivity of COL due to the restriction effect of UiO-66 channels. By contrasting the catalytic efficiency of the samples, it was proved that the double-shell not only served as a stabilizer to restrict Pt nanoparticles with a high dispersion, but also as a sieve to regulate the contact direction of cinnamaldehyde to Pt site in light of the medium-sized channel formed on the outer shell.

However, considering the high cost of noble metal catalysts, it is desirable to develop inexpensive, non-noble metal catalysts with good catalytic activities. One widely used strategy is to prepare oxide supported transition metal catalysts, which have been applied in chemical synthesis and energy conversion process [13]. Pecchi et al. [14] prepared a SiO₂ encapsulated cobalt core-shell catalyst using a solvothermal method for the core and a modified Stöber method for the shell. They adjusted the reduction temperature to improve Co/CoO surface distribution and, thus, enhanced both the dissociation of dissolved hydrogen and adsorption the C=O bond, obtaining the selectivity of more than 60% over Co-CoO@SiO₂-500 °C sample. In addition to Co, some transition metals, like Ni [15], Fe, and Cu are also commonly used as hydrogenation catalysts, usually being designed in the form of monometal [16], alloys [17,18], intermetallic compounds [19], and so on. In the same way, oxide supports also play important roles in improving catalytic stability and selectivity. They may have some differences in morphology, specific surface area, acidity and alkalinity, electronic structure and geometry, and some of them also have catalytic activity. For example, ceria, which has good oxygen storage capacity, is often used as the catalyst support [20]. In addition, SiO₂ [21], Al₂O₃ [22], and La₂O₃ [23] are also commonly considered as supports. Generally, based on these supports, high dispersion and low metal loaded capacity are the conventional ideas for the preparation of metal-based supported catalysts [24]. Recently, an inverse ZrO₂/Cu catalyst, composed of 10% of ZrO₂ supported over 90% of Cu, was reported by Ma and his co-worker to use for CO₂ hydrogenation, exhibiting the high hydrogenation conversion to methanol [25]. Under optimal condition, the catalyst composed by 10% of ZrO₂ supported over 90% of Cu exhibited the highest methanol formation rate of 524 g_{MeOH}kg_{cat}^{−1} h^{−1} at 220 °C, 3.3 times higher than the activity of traditional Cu/ZrO₂ catalysts (159 g_{MeOH}kg_{cat}^{−1} h^{−1}). Despite making many attempts, an inverse loading idea to design catalysts for cinnamaldehyde hydrogenation has not yet been developed.

Herein, a transition-metal-based supported oxide catalyst was prepared for the highly selective hydrogenation of cinnamaldehyde to hydro-cinnamaldehyde using a high loading

strategy. A one-pot hydrothermal approach via mixed metal salt solution was employed to achieve the controllable synthesis of La_2O_3 supported Ni catalysts with different metal loading. At the same time, we also used cobalt nitrate to prepare corresponding Co- La_2O_3 catalysts as the reference sample for the performance test. Through performance tests, the Ni- La_2O_3 catalyst with an Ni/La molar ratio of four could simultaneously accomplish a high HCAL selectivity of 87.4% at a CAL conversion of 88.1%, verifying the idea of using inverse oxide/nickel focusing on a simple design of available catalysts for the cinnamaldehyde hydrogenation conversion.

2. Results and Discussion

2.1. Characterization of the Catalysts

The XRD patterns of the prepared catalysts are shown in Figure 1a. It is clear that the diffraction peaks corresponding to the $\text{La}_2\text{O}_2(\text{CO}_3)$ phase (PDF#84-1963) were observed in the calcined samples. Furthermore, NiO peaks were also detected in $\text{Ni}_4\text{-La}_2\text{O}_3$, while there were no obvious NiO peaks in $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$. After reduction, characteristic peaks at 44.6° , 51.9° , and 76.5° were indexed in $\text{Ni}_4\text{-La}_2\text{O}_3$, which were attributed to the (111), (200), and (220) lattice planes of metallic Ni^0 species (PDF#70-0989), respectively. However, the $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$ presented the absence of Ni^0 peaks, mainly due to the low Ni content compared to that of $\text{Ni}_4\text{-La}_2\text{O}_3$. In addition, the remaining peaks at different positions were assigned to La_2O_3 (PDF#83-1344). Based on the XRD results, the $\text{La}_2\text{O}_2(\text{CO}_3)$ phases were formed on the calcined samples, which originated from the low-temperature calcination of the hydrothermal precursors ($\leq 500^\circ\text{C}$) [26]. HRTEM images of $\text{Ni}_4\text{-La}_2\text{O}_3$ and $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$ are shown in Figure 1b,c. The lattice spacings measured at 0.175 nm and 0.203 nm were attributed to (200) and (111) crystal planes of Ni^0 , respectively. Although the reduced $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$ displayed the absence of Ni^0 peaks, the TEM image gave a clear indication for the presence of Ni^0 . Furthermore, element mappings showed the uniform distribution of La, Ni, and O elements on the $\text{Ni}_4\text{-La}_2\text{O}_3$ framework. Clearly, the point density of the Ni mapping image is higher than that of the La mapping image, indicating the higher Ni ratio over La in the $\text{Ni}_4\text{-La}_2\text{O}_3$ sample.

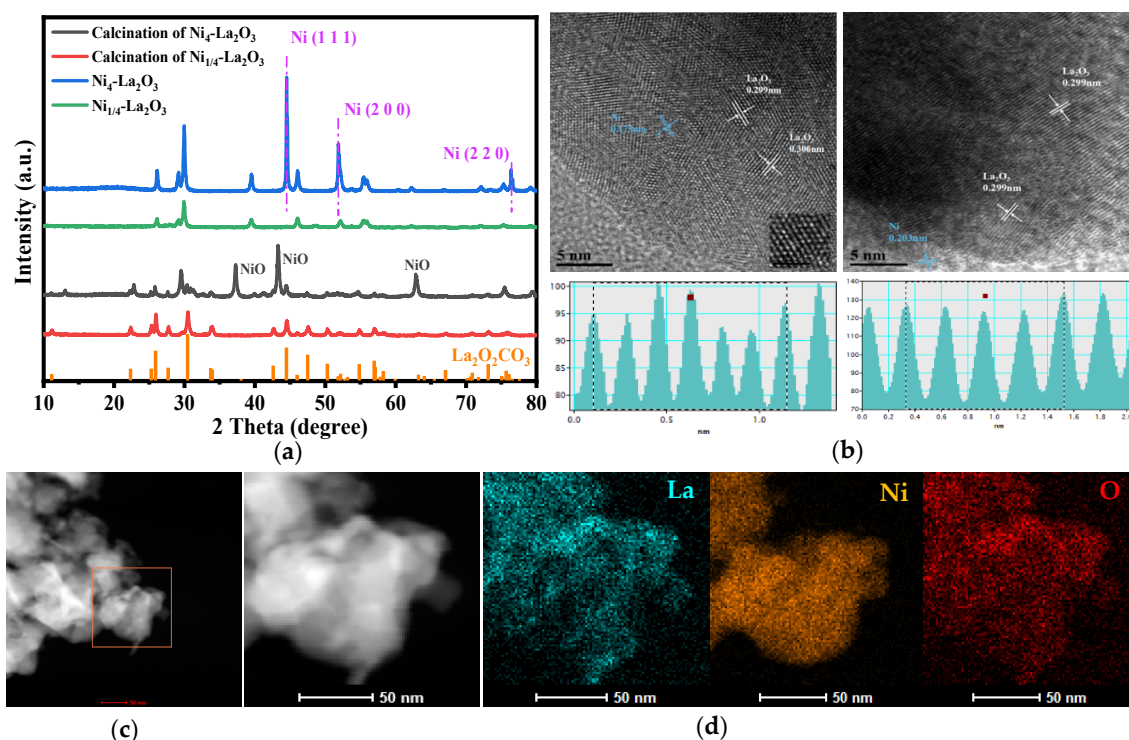


Figure 1. (a) XRD pattern of $\text{Ni}_x\text{-La}_2\text{O}_3$ samples, (b) HRTEM images of $\text{Ni}_4\text{-La}_2\text{O}_3$ and $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$, (c) STEM-HAADF image, and (d) element mappings of the $\text{Ni}_4\text{-La}_2\text{O}_3$ sample.

The chemical state and surface composition of the prepared catalysts were obtained with XPS. Figure 2a showed Ni 2p spectra of $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$, $\text{Ni}_1\text{-La}_2\text{O}_3$ and $\text{Ni}_4\text{-La}_2\text{O}_3$, where two obvious peaks at 851.7 eV and 855.5 eV were attributed to the Ni^0 and Ni^{2+} [27]. This result indicated that, after the reduction of samples, the majority of the Ni species were in the form of metallic Ni, with part of the Ni^{2+} species remaining [28]. In addition, the concentration of Ni in $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$, $\text{Ni}_1\text{-La}_2\text{O}_3$, and $\text{Ni}_4\text{-La}_2\text{O}_3$ were 4.21 wt%, 14.25 wt%, and 40.90 wt%, respectively. The spectra of La 3d were shown in Figure 2c, and the four peaks detected were assigned to La $3d_{5/2}$ (at 838.5 and 834.8 eV) and La $3d_{3/2}$ (at 855.5, 851.7 eV). The O 1s spectra were divided into three peaks, meaning various oxygen species related to oxygen vacancy. The first one at 529.1 eV was ascribed to lattice oxygen (O^{2-}); the middle one at 530.9 eV was due to the oxygen species ($\text{O}^-/\text{O}_2^{2-}$) adsorbed on oxygen vacancies; and the final peak at 531.8 eV was accorded with carbonate species (CO_3^{2-}). The above characterization observations illustrated the presence of a certain amount of oxygen vacancies and trace amounts of unreduced $\text{La}_2\text{O}_2(\text{CO}_3)$ species on $\text{Ni}_x\text{-La}_2\text{O}_3$ catalysts [26]. The existence of oxygen vacancies on $\text{Ni}_x\text{-La}_2\text{O}_3$ catalysts provided the possibility for adsorption of C=O bonds [29].

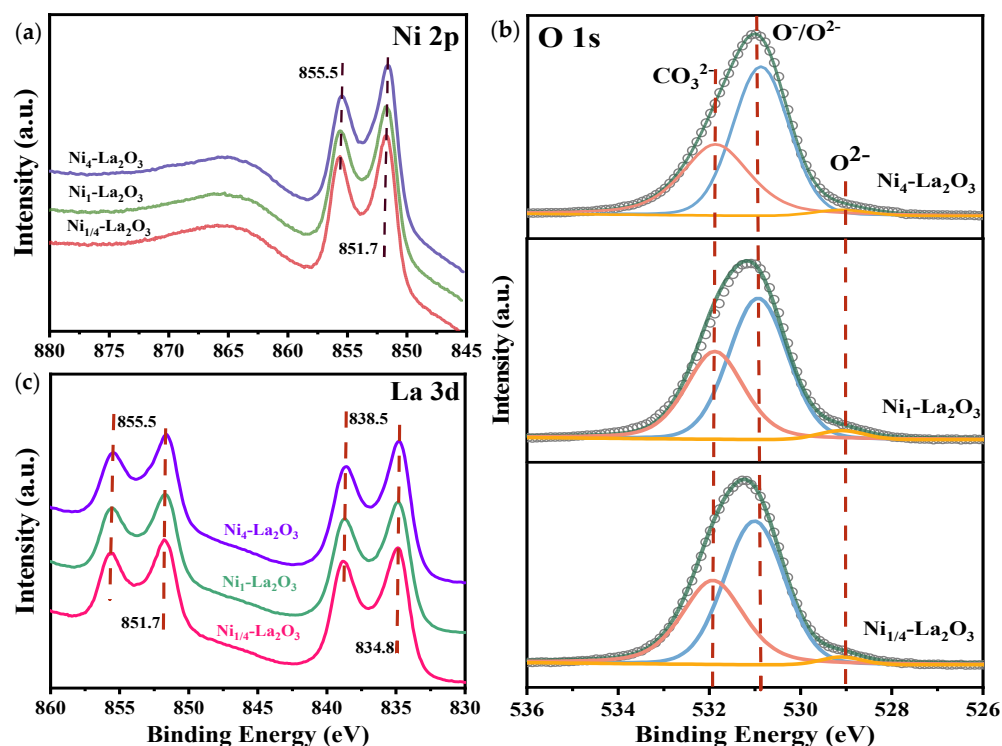


Figure 2. XPS spectra of $\text{Ni}_x\text{-La}_2\text{O}_3$ catalysts with different nickel capacities: (a) Ni 2p; (b) O 1s; (c) La 3d.

To discuss the reduction behavior of the calcined catalysts, Figure 3 exhibits H_2 -TPR data for the calcined samples. As shown in Figure 3, the oxide precursors of the $\text{Ni}_x\text{-La}_2\text{O}_3$ samples display two sets of reduction peaks. The reduction peak between 300–400 °C could be assigned to the reduction of NiO species. Regarding the peak at around 350–370 °C, it was caused by weak interaction between the NiO and La_2O_3 support. At the same time, the H_2 -TPR profiles also show reduction peaks at 400 °C, meaning that the higher the reduction temperature, the stronger the interaction between Ni nanoparticles and support might be [30]. However, for the La_2O_3 sample without loaded Ni nanoparticles, no reduction peaks were found below 700 °C, while one peak observed at around 750 °C was attributed to the reduction of the La-O bond. In light of the oxide precursors of $\text{Ni}_x\text{-La}_2\text{O}_3$, especially of those on $\text{Ni}_4\text{-La}_2\text{O}_3$ and $\text{Ni}_1\text{-La}_2\text{O}_3$, the reduction temperature was lower compared to that of La_2O_3 , indicating that the La-O bond of the oxide precursors of $\text{Ni}_x\text{-La}_2\text{O}_3$ was more readily reduced in the presence of the active metal, thus resulting in more oxygen vacancies upon H_2 reduction [31].

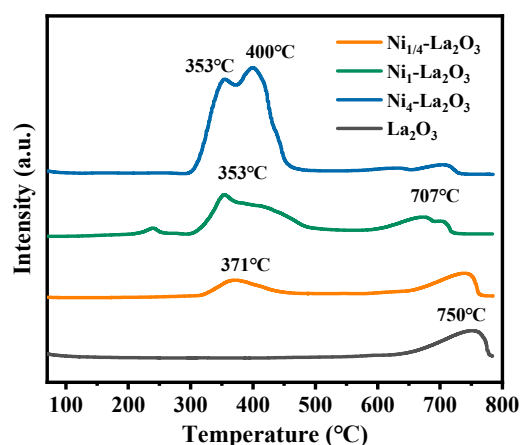


Figure 3. H₂-TPR profiles of oxide precursors of Ni_x-La₂O₃ catalysts.

2.2. Catalytic Selective Hydrogenation of Cinnamaldehyde

In order to further investigate the synergistic effect of metal and support in the reaction process, the catalytic performance tests were evaluated in the selective hydrogenation of cinnamaldehyde (CAL) over Ni_x-La₂O₃ and Co_x-La₂O₃ catalysts (x represented the molar ratio of Ni/Co and La), as shown in Figure 4.

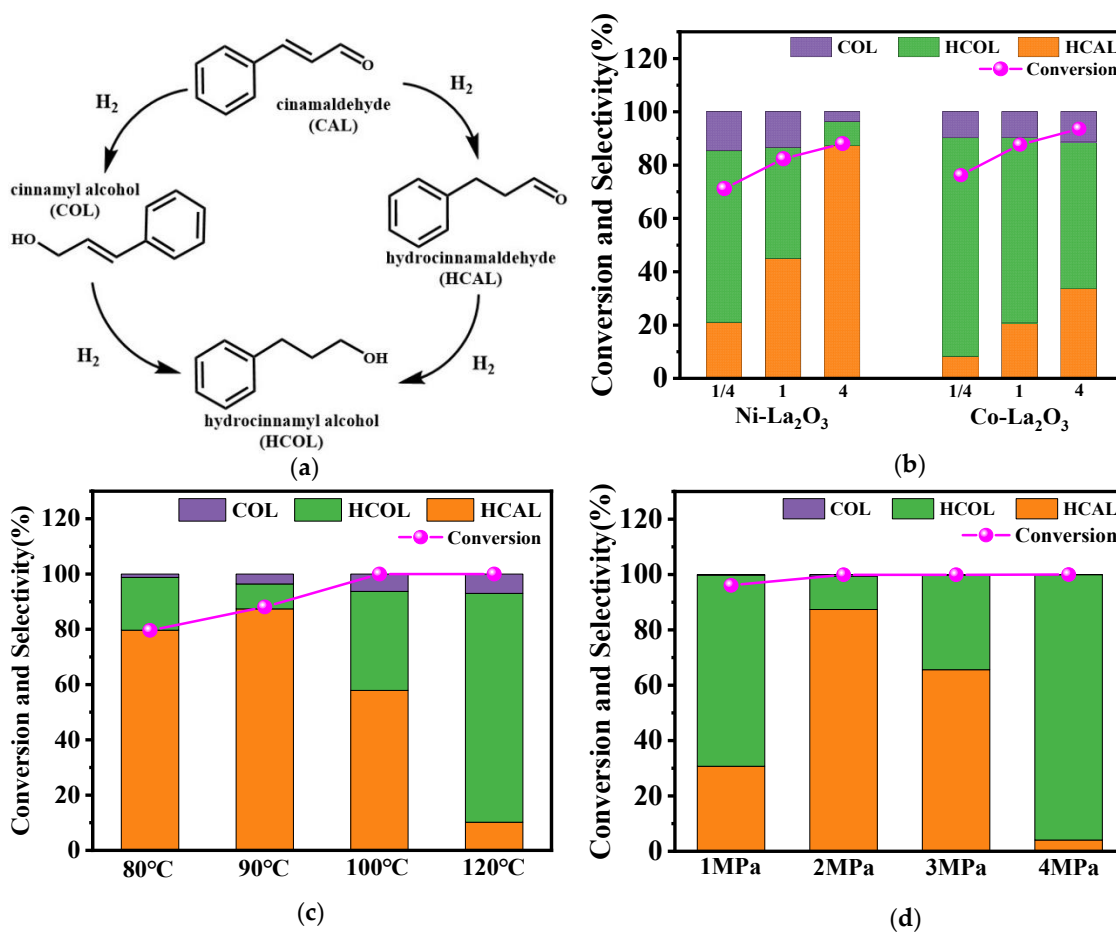


Figure 4. The process for selective hydrogenation of CAL (a), catalytic performance over various Ni_x-La₂O₃ and Co_x-La₂O₃ catalysts (b), reaction conditions: 0.55 mmol CAL, 50 mg catalyst, 6 mL absolute ethanol as solvent, 2 MPa H₂, reaction temperature 90 °C, reaction time 2 h. Influence of reaction temperature (c) and hydrogenation pressure (d) on the selective hydrogenation of CAL over Ni₄-La₂O₃.

The CAL could be hydrogenated to form HCAL and COL with selective hydrogenation of C=C and C=O bonds, respectively. Meanwhile, the obtained HCAL and COL could be further hydrogenated to hydrocinnamyl alcohol (HCOL). Therefore, designing an effective catalyst was critical for improving the selectivity of key products. The catalytic performance of $\text{Ni}_x\text{-La}_2\text{O}_3$ and $\text{Co}_x\text{-La}_2\text{O}_3$ catalysts are shown in Figure 4b. As the metal content increased, the conversion of CAL for $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$, $\text{Ni}_1\text{-La}_2\text{O}_3$, and $\text{Ni}_4\text{-La}_2\text{O}_3$ catalysts was respectively increased from 71.2% to 88.1%, along with the selectivity of HCAL obtained from 20.9% to 87.4%. In particular, the $\text{Ni}_4\text{-La}_2\text{O}_3$ exhibited not only the highest CAL conversion but also the largest selectivity to HCAL. Different from the results over $\text{Ni}_x\text{-La}_2\text{O}_3$ catalysts, the $\text{Co}_x\text{-La}_2\text{O}_3$ catalysts exhibited distinctive catalytic behaviors. The conversion of CAL increased from 76.2% to 93.6% by gradually increasing Co loading amounts on $\text{Co}_x\text{-La}_2\text{O}_3$ samples, whereas the highest HCAL selectivity was only 33.5% over the $\text{Co}_4\text{-La}_2\text{O}_3$ catalyst. These results showed that the $\text{Ni}_x\text{-La}_2\text{O}_3$ catalyst preferred to perform the hydrogenation for the C=C group, while the $\text{Co}_x\text{-La}_2\text{O}_3$ catalysts showed over-hydrogenation for CAL conversion.

The influence of reaction temperature and H_2 pressure on CAL hydrogenation over $\text{Ni}_4\text{-La}_2\text{O}_3$ had also been investigated (Figure 4c,d). Firstly, to determine the suitable reaction temperature, the catalytic hydrogenation of CAL was carried out at different temperatures with 2 MPa of H_2 pressure. Figure 4c displays that the reaction temperature had a remarkable influence on CAL hydrogenation reaction, especially for the process of C=C hydrogenation to HCAL. In addition, the optimal reaction temperature was determined to be 90 °C, as either higher or lower reaction temperatures resulted in comparatively lower HCAL selectivity, due to the formation of HCOL. It might be interpreted that the low reaction temperature was insufficient to obtain high CAL conversion, and the high reaction temperature was prone to over-hydrogenation of CAL to HCOL. Figure 4d shows the distribution of products at 90 °C with different H_2 pressures over the representative $\text{Ni}_4\text{-La}_2\text{O}_3$ catalyst sample. The effect of H_2 pressure on catalytic performance was evaluated in the range of 1–4 MPa H_2 . The highest HCAL selectivity was achieved at 2 MPa H_2 pressure with 87.4%. As the H_2 pressure gradually increased to 4 MPa, the CAL conversion was almost unchanged, but the selectivity of HCAL decreased to 4.07%. This indicated that the excessive reaction pressure led to the over-hydrogenation of CAL to HCOL. Through exploring the reaction conditions, high CAL conversion and HCAL selectivity were obtained over $\text{Ni}_4\text{-La}_2\text{O}_3$ at 90 °C with 2 MPa of H_2 pressure.

Besides reaction temperature and H_2 pressure, reaction time is also another essential factor in measuring catalytic activity and selectivity of $\text{Ni}_4\text{-La}_2\text{O}_3$ for the CAL hydrogenation reaction. As shown in Table 1, it is obvious that the process of cinnamaldehyde hydrogenation required the participation of a catalyst (entry 1) [32]. Meanwhile, the results (entry 2) were obtained by examining the effect of reaction time on the CAL conversion. With the increase in reaction time, the conversion of CAL approached to 100%, while the selectivity of HCAL was gradually decreased. Notably, the HCAL selectivity was only at 3.8% in a 4 h reaction, which was attributed to the over-hydrogenation of CAL. It has been proposed that oxygen vacancies can be used as active sites for activation of C=O bonds [29]. Furthermore, based on the characterization of XPS and H_2 -TPR, as well as the above catalytic performances, it was determined that the dissociative adsorption of the C=C and C=O bonds was carried out on the metallic nickel active sites and oxygen vacancies of La_2O_3 support. Meanwhile, hydrogenation of the C=C bond was more accessible in comparison to that of C=O bond, both thermodynamically and kinetically [33]. When the nickel content increased, the hydrogenation of the C=C bonds over $\text{Ni}_4\text{-La}_2\text{O}_3$ was more readily realized, which might be the reason for the high selectivity of HCAL. However, after 3–4 h of the hydrogenation reaction, an uncontrollable over-hydrogenation occurred, leading to the formation of HCOL.

Table 1. Catalytic hydrogenation of CAL over different reaction conditions.

Entry	Sample	Time (h)	Solvent	Conv. (%)	Selectivity (%)		
					COL	HCAL	HCOL
entry 1 ¹	Blank	2	Ethanol	0	0	0	0
entry 2 ¹	Ni ₄ -La ₂ O ₃	1	Ethanol	79.72	0.51	83.16	16.33
		3		99.92	0.51	14.95	84.54
		4		99.28	0.4	3.8	95.8
entry 3 ¹	Ni ₄ -La ₂ O ₃	2	Methanol	77.65	0.28	39.76	59.96
			Isopropanol	47.07	1.27	80.16	18.57
			N-hexane	99.62	0.06	37.35	62.59
entry 4 ¹	10% Pd/C	2	Ethanol	100	4.0	69.2	26.8

¹ Reaction conditions: 0.55 mmol CAL, 50 mg catalyst, 6 mL solvent, 2 MPa H₂, reaction temperature 90 °C.

Additionally, the solvent might play an important role in the CAL hydrogenation reaction, mostly reflected in the effective diffusion of hydrogen at the gas-liquid and liquid-solid interfaces. The CAL hydrogenation reactions were performed under different solvents over the Ni₄-La₂O₃ catalyst, as shown in entry 3, and corresponded, in turn, to methanol, isopropanol, N-hexane. With Methanol and N-hexane as solvents, the high CAL conversion was obtained but with low HCAL selectivity. In contrast, the conversion of isopropanol was lower, while achieving higher HCAL selectivity. By comparison, ethanol was selected as the most suitable solvent for CAL hydrogenation. In order to illustrate the catalytic activity of the as-prepared Ni₄-La₂O₃ catalyst, a commercial Pd/C catalyst was also tested for cinnamaldehyde hydrogenation, with results shown in entry 4. An excellent conversion was exhibited when 10% Pd/C was used as the catalyst, but the selectivity of HCAL was relatively lower, which was attributed to the strong hydrogenation activity of Pd.

As displayed in Figure 5, the recycling tests were recorded by carrying out the CAL hydrogenation reaction where the reusability of Ni₄-La₂O₃ was investigated for five runs, including the fresh one and four repeat experiments. After each run reaction, the sample was recovered with centrifugation to remove the reaction substances. Subsequently, the recovered sample was washed several times with water and ethanol to remove substrate residues and was dried overnight at 60 °C under vacuum before the next cycle. For the first run reaction, the catalyst reached 68.1% conversion of CAL and 85.4% selectivity to HCAL at 90 °C and 2 MPa H₂ pressure after 2 h. After five cycles, the sample still kept good catalytic activity with 85.46% selectivity to HCAL at 66.37% CAL conversion, and no activity loss was observed. These results demonstrated that the Ni₄-La₂O₃ catalyst sample has achieved acceptable reaction stability of cinnamaldehyde hydrogenation.

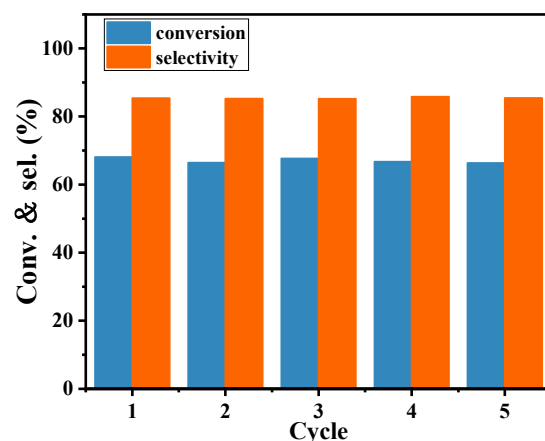


Figure 5. Recycling tests of selective hydrogenation of cinnamaldehyde over Ni₄-La₂O₃ catalyst. Reaction conditions: 0.8 mmol CAL, 50 mg catalyst, 6 mL absolute ethanol as solvent, 2 MPa H₂, reaction temperature 90 °C, reaction time 2 h.

3. Materials and Methods

3.1. Materials

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR grade, >99%), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR grade, >99%), $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (AR grade, >99%), Urea (AR grade, >99%), absolute ethanol (AR grade, >99%), and Cinnamic aldehyde (AR grade, 99%) were purchased from Aladdin Reagent Co., Ltd. in Shanghai, China. All of the above reagents were used directly without any treatment. All gases (H_2 , N_2) used for catalyst preparation and reaction processes were of ultrahigh purity (>99%).

3.2. Synthesis of $\text{Ni}_x\text{-La}_2\text{O}_3$

$\text{Ni}_x\text{-La}_2\text{O}_3$ catalysts were prepared using a hydrothermal synthesis method in sealed Teflon-lined autoclaves. Typically, 8.14 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (as nickel source), 3.03 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 4.62 g urea were dissolved in 100 mL of deionized water with rigorous stirring. After being dissolved completely, the above solution was added into a Teflon-lined autoclave and then heated to 120 °C for 20 h. The obtained precipitations were centrifugally washed with deionized water several times, dried at 100 °C overnight, and calcined at 500 °C (5 °C/min) for 2 h in air. Finally, the resulting powders were reduced under H_2 (10 vol% H_2/N_2) at 600 °C for 2 h to gain the $\text{Ni}_x\text{-La}_2\text{O}_3$ catalysts (x represented the molar ratio of Ni and La). These prepared samples were designated as $\text{Ni}_{1/4}\text{-La}_2\text{O}_3$, $\text{Ni}_1\text{-La}_2\text{O}_3$ and $\text{Ni}_4\text{-La}_2\text{O}_3$, respectively. Similarly, the $\text{Co}_x\text{-La}_2\text{O}_3$ catalysts were also synthesized as that of $\text{Ni}_x\text{-La}_2\text{O}_3$ above, using the same steps, just replacing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

3.3. Catalyst Characterization

The X-ray diffraction (XRD) spectra were recorded using a DX-2700 diffractometer (Haoyuan Corporation, Dandong, China) with $\text{CuK}\alpha$ source ($\lambda = 1.5406 \text{ \AA}$) at the condition of 40 kV, 30 mA and a scan rate of $0.02^\circ/\text{s}$. Diffraction patterns were recorded from 2θ as 10° to 80° . The transmission electron microscopy (TEM) images and scanning transmission electron microscopy images with a high-angle annular dark field scanning pattern (STEM-HAADF) equipped with an energy-dispersive spectroscopy (FlatQuad 5060 F, EDS) were filmed on a JEM-2100 (JEOL, Tokyo, Japan). Prior to the measurement, the samples were dispersed in ethanol using ultrasound and the resulting suspension was dropped on a copper grid coated with a carbon film. X-ray photoelectron spectroscopy (XPS) spectra were carried out using an Axis Ultra DLD (Kratos Analytical, Manchester, UK) with a monochromatic Al $\text{K}\alpha$ X-ray source and the pass energy was 100.0 eV with an energy step of 1.000 eV. All of the binding energies (BEs) were calibrated with using that of C 1s (284.8 eV). Hydrogen temperature programmed reduction (H_2 -TPR) experiments were carried out on a TP-5080 chemical adsorption analyzer (Xianquan, Tianjin, China). Before the H_2 -TPR measurement, 0.05 g of the catalyst was loaded to a fixed-bed quartz tube and pretreated in an Ar flow of 15 mL/min at 300 °C for 1 h. After being cooled at the same atmosphere to 30 °C, the pretreated sample was reduced from 30 °C to 800 °C in a flow (15 mL/min) of 5 % H_2/Ar at a ramp of 10 °C/min.

3.4. Catalytic Reaction

The hydrogenation reaction of CAL was carried out in a sealed Teflon-lined stainless steel automatic high-pressure autoclave. In a typical test, 70 μL (0.55 mmol) of CAL dispersed in 6 mL of absolute alcohol was put into an autoclave (20 mL). Then, 50 mg of the prepared catalyst sample was added into the autoclave above. Then, after sealing the reactor, hydrogen was first purged three times to remove the air inside before 2 MPa of hydrogen was introduced as the reaction gas. After that, the reaction temperature was heated to 90 °C to carry out the reaction for a certain period of time, with the heating mantle stirring at a rate of 600 rpm. After the reaction, the obtained product was analyzed with gas chromatography equipped with a HP-5 MS column. The conversion of the reactant and the selectivity of the target product were calculated using the following Formulas (1) and (2):

$$\text{Conversion (\%)} = [\text{CAL feed (mol)} - \text{CAL residue (mol)}] \times 100\% / \text{CAL feed (mol)} \quad (1)$$

$$\text{Selectivity (\%)} = \text{target product (mol)} \times 100\% / [\text{CAL feed (mol)} - \text{CAL residue (mol)}] \quad (2)$$

4. Conclusions

In summary, a La_2O_3 oxide supported high Ni loading amount catalyst has been prepared successfully with a one-pot hydrothermal synthesis method. In the performance test of cinnamaldehyde hydrogenation reaction, a $\text{Ni}_4\text{-La}_2\text{O}_3$ catalyst displayed excellent catalytic performance with a high CAL conversion of 88.1% and superior HCAL selectivity of 87.4% at 90 °C and 2 MPa H_2 pressure, which was better than that of the $\text{Co}_x\text{-La}_2\text{O}_3$ catalysts under the same reaction conditions. Moreover, combined with XRD, XPS and TPR characterization results, this outstanding catalytic performance could be attributed to the excellent adsorption and dissociation of metallic Ni on C=C bonds and hydrogen molecules along with the adsorption of C=O bonds by oxygen vacancies occurring simultaneously on the Ni/ La_2O_3 support. Finally, the optimal $\text{Ni}_4\text{-La}_2\text{O}_3$ catalyst also maintain excellent catalytic repeatability and chemical stability after five consecutive recycling tests. Overall, the catalyst design consisting of oxide support with oxygen vacancy and high metal loading also provided a new idea for chemoselective hydrogenation of α , β -unsaturated aldehydes.

Author Contributions: Conceptualization, H.Y. and Y.R.; methodology, H.Y. and R.Z.; formal analysis, H.Y. and F.C.; data curation, H.Y.; writing—original draft preparation, H.Y.; supervision, Q.W. and J.X. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (grant number 22202180) and the Natural Science Foundation of Zhejiang Province of China (grant number LQ20B030010).

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

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