Ultrasound-assisted green synthesis of Ru supported on LDH-CNT composites as an efficient catalyst for N-ethylcarbazole hydrogenation

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ABSTRACT

N-ethylcarbazole/dodecahydro-N-ethylcarbazole (NEC/12H-NEC) is one of the most attractive LOHCs, and it is of great significance to develop catalysts with high activity and reduce the hydrogen storage temperature. Layered double hydroxides-carbon nanotubes composites (LDH-CNT) were synthesized by a simple in-situ assembly method. Due to the introduction of CNT, a strong interaction occurred between LDH and CNT, which effectively improved the electron transfer ability of LDH-CNT. Ru/LDH-CNT catalysts were prepared via ultrasound-assisted reduction method without adding reducing agents and stabilizers. Under the cavitation effect of ultrasound, the hydroxyl groups on the surface of LDH were excited to generate hydrogen radicals (•H) with high reducibility, which successfully reduced Ru3+ to Ru NPs. Ru/LDH-3.9CNT-(300-1) catalyst was of 1.63 nm average Ru particle size with CNT amount of 3.9 wt% and the ultrasonic power of 300 W at 1 h, and its electron transfer resistance was less than that of Ru/LDH-(300-1). The synergy of ultrasound Ru NPs and fast electron transfer made it exhibit exceptional catalytic performance in NEC hydrogenation. Even if the reaction temperature was lowered to 80 °C, its hydrogenation performance was better than that of commercial Ru/Al2O3 catalyst at 120 °C. The ultrasound-assisted method is efficient, green and environmentally friendly, and the operation process is simple and economical. It is expected to be used in practical industrial production, which provides a reference for the preparation of high-activity and low-temperature hydrogen storage catalysts.

1. Introduction

Exploring clean and sustainable energy to solve the current problems of energy shortage and serious pollution is one of the urgent tasks to be solved at present [1-3]. Hydrogen is an important energy source for energy transition and carbon neutrality because of its high energy density, green and low carbon, etc. However, due to the low bulk density of hydrogen (0.08988 g/L at 1 atm) and its flammable and explosive characteristics, the safe storage and transportation of hydrogen is the main factor hindering its rapid popularization as an alternative fuel [4,5].

Traditional hydrogen storage technologies, such as high-pressure compression and low-temperature liquefaction, have the disadvantages of high safety risk factor, low storage density, high energy consumption and cost. However, the emerging liquid organic hydrogen carrier (LOHC) has the advantages of low cost, large hydrogen storage capacity, and compatibility with existing infrastructure equipment. It is considered as a green, safe, controllable hydrogen storage technology with great social and economic benefits [6]. The LOHC system is composed of a pair of hydrogen-poor and hydrogen-rich organic compounds, which can store and release hydrogen through reversible hydrogenation and dehydrogenation between them [7,8]. N-ethylcarbazole/perhydro-N-ethylcarbazole (NEC/12H-NEC) has a higher hydrogen capacity (5.79 wt%) and milder hydrogenation/dehydrogenation temperature, which has attracted widespread attention.

Ru-, Pt-, Rh- and Ni-based catalysts have been widely studied in the hydrogenation of NEC [6,9-12], among which Ru metal has the appropriate d-band center value and shows the highest catalytic activity [13]. In addition, Ru-based catalysts can also be used in a variety of different hydrogenation reactions [14] and exhibit excellent hydrogenation performance, such as the hydrogenation of nitroarenes to produce aniline [15], the carbonyl compound reduction amination to produce primary amines [16], etc. However, the reaction temperature of NEC hydrogenation over Ru-based catalysts is generally high, basically

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120 °C–200 °C. A higher reaction temperature usually leads to sintering of the active components and carbon deposition on the surface of the catalyst, thus reducing its lifetime [17,18]. Therefore, it is of great significance to develop low-temperature hydrogen storage catalysts with high activity and stability for this process. The catalyst support can not only disperse the active components and prevent the aggregation of nanoparticles, but also change the electron density of the metal through the interaction between the support and the active metal, or provide additional active sites for substrate adsorption, thus affecting the catalytic performance of the reaction [19,20]. Eblagon [9] carefully studied the catalytic performance of Ru-based catalysts supported on Al2O3, TiO2 and activated carbon in NLEC hydrogenation reaction, and found that the hydrophilic surface on the metal–metal oxide interface would affect the adsorption of intermediates, which in turn affected the distribution of hydrogenation products. Therefore, the choice of support in the catalyst is also important.

Layered double hydroxides (LDH) have unique structures and properties, such as flexible adjustment of the type and proportion of metal cations on brucite layers, abundant hydroxyl (−OH) groups on the surface, and exchangeability of intercalated anions [21,22]. In recent years, researchers have carried out extensive research on LDH, which have been applied in many fields, and one of the important applications is to use LDH as catalyst support. Li [19] prepared Pd nanoclusters with captopril as a protective agent and NaBH4 as a reducing agent, which were adsorbed on NiAl LDH support by electrostatic interaction and then calcined in N2 atmosphere to remove protective agent to obtain Pd nanoclusters supported on LDH. And it exhibited an extremely high turnover frequency in the oxidation of benzyl alcohol. However, this preparation method is complicated and tedious, and uses an organic protective agent, which will generate polluting gas when it is removed, which goes against the concept of green chemistry, so it is of great significance to develop a green and environmentally friendly catalyst preparation method. In addition, the interlayer electrostatic force of the LDH makes it more prone to stack or aggregate, which usually leads to the reduction of specific surface area and the coverage of active sites, thus reducing its catalytic activity [23–25]. However, carbon nanotubes (CNT) have a high specific surface area, good thermal stability and electronic conductivity, and abundant surface functional groups after modification. After CNT is introduced into LDH, LDH can not only maintain its inherent structure, but also reduce its accumulation, and promote heat, mass and electron transfer in the reaction process [26,27]. Xu [28] prepared Ce-doped NiFe LDH/CNT composites by in-situ self-assembly method. Due to the stronger electron transfer ability between the LDH and CNT, as well as the higher specific surface area and more lattice defect sites, it exhibited high catalytic efficiency in the electrochemical oxygen evolution reaction (OER), which was superior to that of the commercial Ir/C catalyst. However, LDH/CNT composites reported in literatures are usually used in electrochemical reactions [29–31], rather than in traditional thermal catalysis, especially as a support for NEC hydrogenation catalysts, which has not yet been reported.

Different preparation methods of supported metal nanomaterials will affect their physical and chemical properties. Among them, the ultrasound-assisted method has a unique reaction effect, and its application has been rapidly developed [32]. Cavitation occurs during ultrasound, and bubbles are generated, grown and violently collapsed, resulting in extreme temperatures and pressures in the liquid. This extraordinary high-energy environment provides a special platform for the growth of novel nanostructures [33,34]. Our previous study found that under ultrasonic conditions, the hydroxyl groups on the surface of LDH were excited to generate highly reducing hydrogen radicals (H•), which successfully reduced the supported noble metal cations [35,36]. Compared with the traditional chemical reduction method, this method does not require the addition of chemical reducing agents and stabilizers, and the obtained metal nanoparticles are smaller and highly dispersed.

In this study, LDH-CNT composites are prepared by a simple in-situ assembly method and used as the support to prepare Ru/LDH-CNT catalysts under the assistance of ultrasound. The preparation method is efficient, green and environmentally friendly, and the operation process is simple and economical, which has good industrial application prospects. The catalyst preparation conditions and NEC hydrogenation reaction conditions are optimized. It is found that the Ru/LDH-3.9CNT- (300-1) catalyst prepared by ultrasound-assisted reduction method has extremely high catalytic activity in NEC hydrogenation even under mild reaction conditions, far superior to commercial Ru/Al2O3.

2. Experimental

2.1. Chemicals and material

MgCl2·6H2O (98.0 %), AlCl3·6H2O (97.0 %) and cyclohexane (99.5 %) were purchased from Shanghai Macklin Biochemical Co., ltd. NaOH (96.0 %) and Na2CO3 (99.8 %) were provided by Tianjin Guangfu Technology Development Co., ltd. Carboxyl-functionalized CNT (diameter 20–30 nm, length 0.5–2 μm) was manufactured by Nanning Xianfeng Nanomaterials Technology Co., ltd. RuCl3·3H2O and NEC (98 %) were produced by Zhejiang Metallurgical Research Institute Co., ltd. and Beijing Coupling Technology Co., ltd., respectively. H2 (99.999 %) and N2 (99.999 %) were purchased from Harbin Qinghua Industrial Gas Co., ltd. Commercial Ru/Al2O3 (5 wt%) catalyst was produced at Alfa Aesar Chemical Co., ltd.

2.2. Synthesis of LDH-xCNT composites

LDH-xCNT composites with Mg2+ and Al3+ as layer cations and CO32− as intercalated anions are prepared by a simple in-situ assembly method. The preparation process was as follows: first, a certain mass of CNT (0.025 g, 0.05 g, 0.075 g, 0.1 g) was ultrasonically dispersed in 40 mL deionized water. Then, MgCl2·6H2O (3.05 g) and AlCl3·6H2O (2.41 g) were added and fully dissolved, recorded as liquid M. NaOH (1.44 g) and Na2CO3 (2.12 g) were dissolved in another 40 mL deionized water, denoted as liquid N. After ultrasonication, it was separated by centrifugation, washed, dried, and denoted as Ru/Al2O3.

2.3. Synthesis of Ru/LDH-xCNT catalysts

In the process of Ru/LDH-xCNT catalysts preparation, an XH-2008D ultrasonic instrument was used, which was produced by Beijing Xiangtu Technology Development Co., ltd., with an ultrasonic frequency of 25 kHz and a probe diameter of 18 mm. LDH-xCNT (0.2 g) was dispersed in 20 mL deionized water, and 10.42 mL 0.01 mol/L RuCl3 solution was added according to the theoretical loading of Ru of 5 wt%. Then it was treated at a certain ultrasonic power (P: 100 W, 300 W, 500 W) for a period of time (t: 0.5 h, 1 h, 1.5 h), and N2 was continuously introduced to abrogate the interference of dissolved oxygen. After ultrasonication, it was separated by centrifugation, washed, dried, and denoted as Ru/LDH-xCNT (P-t).

2.4. Characterisation

The electron transfer resistances of the catalysts were measured by electrochemical impedance spectroscopy (EIS) on a CHI-760E electrochemical workstation from Shanghai Chenhua, China. The CNT content in the LDH-CNT composites was analyzed by a TGA Q50.
States. The test conditions were from 30 °C to 900 °C at a temperature rise rate of 10 °C/min in air atmosphere. Powder X-ray diffraction (XRD) tests were performed on a Shimadzu XRD7000 instrument equipped with Cu Kα radiation (λ = 1.5418 Å). The voltage and current are 40 kV and 30 mA, respectively, and the scan ranges 20 from 5° to 90° with a scan speed of 4°/min. The N₂ adsorption–desorption isotherm was measured at 77 K using the Autosorb-1 automatic specific surface and porosity analyzer manufactured by Quantachrome, USA. The specific surface area of the sample was calculated by the Brunauer Emmett Teller (BET) method, and the pore size distribution was calculated by the Barrett Joyner Halenda (BJH) method. Fourier transform infrared (FT-IR) analysis was carried out on an IN10 instrument from Thermo Scientific, USA. A certain amount of catalyst powder and KBr were mixed and pressed into tablets, and the scanning range was 400 ~ 4000 cm⁻¹.

2.5. NEC hydrogenation tests

The NEC hydrogenation process was carried out in an autoclave reactor, which was the SLM-50 model manufactured by Beijing Century Senlang Experimental Equipment Co., Ltd. First, 0.5 g NEC, 20 mL cyclohexane and 0.015 g 5 wt% Ru-based catalyst (m_{Ru}/m_{NEC} = 0.15 %) were added. After the reactor was sealed, the air in the reaction system was replaced with H₂. The temperature was raised to the set reaction temperature under a stirring speed of 900 rpm. Then, a certain pressure of H₂ was introduced, after which the pressure change with time was recorded. After 80 min of reaction, the liquid products were analyzed by GC-MS-2030.

The following formulas were used to calculate the capacity and percentage of hydrogen storage in NEC hydrogenation.

\[
\text{Hydrogen Capacity (wt%)} = \frac{\text{Yield}_{12\text{H}-\text{NEC}} + \frac{12}{8} \text{Yield}_{8\text{H}-\text{NEC}}}{\text{M}_{\text{NEC}}} \times 100\%
\]

\[
\text{Percentage of hydrogen storage (%) = } \frac{\text{Hydrogen Capacity (wt%)} \times 5.79 (\text{wt%})}{1} \times 100\%
\]

3. Results and discussion

3.1. Effect of the CNT amount on the catalytic performance in NEC hydrogenation

In order to screen out the appropriate amount of CNT introduced in the Ru/LDH-xCNT-(300-1) catalyst, the catalytic performance of this series of catalysts in NEC hydrogenation was evaluated, as shown in Fig. 1. It can be seen that when a certain amount of CNT is introduced, its catalytic activity in the hydrogenation of NEC is improved. The hydrogenation rate of NEC changes little with the CNT amount of 1.3 %, which may be related to the low amount of CNT introduced. The initial hydrogenation rate of NEC increases significantly when the amount of CNT is increased to 2.6 % and 3.9 %. When Ru/LDH-3.9CNT-(300-1) is used as the catalyst, it has the optimal catalytic activity. After 24 min of reaction, the selectivity of 12H-NEC and 8H-NEC are 98.31 % and 1.69 %, and the capacity and percentage of hydrogen storage reach 5.76 wt% and 99.5 %, respectively, basically realizing complete hydrogenation.

After extending the reaction time to 80 min, the hydrogen capacity does not change. This indicates that the reaction equilibrium has been reached after 24 min under the reaction conditions (120 °C, 6 MPa). When the amount of introduced CNT is further increased to 5.2 %, the initial hydrogenation rate decreases slightly. In conclusion, the optimal amount of CNT is 3.9 %. To study the influence of the introduction of CNT in the Ru/LDH-3.9CNT-(300-1) catalyst on its physical and chemical properties, the following series of characterizations were carried out.

3.2. Catalyst characterization

To explore the influence of the introduction of CNT on the electrochemical performance, electrochemical impedance spectroscopy (EIS) analysis was performed on Ru/LDH-(300-1) and Ru/LDH-3.9CNT-(300-1) catalysts. In Fig. 2, the electron transfer resistance of the catalyst is proportional to the diameter of the semicircle in the high frequency region of the Nyquist plot [37]. For Ru/LDH-3.9CNT-(300-1) sample, the diameter of the semicircle in the high frequency region is significantly lower than that of Ru/LDH-(300-1), which indicates that the electron transfer resistance in the Ru/LDH-3.9CNT-(300-1) catalyst is lower and the conductivity is higher. Therefore, the introduction of CNT is beneficial for improving the conductivity and electron transport ability of the material. The enhancement of electron transfer ability indicates that it may be an excellent material for promoting electron transfer in catalytic reactions [38], which is conducive to the better...
The CNT content in LDH-xCNT was verified by thermogravimetric (TG) analysis of LDH and LDH-xCNT in air atmosphere. Taking LDH-3.9CNT as an example, the TG analysis is shown in Fig. 3. LDH has two stages of weight loss, and the first stage is the removal of physically adsorbed water and interlayer water molecules when the temperature is lower than 250 °C. The second stage is 250 ~ 900 °C, which corresponds to the weight loss of surface hydroxyl groups and interlayer CO$_3^{2-}$, and finally becomes spinel. However, the weight loss of LDH-3.9CNT occurs in three stages. The first stage is the same as that of LDH, the second stage is 250 ~ 500 °C, mainly due to the weight loss of surface hydroxyl groups and interlayer CO$_3^{2-}$, and the third stage is the removal of CNT in the LDH-3.9CNT composite above 500 °C. According to the difference between the residual amounts of the two samples at 900 °C, it is 4.0 %, which is the content of CNT in LDH-3.9CNT, and it is very close to the theoretical value (3.9 %).

Fig. S1 and Fig. 4 show the XRD patterns of CNT and samples, respectively. In Fig. 4, compared with LDH, a weak characteristic diffraction peak corresponding to the (0 0 2) crystal plane of CNT appears at 2θ = 26.3° after the introduction of CNT, demonstrating the successful combination of LDH and CNT [31]. The characteristic diffraction peaks corresponding to LDH appear in all samples, indicating that it has a hexagonal lattice with R3m rhomboic space group symmetry [39]. The lattice parameter a = 2d(1 1 0) corresponds to the metal–metal distance on the LDH layer. c = 3d(003), where d(003) is the thickness composed of a single layer of brucite and the interlayer [40]. The structural parameters of each sample calculated from the XRD data are shown in Table 1. The d(003) value of LDH calculated by the Bragg formula is 7.583 Å, which is consistent with the reported layer spacing of CO$_3^{2-}$ as intercalation anion [41,42]. When a certain amount of CNT is introduced, the value of d(003) slightly increases. This is due to the hydrogen bonding between the hydroxyl groups of the layer and the interlayer anions and water molecules in LDH. The surface of carboxyl-functionalized CNT is negatively charged and can attract Mg$^{2+}$ and Al$^{3+}$ metal cations. When alkaline solution is added, the surface of the carboxyl group becomes the nucleation center of LDH. That is, when the carboxyl groups on the surface of CNT have a strong interaction with the LDH layer, the interaction between the brucite layer and interlayer CO$_3^{2-}$ is weakened, and the interlayer spacing is slightly increased [43]. However, there is no change for d(1 1 0), because the introduction of CNT does not change the metal–metal composition and distance on the LDH layer. According to the Scherrer formula, the crystal grain size is inversely proportional to its full width at half maximum (FWHM); that is, the smaller the FWHM is, the larger the crystal size, and the more complete the crystal structure [44]. From the data in Table 1, the FWHM$_{003}$ and FWHM$_{110}$ values of LDH decrease after a certain amount of CNT is introduced, which indicates that its growth along the c-axis and a-axis is promoted.

For the sample of Ru/LDH-3.9CNT-(300-1) prepared under the condition of ultrasound-assisted reduction, no characteristic diffraction peak corresponding to elemental Ru is detected in Fig. 4, implying the Ru NPs with ultrafine size and high dispersion. In Table 1, compared with LDH-3.9CNT, the layer spacing corresponding to d(003) in Ru/LDH-3.9CNT-(300-1) decreases, and the values of FWHM$_{003}$ and FWHM$_{110}$ increase. This may be due to the effect of ultrasound and the formation of Ru NPs in the interlayer affecting the distribution of species and the integrity of the crystal structure.

The specific surface area and pore structure of the samples were analyzed by N$_2$ adsorption–desorption characterization, as shown in Fig. 5 and Table 2. From the N$_2$ adsorption–desorption isotherms in Fig. 5(a), all samples are type IV isotherms and H3 hysteresis loops. In Fig. 5(b), the pore size distribution of CNT is broad, mainly centered at about 45 nm. And the pore size of LDH ranges from 10 to 37 nm, mainly concentrated at approximately 32 nm. The pore size range of the LDH-3.9CNT composite is basically unchanged. However, for Ru/LDH-3.9CNT-(300-1) samples after ultrasound-assisted reduction, the pore size range is significantly smaller, ranging from 10 nm to 32 nm, mainly around about 25 nm. From the data in Table 2, after introducing a certain amount of CNT into LDH, the BET surface area and total pore volume increase, which may be explained by the fact that most of the LDH grows on the surface of CNT, which reduces the accumulation of LDH. Compared with LDH-3.9CNT, the specific surface area and total pore volume of Ru/LDH-3.9CNT-(300-1) decrease, which is consistent with the result of decreasing interlayer spacing obtained by XRD. A possible explanation is that the Ru NPs formed by the reduction under
the action of ultrasound are formed in the pores of the support, and the instantaneous extremely high temperature and high pressure generated by the ultrasonic cavitation act on the \( \text{CO}_3^{2-} \) anions between the LDH layers, causing part of the \( \text{CO}_3^{2-} \) to decompose and produce \( \text{CO}_2 \). In order to maintain the charge balance of the LDH structure, part of \( \text{Cl}^- \) in the RuCl\(_3\) precursor acts as an intercalation anion to supplement the missing \( \text{CO}_3^{2-} \), thus affecting its pore structure.

The surface functional groups on the support and catalyst were analyzed by FT-IR, as shown in Fig. 6. For LDH, the absorption peaks at 3440 cm\(^{-1}\) and 1564 cm\(^{-1}\) correspond to the stretching vibration and bending vibration peaks of \( \text{O}^--\text{H} \) on the LDH layer or interlayer water molecules, respectively [41]. The peak at 1360 cm\(^{-1}\) is assigned to the antisymmetric stretching vibration of the C–O bond, indicating the presence of \( \text{CO}_3^{2-} \). The \( \upsilon_2 \) and \( \upsilon_4 \) vibration peaks of \( \text{CO}_3^{2-} \) appear at 958 cm\(^{-1}\) and 681 cm\(^{-1}\), respectively, and the peaks at 792 cm\(^{-1}\) and 557 cm\(^{-1}\) represent the interaction between \( \text{CO}_3^{2-} \) and the brucite layer [45]. In addition, the peak at 450 cm\(^{-1}\) is due to the stretching vibration of M–O [46]. For LDH-3.9CNT, the characteristic peaks of the functional groups of LDH all exist, but the intensity of the peak at 557 cm\(^{-1}\) is weakened. This may be because the surface carboxyl groups of CNT have a strong interaction with the LDH layer, weakening the interactions between brucite layers and interlayer species, which is consistent with the XRD results. In Fig. 6(b), after the ultrasound-assisted reduction of Ru NPs, the peak intensity of hydroxyl groups at 3440 cm\(^{-1}\) is reduced, which is due to the excitation of hydroxyl groups on the LDH layer under ultrasonic cavitation to generate reducing hydrogen radicals, reducing Ru\(^{3+}\) to Ru\(^0\), and anchors on the support through Ru–O coordination.

The intensity of peaks corresponding to \( \text{CO}_3^{2-} \) is also significantly weakened, which further proves that part of the \( \text{CO}_3^{2-} \) anions between LDH layers are decomposed under the action of ultrasonic cavitation. The FT-IR spectrum of CNT is shown in Fig. S2. For the LDH-3.9CNT and Ru/LDH-(300–1) samples in Fig. 6, there is no characteristic vibration peak corresponding to the C–O groups in the carboxyl groups on the surface of CNT at 1720 cm\(^{-1}\) [47], which may be due to the low content of CNT.

The valence states of Ru in the Ru/LDH-(300–1) and Ru/LDH-3.9CNT-(300–1) samples were analyzed by XPS, as shown in Fig. 7. It appears in the spectrum as a double state of 3p\(^3/2\) and 3p\(^1/2\). For Ru/LDH-(300–1) and Ru/LDH-3.9CNT-(300–1), the Ru 3p\(^3/2\) peaks are weak. The FT-IR spectra of the samples are shown in Fig. 6.
both deconvoluted at 462.5 eV and 464.2 eV, corresponding to Ru$^{0}$ and RuO$_2$, respectively [48]. Similarly, the Ru 3p1/2 peaks are deconvoluted into two peaks at 484.6 eV and 486.2 eV, which are ascribed to Ru$^{0}$ and RuO$_2$, respectively [49]. The existence of Ru$^{0}$ indicates that in ultrasound-assisted reduction, the –OH groups on the surface of LDH are excited to generate hydrogen radicals with high reducibility, and Ru$^{3+}$ is successfully reduced to Ru NPs.

To further explore the interfacial interaction between CNT and LDH, Raman analysis was performed, as shown in Fig. 8. The D and G bands of CNT at 1340 cm$^{-1}$ and 1580 cm$^{-1}$ represent the defect sites and the in-plane stretching vibration of sp$^2$ hybridization of C atoms, respectively. The intensity ratio of I$_D$/I$_G$ is used to evaluate the surface defect density in the CNT [50]. The I$_D$/I$_G$ value in LDH-CNT (1.53) is lower than that in CNT (1.75), indicating a decrease in defect density, which may be because the electron-rich defect sites could also act as the nucleation center of LDH, thus forming a strong interface interaction between CNT and LDH [51]. For the sample Ru/LDH-3.9CNT-(300–1), the I$_D$/I$_G$ value (1.35) is further decreased, which may be due to the fact that some Ru NPs are anchored at the defect site center on the CNT surface. The Raman vibration peak corresponding to LDH appears near 1054 cm$^{-1}$ for both LDH-3.9CNT and Ru/LDH-3.9CNT-(300–1) samples, which further indicates the successful combination of CNT and LDH [52].

To obtain the interface state between LDH and CNT more intuitively and the particle size of Ru NPs, TEM and EDS mapping were performed on Ru/LDH-3.9CNT-(300–1), as shown in Fig. 9. From Fig. 9(a) to (g), it can be clearly seen that LDH is attached to the surface of CNT, indicating that there is a certain interaction between them. This is because both the defect sites and negatively charged carboxyl groups on the surface of CNT can become the nucleation centers of LDH, which is conducive to the growth of LDH on the surface of CNT, effectively attenuating the accumulation between LDH and increasing the specific surface area of the catalyst. In Fig. 9(h), Ru NPs are highly dispersed on the LDH-3.9CNT support. The inset in Fig. 9(h) shows the particle size distribution of Ru NPs, ranging from 0.85 nm to 2.57 nm, with an average particle size of 1.63 nm. The lattice fringe of Ru NPs is 0.205 nm in Fig. S3, which corresponds to the (1 0 1) crystal plane of Ru$^{0}$.

3.3. NEC hydrogenation performance

3.3.1. Optimisation of catalyst preparation conditions

Previous studies have found that when using the ultrasound-assisted reduction method to prepare Ru-based catalysts supported on LDH, if the ultrasonic power is too low or the ultrasonic time is too short, the generated energy is not enough to excite the –OH groups on the surface of LDH to produce enough •H, resulting in incomplete reduction of Ru$^{3+}$. However, too high ultrasonic power and too long ultrasonic time can easily cause Ru NPs to agglomerate, leading to a decrease in the number of exposed active sites [36]. Therefore, the selection of ultrasonic preparation conditions is necessary. By comparing the NEC hydrogenation performance of Ru/LDH-3.9CNT-(P–t) catalysts prepared under different ultrasonic powers and times in Fig. 10, the most appropriate ultrasonic power and time are obtained as 300 W and 1 h, respectively.

3.3.2. Optimisation of the NEC hydrogenation reaction conditions

Ru/LDH-3.9CNT-(300–1) is used as the catalyst, and different reaction temperatures in NEC hydrogenation are investigated under the hydrogenation pressure of 6 MPa, which are shown in Fig. 11(a) and Table 3. As shown in Fig. 11(a), with the increase of reaction temperature, the initial hydrogenation rate is significantly accelerated. However, from the data after 80 min of reaction in Table 3, the selectivity of 12H-NEC and hydrogen capacity first increase and then decrease as the reaction temperature increases, while the selectivity of 8H-NEC shows the opposite trend. This is because NEC hydrogenation is an exothermic reaction. Although an excessively high reaction temperature can accelerate the reaction rate, it is not conducive to the reaction equilibrium in the direction of hydrogenation. When the reaction temperature is 90 °C, the selectivity of 12H-NEC reaches the highest value (99.29 %), and the percentage of hydrogen storage is 99.8%.

When the reaction temperature is 90 °C, the effect of hydrogen
pressure on the hydrogenation performance of NEC is investigated, and the results are shown in Fig. 11(b) and Table 4. As shown in Fig. 11(b), with the increase of hydrogen pressure, the initial hydrogenation rate is obviously accelerated. According to the data in Table 4 after 80 min of reaction, with the increase of hydrogen pressure, the selectivity of 12H-NEC and hydrogen capacity increase continuously, while the selectivity of 8H-NEC decreases. This is because high pressure can not only increase the reaction rate of NEC hydrogenation, but also promote the reaction balance to move toward the hydrogenation direction. When the hydrogen pressure is 7 MPa, the selectivity of 12H-NEC reaches 99.75%, and the corresponding percentage of hydrogen storage is 100%. Even under the relatively mild reaction conditions (reaction temperature 90 °C and hydrogen pressure 5 MPa), the percentage of hydrogen storage can also reach 99.3%, which further illustrates that the catalyst has high activity.

3.3.3. Comparison of NEC hydrogenation performance over different catalysts

Under the same reaction conditions (reaction temperature 120 °C, hydrogen pressure 6 MPa), the catalytic performance of Ru/LDH-3.9CNT-(300–1), Ru/LDH-(300–1) and commercial Ru/Al₂O₃ catalysts in NEC hydrogenation are compared, as shown in Fig. 12(a). The catalytic activity of Ru/LDH-3.9CNT-(300–1) is much higher than that of Ru/LDH-(300–1) and Ru/Al₂O₃. When Ru/LDH-3.9CNT-(300–1) is used as the catalyst, the conversion of NEC is 100%, the selectivity of 12H-NEC and hydrogen capacity reach 98.31% and 5.76 wt% after 24 min of reaction. Although the NEC conversion rate can reach 100% over Ru/Al₂O₃ catalyst after 80 min of reaction, the selectivity of 8H-NEC is higher (24.10%), and the selectivity of 12H-NEC and hydrogen capacity are 75.90% and 5.34 wt%, respectively.

To further contrast the catalytic performance of Ru/LDH-3.9CNT-(300–1), Ru/LDH-(300–1) and commercial Ru/Al₂O₃ catalysts in NEC hydrogenation, the NEC conversion and hydrogen capacity after 80 min at different hydrogenation temperatures (80 ~ 120 °C) are shown in Fig. 12(b, c). NEC can be completely transformed over Ru/LDH-3.9CNT-(300–1) catalyst during the reaction temperature from 80 °C to 120 °C, and the hydrogen capacity is more than 5.63 wt%. However, the complete conversion of NEC can only be achieved at temperatures higher
than 100 °C over Ru/LDH-(300–1) and commercial Ru/Al₂O₃ catalyst. When the temperature is 80 °C, the conversion of NEC is very low over Ru/LDH-(300–1) and commercial Ru/Al₂O₃ catalysts, only 40.90 % and 15.31 %, respectively. Moreover, the catalytic performance of Ru/LDH-3.9CNT-(300–1) at 80 °C is better than that of commercial Ru/Al₂O₃ at 120 °C. This result sufficiently indicates that the Ru/LDH-3.9CNT-(300–1) catalyst still has high catalytic activity even at lower reaction temperatures. The main reasons may be as follows: (1) The introduction of CNT makes the catalyst have a higher electron transfer ability and larger specific surface area, which is conducive to heat and mass transfer, and facilitates the hydrogenation of NEC. (2) For the catalyst prepared by the ultrasound-assisted method, Ru NPs are highly dispersed on the support, providing more active sites. Therefore, the synergy of ultrafine Ru NPs and fast electron transfer in the catalyst makes it exhibit exceptional catalytic performance in NEC hydrogenation.

Table 3
Data of NEC hydrogenation after 80 min at different reaction temperatures (hydrogen pressure 6 MPa).

| Temperature (°C) | Conversion (%) | Selectivity (%) | H₂ Capacity (wt%) | Percentage of hydrogen storage (%) |
|-----------------|----------------|----------------|-------------------|-------------------------------------|
|                 |                | 12H-NEC | 8H-NEC     |                                   |
| 80 °C           | 100            | 91.36   | 8.64        | 5.63                               | 97.2                                |
| 90 °C           | 100            | 99.29   | 0.71        | 5.78                               | 99.8                                |
| 100 °C          | 100            | 99.27   | 0.73        | 5.78                               | 99.8                                |
| 110 °C          | 100            | 98.88   | 1.12        | 5.77                               | 99.7                                |
| 120 °C          | 100            | 98.31   | 1.69        | 5.76                               | 99.5                                |

Table 4
Data of NEC hydrogenation after 80 min under different reaction pressures (reaction temperature 90 °C).

| Pressure (MPa) | Conversion (%) | Selectivity (%) | H₂ Capacity (wt%) | Percentage of hydrogen storage (%) |
|----------------|----------------|-----------------|-------------------|-------------------------------------|
|                |                | 12H-NEC | 8H-NEC     |                                   |
| 5 MPa          | 100            | 97.70   | 2.30        | 5.75                               | 99.3                                |
| 6 MPa          | 100            | 99.29   | 0.71        | 5.78                               | 99.8                                |
| 7 MPa          | 100            | 99.75   | 0.25        | 5.79                               | 100                                 |

3.3.4. Calculation of apparent activation energy

The influence of external diffusion and internal diffusion should be considered when studying the kinetics of NEC hydrogenation. Due to the extremely fast stirring speed in the reaction process and the small particle size of the catalyst, external diffusion and internal diffusion can be neglected [11,53]. Kinetic studies show that the reaction rate is zero order for the NEC concentration and first order for the H₂ concentration [12,54]. The apparent activation energy of NEC hydrogenation on Ru/LDH-3.9CNT-(300–1) catalyst was calculated at the reaction temperature of 80 °C–120 °C. It can be seen from ln(P₀/Pₜ) ~ t in Fig. 13(a) that they all present a good linear relationship, and its slope is the apparent reaction constant (k). On the basis of lnk ~ 1/T in Fig. 13(b), the apparent activation energy (Eₐ) is calculated to be 34.95 kJ/mol. By comparison in Table S1, it is found that the Eₐ on Ru/LDH-3.9CNT-(300–1) catalyst is lower than most values reported in the literatures.

Fig. 11. NEC hydrogenation performance over the Ru/LDH-3.9CNT-(300–1) catalyst at different reaction temperatures (hydrogen pressure 6 MPa) (a) and different hydrogen pressures (reaction temperature 90 °C) (b).

Fig. 12. Hydrogenation curves in NEC hydrogenation over Ru/LDH-3.9CNT-(300–1), Ru/LDH-(300–1) and commercial Ru/Al₂O₃ catalysts (reaction temperature 120 °C, hydrogen pressure 6 MPa) (a), NEC conversion (b) and hydrogen capacity (c) at different hydrogenation temperatures for 80 min (hydrogen pressure 6 MPa).
3.3.5. Stability of catalyst

In order to determine whether Ru/LDH-3.9CNT-(300–1) is a heterogeneous catalyst in the NEC hydrogenation reaction, the leaching test was performed, as shown in Fig. 54. After 10 min of reaction, the hydrogen capacity is 3.86 wt%. After removing the catalyst by centrifugation and continuing the hydrogenation reaction for 70 min, the hydrogen capacity does not change, indicating that no Ru NPs leaching occurs in the reaction process, and the catalyst is truly heterogeneous.

A long-term stability test is very important to evaluate the application value of a catalyst. The stability of Ru/LDH-3.9CNT-(300–1) catalyst in NEC hydrogenation was investigated at the hydrogenation temperature of 120 °C and pressure of 6 MPa. After completing a hydrogenation test, it can be put into the next use after simple centrifugal separation and cyclohexane washing. Fig. 14 shows that after the catalyst is recycled 6 times, the selectivity of 12H-NEC is 97.19 %, and the hydrogen capacity can still reach 5.74 wt%. Even after the 8th cycle, NEC can still be completely converted, the selectivity of 12H-NEC and 8H-NEC are 95.17 % and 4.83 %, respectively, the hydrogen capacity is 5.70 wt%, and the corresponding percentage of hydrogen storage is 98.4 %. This indicates that the catalyst has high stability, which is attributed to the strong interaction between Ru NPs and the support.

The TEM analysis of Ru/LDH-3.9CNT-(300–1) catalyst after eight recycling uses is shown in Fig. 14 (b) and (c). It can be seen that the average size of Ru NPs increases from 1.63 nm to 2.19 nm after eight recycling uses, and the agglomeration of Ru NPs may be the main reason for the slight decrease in catalytic activity.

4. Conclusion

It is crucial to develop catalysts with high activity and stability to reduce the reaction temperature of NEC hydrogenation. Ru-based catalysts supported on LDH-CNT are prepared using ultrasound-assisted green reduction method without introducing other chemical reducing agents and organic stabilizers. The –OH groups on the LDH are excited by the special cavitation of ultrasound to generate reducing •H, reducing Ru³⁺ to Ru NPs, which are anchored on the support. For Ru/LDH-3.9CNT-(300–1) catalysts prepared under optimal ultrasonic conditions, the average particle size of Ru NPs is 1.63 nm and they are highly dispersed on the support. After the introduction of CNT, LDH has a strong interaction with CNT, which increases its specific surface area and enhances the electron transfer ability. Due to the synergy of ultrafine Ru NPs and enhanced electron transfer ability, the series catalysts show extremely high catalytic activity in NEC hydrogenation with an apparent activation energy of only 34.95 kJ/mol. When the reaction temperature is 120 °C and the pressure is 6 MPa, the selectivity of 12H-NEC and 8H-NEC are 98.31 % and 1.69 %, respectively, and the hydrogen capacity and percentage of hydrogen storage are 5.76 wt% and 99.5 % after 24 min, which basically achieves complete hydrogenation in a relatively short time. Meanwhile, the catalyst has high stability, NEC can still be fully converted after the 8th cycle, and the percentage of hydrogen storage can reach 98.4 %. In addition, the hydrogenation performance of Ru/LDH-3.9CNT-(300–1) catalyst at 80 °C is better than that of the commercial Ru/Al₂O₃ catalyst at 120 °C, which fully reflects that Ru/LDH-3.9CNT-(300–1) still has high activity at lower temperatures. This method provides a reference for the preparation of NEC hydrogen storage catalysts with high activity.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultrasch.2022.106227.

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