Ultrasound-excited hydrogen radical from NiFe layered double hydroxide for preparation of ultrafine supported Ru nanocatalysts in hydrogen storage of N-ethylcarbazole

Xiaoran Liu, Jiaming Shi, Xuefeng Bai, Wei Wu

School of Chemistry and Material Science, Heilongjiang University, Harbin 150080, China
Institute of Petrochemistry, Heilongjiang Academy of Sciences, Harbin 150040, China

ARTICLE INFO

Keywords:
Ultrafine Ru nanoparticles
Ultrasound-excited
N-ethylcarbazole
Hydrogen storage
NiFe layered double hydroxide

ABSTRACT

Highly active Ru nanoparticles (Ru NPs) supported on NiFe layered double hydroxide (Ru/NiFe-LDH) are prepared easily using ultrasound-assisted reduction method without chemical reductants and stabilizers. The plentiful hydroxyls on NiFe-LDH are excited into hydrogen radicals (H) under the action of ultrasound for reducing Ru$^{3+}$ to Ru$^{0}$. Ru NPs with an average particle size of 1.26 nm highly disperse on the mesopore-like surface of NiFe-LDH, which improve the catalytic performance for N-ethylcarbazole (NEC) hydrogenation. The experimental results show that 5Ru/NiFe-LDH-300-60 exhibits the best catalytic performance with 100% conversion of NEC, 98.88% yield of dodecahydro-N-ethylcarbazole (12H-NEC) and 5.77 wt% mass hydrogen storage capacity under the reaction conditions of 110 $^o$C, 6 MPa and m$_{Ru/NiFe-LDH}$ = 0.15 wt% for 80 min. The kinetics study shows that the apparent activation energy is only 25.15 kJ/mol, which is the lowest in the reported literatures. Ru complexes with O-contained groups on NiFe-LDH, improving the catalytic stability in NEC hydrogenation.

1. Introduction

With the development of society and economy, energy shortage and environmental pollution caused by the burning of fossil fuels have become two major problems in the 21st century. Hydrogen energy is considered as the best way to solve environmental pollution and energy shortage due to its abundant reserves, wide sources, high energy density, and clean combustion without pollution. However, hydrogen storage and transportation issues limit the wide application of hydrogen energy [1–3]. Traditional hydrogen storage methods mainly include high pressure compression [4–5], metal hydride [6–8], cryogenic liquefaction [9–10], complex hydride [11] and porous materials for hydrogen storage [12–13]. However, the current hydrogen storage technologies mainly have some problems, such as extreme conditions for hydrogen storage and release, low hydrogen storage capacity, high cost, inconvenient transportation, and difficult to recycle. Compared with the above-mentioned hydrogen storage methods, liquid organic hydrogen carriers (LOHCs) have higher storage capacity, recyclable use, clean and pollution-free, low cost, high safety, and can be transported and stored using existing gasoline pipelines, which can solve the problems of environmental pollution and energy shortage at the same time, and it provides a new hydrogen storage and transportation way for the hydrogen fuel cell and hydrogen energy vehicles [14].

The NEC/12H-NEC system is one of the most popular LOHCs because of its high mass hydrogen storage capacity (5.79 wt%) and low dehydrogenation enthalpy (50.6 kJ/mol), which meets the requirements of the U.S. Department of Energy [15]. Eblagon et al. [16–17] systematically compared the effects of unsupported Pd, Ru, Pt, and Ni catalysts on the catalytic performance in NEC hydrogenation, and it was found that Ru was the most active metal for the reaction. In addition, they also discovered the catalytic activity of the supported Ru catalyst was significantly better than that of the unsupported Ru catalyst. Yu et al. [18] found that the catalytic activity in NEC hydrogenation over Ru/TiO$_2$-P25 (anatase/rutile = 1/4 mixture) was significantly better than that of Ru/TiO$_2$-rutile and Ru/TiO$_2$-anatase catalysts, indicating that the different crystal structures of support also affected the catalytic performance. Therefore, choosing a suitable catalyst support and active metal is the key to prepare a high catalytic performance catalyst for NEC hydroygenation. Although great achievements have been made in the LOHCs hydrogenation, most of current catalysts still have disadvantages
of complex preparation methods, poor activity and stability. So it is urgent to prepare an efficient and stable Ru-based catalyst via a simple synthesis method for decreasing the pressure and temperature of the hydrogenation reaction, thereby realizing the cost reduction of the hydrogenation of LOHCs.

Layered double hydroxides (LDHs) are a large family of 2D natural and/or synthetic anionic clay materials [19]. The general formula for LDH is \[M^{2+}\rm{A}^{n-}(\rm{OH})\alpha^{\delta}\rm{H}_2\rm{O}\], where M is the metal cation and A is the interlayer anion to compensate for the net positive charge. The controllability of the composition and structure of the layer, the exchangeability of interlayer anions, and the memory effect make it become an ideal support of supported nanocatalysts, which has attracted extensive attention from researchers [20–23]. In addition, a suitable preparation method is the key to the preparation of ultrafine nanocatalysts with excellent catalytic performance. The preparation methods of supported nanocatalysts mainly include traditional chemical reduction methods [24] and new reduction methods, such as thermal reduction method [25], plasma reduction method [26], microwave-assisted reduction method [27] and ultrasound-assisted reduction method [28–30]. Traditional chemical reduction methods usually require a large number of surfactants and stabilizers to prevent agglomeration of nanoparticles to prepare ultrafine nanocatalysts with high dispersibility. However, they will be strongly adsorbed around the active sites during the synthesis process, which significantly decreases its catalytic activity. In addition, the use of chemical reducing agents and the removal of stabilizers will pollute the environment, which does not conform to the concept of green chemistry. Thermal reduction, plasma reduction, and microwave-assisted reduction are not suitable for large-scale preparation of nanocatalysts because of the high energy consumption and complex preparation process. The ultrasonic mechanism is the acoustic cavitation effect, that is, the formation, growth and collapse of cavitation bubbles in the liquid medium by ultrasonic waves. The collapse of cavitation bubbles will produce extreme conditions such as high temperature and high pressure, and accompany by the generation of powerful shock waves and high-speed microjets to promote the dispersion of active sites and accelerate the reaction process [31]. Therefore, ultrasonic technology based on acoustic cavitation effect has been widely used in the preparation of metal nanocatalysts. Li et al. [32] successfully prepared one-dimensional rod-like SBA-15 supported Ru nanorods with particle size of 2–6 nm by ultrasound-assisted ethylene glycol reduction method, and Ru NPs were embedded into one-dimensional channels of SBA-15. Ultrasonic waves played two important roles in the preparation of the catalyst. Firstly, the hydroxyls in ethylene glycol were dissociated into hydrogen radicals under the action of ultrasound to reduce \(\text{Ru}^{3+}\) to \(\text{Ru}^0\); Secondly, the microjet and bubble oscillation effect of ultrasound promoted Ru NPs to be embedded in the one-dimensional channel of SBA-15. In our previous work, Li et al. [33] used two-dimensional layered MgAl-LDH as support, the hydroxyls on the surface of MgAl-LDH were successfully dissociated into the hydrogen radicals under the action of ultrasound without adding any reducing agents and stabilizers to reduce \(\text{Pd}^{2+}\), thereby obtaining highly dispersed Pd NPs, which showed excellent catalytic performance in Suzuki reaction. However, some studies have indicated that LDH materials composed of transition metals (such as NiFe-LDH) generally showed more attractive catalytic performance due to their different band gap and band edge positions [19,34–35].

In order to synthesize efficient and environmentally friendly supported NPs catalysts, we designed and prepared ultrafine Ru NPs catalysts supported on NiFe-LDH by ultrasound-assisted reduction method without adding any stabilizers or chemical reductants. The surface hydroxyls of NiFe-LDH were excited into hydrogen radicals under ultrasonic cavitation for reducing \(\text{Ru}^{3+}\). The O-contained groups on NiFe-LDH played an important role in immobilizing Ru NPs, thus improving its catalytic stability. What is more, the effects of ultrasound preparation conditions and NEC hydrogenation reaction conditions were studied.

2. Experimental

2.1. Preparation of NiFe-LDH support

Traditional coprecipitation-hydrothermal method was used to prepare NiFe-LDH support \((\text{Ni}^{2+} :\text{Fe}^{3+} = 3)\), and its detailed synthesis process was described in the Supplementary Material.

2.2. Preparation of Ru/NiFe-LDH catalyst

The XH-2008D ultrasonic reactor (Beijing Xinghao Science and Technology Development Co., Ltd) was used in the preparation process with 18 mm diameter titanium alloy probe and 25 kHz ultrasonic frequency. In the ultrasonic process, the temperature of the liquid storage tank was controlled at 25 ± 3 °C. 0.2 g NiFe-LDH powder was dispersed in 20 mL deionized water, then nitrogen was introduced as the protective gas, which was treated with an ultrasonic power of 100 W for 30 min to make the support uniformly dispersed. A certain amount of 0.01 mol/L \(\text{RuCl}_3\) solution was added according to the theoretical Ru loading amount, then the suspension was sonicated under different ultrasonic power (100, 300, 500 or 700 W) and time (30, 60, 90 or 120 min). After that, it was centrifuged and dried overnight in an oven at 60 °C and obtained the Ru NPs supported on NiFe-LDH, denoted as \(\text{Ru}/\text{NiFe-LDH}\). In our previous work, Li et al. [33] successfully prepared one-dimensional rod-like SBA-15 supported Ru nanorods with particle size of 2–6 nm by ultrasound-assisted ethylene glycol reduction method, and Ru NPs were embedded into one-dimensional channels of SBA-15. Ultrasonic waves played two important roles in the preparation of the catalyst. Firstly, the hydroxyls in ethylene glycol were dissociated into hydrogen radicals under the action of ultrasound to reduce \(\text{Ru}^{3+}\) to \(\text{Ru}^0\); Secondly, the microjet and bubble oscillation effect of ultrasound promoted Ru NPs to be embedded in the one-dimensional channel of SBA-15. In our previous work, Li et al. [33] used two-dimensional layered MgAl-LDH as support, the hydroxyls on the surface of MgAl-LDH were successfully dissociated into the hydrogen radicals under the action of ultrasound without adding any reducing agents and stabilizers to reduce \(\text{Pd}^{2+}\), thereby obtaining highly dispersed Pd NPs, which showed excellent catalytic performance in Suzuki reaction. However, some studies have indicated that LDH materials composed of transition metals (such as NiFe-LDH) generally showed more attractive catalytic performance due to their different band gap and band edge positions [19,34–35].

In order to synthesize efficient and environmentally friendly supported NPs catalysts, we designed and prepared ultrafine Ru NPs catalysts supported on NiFe-LDH by ultrasound-assisted reduction method without adding any stabilizers or chemical reductants. The surface hydroxyls of NiFe-LDH were excited into hydrogen radicals under ultrasonic cavitation for reducing \(\text{Ru}^{3+}\). The O-contained groups on NiFe-LDH played an important role in immobilizing Ru NPs, thus improving its catalytic stability. What is more, the effects of ultrasound preparation conditions and NEC hydrogenation reaction conditions were studied.

2.3. Catalyst characterization

NiFe-LDH support and Ru/NiFe-LDH catalysts were characterized by XRD, XPS, TEM, SEM, FT-IR, UV–Vis and N\textsubscript{2} adsorption–desorption, and the detailed process was described in the Supplementary Material.

2.4. Catalytic hydrogenation of NEC

The catalytic performance of Ru/NiFe-LDH catalysts was evaluated in NEC hydrogenation reaction. A stainless steel autoclave with magnetic stirring was used as the reactor of NEC hydrogenation. Its volume was 50 mL and the model was SLM-50, which was produced by Beijing Century Senlang Experimental Equipment Co., Ltd. A certain mass of catalyst \((\text{m}_{\text{Ru}} :\text{m}_{\text{NEC}} = 0.15 \text{wt%})\), 20 mL cyclohexane as solvent and 0.5 g NEC as reactant were added to the reactor. It was sealed and purged with high purity hydrogen to remove the air in the reaction system, then heated to the reaction temperature. When the temperature was reached, high purity hydrogen with a certain pressure was introduced and the change of hydrogen pressure with the reaction time was recorded. After the reaction for 80 min, the autoclave was cooled down to room temperature using a water bath, the pressure was then released. Then Nxis GC–MS-2030 of Shimadzu Company with the SH-Rtx-5 capillary column was used to analyze the liquid products. The calculation formula of mass hydrogen storage was described in our previous work [36]. The initial
hydrogenation rate was calculated based on the consumption of $H_2$ within 10 min of the initial reaction, that is, the number of $H_2$ moles consumed on Ru catalyst per unit time and per unit mass ($mol_{H_2}^{-1}min^{-1}g_{Ru}^{-1}$) \[18,37\].

2.5. Catalyst stability test

At the end of the each reaction, the catalyst was separated by centrifugation, and washed with cyclohexane, then applied to the next catalytic reaction.

3. Results and discussion

3.1. The effects of ultrasound-assisted reduction on the physicochemical properties of Ru/NiFe-LDH catalysts

3.1.1. XRD analysis

The crystal structures of the NiFe-LDH support and 5Ru/NiFe-LDH-y-60 synthesized under different ultrasonic power were analyzed by XRD, and the results were shown in Fig. 1. As can be seen from Fig. 1 (a), it appeared seven characteristic diffraction peaks, which were respectively attributed to the (003), (006), (009), (015), (018), (110) and (113) crystal planes of the NiFe-LDH (PDF#40–0215) layered material. According to Fig. 1 (b ~ e), the diffraction peaks of Ru NPs corresponding to 2θ of 38.8°, 42.2°, 43.8°, 58.2° and 69.6° (PDF#06–0663) were not observed, and it was probably caused by the fact that Ru NPs were well dispersed on the support and the particle size was too small to be detected by XRD \[38–39\]. With the increase of ultrasonic power from 100 W to 300 W, the characteristic diffraction peak intensity of NiFe-LDH decreased, but they did not change significantly with increasing from 300 W to 700 W. In addition, compared with NiFe-LDH, the position of the (003) diffraction peak was slightly offset to the lower angle after ultrasound with different power, indicating that the interlayer spacing increased.

3.1.2. $N_2$ adsorption-desorption analysis

In order to explore the effect of ultrasonic power on the pore structure of 5Ru/NiFe-LDH catalyst, $N_2$ physical adsorption and desorption were performed, and the results were shown in Fig. 2 and Table 1.

As for 5Ru/NiFe-LDH-y-60 catalysts, with the rise of ultrasonic power, the specific surface area and pore volume decreased, but the pore diameter increased gradually. It may be because the action of ultrasound promoted Ru NPs easily diffuse into the mesopore-like of NiFe-LDH, which reduced the pore volume and specific surface area. However, as for 5Ru/NiFe-LDH-A catalyst obtained by AA reduction, its specific surface area had no distinct change, which indicated that most of Ru NPs prepared via the chemical reduction process only were supported on the outer part of pores.

3.1.3. SEM-EDS analysis

In order to investigate the morphology and composition of the catalyst, NiFe-LDH support and 5Ru/NiFe-LDH-300–60 sample were characterized by SEM-EDS in Fig. 3. From Fig. 3 (a), there were many small nanosheet particles stacked together and formed intergranular mesopores, which was characteristics of most clay hydroxylate materials \[40\]. As can be known from Fig. 3 (b) that NiFe-LDH support was mainly composed of the elements C, O, Fe and Ni. In addition, the mole

| Sample                  | $S_{\text{total}}$ (m$^2$/g) | $V_{\text{total}}$ (cm$^3$/g) | $D_{\text{BJH}}$ (nm) |
|------------------------|-------------------------------|-------------------------------|------------------------|
| NiFe-LDH               | 244                           | 3.36                          | 6.23                   |
| 5Ru/NiFe-LDH-100–60    | 235                           | 3.24                          | 3.43                   |
| 5Ru/NiFe-LDH-300–60    | 226                           | 3.23                          | 3.64                   |
| 5Ru/NiFe-LDH-500–60    | 215                           | 3.15                          | 3.95                   |
| 5Ru/NiFe-LDH-A         | 238                           | 3.23                          | 3.35                   |

$S_{\text{total}}$ calculated by BET method; $V_{\text{total}}$ and $D_{\text{BJH}}$ calculated by BJH method.

Fig. 2. (a) $N_2$ adsorption–desorption isotherms and (b) pore size distribution of catalysts.
ratio of Ni to Fe was 2.64, which was close to its theoretical ratio of 3. As for 5Ru/NiFe-LDH-300–60 catalyst, the Ru-mapping in Fig. 3 (f) further illustrated that Ru NPs were well dispersed on the support.

3.1.4. XPS analysis

XPS was used to analyze the elemental valence of 5Ru/NiFe-LDH-300–60 catalyst, as shown in Fig. 4.

Since the peaks of Ru 3d overlapped with the peaks of C 1 s at about 284.0 eV and were masked, the Ru 3p signal was selected instead of the Ru 3d signal. As shown in Fig. 4 (a), the peaks appeared at 484.3 eV and 462.1 eV, which were ascribed to Ru3p1/2 and Ru3p3/2 of Ru0, respectively. This proved that the ruthenium precursor was successfully supported on the NiFe-LDH support and reduced to Ru0 by the hydrogen radicals excited from the hydroxyl group on the support under the action of ultrasonic cavitation [33]. The other two peaks at 486.2 eV and 464.1 eV ascribed to Ru3p1/2 and Ru3p3/2 of the oxidized from of ruthenium (Ruδ+), respectively [41–42]. The formation of oxidized ruthenium might be result from the partial oxidation of ultrafine Ru NPs during XPS testing and the interaction of Ru NPs with O-contained groups on NiFe-LDH surface [43]. From Fig. 4 (b), two peaks appeared at 855.6 eV and 873.4 eV, which corresponded to 2p3/2 and 2p1/2 of Ni2+ [44]. From Fig. 4 (c), there were two peaks at 712.7 eV and 726.3 eV, which ascribed to 2p3/2 and 2p1/2 of Fe3+ [45].

3.1.5. TEM analysis

The distribution and particle size of Ru NPs on the support were analyzed by TEM, and the results were shown in Fig. 5.

From Fig. 5, Ru NPs were small spherical and uniformly dispersed on NiFe-LDH support. As for 5Ru/NiFe-LDH-300–60 catalyst, the Ru NPs size distribution was 0.78 ~ 2.20 nm, and its average particle size was mainly concentrated in 1.26 nm. When the ultrasonic power increased to 700 W, the Ru NPs average particle size increased to 1.90 nm. However, as for 5Ru/NiFe-LDH-A catalyst prepared by AA reduction, the Ru NPs average particle size was larger (2.34 nm). The Ru NPs lattice fringes on 5Ru/NiFe-LDH-300–60 catalyst prepared by the ultrasound-assisted reduction method can be seen according to HRTEM (Fig. 5 (b)). The lattice fringe spacing was 0.205 nm, which was attributed to (1 0 1) crystal plane of Ru [46], and it further indicated that Ru3+ was reduced to Ru0.

3.1.6. FT-IR analysis

In order to study the changes of functional groups on 5Ru/NiFe-LDH catalyst, they were characterized by FT-IR, which were shown in Fig. 6.

As shown in Fig. 6 (a) and (b), compared with NiFe-LDH support, the peaks of 5Ru/NiFe-LDH-A catalyst had no obvious changes. For NiFe-LDH, the peak at 3442 cm⁻¹ was ascribed to the stretching vibration peak of the hydroxyl groups on the layer and interlayer water molecules [47]. However, the hydroxyls peak position of 5Ru/NiFe-LDH-300–60 obtained by ultrasound-assisted reduction moved to the lower
wavenumber. This may be because ultrasonic wave can promote the complexation of Ru NPs with the hydroxyls on the surface of NiFe-LDH support, and enhance the interaction between them. The peak near the wavenumber of 1637 cm$^{-1}$ was ascribed to the flexural vibration of hydroxyls on the layer. This corresponding peak of 5Ru/NiFe-LDH-300–60 also moved to the lower wavenumber, and it may be due to the fact that Ru$^0$ was immobilized to the NiFe-LDH support through Ru–O coordination effect, which caused the electron cloud of the O surface shifted to Ru and reduced the affinity of O to H. The peak near the wavenumber of 1359 cm$^{-1}$ belonged to the anti-symmetric stretching peak of CO$_3^{2-}$, and that at the wavenumber of 761 cm$^{-1}$ belonged to the interaction between CO$_3^{2-}$ and NiFe-LDH layer [48]. After ultrasound-assisted reduction, the peak intensity at 1359 cm$^{-1}$ decreased, which may be caused by the decrease of the number of CO$_3^{2-}$ in the interlayer during ultrasound-assisted reduction. In addition, the peak position at 761 cm$^{-1}$ shifted to the lower wavenumber. This may be caused by the increase of the interlayer spacing in NiFe-LDH after ultrasound, which reduced the interaction between CO$_3^{2-}$ and the layers.

3.2. Mechanism of ultrasound-assisted reduction

To determine the reducing hydrogen radicals coming from the water or the NiFe-LDH support, 30 mL 0.15 mmol/L RuCl$_3$ aqueous solution without NiFe-LDH support was sonicated at 300 W, and the
concentration change of Ru$^{3+}$ in the solution was monitored by UV–Vis, as shown in Fig. 7. The characteristic absorption peak of Ru$^{3+}$ at 307 nm [49] did not change after ultrasound at 300 W for 4 h, which indicated that it was not enough to excite water to generate enough hydrogen radicals to reduce Ru$^{3+}$ under 300 W ultrasonic power. So it was further determined that the reducing hydrogen radicals came from the hydroxyl groups on NiFe-LDH support.

The mechanism of Ru/NiFe-LDH catalyst prepared by the ultrasound-assisted reduction method was shown in Fig. 8.

\[
\text{Ni}_2\text{Fe}_4\text{CO}_3\text{-LDH} \xrightarrow{\text{Ultrasound}} \text{H} + \left[ \begin{array}{c} \text{Ni(OH)} \\ \text{Fe(OH)} \end{array} \right]
\]

The hydroxyl groups on NiFe-LDH were excited into highly reducing hydrogen radicals under the effect of ultrasonic cavitation [33]. Subsequently, hydrogen radicals reduced Ru$^{3+}$ to Ru$^0$. Meanwhile, Ru$^0$ was immobilized to the NiFe-LDH support through Ru–O coordination effect, then ultrafine supported Ru nanocatalyst was successfully prepared, which had higher catalytic stability in NEC hydrogenation.

3.3. Catalytic performance for NEC hydrogenation

3.3.1. The effects of catalyst preparation conditions

As for xRu/NiFe-LDH-x catalysts, the influences of the preparation conditions, including Ru loading amount, ultrasonic power and ultrasonic time on the mass hydrogen storage capacity in NEC hydrogenation were studied, which were shown in Fig. 9. The corresponding initial hydrogenation rate were listed in Table S1.

As can be seen from Fig. 9, the mass hydrogen storage capacity increased with the reaction time until the reaction equilibrium was reached. In Fig. 9 (a) and Table S1, with the rise of ultrasonic power, NEC hydrogenation rate firstly increased and then decreased. When the ultrasonic power was 300 W, the hydrogenation rate was the fastest. And after the NEC hydrogenation reaction of 40 min, the mass hydrogen storage capacity remained unchanged. In Fig. 9 (b), the influence of ultrasonic time on hydrogenation rate was similar to that of ultrasonic power. When the ultrasonic time was 60 min, the hydrogenation rate was the fastest. Therefore, the optimal preparation conditions of the catalyst were the ultrasonic power of 300 W and the ultrasonic time of 60 min. The 100% conversion of NEC, 97.64% yield of 12H-NEC and 5.75 wt% mass hydrogen storage capacity were reached over 5Ru/NiFe-LDH-300-60 catalyst.

![Fig. 7. UV–Vis spectra of RuCl$_3$ aqueous solution with 300 W ultrasonic power.](image)

![Fig. 8. Mechanism diagram of Ru/NiFe-LDH prepared by ultrasound-assisted reduction method.](image)

![Fig. 9. Hydrogenation curves over xRu/NiFe-LDH-y-z catalysts prepared under different conditions (a) ultrasonic power, (b) ultrasonic time and (c) Ru loading amount (6 MPa, 120 °C, 0.15 wt%).](image)
In the NEC hydrogenation reaction, the addition amount of catalyst remained $m_{\text{Ru}}/m_{\text{NEC}} = 0.15$ wt%. The influence of Ru loading amount on NEC hydrogenation reaction was studied, which was shown in Fig. 9 (c). It can be seen that the hydrogenation rate was slow when the loading amount of Ru was too low (1 wt%) or too high (10 wt%). This may be due to the relatively long distance between the active sites, the contact frequency between the active sites and the reactant was limited when the Ru loading amount was too low. In addition, when the Ru loading amount was too high, the Ru NPs dispersion and Ru$^{3+}$ reduction degree was low. When the Ru loading amount was 5 wt%, it had the highest hydrogenation activity. Besides, as a blank control experiment, it showed no catalytic activity in NEC hydrogenation reaction over NiFe-LDH-300–60 catalyst.

3.3.2. The effects of NEC hydrogenation reaction conditions

The influences of reaction conditions on the mass hydrogen storage capacity in NEC hydrogenation reaction were investigated, including reaction temperature and hydrogen pressure, which were shown in Fig. 10, Table S2 and Table S3. As can be seen from Fig. 10 (a), the higher the reaction temperature, the faster NEC hydrogenation rate, the shorter time to reach the reaction equilibrium. When the reaction temperature was 130 °C, the reaction equilibrium was reached after 30 min, and then the hydrogen storage capacity remained unchanged. As shown in Table S2, after the NEC hydrogenation reaction of 80 min, the yield of 12H-NEC firstly increased, then decreased with the rise of temperature, which probably due to the influence of reaction temperature and the solubility of hydrogen in the liquid phase. At the reaction temperature of 110 °C, 98.88% yield of 12H-NEC and 5.77 wt% mass hydrogen storage capacity were reached, indicating that the Ru/NiFe-LDH catalyst prepared by ultrasound-assisted reduction method had high catalytic activity. From Fig. 10 (b), when the hydrogen pressure increased from 4 MPa to 6 MPa, the hydrogenation rate of NEC was significantly accelerated. However, when the hydrogen pressure continued to increase to 7 MPa, it had little effect on the hydrogenation rate. However, as shown in Table S3, when the hydrogen pressure was 7 MPa, the yield of 12H-NEC and its mass hydrogen storage capacity were the highest, reaching 99.30% and 5.78 wt%, respectively. And it was because the high pressure was conducive to the forward movement of the NEC hydrogenation reaction.

3.3.3. Comparative experiments over Ru-based catalysts prepared by different method

The TG analysis of NiFe-LDH was shown in Fig. S2. It can be seen that when the temperature was above 200 °C, NiFe-LDH began to decompose. However, hydrogen reduction method usually needs to be carried out at about 400 °C, it may destroy the structure of the NiFe-LDH support. Therefore, the chemical reduction method was used as the comparative experiment. In order to compare the catalytic performance of 5Ru/NiFe-LDH catalysts prepared by ultrasound-assisted method and chemical reduction method, and commercial 5Ru/C catalyst in NEC hydrogenation reaction, the results of mass hydrogen storage capacity under the same hydrogenation reaction conditions were shown in Fig. 11 and Table S4. From Fig. 11, in NEC hydrogenation reaction, the following list was ordered from highest catalytic activity to lowest: 5Ru/NiFe-LDH-300–60 > 5Ru/C > 5Ru/NiFe-LDH-B > 5Ru/NiFe-LDH-A. However, as can be seen from Table S4, the hydrogen storage capacity over 5Ru/NiFe-LDH-300–60 catalyst was the highest (5.77 wt%), while the hydrogen storage capacity over 5Ru/NiFe-LDH-A, 5Ru/NiFe-LDH-B and 5Ru/C catalysts was almost about 5.51 wt%. Therefore, through the comparative experiments over different catalysts, it was further demonstrated that 5Ru/NiFe-LDH-300–60 catalyst prepared by ultrasound-assisted reduction method showed excellent catalytic performance.

![Fig. 10.](attachment:fig10.png) Hydrogenation curves over 5Ru/NiFe-LDH-300–60 catalyst under different (a) temperatures and (b) hydrogen pressures ((a) 6 MPa, 0.15 wt%, (b) 120 °C, 0.15 wt%).

![Fig. 11.](attachment:fig11.png) Hydrogenation curves over different catalysts (6 MPa, 110 °C, 0.15 wt%).
3.3.4. Catalyst stability in NEC hydrogenation reaction

The catalyst stability is one of the important evaluation indexes, so the stability of 5Ru/NiFe-LDH-300-60 prepared by ultrasound-assisted reduction method and 5Ru/NiFe-LDH-A prepared by chemical reduction method in NEC hydrogenation reaction were studied, which was shown in Fig. 12.

The yield of 12H-NEC remained above 90% over 5Ru/NiFe-LDH-300-60 catalyst after seven recycle use. However, for 5Ru/NiFe-LDH-A catalyst, the yield of 12H-NEC decreased significantly during recycle use, which was only 28.11% after eight cycles. In addition, our previous

Fig. 12. Stability experiments in NEC hydrogenation: (a) 5Ru/NiFe-LDH-300-60, (b) 5Ru/NiFe-LDH-A (6 MPa, 110 °C, 0.15 wt%).

Fig. 13. TEM images (a) and Ru NPs size distribution (b) of 5Ru/NiFe-LDH-300-60 catalyst after eight recycle use.

Fig. 14. (a) relationship between ln (Pf/P0) and time in NEC hydrogenation at 100 ~ 130 °C over 5Ru/NiFe-LDH-300-60 catalyst, (b) relationship of lnk ~ 1/T in NEC hydrogenation.
work also investigated the stability of commercial 5Ru/C catalyst and found that the yield of 12H-NEC was only 52.1% after eight cycles when the reaction temperature was 120 °C [36]. The above results showed the superiority of 5Ru/NiFe-LDH-300–60 catalyst prepared by ultrasound-assisted reduction method, and it was attributed to the fact that ultrasound was beneficial for Ru NPs to enter the mesopore-like NiFe-LDH and the complexion effect of Ru NPs with O-contained groups on NiFe-LDH.

The 5Ru/NiFe-LDH-300–60 catalyst after eight recycle use in NEC hydrogenation was analyzed by TEM in Fig. 13. It can be seen that after eight recycle use, the average size of Ru NPs increased from 1.26 nm to 2.46 nm. Therefore, the agglomeration of Ru NPs may be the main reason for the decrease of catalytic activity.

3.3.5. The kinetics study of NEC hydrogenation

It is proved that the apparent reaction rate of NEC concentration is zero-order and that of hydrogen pressure is first-order in NEC hydrogenation [50–52]. The hydrogenation kinetic model can be expressed as:

$$r = -\frac{dc}{dt} = kP_H$$

$$\ln k = -\frac{E_a}{RT} + \ln k_0$$

The kinetics of 5Ru/NiFe-LDH-300–60 catalyst in NEC hydrogenation was studied according to the above model. In (Pc/P0) changed with time, and its relation was shown in Fig. 14 (a). It can be seen that all of them presented a linear relationship, and the slope was the apparent reaction rate constant k. According to the linear relationship of $\ln k \sim 1/T$ (Fig. 14 (b)), the apparent activation energy (Ea) of the reaction was calculated only 25.15 kJ/mol by the slope.

The Ea of NEC hydrogenation reaction over 5Ru/NiFe-LDH-300–60 and the reported catalysts were summarized in Table 2. Compared with other catalysts, 5Ru/NiFe-LDH-300–60 prepared by ultrasound-assisted reduction method had the lowest apparent activation energy and could react at lower temperature and catalyst dosage. Therefore, not only the preparation method of 5Ru/NiFe-LDH-300–60 catalyst was simple and green, but also it showed high activity and stability in the hydrogenation of NEC.

### 4. Conclusion

The plentiful hydroxyls on NiFe-LDH were excited into hydrogen radicals (•H) under the action of ultrasound for reducing Ru3+ to Ru0 without adding any chemical reductants and stabilizers. The layered O-contained groups played an important role in immobilizing Ru NPs, which enhanced the interaction between NiFe-LDH support and Ru NPs, thereby obtaining ultrafine Ru NPs supported on NiFe-LDH with higher stability in NEC hydrogenation. The 5Ru/NiFe-LDH-300–60 catalyst prepared by ultrasound-assisted reduction method showed outstanding catalytic performance. When the reaction conditions were 110 °C, 6 MPa and mRu/mNEC = 0.15 wt%, the yield of 12H-NEC and mass hydrogen storage capacity can reach 98.88% and 5.77 wt%, respectively, which were higher than other catalysts prepared by chemical reduction method and commercial 5Ru/C. The yield of 12H-NEC remained above 90% after seven recycle use, and the apparent activation energy was only 25.15 kJ/mol, which was the lowest in the reported literatures about NEC hydrogenation reaction. In general, the ultrasound-assisted reduction method was simple and environmentally friendly without any chemical reductants and stabilizers, which provided a new idea for the preparation of ultrafine nanocatalysts with high dispersion and catalytic activity.

### References

[1] T. He, P. Pachfule, H. Wu, Q. Xu, P. Chen, Hydrogen carriers, Nat. Rev. Mater. 1 (2016) 16059–16075, https://doi.org/10.1038/natrevmats.2016.59.

[2] L. Schlaphach, A. Züttel, Hydrogen-storage materials for mobile applications, Nature 414 (6861) (2001) 353–358, https://doi.org/10.1038/35104634.

[3] Q.-L. Zhu, Q. Xu, Liquid organic and inorganic chemical hydrides for high-capacity hydrogen storage, Energy Environ. Sci. 8 (2) (2015) 478–512, https://doi.org/10.1039/C4EE03608B.

[4] J. Zheng, X. Liu, P. Xu, P. Liu, Y. Zhao, J. Yang, Development of high pressure gaseous hydrogen storage technologies, Int. J. Hydrogen Energ. 37 (1) (2012) 1046–1057, https://doi.org/10.1016/j.ijhydene.2011.02.125.

[5] H. Wang, X. Zhou, M. Ouyang, Efficiency analysis of novel liquid organic hydrogen carrier technology and comparison with high pressure storage pathway, Int. J. Hydrogen Energ. 41 (40) (2016) 18062–18071, https://doi.org/10.1016/j.ijhydene.2016.08.002.

[6] B. Sakintuna, F. Lamari-Darkim, M. Hirscher, Metal hydride materials for solid hydrogen storage: A review, Int. J. Hydrogen Energ. 32 (9) (2007) 1121–1140, https://doi.org/10.1016/j.ijhydene.2006.11.022.

[7] A.M. Abdalla, S. Hossain, O.B. Nifinthy, A.T. Azad, M. Dawood, A.K. Azad, Hydrogen production, storage, transportation and key challenges with application: A review, Energ. Convers. Manage. 165 (2018) 602–627, https://doi.org/10.1016/j.enconman.2018.03.086.

[8] F. Zhang, P. Zhao, M. Niu, J. Maddy, The survey of key technologies in hydrogen energy storage, Int. J. Hydrogen Energ. 41 (33) (2016) 14535–14552, https://doi.org/10.1016/j.ijhydene.2016.05.293.

[9] A. Züttel, Materials for hydrogen storage, Mater. Today 6 (9) (2003) 24–33, https://doi.org/10.1016/S1369-7021(03)00552-2.
K.M. Eblagon, K. Tam, K.M.K. Yu, S.C.E. Tsang, Comparative study of catalytic hydrogenation of 9-ethylcarbazole for hydrogen storage over noble metal surfaces, J. Phys. Chem. C 116 (13) (2012) 4721–4729, https://doi.org/10.1021/jp212269q.

K.M. Eblagon, D. Rentsch, O. Friedrichs, A. Remhof, A. Zuetell, A.J. Ramirez-Cuesta, S.C. Tsang, Hydrogenation of 9-ethylcarbazole as a prototype of a liquid hydrogen carrier, Int. J. Hydrogen Energy 35 (20) (2010) 11609–11621, https://doi.org/10.1016/j.ijhydene.2010.04.118.

Y.I. Choi, B.S. Shin, S.K. Kwak, K.S. Kang, C.W. Yoon, J.W. Kang, Thermodynamic efficiencies of hydrogen storage processes using carbazole-based compounds, Int. J. Hydrogen Energy 41 (22) (2016) 9367–9373, https://doi.org/10.1016/j.ijhydene.2016.04.118.

K.-R. Kim, K.-J. Kim, S.-C. Kim, Hydrogenation of 9-ethylcarbazole as a prototype of a liquid hydrogen carrier, Int. J. Hydrogen Energ. 35 (20) (2010) 11609–11621, https://doi.org/10.1016/j.ijhydene.2010.04.118.

F. Su, L. Lv, F.Y. Lee, T. Liu, A.I. Cooper, X.S. Zhao, Thermally reduced ruthenium ultrafine supported Pd nanocatalysts by hydroxyl groups on the surfaces of layered double hydroxides and their catalytic properties, Ultrason. Sonochem. 60 (2020) 104764–104775, https://doi.org/10.1016/j.ultsonch.2020.104746.

J.F. Ma, J.F. Ding, L.M. Yu, L.Y. Li, Y. Kong, S. Komarneni, BiOCl dispersed on NiFe-LDH leads to enhanced photo-degradation of Rhodamine B dye, Appl. Clay Sci. 109 (2015) 76–82, https://doi.org/10.1016/j.claysci.2015.02.009.

M.G. Yang, T.L. Feng, Y.X. Chen, J.J. Liu, X.H. Zhao, B. Yang, Synchronously integration of Co, Fe-dual-metal doping in RuO2 and CDs for boosted water splitting performances, Nano Energy 58 (2019) 116578–116665, https://doi.org/10.1016/j.nanoen.2019.116578.

K. Qadir, S.H. Joo, B.S. Mun, D.R. Butcher, J.R. Renzas, F. Akoly, Z. Liu, G. A. Somorjai, J.Y. Park, Intrinsic relationship between catalytic activity of CD oxidation on nickel nanoparticles and the catalytic reaction mechanism of Ni-CD oxidation, Nano Lett. 12 (11) (2012) 5761–5768, https://doi.org/10.1021/nl303072d.

B. Wang, T.Y. Chang, X. Gong, Z. Jiang, S. Yang, Y.-S. Chen, T. Fang, One-port synthesis of Au/Pd/shell nanoparticles supported on reduced graphene oxide with enhanced dehydrogenation performance for dodecahydro-N-ethylcarbazole, ACS Sustainable Chem. Eng. 7 (1) (2019) 1766–1768, https://doi.org/10.1021/acssuschemeng.8b05002.

J. Shen, P. Zhang, R.S. Xie, L. Chen, M.T. Li, J.P. Li, B.O. Ji, Y.Z. Hu, J.I. Li, L. X. Zhang, J.P. Wu, X.L. Liu, Enhanced self-supported NiFe-Layered double hydroxides/reduced graphene oxide nanohybrids based on solid phase exfoliation strategy as an excellent electrocatalyst for the oxygen evolution reaction, ACS Appl. Mater. Interfaces 11 (2019) 13545–13556, https://doi.org/10.1021/acsami.9b10696.

S. Nayak, L. Mohapatra, K. Parida, Visible light-driven n-CuN/ NiFe-LDH composite photocatalyst with enhanced photocatalytic activity towards water oxidation and reduction reaction, J. Mater. Chem. A 3 (36) (2015) 18622–18635, https://doi.org/10.1039/C5TA00826D.

L. Jiang, J. Chen, Y. An, D. Han, S. Chang, Y. Liu, R. Yang, Enhanced electrochemical performance by nickel-iron layered double hydroxides (LDH) coated on Fe3O4 as a cathode catalyst for single-chamber microbial fuel cells, Sci. Total Environ. 745 (2020) 141163, https://doi.org/10.1016/j.scitotenv.2020.141163.

J.A. Carrasco, R. Sanchís-Gual, A.-D. Silva, G. Abellán, E. Coronado, Influence of the interlayer space on the water oxidation performance in a family of surfacetant-intercalated layered double hydroxides, Chem. Mater. 31 (17) (2019) 6798–6807, https://doi.org/10.1021/acs.chemmater.9b01261.

I. Simakova, V. Demidova, I. Provyrin, D.Y. Murzin, A. Simakov, Development of polyol method for the synthesis of concentrated colloids of PVDF-stabilized Ru nanoparticles, Int. J. Nanotechnol. 13 (2016) 15–27, https://doi.org/10.1504/IJN.2016.074520.

X. Ye, Y. An, X. Xu, Kinetics of 9-ethylcarbazole hydrogenation over Raney-Ni catalyst for hydrogen storage, J. Alloy. Compd. 509 (1) (2011) 152–156, https://doi.org/10.1016/j.jallcom.2011.02.048.

C. Wan, Y. An, F. Chen, D. Cheng, F. Wu, G. Xu, Kinetics of N-ethylcarbazole hydrogenation over a supported Ru catalyst for hydrogen storage, Int. J. Hydrogen Energy 38 (17) (2013) 7065–7069, https://doi.org/10.1016/j.ijhydene.2013.04.022.

F. Su, Y. An, L. Lei, F. Wu, J. Zhu, X. Zhang, Identification of the starting reaction position in the hydrogenation of N-ethylcarbazole over Raney-Ni, J. Energy Chem. 24 (2) (2015) 219–224, https://doi.org/10.1016/j.jenergy.2015.03.004.

C. Wan, Y. An, G. Xu, Kinetics of the catalytic hydrogenation of N-ethylcarbazole over ruthenium catalyst, Int. J. Hydrogen Energy 37 (17) (2012) 13092–13096, https://doi.org/10.1016/j.ijhydene.2012.04.123.

Y. Qin, J. Shi, X. Bai, Preparing ultra-stable Ru nanoparticles supported on partially graphitized carbon biomass via microwave-assisted synthesis for reduction for hydrogen storage of N-ethylcarbazole, Int. J. Hydrogen Energy 46 (50) (2021) 25543–25554, https://doi.org/10.1016/j.ijhydene.2021.05.074.

S.-S. Kim, S. Kim, B. Kwon, J. Kim, Plasma catalytic methane conversion over sol-gel derived Ru/TiO2 catalyst in a dielectric-barrier discharge reactor, Catal. Commun. 8 (12) (2007) 2204–2207, https://doi.org/10.1016/j.catcom.2007.04.029.

S.-S. Kim, B. Kwon, J. Kim, Plasma catalytic methane conversion over sol-gel derived Ru/TiO2 catalyst in a dielectric-barrier discharge reactor, Catal. Commun. 8 (12) (2007) 2204–2207, https://doi.org/10.1016/j.catcom.2007.04.029.