Ultrasonic-assisted preparation of ultrafine Pd nanocatalysts loaded on Cl⁻-intercalated MgAl layered double hydroxides for the catalytic dehydrogenation of dodecahydro-N-ethylcarbazole

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ABSTRACT

N-ethylcarbazole/dodecahydro-N-ethylcarbazole (NEC/H12-NEC) is a promising LOHC, and the development of a catalyst with high activity and stability is the key to realizing its reversible hydrogen storage process. In this paper, ultrafine Pd nanocrystalline catalysts (Pd/LDHs-us) supported on Cl⁻-intercalated MgAl LDHs were prepared by a simple ultrasonic-assisted reduction method and applied in the dehydrogenation of 12H-NEC. In the process of ultrasonic-assisted reduction, the instantaneous high temperature generated by cavitation decomposed part of the CO₃²⁻ in LDHs interlayer, and promoted PdCl₂ to enter the interlayer and become new intercalated ions. At the same time, hydroxyl groups on the surface of LDHs were excited to generate hydrogen radicals (•H) with strong reducibility, which reduced PdCl₂ to Pd nanoparticles (PdNPs) in situ. The remaining Cl⁻ ions continued to exist in the interlayer as intercalated ions. The agglomeration of PdNPs was effectively inhibited, and the average particle size was 1.8 nm, which was uniformly dispersed on LDHs, which improved the catalytic activity of Pd/LDHs-us. The coordination between PdNPs and oxygen in the hydroxyl groups on the surface of LDHs improved its catalytic stability. Using Pd/LDHs-us catalyst, the conversion rate of H12-NEC was 100.0 %, and the dehydrogenation efficiency was 99.3 % at 180 °C. When the reaction temperature drops to 170 °C, the dehydrogenation efficiency can still reach 94.6 %, showing excellent catalytic performance. The study of dehydrogenation kinetics shows that the apparent activation energy of Pd/LDHs-us catalyst is only 90.97 kJ/mol. This provides a new method and idea for the preparation of efficient dehydrogenation catalysts in the future.

1. Introduction

In recent years, with the continuous growth of the population and development of social industries, the global demand for energy has increased [1]. However, coal, natural gas, oil and other fossil energy are the most used at present [2]. Their extensive use has led to energy shortages and environmental pollution problems, and has brought great challenges to the sustainable development of the global economy [3]. It is becoming increasingly urgent to replace fossil energy with low-carbon and clean renewable energy [4,5].

Hydrogen energy is an ideal energy source that can be stored and transferred in a usable way. Hydrogen has an extremely high energy density, typically between 120 MJ/kg (LHV) and 142 MJ/kg (HHV), which is 2–3 times that of other fossil fuels [6,7]. The combustion of hydrogen only produces water, which will not cause any pollution to the environment and is the cleanest fuel [8].

The production, storage, transportation and application of hydrogen are the main problems that need to be solved for the use of hydrogen energy [9–13]. At present, the common methods of hydrogen storage include high-pressure gaseous hydrogen storage [14], low-temperature liquefied hydrogen storage [15], metal alloy hydrogen storage [16], physical adsorption hydrogen storage [17] and liquid organic hydrogen carrier hydrogen storage [18]. To meet the requirement of 40 kg/m³ hydrogen storage volume density, high-pressure gaseous hydrogen storage needs to reach more than 70 MPa, and there are many safety problems in operation [19]. Hydrogen liquefaction requires an extremely low temperature of −253 °C, and the required energy is approximately 35 % of the energy released by the combustion of...
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hydrogen storage also needs to be completed below the usually used in aerospace engineering [20]. Metal alloy hydrogen storage has the highest volumetric hydrogen storage density, but it also requires a high dehydrogenation temperature. Physical adsorption hydrogen storage also needs to be completed below 70 °C, which is difficult to achieve industrially [12].

In general, unsaturated organics are used as liquid organic hydrogen carriers (LOHCs) to store and release hydrogen through hydrogenation and dehydrogenation reactions [21]. LOHCs with a higher flash point are safer and more stable than gasoline. LOHCs have the characteristics of high hydrogen storage density, easy long-distance transportation, use of existing fuel infrastructure, etc., and are more cost-effective [22].

LOHCs mainly include liquid aromatic compounds such as benzene, toluene, biphenyl, benzyl toluene, dibenzyl toluene and naphthalene; small molecular organic compounds such as formic acid and methanol; nitrogen-containing heterocyclic compounds such as alkyl pyridine, alkyl indole and alkyl carbazole; and organoboron-nitrogen unsaturated organic compounds [22–26]. Since the hydrogenation reaction is usually completed in a factory, the production equipment and process are similar to the hydrogenation process of the current product, which is relatively easy to realize. The dehydrogenation reaction is completed in the car, usually under normal pressure, and the dehydrogenation temperature is preferably lower than the working temperature of the solid fuel cell to maximize the use of waste heat. Therefore, the development of highly active catalysts to reduce temperature and improve dehydrogenation rate is of great significance to the application of LOHCs. The hydrogen storage capacity of NEC is 5.8 wt%, which is higher than the US Department of Energy requirement (5.5 wt%), and is considered as a promising LOHCs [27].

H12-NEC dehydrogenation catalysts are mainly based on Pd-based catalysts in related research. Yang [28] used Al2O3 as the carrier to prepare the Pd/Al2O3 catalyst by the traditional hydrogen reduction method. At 180°C, the amount of hydrogen released in H12-NEC dehydrogenation can reach 3.30 wt% in 1 h, and the dehydrogenation can be complete in 4 h. Sotoodeh [29] synthesized Pd/SiO2 catalyst prepared by incipient wetness and H2 reduction method and found that the catalytic activity in H12-NEC dehydrogenation and selectivity of NEC depended on the particle size of the PdNPs. Feng [30] studied the dehydrogenation of H12-NEC over Pd-based catalysts supported on NEC. Catalyst preparation was carried out in the XH-2008D ultrasonic oven. The prepared catalyst was denoted as xPd/LDHs-us-P-t, where x indicates the mass loading amount of Pd (wt.%), P means ultrasonic power (W), and t means ultrasonic time (min).

To prepare highly dispersed nanocatalysts, except for the selection of the carrier, the appropriate preparation method is also key. The most commonly used method for preparing loaded nanocatalysts is the traditional chemical reduction method, in which stabilizers are usually used. However, stabilizers may be adsorbed on the active surface, and removing the stabilizer will not only destroy the structure and morphology of nanoparticles, but also produce pollution such as wastewater, exhaust gas and toxic byproducts [35,36]. Therefore, other new and green reduction methods have also emerged and been applied, such as thermal reduction [37], plasma reduction [38], microwave-assisted reduction [39,40] and ultrasonic-assisted reduction [41,42]. Among them, the ultrasonic-assisted method is simple and easy to control in operation, which has potential application prospects in industry. The formation, growth and collapse of cavitation bubbles occur in liquid media under the action of ultrasound. The collapse of cavitation bubbles will produce high temperature, high pressure and so on of special physical and chemical changes, which provides favorable conditions for the rapid synthesis of nanomaterials with uniform particle size distributions. Liu [43] prepared RuNPs loaded on NiFe-LDHs by ultrasonic-assisted reduction, showing excellent catalytic activity in NEC hydrogenation. The surface hydroxyg groups of the carrier were excited into •OH under ultrasound to reduce RuCl4. The O-containing groups on NiFe-LDHs can anchor RuNPs, thereby enhancing its catalytic stability.

In this paper, Pd nanocatalysts supported on Cl–intercalated LDHs-w (Pd/LDHs-us) were prepared by ultrasonic-assisted reduction. First, MgAl–CO3 LDHs was calcined to remove interlayer water and a small amount of interlayer anion CO32– to prepare dehydrated layered double hydroxides (LDHs-w). Then, under the action of ultrasound, the interlayer water of LDHs-w was restored, and at the same time, it promoted PdCl2 to replace CO32– and intercalated into the interlayer of LDHs. Therefore, PdCl2 was reduced to Pd0 in situ by the strong reduction of •OH generated by ultrasonic excitation of surface hydroxyl groups. The remaining Cl– ions continued to exist in the interlayer as intercalated ions. The catalytic performance of Pd/LDHs-us prepared by different ultrasonic conditions was investigated in the dehydrogenation of H12-NEC.

2. Experimental

2.1. Material

Materials used in the experiment were shown in the Supplementary Material.

2.2. Preparation of catalysts

For the preparation of MgAl–CO3 LDHs, the co-precipitation method was used, and the specific preparation process was shown in the Supplementary Material. Then, the dehydrated LDHs was obtained by calcining the prepared LDHs at 300°C for 2 h, which was recorded as LDHs-w.

Catalyst preparation was carried out in the XH-2008D ultrasonic reactor, which was provided by Beijing Xianghu Science & Technology Development Co., Ltd. The diameter of titanium alloy probe was 18 mm and the ultrasonic frequency was 25 kHz. 0.2 g LDHs-w powder was added to 30 mL H2O, which was treated by ultrasound with the power of 100 W and time of 30 min to make sure it dispersed evenly. According to the theoretical loading amount of Pd in the catalyst, a certain amount of 0.01 mol/L Na2PdCl4 was added and sonicated at a certain ultrasonic power (100, 200, 300 or 400 W) within a certain amount of time (20, 40, 60 or 80 min). Then it was washed three times and dried overnight in an oven. The prepared catalyst was denoted as xPd/LDHs-us-P-t, where x means the mass loading amount of Pd (wt.%), P means ultrasonic power (W) and t means ultrasonic time (min). Pd/LDHs-us-P represents the catalyst prepared at different powers (100 W, 200 W, 300 W, 400 W) with ultrasonic time of 80 min, and Pd loading amount of 2.5 wt%. Pd/LDHs-us represents the optimal catalyst prepared under the conditions of ultrasonic power of 200 W, time of 80 min and Pd loading amount of 2.5 wt%. According to the results of ICP characterization, the actual weight ratio of Pd is 2.2 wt%.

To compare the reduction methods, the catalyst with Pd loading...
amount of 2.5 wt% was prepared by NaBH₄ conventional chemical reduction method. First, 0.2 g LDHs-w was evenly dispersed in 30 mL H₂O, and then 4.75 mL 0.01 M Na₂PdCl₄ was added and stirred for 12 h, in which NaBH₄ solution was added for reduction. Subsequently, it was centrifuged, washed and dried to obtain Pd/LDHs-c.

2.3. Preparation of H12-NEC and catalytic dehydrogenation of H12-NEC

According to the literature [30], H12-NEC was prepared by hydrogenation of NEC using commercial Ru/Al₂O₃ as catalyst.

The Pd/LDHs catalysts were applied to the dehydrogenation of H12-NEC, and the detailed operation process and calculation method were described in the Supplementary Material.

2.4. Characterization

The Pd/LDHs catalysts were characterized by TG, XRD, FT-IR, SEM, TEM, HRTEM, SEM, N₂ adsorption-desorption, EDS, H₂ chemisorption and XPS. For test instrument models and characterization methods, please see the Supplementary Material.

3. Results and discussion

3.1. TG

In order to investigate the changes in intercalated anions and adsorbed water during ultrasonic-assisted reduction and conventional chemical reduction, LDHs-w, Pd/LDHs-us, and Pd/LDHs-c were analyzed by TG, as shown in Fig. 1.

In Fig. 1(a), all of three samples had three weight loss peaks, of which the second peak had the largest weight loss. Fig. 1(b) showed that the peak temperatures of LDHs-w, Pd/LDHs-us and Pd/LDHs-c corresponding to the second weight loss peak are 430.3°C, 418.6°C and 421.7°C, respectively. This peak was mainly due to the removal of the interlayer anions and the hydroxyl groups on the LDHs layer. The Mg²⁺ and Al³⁺ cations were converted into magnesium-aluminum oxides, resulting in the disappearance of the original layered structure. Because of the strongest affinity between CO₃²⁻ and the LDHs layer, the weight loss peak temperature of LDHs-w was the highest. Since cavitation by ultrasound could cause the in-situ reduction of PdCl₂ in the interlayer, which made part of Cl⁻ become intercalation ions and reduced the content of CO₃²⁻ in the interlayer, the weight loss peak temperature of Pd/LDHs-us was the lowest. A small amount of CO₃²⁻ was replaced in Pd/LDHs-c, which made its peak temperature intermediate. The first weight loss peak was from room temperature to 200°C, mainly caused by the process of removing interlayer water. Because the interlayer water of LDHs-w had been removed after calcination at 300°C, the weight loss was very low, attributed to a small amount of adsorbed water. Since CO₃²⁻ can form hydrogen bonds with interlayer water, but PdCl₂ and Cl⁻ cannot form hydrogen bonds with interlayer water, Pd/LDHs-us was easier to dehydrate than Pd/LDHs-c. The peak temperatures of Pd/LDHs-us and Pd/LDHs-c were 87.2°C and 102°C, respectively, which also indicated that ultrasound can promote PdCl₂ to enter the interlayer of LDHs and be reduced to PdNPs. In addition, compared with LDHs-w, both Pd/LDHs-us and Pd/LDHs-c showed a third weight loss peak at approximately 870°C. This was because PdNPs with a small particle size and good dispersion were easily oxidized to PdO on the surface. PdO was decomposed to Pd at 850-870°C [44]. The third weight loss peak was attributed to the decomposition of surface PdO.

3.2. XRD

In order to study the crystal structure changes of LDHs, LDHs-w and Pd/LDHs, XRD analysis were carried out, as shown in Fig. 2, and the corresponding calculated crystal cell parameters were shown in Table S1.

As shown in Fig. 2, for LDHs, it appeared characteristic diffraction peaks corresponding to the (003), (006), (009), (015), (018), (110) and (113) crystal planes, indicating that LDHs had R3m hexagonal lattice with rhombohedral space group symmetry. After calcination at 300°C, the characteristic diffraction peaks corresponding to LDHs in LDHs-w weakened but did not disappear, which indicated that its layered structure still existed, and the crystallinity decreased due to the removal of interlayer water molecules and a small amount of CO₃²⁻. For LDHs-w, the peak position of the (003) crystal plane was shifted from 11.65° to 13.32°, indicating that the removal of interlayer water molecules and a small amount of CO₃²⁻ led to a smaller LDHs-w layer spacing.

![Fig. 2. XRD patterns of samples (a) LDHs, (b) LDHs-w, (c) Pd/LDHs-us-100, (d) Pd/LDHs-us-200, (e) Pd/LDHs-us-300, (f) Pd/LDHs-us-400, (g) Pd/LDHs-c.](image-url)
For Pd/LDHs-us-P samples prepared by ultrasonic-assisted reduction under different powers, the peak positions of the (003) crystal plane shifted from 13.32° to 12.20°, 12.28°, 12.33°, 12.44°, respectively. The d(003) value increased from 6.6427 Å to 7.2493 Å, 7.2018 Å, 7.1754 Å and 7.1083 Å, respectively. Compared with the interlayer spacing of LDHs-w, the increase in interlayer spacing indicated the recovery and replacement of interlayer water and anions in Pd/LDHs-us-P [34]. When the ultrasonic power increased from 100 W to 400 W, the ability of PdCl$_2$ to replace the intercalation gradually increased, and the reduction degree of PdCl$_2$ decreased gradually, which resulted in less Cl intercalation so that the interlayer spacing gradually decreased. This was due to the fact that the PdCl$_2$ had a planar square structure, and the radius of Pd$^{2+}$ in the tetracoordinate compound was 0.075 nm [45], which was smaller than that of CO$_3^{2-}$ (0.164 nm). When PdCl$_2$ was intercalated in the LDHs interlayer, the plane of the ions was parallel to the layer, resulting in a decrease in the interlayer spacing. As for the Pd/LDHs-c prepared by chemical reduction method, the interlayer spacing was larger than that of the catalyst prepared by ultrasonic-assisted reduction method, because the anion replacement of ordinary impregnation was very small. The characteristic diffraction peak of Pd was not observed in the XRD patterns, which may be due to the PdNPs loaded on the LDHs being too small to be detected.

### 3.3. FT-IR

The functional groups on the surface of the carrier and catalysts prepared by different methods were analyzed by FT-IR, which was shown in Fig. 3. In Fig. 3(a), the absorption peak at 3466 cm$^{-1}$ belonged to the stretching vibration of adsorbed water molecules and hydroxyl groups on the LDHs layer [34], and the deformation vibration peak corresponding to the hydroxyl group at 1535 cm$^{-1}$ [34,46]. The area of Pd/LDHs-us corresponding to the hydroxyl vibration peak at 1535 cm$^{-1}$ was smaller than that in LDHs-w, which was due to the excitation of the hydroxyl groups on the surface of LDHs under the cavitation of ultrasound to produce reducing hydrogen radicals, reducing Pd$^{2+}$ to Pd$^{0}$, and anchoring on the LDHs through Pd–O coordination, resulting in a reduction in the number of hydroxyl groups. The peak at 1532 cm$^{-1}$ was ascribed to the antisymmetric stretching vibration of the C–O bond [47,48], which proved the existence of CO$_3^{2-}$ in the interlayer of LDHs, indicating that calcination at 300 °C did not completely destroy the layered structure of LDHs. In Fig. 3(b), for Pd/LDHs-c prepared by NaBH$_4$ reduction, the absorption peak area at 1352 cm$^{-1}$ was smaller than that in LDHs-w, which was due to the excitation of the hydroxyl groups on the surface of LDHs under the cavitation of ultrasound to produce reducing hydrogen radicals, reducing Pd$^{2+}$ to Pd$^{0}$, and anchoring on the LDHs through Pd–O coordination, resulting in a reduction in the number of hydroxyl groups. The peak at 1532 cm$^{-1}$ was ascribed to the antisymmetric stretching vibration of the C–O bond [47,48], which proved the existence of CO$_3^{2-}$ in the interlayer of LDHs, indicating that calcination at 300 °C did not completely destroy the layered structure of LDHs. In Fig. 3(b), for Pd/LDHs-c prepared by NaBH$_4$ reduction, the absorption peak area at 1352 cm$^{-1}$ corresponded to the C–O bond decreased, which might be because CO$_3^{2-}$ in the process of preparing the catalyst was replaced by PdCl$_2$. However, for Pd/LDHs-us prepared by the ultrasonic-assisted reduction method, the area of the peak at 1352 cm$^{-1}$ was greatly reduced. This was because the ultrasonic cavitation caused high temperature and high pressure [49], and more interlayer CO$_3^{2-}$ was converted into CO$_2$. As a result, more PdCl$_2$ entered the interlayer of LDHs and was reduced to PdNPs in situ, forming Cl- intercalated LDHs. In addition, the characteristic peaks of each functional group of LDHs were present, which indicated that ultrasound did not destroy the layered structure of LDHs.

### 3.4. SEM

Fig. S1 showed the SEM images of the LDHs-w and Pd/LDHs-us. In Fig. S1(a), LDHs-w formed an irregular morphology through layer-to-layer alternate stacking. As shown in Fig. S1(b), ultrasound did not destroy this structure during the preparation of catalyst by ultrasonic-assisted reduction method.

### 3.5. TEM

TEM images of catalysts prepared by two different reduction methods and the particle size distribution of PdNPs were shown in Fig. 4. For the Pd/LDHs-us catalyst in Fig. 4(a), with the Pd loading amount of 2.5 wt% prepared by the ultrasonic-assisted reduction at the power of 200 W for 80 min, the PdNPs were highly dispersed on the LDHs with an average particle size of 1.80 nm, and the dispersity degree of PdNPs measured by hydrogen chemisorption was 80 %. For the Pd/LDHs-c catalyst prepared by NaBH$_4$ reduction in Fig. 4(b), the average particle size of PdNPs was 2.34 nm, and the dispersion degree of PdNPs (55 %) was lower than that of Pd/LDHs-us. The reason for the smaller PdNPs of the Pd/LDHs-us catalyst might be that the ultrasound can accelerate the crystal nucleation and form small metal nanoparticles. For the Pd/LDHs-c catalyst, due to the strong reducibility of NaBH$_4$, the crystal nucleus grew rapidly, leading to nucleus agglomeration. When the loading amount is the same, the smaller the particle size of Pd nanoparticles, and the better the dispersion of Pd nanoparticles, the more active components are exposed, which leads to the higher catalytic activity [50]. Therefore, Pd/LDHs-us exhibited higher catalytic activity in the H12-NEC dehydrogenation. In addition, Fig. 4(c) showed the HRTEM of Pd/LDHs-us, it can be clearly concluded that the lattice fringe spacing of PdNPs was 2.29 Å, corresponding to the Pd (1 1 1) crystal plane. This showed that the ultrasonic-assisted reduction method was a good method for preparing loaded metal catalysts.

### 3.6. EDS

In order to further analyze the distribution and content of Mg, Al, Pd, Cl and O elements in the catalysts prepared by two different reduction methods, they were characterized by EDS in Fig. 5. Compared with Pd/LDHs-c, the distribution of Pd in Pd/LDHs-us was more uniform, and there was no agglomeration of PdNPs, which was consistent with the
5. TEM results in Fig. 4. In addition, according to the analysis results of EDS element content, the percentages of Cl in Pd/LDHs-c and Pd/LDHs-us were 0.03 % and 0.17 %, respectively. It can be seen that the Cl content of Pd/LDHs-us prepared by ultrasonic-assisted reduction was more than 5 times that of Pd/LDHs-c prepared by chemical reduction, which further proved the existence of Cl intercalation under ultrasound action. Moreover, compared with Pd/LDHs-c, the content of O in Pd/LDHs-us was lower, which further indicated the decomposition of CO\(_3^{2-}\) in ultrasonic cavitation, which was in agreement with the XRD and FT-IR characterization results.

3.7. \(N_2\) adsorption–desorption

In order to explore the pore structure of the samples, \(N_2\) physical adsorption and desorption were performed, and the results were shown in Fig. S2 and Table S2. It can be seen from Table S2 that LDHs had larger specific surface area, total pore volume and average pore size than LDHs-w. This was because after calcination at 300℃, the interlayer water of LDHs was removed, which reduced the interlayer spacing and made the layers more tightly stacked. As for Pd/LDHs-us, PdCl\(_4^{2-}\) was reduced to PdNPs in situ between layers during the ultrasonic-assisted preparation process, so the specific surface area, pore volume and pore diameter were decreased. For Pd/LDHs-c, there was little change since most of the PdNPs were on the surface of the carrier.

3.8. XPS

In order to study the chemical states of the elements in the catalyst and the electronic effects between them, the samples were characterized by XPS. From the XPS spectra of Pd 3d in Fig. 6, all of them had two peaks at about the binding energies of 335.5 eV and 340.5 eV, corresponding to Pd\(^0\) 3d\(_{5/2}\) and 3d\(_{3/2}\), respectively. Two peaks appeared near the binding energies of 337.4 eV and 341.8 eV, which corresponded to Pd\(^{2+}\) 3d\(_{5/2}\) and 3d\(_{3/2}\), respectively [51]. Pd\(^0\) represented the
Table 1

| Catalysts          | Pd 3d_{3/2} Binding Energy (eV) | Pd 3d_{5/2} Binding Energy (eV) | Pd^{2+}/Pd^{2+} |
|--------------------|---------------------------------|---------------------------------|------------------|
|                    | Pd^{2+}                         | Pd^{4+}                         |                  |
| Pd/LDHs-us-100     | 336.8                           | 338.2                           | 341.5            |
| Pd/LDHs-us-200     | 336.8                           | 338.2                           | 341.5            |
| Pd/LDHs-us-300     | 336.8                           | 338.2                           | 341.5            |
| Pd/LDHs-us-400     | 336.8                           | 338.2                           | 341.5            |
| Pd/LDHs-c          | 337.0                           | 338.3                           | 341.7            |

Fig. 6. XPS spectra of Pd 3d (a) Pd/LDHs-us-100, (b) Pd/LDHs-us-200, (c) Pd/LDHs-us-300, (d) Pd/LDHs-us-400, (e) Pd/LDHs-c.

reduced Pd, and Pd^{2+} was derived from the oxidation state of Pd exposed to the air and PdCl_{2} in the LDHs interlayer. The binding energies of Pd in different valence states and the content ratios of Pd^{2+}/Pd^{2+} were shown in Table 1. The Pd^{2+} binding energies of Pd/LDHs-c and Pd/LDHs-us shifted to higher binding energy. The main influencing factor of the offset was the particle size of the noble metal nanoparticles loaded on the carrier. When the particle size was small, the binding energy shifted to a higher position [52]. However, compared with Pd/LDHs-c, the Pd^{0} binding energy of Pd/LDHs-us prepared by ultrasonic-assisted reduction had a smaller shift, which might be due to the coordination effect occurred between Pd and O. In addition, according to the content ratio change of Pd^{2+}/Pd^{2+}, the catalysts prepared by ultrasonic-assisted reduction method had higher Pd^{2+} content than those prepared by chemical reduction method. This was caused by two aspects. On the one hand, PdNPs had a higher dispersion on LDHs, and the metal nanoparticles were finer and more easily oxidized by oxygen in the air [53]; on the other hand, more PdCl_{2} entered the interlayer to replace CO_{2} under the action of ultrasound, which was consistent with the results of the FT-IR characterization. Under the ultrasonic power of 100 W, the number of excited •H were relatively low, so the content of Pd^{2+}/Pd^{2+} was slightly lower. As the ultrasonic power increased from 200 W to 400 W, the content of Pd^{2+} increased, because the greater the ultrasonic power, the more PdCl_{2} entered the interlayer, which was difficult to be reduced. Therefore, the ultrasonic power of 200 W was the most suitable, which was consistent with the results of the catalytic performance later.

The chemical state of O on the catalyst surface was further analyzed, as shown in Fig. 7, the spectrum of O 1s can be fitted to four peaks at the binding energies of 530.0, 531.2, 532.2 and 533.1 eV [54], which corresponded to Al-O, Mg-O, M–OH and H_{2}O. By calculating and comparing the proportion of the M–OH peak area in each catalyst in Table 2, it was found that the M–OH content of Pd/LDHs-us prepared under different ultrasonic powers was lower than that of Pd/LDHs-c, which was due to the fact that the hydroxyl groups were excited to •H by ultrasound, then Pd^{2+} was reduced, and at the same time the coordination effect between Pd and O was formed. This not only led to a decrease in hydroxyl content, but also formed stronger interactions between the metal and the carrier, enhancing the stability of the catalyst, which was confirmed in the catalyst recycling experiments discussed later. Fig. S3 showed the XPS spectrum of Cl 2p, each catalyst had a peak at 198.8 eV, which was attributed to the interlayer Cl\textsuperscript{-}, which further proved the existence of Cl\textsuperscript{-}-intercalated between the interlayers of LDHs.

3.9. Catalytic dehydrogenation performance

3.9.1. Study on the preparation conditions of catalyst

In order to optimize the preparation conditions of the catalyst, H12-NEC dehydrogenation was used as the probe reaction, and the effects of ultrasonic power, ultrasonic time and Pd loading amount on the catalytic performance of H12-NEC dehydrogenation were studied at 180℃, which were shown in Fig. 8. With the progress of the dehydrogenation reaction, the amount of hydrogen released increased rapidly at the initial stage of the reaction and gradually reached a stable level. In Fig. 8 (a), the ultrasonic power in preparation of the catalyst had little effect on its catalytic performance in 12H-NEC dehydrogenation. In Fig. 8 (b), when the ultrasonic time was 80 min, it had the highest catalytic performance. With the extension of ultrasonic time to 100 min, the catalyst performance did not improve further. As shown in Fig. 8 (c), the optimum loading amount of the catalyst was 2.5 wt%. When the Pd loading
amount was 1 wt%, although it had better dispersion, there was a larger distance between each active site, which reduced the contact frequency between the active site and the reactant. When the Pd loading amount was 5 wt%, it had poor dispersion, larger particle size of PdNPs, and fewer active sites were exposed, leading to poor catalyst performance. The catalyst prepared under the conditions of 200 W for 80 min and loading amount of 2.5 wt% presented the best catalytic performance in H12-NEC dehydrogenation, and the amount of hydrogen released of 1 h and 6 h can reach 4.65 wt% and 5.72 wt% respectively.

3.9.2. Comparative experiments over Pd-based catalysts

The performance of Pd/LDHs-us prepared under the optimal ultrasonic conditions, Pd/LDHs-c prepared by NaBH₄ reduction, and the commercial Pd/Al₂O₃ catalyst in H12-NEC dehydrogenation were compared. The experimental results were shown in Fig. 9(a) and Table 3. The catalytic activity of Pd/LDHs-us was higher than that of Pd/LDHs-c and commercial Pd/Al₂O₃ catalyst. The dehydrogenation efficiency at 1 h and 6 h was 80.3 % and 99.3 %, respectively. In addition, the catalytic performance of Pd/LDHs-us was compared with the reported literatures about H12-NEC dehydrogenation catalysts, and the results were shown in Table S3. It can be seen that the catalytic performance of Pd/LDHs-us is significantly higher than most of the results reported in studies, which fully reflects the superiority of catalysts.

Fig. 9(b–e) showed the distribution curve of the H12-NEC dehydrogenation product over time on different catalysts. As shown in Fig. 9(b),

Table 2

| Catalysts   | O 1s Binding Energy (eV) | Proportion of M-OH |
|-------------|--------------------------|-------------------|
|             | Al-O | Mg-O | M-OH | H₂O |
| Pd/LDHs-c   | 530.0, 531.2, 532.2, 533.1 | 37.84 % |
| Pd/LDHs-us-200 | 530.0, 531.2, 532.2, 533.1 | 33.02 % |
| Pd/LDHs-us-300 | 530.0, 531.2, 532.2, 533.1 | 33.58 % |
| Pd/LDHs-us-400 | 530.0, 531.2, 532.2, 533.1 | 32.97 % |
| Pd/LDHs-us-100 | 530.0, 531.2, 532.2, 533.1 | 34.02 % |

Fig. 7. XPS spectra of O 1s (a) Pd/LDHs-us-100, (b) Pd/LDHs-us-200, (c) Pd/LDHs-us-300, (d) Pd/LDHs-us-400, (e) Pd/LDHs-c.

Fig. 8. Dehydrogenation curves over xPd/LDHs-y-z catalysts (a) ultrasonic power, (b) ultrasonic time and (c) Pd loading amount.
H12-NEC was rapidly consumed, and when Pd/LDHs-us was used as the catalyst, the consumption rate of H12-NEC was the fastest, that is, it showed the best catalytic activity. As seen from the Fig. 9 (c) and (d), when Pd/LDHs-c and commercial Pd/Al$_2$O$_3$ catalyzed H12-NEC dehydrogenation reaction, the intermediate products H8-NEC and H4-NEC formed the deposition without further rapid dehydrogenation to NEC, and the commercial Pd/Al$_2$O$_3$ catalyst showed the lowest catalytic activity. For Pd/LDHs-us catalyst, although a large number of intermediate products were rapidly formed, they were converted immediately without accumulation. Therefore, it displayed excellent catalytic performance in the dehydrogenation of H12-NEC over Pd/LDHs-us catalyst, and it was proved that ultrasonic-assisted reduction was an effective preparation method.

### 3.9.3. Study on the reaction temperature of H12-NEC dehydrogenation catalyzed by Pd/LDHs-us

The dehydrogenation curves of H12-NEC over Pd/LDHs-us catalyst at different temperatures were shown in the Fig. 10(a). With the increase of temperature, the rate of dehydrogenation was accelerated. At 180°C, dehydrogenation efficiency of 99.3 % was achieved at 6 h, and it also reached 94.6 % at a lower temperature of 170 °C for 6 h. Dehydrogenation kinetics were obtained by dehydrogenation at different temperatures. In Fig. 10(b), according to the results of dehydrogenation at 165–180 °C, the reaction rate constants (k) at different temperatures were obtained. As shown in Fig. 10(c), according to the Arrhenius equation, with 1/RT $\times 10^3$ as the x-axis and ln(k) as the y-axis, a straight line was fitted, and the linear correlation coefficient was 98.48 %. The slope was the apparent activation energy for H12-NEC dehydrogenation over Pd/LDHs-us, which was 90.97 kJ/mol.

### 3.9.4. Study of catalyst stability

In order to evaluate the leaching of Pd supported on the catalyst, a thermal filtration experiment was carried out. The specific methods were described in the Supplementary Material, and the result was shown in Fig. S4, which indicated that the prepared Pd/LDHs-us catalyst was a heterogeneous catalyst with high stability. To further study the stability of the catalyst, reuse experiments of Pd/LDHs-us and Pd/LDHs-c catalysts were carried out in H12-NEC dehydrogenation, as shown in Fig. 11. The hydrogen release of 6 h over the Pd/LDHs-us catalyst remained 98 % of the initial hydrogen release after 4 continuous operations, and decreased to 93 % of the initial hydrogen release after 6 continuous operations. As for Pd/LDHs-c catalyst, the hydrogen release after 6 h decreased to 86 % of its initial hydrogen release after 3 consecutive reactions.

In order to explore the particle size change of PdNPs, TEM characterization was carried out for the two catalysts after being reused. As shown in Fig. 12(a), for Pd/LDHs-us catalyst after six reuse experiments, the average particle size of PdNPs was 3.77 nm. Fig. 12(b) showed TEM images of Pd/LDHs-c after three repeated experiments, the average

| Catalysts | Temperature (°C) | Catalytic activity (mol$_{12H-NEC}$ Pd$^{-1}$ s$^{-1}$) | Hydrogen release of 1 h (wt.%) | Dehydrogenation efficiency (%) |
|-----------|-----------------|-------------------------------------------------|-------------------------------|--------------------------------|
| Pd/LDHs-us | 180             | 2.59$\times 10^{-3}$                            | 4.65                          | 99.3(6 h)                      |
| Pd/LDHs-us | 175             | 2.23$\times 10^{-3}$                            | 4.18                          | 98.5(6 h)                      |
| Pd/LDHs-us | 170             | 1.28$\times 10^{-3}$                            | 2.98                          | 94.6(6 h)                      |
| Pd/LDHs-c  | 180             | 1.41$\times 10^{-3}$                            | 3.48                          | 98.3(6 h)                      |
| Pd/Al$_2$O$_3$ | 180          | 1.48$\times 10^{-3}$                            | 2.94                          | 96.5(6 h)                      |
particle size of PdNPs was 4.26 nm. After reuse experiments, due to the agglomeration of PdNPs, the number of active sites decreased, resulting in a decrease in catalytic activity. For Pd/LDHs-us, owing to the coordination effect between Pd and O, the agglomeration was effectively inhibited and showed better stability, which was consistent with the previous characterization results.

4. Conclusion

In this study, without the use of chemical reductants and stabilizers, hydroxyl groups on the surface of LDHs-w were excited by the action of ultrasound and obtained •H. Then, PdCl$_4^{2-}$ adsorbed in the interlayer of LDHs-w was further reduced to PdNPs in situ. It effectively improved the catalytic dehydrogenation activity and stability of the catalyst. By investigating the preparation conditions of the catalyst, it was found that the catalyst was prepared under the conditions of ultrasonic power of 200 W, time of 80 min and Pd loading amount of 2.5 wt%, which had the best catalytic performance. When the dehydrogenation temperature was 180°C, the hydrogen release of 1 h and 6 h reached 4.65 wt% and 5.72 wt%, respectively, higher than Pd/LDHs-c prepared by chemical reduction and commercial Pd/Al$_2$O$_3$ catalyst. After four consecutive dehydrogenation reactions, the hydrogen release remained 98% of the initial hydrogen release. The catalytic performance was better than most of the values reported in the literatures. In conclusion, ultrasonic-assisted reduction is an excellent and environmentally friendly preparation method.

CRediT authorship contribution statement

Yanpeng Wu: Investigation, Formal analysis, Data curation, Writing – original draft, Visualization. Xiaoran Liu: Investigation, Formal analysis, Data curation, Software, Validation. Xuefeng Bai: Conceptualization, Methodology, Resources, Formal analysis, Writing – review & editing, Funding acquisition, Supervision, Project administration. Wei Wu: Conceptualization, Methodology, Resources, Formal analysis, Writing – review & editing, Funding acquisition, Supervision, Project administration.

Fig. 10. (a) Dehydrogenation curves of H$_{12}$-NEC dehydrogenation over Pd/LDHs-us catalyst at different temperature, (b) the curve of ln(C$_{H_{12}}$/C$_0$) ~ t, (c) the curve of lnk ~ 1/RT $\times$ 10$^3$.

Fig. 11. Reusability of Pd/LDHs-us and Pd/LDHs-c.

Fig. 12. TEM images of Pd/LDHs-us after 6 reuse (a) and Pd/LDHs-c after 3 reuse (b).
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