Novel Pt–Ni Bimetallic Catalysts Pt(Ni)–LaFeO₃/SiO₂ via Lattice Atomic-Confined Reduction for Highly Efficient Isobutane Dehydrogenation

Xiao Yang¹ · Guilong Liu² · Yingxia Li¹ · Lihong Zhang¹ · Xitao Wang¹ · Yuan Liu¹

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Abstract

In this study, a series of novel Pt–Ni bimetallic catalysts supported on LaFeO₃/SiO₂ with different amounts of Ni were prepared by the lattice atomic-confined reduction of LaFe_{1-x}(Ni, Pt)_xO₃/SiO₂ perovskite precursors and applied in isobutane dehydrogenation to isobutene reaction. The catalysts were characterized by X-ray diffraction, H₂-temperature-programmed reduction, Brunauer–Emmett–Teller analysis, transmission electron microscopy, energy dispersive X-ray, CO chemisorption, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The as-synthesized Pt–Ni bimetallic catalysts possessed smaller most probable particle size with tunable Pt–Ni interaction, depending on the Ni content. The catalyst with Ni content of 3.0 wt% showed excellent activity and stability (the isobutane conversion and isobutene selectivity remained at about 38% and 92%, respectively, after 310 min) for the isobutane dehydrogenation reaction. It also provided approximately six times turnover frequency of the catalyst without Ni. The excellent activity and stability of the 3.0 wt% Ni-containing catalyst can be attributed to its small metal nanoparticles with high dispersion and suitable Pt–Ni interaction. Moreover, the Pt(Ni)–LaFeO₃/SiO₂ catalyst with Ni content of 3.0 wt% had been run for more than 35 h without obvious loss of activity, indicating its long-term stability, and the decrease in the Pt–Ni interaction that accompanied the formation of the FeNi alloy phase was thought to be responsible for the slight decrease in activity.

Keywords Perovskite · Isobutane dehydrogenation · Isobutene · Pt–Ni interaction · Silica

Introduction

Olefins, especially isobutene, are indispensable chemical raw materials for producing commodities such as plastic, fiber, and rubber [1]. In recent decades, isobutene is mainly produced by the steam naphtha cracking and fluidized catalytic cracking of heavy oil, which are high-cost processes with serious and unavoidable environmental consequences. Recently, the direct dehydrogenation of isobutane to isobutene has been regarded as one of the most promising routes for isobutene production [2].

Among the commercial processes, Pt/Al₂O₃ demonstrates excellent catalytic performance for isobutane dehydrogenation; however, their carbon deposition and Pt sintering problems are urgent and must be resolved [3]. The modification of Pt-based catalysts is mainly performed by adding additives (such as alkaline metals [4], Mg [5], La [6], Sn [7] and Zn [8]); alloying Pt with other metals (Cu [9] and Sn [10], etc.); or using functional supports [1, 11–13]. However, these active species, additives, and support are usually assembled together by the traditional impregnation method [10–13]. As a result, their interaction must be restricted to some degree. Therefore, there remains a need to design a highly efficient Pt-based catalyst to improve the performance of isobutane dehydrogenation.

A perovskite-type oxide (PTO), which is typically expressed as ABO₃, is not only structurally stable because of its well-balanced geometrical array of constituent atoms, but its A- and B-site ions confined in the lattice can also be partially replaced by other metal ions to yield many complex metal oxides with various compositions

✉ Lihong Zhang
zlh_224@163.com

¹ School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China

² College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, China

[14–16]. More importantly, all the ions at the A- and B-sites are uniformly mixed at the atomic level, which favors the adjustment and control of the interaction among species [17–21].

In this paper, to ensure the maintenance of the perovskite structure [17], LaFeO_3 PTO is chosen as the skeleton structure, in light of the anti-sintering performance and dispersion effect of La^{3+} ions [6, 22] and the dehydrogenation ability of Fe^{3+} ions [23], as well as their good anti-reduction stability. Given that supported Ni-based catalysts have been widely researched in the dehydrogenation reactions [23–25], Ni and Pt species are introduced into LaFeO_3 PTO together. In this way, the B-site of LaFeO_3 can be partially substituted by active Pt species and Ni assistant to obtain $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$, in which the Pt and Ni elements can be atomic-confined. By reduction, $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$ will be transformed into Pt–Ni/ LaFeO_3 .

Furthermore, in order to inhibit the sintering of metal species, it is necessary to divide PTO nanoparticles (NPs) into small sizes. One of the most effective ways is to load PTO NPs onto a support with channels, high specific surface area, and thermal stability [22, 26–28]. Among the available supports, mesoporous SiO_2 is a desired support for isobutane dehydrogenation [25, 29–31] and can be used to facilitate an understanding of the structural features.

Therefore, a series of Pt–Ni bimetallic catalysts supported on La_2O_3 – LaFeO_3 / SiO_2 with different amounts of Ni were prepared by the lattice atomic-confined reduction of SiO_2 -supported $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$ PTO precursors. Then, they were applied in isobutane dehydrogenation to isobutene reaction. The essential relationship between the high activity and structure of the as-synthesized catalysts was studied. The deactivation behaviors of the catalysts were also described according to their characteristics before and after the reaction.

Experimental

Catalyst Preparation

Raw Materials

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR) and citric acid (AR) were purchased from Aladdin Industrial Corporation, USA. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (AR), and ethylene glycol (AR) were purchased from Tianjin Real & Lead Chemical Co., Ltd, China. Support SiO_2 powders (>98%, specific surface area: $150 \text{ m}^2 \text{ g}^{-1}$; average pore diameter: 20.7 nm) were purchased from Nanjing TANSAIL Advanced Materials Co., Ltd, China, and calcined at 700°C for 5 h in air.

Catalyst Preparation

The SiO_2 -supported $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$ PTO precursors were prepared by citrate complexing method accompanied by impregnation. As is typical, SiO_2 powders were impregnated with a mixed solution of lanthanum nitrate, iron nitrate, nickel nitrate, and chloroplatinic acid at $\text{La}/\text{Fe}/(\text{Ni} + \text{Pt})$ molar ratio of $1:1-x:x$. Then, citrate acid and glycol were added into the above solution, in which the [citrate acid]/[glycol] molar ratio was 5.0 and the [citrate acid]/[total metal cations] molar ratio was 1.2. The resulting solid was left for 24 h and then dried at 80 and 120°C for 6 and 12 h, respectively. Subsequently, the samples were calcined at 350 and 700°C for 2 and 5 h, respectively, at a heating rate of 2°C min^{-1} , and then SiO_2 -supported $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$ perovskite precursors were obtained. In this paper, the precursors were denoted as LFNP- ω , where ω ($\omega = 0.6, 3.0, 6.0\%$) represents the mass fraction of Ni in the catalysts. The mass loadings of PTO and Pt in the calcined catalysts were kept at 30.0 and 0.3 wt%, respectively. For comparison, SiO_2 -supported LaFeO_3 , $\text{LaFe}_{1-y}\text{Pt}_y\text{O}_3$ and $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3$ were also synthesized and labeled as LF, LFP, and LFN-3.0%, respectively.

The Pt–Ni bimetallic catalysts were prepared by the lattice atomic-confined reduction of the $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$ / SiO_2 perovskite precursors as follows: the precursors were reduced at 580°C for 2 h at a heating rate of 2°C min^{-1} in 5 vol% H_2/N_2 atmosphere.

Characterization

X-ray diffraction (XRD) measurements were examined on a PANalytical X'Pert Pro X-ray diffractometer (PANalytical, Holland) with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The spectra were collected at 2θ range of 15° – 60° at a scanning speed of 5° min^{-1} .

Temperature-programmed reduction (TPR) experiments were carried out in self-made instrument, and the thermal conductivity detector was used to detect concentration variation of H_2 . In each run, 50 mg of catalyst with 40–60 mesh grain size was loaded into a quartz tube reactor and then heated to 850°C from room temperature at a heating rate of $10^\circ\text{C min}^{-1}$ in the presence of 5% H_2/N_2 at a flow rate of 30 mL min^{-1} .

Transmission electron microscopy (TEM) experiments and energy dispersive X-ray (EDX) spectroscopy analyses were performed on a JEM-2100F field-emission transmission electron microscope (JEOL, Japan). Before testing, the catalysts were ground into powder and dispersed in absolute ethanol using ultrasonic dispersion instrument. At last, the samples were deposited onto a copper grid covered by holey carbon film.

X-ray photoelectron spectroscopy (XPS) tests were performed using Al K α ($h\nu = 1253.6$ eV) radiation on a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA). The residual pressure in the analysis room was approximately 266.6×10^{-10} Pa during the analysis.

To determine the amount of carbon deposited on the spent catalysts, thermogravimetry (TG) analysis and differential thermal analysis (DTA) were performed on a DTG-50/50H thermal analyzer (PerkinElmer, USA). 40 mg of the samples was heated from room temperature to 850 °C at a heating rate of 10 °C min⁻¹ in the presence of air. The total weight loss was calculated by the following formula:

$$\frac{W_1 - W_2}{W_1} \times 100\% \quad (1)$$

where W_1 is the weight of the reacted catalyst prior to the TG test and W_2 is the weight of the reacted catalyst after the TG test.

Nitrogen adsorption and desorption isotherms were performed on a TriStar 3000 micromeritics apparatus (Micromeritics, USA) at -196 °C. The specific surface areas were calculated based on the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were derived from the desorption branch of isotherms using the Barrett–Joyner–Halenda (BJH) model. All samples were outgassed under vacuum at 300 °C for 4 h prior to analysis.

Dispersion degree (D) of the Pt was calculated by CO chemisorption. CO chemisorption was conducted on AutoChem II 2920 analyzer (Micromeritics, USA). 100 mg of the samples was reduced under 10 vol% H₂/Ar atmosphere at 580 °C for 2 h at a heating rate of 5 °C min⁻¹. After reduction, the catalysts were swept with He at 580 °C for 30 min to remove H₂ and then cooled down to 40 °C. Subsequently, the CO pulse chemisorption was carried out at 40 °C by injecting pulses of 5 vol% CO/He until the CO was adsorbed to saturation. To calculate the dispersion degree of Pt, it is assumed that the adsorption of CO on Pt is a linear adsorption, i.e., CO/Pt_{surface} = 1 [32], considering that CO chemisorption over Ni/La₂O₃ catalyst is significantly suppressed, which can be attributed to the blocking of Ni sites by the La species [33]. Thus, CO is mainly adsorbed on Pt rather than Ni. And the dispersion degree of Pt was calculated using the following formula:

$$D = \frac{\frac{n_1}{m_1} \times M_{\text{Pt}}}{m_{\text{Pt}}} \quad (2)$$

where n_1 and m_1 represent the molar amounts of CO adsorbed and the mass of catalysts used in the CO chemisorption test, respectively; m_{Pt} is the mass of Pt per gram of catalyst; M_{Pt} is the relative atomic mass of Pt, i.e., 195.08.

Catalytic Reaction

Catalytic performance was evaluated in a stainless-steel fixed-bed continuous-flow reactor at atmospheric pressure. 0.5 g of the precursors (40–60 mesh) was loaded into the reactor and reduced at 580 °C for 2 h at a heating rate of 2 °C min⁻¹ in 5 vol% H₂/N₂ atmosphere. After reduction, the temperature of reactor was cooled to 560 °C, and then isobutane and hydrogen were introduced into the reactor, in which the weight hourly space velocity (WHSV) of isobutane was 3 h⁻¹ and the molar ratio of isobutane to hydrogen was 1. The composition of the off-gases was analyzed by an online gas chromatograph equipped with a flame ionization detector (Al₂O₃ packed column).

The catalytic performance of the catalyst is evaluated by isobutane conversion (Conv.) and selectivity to products (Selec.), which were calculated using the following formulas:

$$\text{Conv.} = \frac{\text{C moles of } C_4 \text{ reacted}}{\text{Total C moles}} \times 100\% \quad (3)$$

$$\text{Selec.} = \frac{\text{C moles of product } x}{\text{C moles of } C_4 \text{ reacted}} \times 100\% \quad (4)$$

where “C moles of C_4 reacted” was calculated by the moles of product generated, including isobutene and other by-products x . Here, x means CH₄, C₂H₆, C₂H₄, C₃H₈, or C₃H₆.

Also, the turnover frequency (TOF) was calculated based on the Pt dispersion, which is defined as the moles of isobutane converted per mole of active Pt per second. The moles of active Pt were obtained through CO chemisorption analysis. And the TOF was calculated by the following formula [34]:

$$\text{TOF (s}^{-1}\text{)} = \frac{\frac{F}{22.4 \times 60 \times 1000} \times X \times M_{\text{Pt}}}{m_{\text{cat}} \times \omega_{\text{Pt}} \times D} \quad (5)$$

where F (mL min⁻¹) is the flow rate of isobutane; X (%) and m_{cat} (g) are the conversion of isobutane and mass of catalysts, respectively; and ω_{Pt} (%) and D (%) are the percentages of Pt mass loading in the catalyst and the Pt dispersion, respectively.

Results and Discussion

Structure and Morphology Characterization

Figure 1a shows the XRD patterns of calcined catalysts. In addition to the diffraction peaks of SiO₂ [JCPDS#39-1425], weak diffraction peaks of PTO can also be detected at about

Fig. 1 XRD patterns of **a** calcined catalysts along with the magnified patterns for 2θ from 31° to 35° and **b** reduced catalysts. Curves: a LF; b LFP; c LFN-3.0%; d LFNP-0.6%; e LFNP-3.0%; f LFNP-6.0%

32.2° , 39.8° and 46.3° . It indicates that small PTO NPs had been successfully loaded on the SiO_2 . Also it is noticeable that the diffraction peaks of the PTO phase shift to higher angles when Pt^{4+} and Ni^{3+} are introduced into the B-site of the LaFeO_3 . With the increase in Ni content from 0.6 to 6.0 wt%, the diffraction peaks of the PTO shift to a higher 2θ value for LFNP- ω . This phenomenon is due to the fact that the ionic radius of Fe^{3+} ions (0.645 Å) is bigger than those of Pt^{4+} (0.625 Å) and Ni^{3+} (0.600 Å) ions [35]. Therefore, the substitution of Fe^{3+} ions by the Pt^{4+} and Ni^{3+} ions leads to the shrinkage of the PTO unit cell. This result also proves that Pt^{4+} and Ni^{3+} ions can be introduced into the PTO unit cell [36, 37]. The peak shifts of LFP and LFNP-0.6% do not follow similar rules, which may be due to the Jahn–Teller effect of Ni^{3+} [38, 39]. When the catalyst has a low Ni content, the local lattice distortion may cause the PTO unit cell to increase in size, thus shifting the PTO diffraction peaks to a lower 2θ value. When the Ni content increases, the PTO unit cell is mainly affected by the ionic radius, just as discussed above. In this view, it can be deduced that the small $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$ NPs with PTOs structures have been successfully loaded on the SiO_2 .

Figure 1b shows the XRD results of samples reduced at 580°C for 2 h. After reduction, the diffraction peaks of PTO and SiO_2 can still be seen, which indicates that the structures of PTO and SiO_2 are stable enough. In the LFP sample, the diffraction peak of metallic Fe [JCPDS#06-0696] can

be observed, which should be due to the reduction of highly dispersed iron from the PTO lattice, as also reported in Ref. [40].

In addition, a new diffraction peak assigned to metallic Ni [JCPDS#01-1258] can be also observed at about 44.4° for LFNP- ω and LFN-3.0%. These broad and low-intensity peaks indicate that small Ni NPs are highly dispersed in the catalysts. Although the diffraction peak in LFNP-0.6% at about 44.4° is not obvious due to the low Ni content of 0.6 wt% and the high dispersion of Ni, it can still be assigned to metallic Ni compared with other samples. Moreover, it is worth emphasizing that Pt^{4+} ions should be more easily reduced than Ni^{3+} ions. However, the diffraction peaks of metallic Pt cannot be found, which may be due to the low loading amount, small size, and high dispersion of the Pt species. At the same time, some La_2O_3 and other metal oxide NPs should be extracted from the PTO structure during the reduction of PTO [41]. Although no corresponding diffraction peaks can be detected, which can be attributed to the interaction among reduced metal species, extracted metal oxides, and the retained PTO structure, the highly dispersed La_2O_3 can still be obtained. In summary, after reduction the catalysts were transferred into the highly dispersed La_2O_3 modified Pt–Ni bimetallic catalysts supported on $\text{LaFeO}_3/\text{SiO}_2$.

Figure 2a shows the nitrogen adsorption and desorption isotherm curves of SiO_2 and catalysts. All catalysts

Fig. 2 **a** Nitrogen adsorption and desorption isotherm curves and **b** pore size distributions of SiO_2 and catalysts. Curves: a LF; b LFP; c LFN-3.0%; d LFNP-0.6%; e LFNP-3.0%; f LFNP-6.0%

Table 1 Metal loading and textural data of SiO₂ and supported catalysts obtained from N₂ adsorption and desorption

Sample	Theoretical metal loading (wt%)		S_{BET} (m ² g ^{−1})	Most probable pore size (nm)	V_{pore} (cm ³ g ^{−1})
	Ni	Pt			
SiO ₂	0	0	127	35	1.0
LF	0	0	88	16	0.5
LFP	0	0.3	92	20	0.5
LFN-3.0%	3.0	0	77	15	0.5
LFNP-0.6%	0.6	0.3	82	22	0.4
LFNP-3.0%	3.0	0.3	95	16	0.4
LFNP-6.0%	6.0	0.3	100	15	0.4

show mixed physisorption isotherms of types II and IV with H3-type hysteresis loop according to the International Union of Pure and Applied Chemistry (IUPAC) classification [42]. The hysteresis loops start at a relative pressure (P/P_0) of around 0.8, which suggests the existence of meso- and macropores.

Figure 2b shows the pore size distributions (PSDs) of SiO₂ and supported PTO NPs, and Table 1 lists the corresponding textural data. It can be seen that the PSD of SiO₂ is broad and arched across the meso- and macropore range, centering at about 35 nm. The loading of PTO NPs results in a decrease in the specific surface area, pore volume, and most probable pore size. These results suggest that the small PTO NPs have been loaded into the pores of SiO₂, which agrees with the XRD results.

Compared to LFP, the increase in Ni from 0.6 to 3.0 wt% and then to 6.0 wt% gives rise to a further shift of PSDs toward a small size range, accompanied by an increase in the specific surface area. These results indicate that it is the dispersion effect of Ni element that decreases the size of PTO NPs and further reduces the stacking pore size of the PTO NPs. Furthermore, all the supported catalysts show high specific surface area, which is high enough to load PTO and makes PTO highly dispersed on SiO₂. These results are also consistent with the XRD results.

To understand the interaction among metallic ions and further confirm the phase structure of samples before and after reduction, H₂-TPR tests on the calcined samples were performed, and the results are shown in Fig. 3. Under reduction conditions, Pt⁴⁺, Ni³⁺, and Fe³⁺ ions in LaFe_{1-x}(Ni, Pt)_xO₃ can be reduced, as shown by the corresponding reduction peaks, which are labeled as α , β and γ , respectively.

For all the samples, the peak at about 520 °C (γ_1) can be assigned to the partial reduction of Fe³⁺ to Fe²⁺ ions within the PTO lattice [43]. In LFP, two big reduction peaks between 400–600 °C can be seen. To maintain

Fig. 3 TPR profiles of catalysts. Curves: a LF; b LFP; c LFN-3.0%; d LFNP-0.6%; e LFNP-3.0%; f LFNP-6.0%

electrical neutrality, some oxygen vacancies [44] and Fe²⁺ ions are generated after the addition of Pt⁴⁺ ions into LF. Combined with the XRD result of the reduced LFP, the peak at about 450 °C can be attributed to the reduction of Pt⁴⁺ ions to Pt⁰ NPs (α) and oxygen vacancies as well as the reduction of Fe²⁺ ions to Fe⁰ (γ_3), where Fe²⁺ ions are generated by the addition of Pt⁴⁺ ions. The big overlapping peak at a low temperature indicates that the formation of Fe⁰ NPs occurs nearly the same time as that of the Pt⁰ NPs, which suggests that the Pt⁰ sites are probably coated by Fe⁰ NPs. Compared with the LF without any Pt element, it can be concluded that the presence of Pt promotes the reduction of Fe³⁺ ions from the PTO structure, which results in the growing γ_1 peak.

In LFN-3.0%, continuous multistage reduction processes occurred. The first small β_1 peak should be related to the partial reduction of Ni³⁺ to Ni²⁺ ions on the surface of the PTO NPs. The broad and strong γ_1 peak is overlapped with that of the reduction of Ni²⁺ to Ni⁰ (β_2 peak) on the surface of the PTO NPs and Ni³⁺ to Ni⁰ (β peak) within the bulk of the PTO NPs. After the introduction of Pt⁴⁺ and Ni³⁺ ions, the weak γ_2 peak can be found at a high temperature, which indicates that the reduction of Fe²⁺ ions in the bulk of the PTO to metallic Fe becomes easier under the catalysis of the Pt and Ni species [44].

In LFNP-0.6%, the overlapping peaks of α and β at a low temperature can be attributed to the co-reduction of Pt⁴⁺ and Ni³⁺ ions in the PTO lattice. In fact, it is the initial reduced Pt⁰ species that accelerate the reduction of Ni³⁺ ions. With the increase in Ni content to 3.0 wt%, the overlapping peak broadens and shifts toward lower temperatures. With a further increase in the content of Ni to 6.0 wt%, the overlapping peak splits into a small α peak toward a lower temperature and a big β peak toward a higher temperature. This means that there is an interaction between the Pt and Ni species and this interaction decreases with the increase in Ni content, which is bound to affect the structure and catalytic properties of the reduced species. The TPR results indicate that the

interaction between Pt and Ni in the catalysts is tunable by changing the Ni content.

Figure 4 presents TEM images and the particle size distributions of reduced LFP and reduced LFNP-3.0%. We can see that the metal NPs are well dispersed on the surface of SiO_2 in both the reduced LFP and reduced LFNP-3.0%. This can be explained by the fact that (1) all the metal NPs are derived from the corresponding metallic ions confined in the PTO lattices, in which each metal element must be uniformly dispersed at the atomic level; (2) during reduction, an interaction between the metallic particles and remaining PTO results in small NP sizes; and (3) meso–macropore SiO_2 with a high surface area provides a platform for the uniform dispersion of metal particles.

Notably, compared with the reduced LFP, we can see that the reduced LFNP-3.0% has a smaller particle size and a narrower particle size distribution of metallic NPs. In particular, the most probable particle size of reduced LFNP-3.0% is only 2.7 nm, which is smaller than that of reduced LFP (3.2 nm). Moreover, in the inset of Fig. 4b, we can see the close contact of Pt and Ni grains, which further indicates that there exists interaction between Pt and Ni species in LFNP-3.0%. Additionally, the interaction between Pt and Ni results in the higher dispersion and smaller particles sizes of metallic NPs in reduced LFNP-3.0%. These results also agree with the XRD and TPR results.

To deeply explore the interaction between metal components, the chemical statuses of the Pt, Ni, and Fe elements are studied by XPS analysis. Figure 5 shows the spectra of the Pt 4f, Ni 2p, and Fe 2p regions for samples after reduction at 580 °C for 2 h in 5% H_2/N_2 , and Table 2 lists their binding energies (BEs).

In Fig. 5a, only one peak at around 74 eV for Pt 4f in the reduced catalysts can be seen, which is attributed to Pt^0 [45]. As for the Ni 2p in Fig. 5b, we can see two relevant fitted peaks, representing two different surface Ni species,

i.e., Ni^{2+} ions and Ni^0 , which are in good agreement with Refs. [25, 46]. This is due to the fact that the surface Ni^0 NPs can be partially oxidized into Ni^{2+} ions during transportation while waiting to be tested. As shown in Fe 2p_{3/2} region spectra (see Fig. 5c), all samples have peaks of Fe^{3+} and Fe^{2+} ions. As expected, Fe^0 peak is observed in the reduced LFP at the BE of 709.0 eV, which coincides with the above XRD and TPR results.

As listed in Table 2, the binding energies of Fe^{3+} and Fe^{2+} ions are 711.7 and 710.0 eV, respectively, and there is no change in the BE values of these ions with the variation of elements. This indicates that Fe has little effect on Pt or Ni. However, Fe species play an important role in maintaining the frame structure of PTO during the reduction treatment and catalytic reaction. As shown in Table 2, the Pt 4f peak at 74.4 eV in the reduced LFP shifts to 74.2 eV after the introduction of the Ni species. At the same time, the BE of 852.2 eV of the Ni^0 spectrum in the reduced LFNP-3.0% increases to 852.4 eV after introducing Pt, which indicates that electrons tend to be transferred from Ni to Pt due to the bigger electronegativity of Pt [47]. In other words, an interaction between the Pt^0 and Ni^0 species does exist in Pt–Ni bimetallic catalysts, which is consistent with the TPR curves and TEM images.

Considering the above structure features and physicochemical properties, the structural evolution of $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3/\text{SiO}_2$ precursors is proposed, as illustrated in Scheme 1. In this work, Pt and Ni ions are atomic-confined and uniformly mixed in $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3/\text{SiO}_2$ PTO precursors. During the reduction process, Pt, Ni, and La_2O_3 are separated in situ from the $\text{LaFe}_{1-x}(\text{Ni}, \text{Pt})_x\text{O}_3$ lattice and the close contact of Pt and Ni NPs provides opportunity for them to interact with each other. Hence, novel Pt–Ni bimetallic catalysts supported on La_2O_3 – $\text{LaFeO}_3/\text{SiO}_2$ are obtained by lattice atomic-confined reduction.

Fig. 4 TEM images and particle size distribution (insets) of **a** reduced LFP and **b** reduced LFNP-3.0%

Fig. 5 XPS analysis results of **a** Pt 4*f*, **b** Ni 2*p* and **c** Fe 2*p* regions for reduced catalysts. Curves: a LFP; b LFN-3.0%; c LFNP-0.6%; d LFNP-3.0%; e LFNP-6.0%

Table 2 XPS characteristics, Pt dispersion, and TOF of representative samples

Reduced sample	Binding energy (eV) ^a						<i>D</i> ^b (%)	TOF ^c (s ^{−1})
	Pt 4 <i>f</i> _{5/2}	Ni 2 <i>p</i> _{3/2}		Fe 2 <i>p</i> _{3/2}				
	Pt ⁰	Ni ²⁺	Ni ⁰	Fe ³⁺	Fe ²⁺	Fe ⁰		
LFP	74.4	–	–	711.7	710.0	709.0	22.5	0.10
LFN-3.0%	–	855.8	852.2	711.7	710.0	–	–	–
LFNP-0.6%	74.2	856.0	852.4	711.7	710.0	–	–	–
LFNP-3.0%	74.2	856.0	852.4	711.7	710.0	–	57.4	0.59
LFNP-6.0%	74.2	856.0	852.4	711.7	710.0	–	–	–

^a Binding energy is derived from the XPS characteristics

^b *D* is calculated from CO chemisorption results

^c TOF is calculated from the Pt dispersion

Scheme 1 Structural evolution of LaFe_{1−*x*}(Ni, Pt)_{*x*}O₃/SiO₂

Fig. 6 **a** Isobutane conversion, **b** selectivity to isobutene, **c** selectivity to methane, and **d** long-term activity test for 35 h of reduced samples (reaction conditions: $T = 560\text{ }^{\circ}\text{C}$; $P = 1\text{ atm}$; $m = 0.5\text{ g}$; $\text{WHSV}(\text{i-C}_4\text{H}_{10}) = 3\text{ h}^{-1}$; $\text{H}_2/\text{i-C}_4\text{H}_{10} = 1$). Curves: **a** LF; **b** LFP; **c** LFN-3.0%; **d** LFNP-0.6%; **e** LFNP-3.0%; **f** LFNP-6.0%

Catalytic Activity and Stability

The isobutane dehydrogenation performance over Pt-based PTO catalysts was carried out in a fixed-bed reactor at $560\text{ }^{\circ}\text{C}$. Figure 6a–c presents the overall catalytic performances of all the catalysts as a function of time on stream. The contrast samples of reduced LF, LFP, and LFN-3.0% show relatively low isobutane conversions of less than 20%. The dehydrogenation activity and selectivity over reduced LFP fluctuated significantly over the run time compared with other samples, which indicates that the structural stability of reduced LFP is very poor during the reaction. The explanation can be found in Section of Structure–catalytic Performance Correlation. The reduced LFN-3.0% also exhibited low isobutane conversion and isobutene selectivity, whereas its methane selectivity was the highest one. This result can be ascribed to the strong cracking activity of metal Ni species in the absence of active Pt centers.

The main aim of introducing Ni element into the supported Pt-based catalysts is to improve the dehydrogenation activity of isobutane and selectivity to isobutene. However, the activity and selectivity of reduced LFNP-0.6% shows no obvious enhancement compared with that of the reduced LFP. According to the above TPR results, this is because that the strong interaction between Pt and Ni constrains the Pt center from fully converting isobutane to isobutene. For the reduced LFNP-0.6%, the isobutane conversion and selectivity to methane show a decreasing trend after about 70 min, due to the buildup of carbon deposition [48]. The carbon immediately disperses the active centers and inhibits

the cracking behavior, and then enhances the selectivity to isobutene after 70 min.

The interaction between Pt and Ni decreases as the Ni content increases from 0.6 to 6.0 wt%. The reduced LFNP-3.0% exhibits the best dehydrogenation performance, in particular the isobutane conversion and isobutene selectivity increase to about 38 and 92%, respectively. When the content of Ni is 6.0 wt%, the corresponding dehydrogenation activity slightly increases, whereas the selectivity to isobutene drops, accompanied by the increase in by-product methane. The best dehydrogenation performance of LFNP-3.0% should be attributed to the most suitable interaction between Pt and Ni. In other words, the moderate electrons transferred from Ni atoms to Pt atoms result in a moderate Pt electron density, which is beneficial for attaining a balance between isobutane adsorption and isobutene desorption, thereby reducing the possibility of deep cracking reaction. In summary, the Ni content affects the interaction strength between Pt and Ni, and then the interaction strength has important influences on the catalytic properties of LFNP- ω .

Table 2 shows the Pt dispersion and TOF values of LFP and LFNP-3.0%. The TOF value of LFNP-3.0% is approximately six times larger than that of LFP, which indicates that the dehydrogenation ability is enhanced significantly after the introduction of Ni, at least for a certain period of time. From the perspective of dispersion, the reduced LFNP-3.0% has a higher Pt dispersion (57.4%) than that of the reduced LFP, as shown in Table 2. Therefore, it is reasonable to infer that the introduction of Ni has a positive effect on the dispersion of Pt species, which is consistent with the BET, XRD,

and TEM results. The metal–metal interaction between Ni and Pt can elevate the dispersion of metallic Pt, which increases the utilization of Pt atoms and thus improves the catalytic performance of LFNP-3.0%.

To investigate stability, the isobutane dehydrogenation over reduced LFP and reduced LFNP-3.0% was carried out for 35 h and the catalytic behaviors are depicted in Fig. 6d, which clearly shows that the dehydrogenation performance of reduced LFNP-3.0% is much more stable than that of reduced LFP. We can see that the isobutane conversion of reduced LFNP-3.0% remains higher than that of LFP during the testing period. However, as time goes on, the conversion and selectivity of reduced LFNP-3.0% decrease gradually. For reduced LFP, both the conversion and selectivity increase in the beginning stage. After reaching the highest point, the reaction shows a slow deactivation followed by slow reactivation. The varying stability of reduced LFNP-3.0% and reduced LFP must be related to their structural evolution. The detailed analyses are shown below.

Structure–Catalytic Performance Correlation

To understand the relationship between structure and activity, the XRD, TGA, TEM, and EDX results of the used catalysts are analyzed.

Figure 7a shows the XRD patterns of the samples after reaction for 310 min. After reaction, the peaks of the original SiO₂, PTO, Ni, and Fe phases can still be seen. This suggests that the original structures of the catalysts are stable enough under reaction conditions. Furthermore, the diffraction peaks of Pt phase still cannot be detected. This is also consistent with the expected result. Additionally, new phase of FeNi alloy can be found in the Ni-containing samples, and Fe⁰ phase can be detected in the used LF and used LFP, which indicates that the partial Feⁿ⁺ ions can be reduced and even reacted with surface Ni to form FeNi alloy in the reductive reaction atmosphere.

The DTA curves in Fig. 7b show two carbon combustion peaks: the peak at the low temperature is attributed to amorphous carbon; the peak at the high temperature is

related to graphitized carbon [1, 5]. The two peaks shift to the low-temperature region due to the introduction of Ni, and the corresponding graphitized carbon peak becomes smaller than that of used LFP. This means that the more serious graphitized carbon can be easily formed on LFP than on LFNP-3.0%, which may not be beneficial to the regeneration treatments. In addition, the total mass losses of the used LFP and used LFNP-3.0% are the same, about 28%. However, the activity of LFNP-3.0% is about twice that of LFP, and the LFNP-3.0% has better anti-carbon deposition ability. In this respect, metallic Ni usually has a strong C–C cleavage capacity to generate a large amount of carbon deposition. The small amount of carbon deposition over used LFNP-3.0% should result from the Pt–Ni interaction, which weakens the C–C cleavage capacity of Ni. In summary, LFNP-3.0% has a better anti-carbon deposition performance than LFP.

Figure 8a, b shows TEM images of used LFP and used LFNP-3.0% after reaction for 310 min, respectively. The most probable particle sizes of used LFP and used LFNP-3.0% show slight increases from 3.2 nm to 4.4 nm and from 2.7 nm to 3.6 nm, respectively, which reveal that the preparation of supported Pt-based catalyst via lattice atomic-confining reduction of supported PTO precursor is an effective way to maintain stable Pt dispersion during reduction treatment and reaction. In fact, the used LFNP-3.0% still exhibits a smaller and narrower particle size than the used LFP during the reaction. At the same time, a small amount of amorphous carbon deposition on the surfaces of the used LFP and used LFNP-3.0% can be seen, respectively. In addition, the FeNi alloy NPs also can be found in the corresponding TEM images of used LFNP-3.0%. The formation of FeNi alloys would weaken the interaction between Pt and Ni and be beneficial to inhibiting the sintering of isolated Ni NPs that are far away from Pt.

The EDX maps of used LFP and used LFNP-3.0% (Fig. 8c, d, respectively) show that every metal element remains uniformly dispersed and no serious sintering has taken place even after the reaction at 560 °C for 310 min. The excellent anti-sintering performance of LFNP-3.0%

Fig. 7 **a** XRD patterns of used catalysts and **b** TG profiles of used LFP and used LFNP-3.0% after reaction for 310 min. Curves: a LF; b LFP; c LFNP-3.0%; d LFNP-0.6%; e LFNP-3.0%; f LFNP-6.0%

Fig. 8 TEM images (insets: statistics of particle size distribution) and EDX maps of used LFP (a, c) and used LFNP-3.0% (b, d) after reaction for 310 min; TEM images of e LFP and f LFNP-3.0% after reaction for 35 h

can be mainly attributed to the interaction between Pt and Ni. In addition, there is no obvious agglomeration of metallic particles after a long reaction time, as shown in Fig. 8e, f, which indicates the excellent anti-sintering ability of catalysts prepared by the lattice atomic-confined reduction of supported PTO precursor.

Based on the characterized results of reduced LFP before and after reaction, it can help to understand the fluctuant isobutane conversion and selectivity to isobutene of reduced LFP. According to the XRD and TPR results of LFP before reaction, it is deduced that the Fe⁰ NPs can be formed under the promotion of Pt⁰ NPs during reduction treatment, indicating that Pt⁰ NPs are quite possible to be covered by Fe⁰ NPs. This phenomenon suggests that the initial low activity and selectivity of the reduced LFP can be ascribed to the wrapping of Fe⁰ NPs at Pt⁰ sites. However, it is worth noting that carbon is mainly deposited on Pt⁰ NPs after a short reaction time over the used LFP (see Fig. 8a). This indicates that the Pt⁰ species can shift to the surface of Fe⁰ NPs in the reductive reaction atmosphere [49], which can gradually enhance the activity and selectivity in a period of time. This process must be accompanied by carbon deposition. Thus, the subsequent decline in activity and selectivity from the highest point can be ascribed to the continual coverage of carbon at the active sites. Nevertheless, the activity and selectivity increase again after about 9 h. In addition, after a long reaction time of 35 h, Fe⁰ NPs are also wrapped by deposited carbon (see Fig. 8e). Thus, it can be deduced that the deposited carbon should also behave as an effective catalyst for the isobutane conversion reaction [50, 51].

By comparing the TEM images of the used LFNP-3.0% in Fig. 8b, f, it can be concluded that the FeNi alloy forms easily in a reductive reaction atmosphere, and the FeNi alloy NPs become the centers of carbon formation with the carbon layer thickening after a long reaction time. Although the amount of carbon deposition is high, it is not the main reason for the deactivation of the reduced LFNP-3.0% catalyst. The slightly decreased activity of reduced LFNP-3.0% should be related to the formation of FeNi alloy phase. This is due to the fact that the formation of FeNi alloy phase weakens the interaction between Pt and Ni. It further suggests that isobutane dehydrogenation to isobutene is determined by the strength of the Pt–Ni interaction, which depends on the Ni content.

Conclusion

In this work, a series of LaFe_{1-x}(Ni, Pt)_xO₃ perovskite precursors supported on SiO₂ were prepared. After lattice atomic-confined reduction, the novel Pt–Ni bimetallic catalysts supported on La₂O₃–LaFeO₃/SiO₂ catalysts were obtained. And these catalysts were applied in isobutane dehydrogenation to isobutene reaction. The results verify that it has interaction between Pt and Ni, which can be tuned by changing the Ni content. And the interaction between Pt and Ni plays an important role in improving the dehydrogenation performance. The reduced LFNP-3.0% exhibited good activity, high selectivity, excellent anti-sintering, good resistance to carbon deposition, and long-term stability for the isobutane dehydrogenation. It is necessary to believe that Pt–Ni bimetallic catalysts prepared by lattice atomic-confined reduction are excellent and promising catalysts for the dehydrogenation reaction.

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