

A Surface Defect-Promoted Ni Nanocatalyst with Simultaneously Enhanced Activity and Stability

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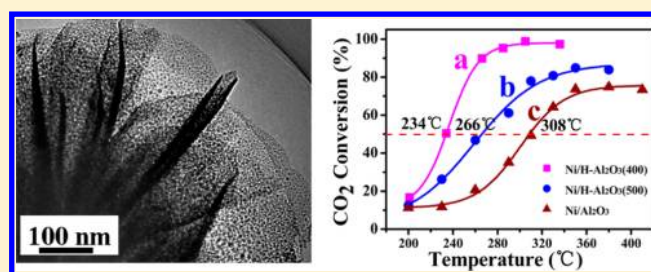
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S Supporting Information

ABSTRACT: How to achieve supported metal nanocatalysts with simultaneously enhanced activity and stability is of vital importance in heterogeneous catalysis and remains a challenging goal. In this work, a surface defect-promoted Ni nanocatalyst with a high dispersion and high particle density embedded on a hierarchical Al₂O₃ matrix was fabricated via a facile method involving an in situ reduction process, which exhibits excellent activity and stability simultaneously for the reaction of CO₂ methanation. HRTEM, HAADF-STEM, EXAFS, and positron annihilation spectroscopy demonstrate the existence of abundant surface vacancy clusters that serve as active sites, accounting for the significantly enhanced low-temperature activity of the supported Ni nanoparticles. In addition, the anchoring effect from the support gives rise to a high reaction stability, without sintering and/or aggregation of active species during long-term use.

KEYWORDS: Ni nanocatalyst, surface defect, low-temperature activation, CO₂ methanation, layered double hydroxides



INTRODUCTION

For many heterogeneous reactions, the formation of metal nanocatalyst particles with effective control over size and morphology and their subsequent immobilization on a suitable support have both been found to be efficient ways of increasing catalyst activity and selectivity.¹ However, how to achieve supported metal nanocatalysts with simultaneously enhanced activity and stability is of vital importance and remains a challenging goal, because many factors (e.g., the surface morphology, electronic structure, and metal–support interaction) would impose significant influences on the catalytic performance. It is widely accepted that the surface defects of nanocatalysts serving as an active site play a decisive role in the adsorption and reactivity in catalytic reactions. The formation or introduction of abundant and specific defect site/defect on the surface of supported nanocatalysts is a promising approach for tailoring the surface morphology and electronic structure to enhance heterogeneous catalytic activity,² but the creation of desirable defects as well as understanding their roles in activity of supported nanocatalysts at the atomic scale is still lacking. Although nanoparticles immobilized on various supports via physicochemical deposition routes often suffer from rapid deactivation (especially at high temperatures) because of sintering and/or aggregation of nanoparticles,³ it has been proposed that if a strong interaction (e.g., a covalent bond) is involved between the metal nanoparticles and the support, the

migration or sintering of nanoparticles should be significantly inhibited.⁴

Given the two problems discussed above, an effective immobilization approach and a suitable support are two key factors in the design and fabrication of highly efficient supported metal nanocatalysts. Recently, considerable interest has been focused on layered double-hydroxide materials (LDHs) as sorbents and heterogeneous catalysts and/or precursors, as a result of their versatility in chemical composition and structural architecture.^{5–7} A unique structural characteristic of LDH materials is that the M^{II} and M^{III} cations are distributed in a highly ordered manner in the hydroxide layers, as verified by Gray et al. by means of multinuclear nuclear magnetic resonance spectroscopy.⁸ Moreover, an in situ topotactic transformation of LDHs materials to metal oxides or metal–metal oxide composites will occur upon heating in air or under reducing conditions, respectively.⁹ This provides a method for obtaining supported metal nanoparticles with specific morphology and/or surface structure and high dispersion.

The catalytic hydrogenation of carbon dioxide to give methane, known as methanation, is an efficient approach to

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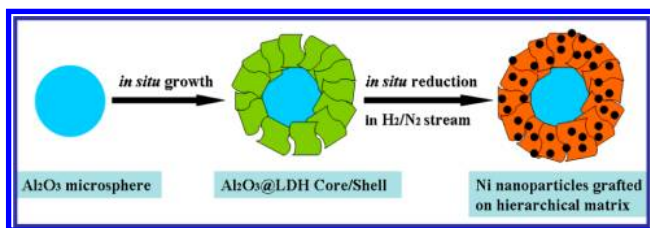
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recycling exhausted CO_2 to give a useful fuel, with potential commercial applications and environmental benefits.¹⁰ Noble metals (e.g., Ru, Rh, and Pd) have been found to be the most effective catalysts of CO_2 methanation under relatively mild reaction conditions (temperature and pressure),¹¹ but the high cost as well as limited availability restricts their practical applications.^{12a} Thus, previous work has been focused on the study of non-noble metal catalysts.¹² Although first-row transition metal catalysts (e.g., Ni, Co, and Cu) have been studied as catalysts of this reaction, they have shown lower activities than noble metals.¹³ Therefore, it is highly necessary to find ways of fabricating supported transition metal catalysts with excellent activity and stability simultaneously for CO_2 methanation, for the purpose of achieving the substitution of noble metals.

In this work, a surface defect-promoted Ni nanocatalyst with a high dispersion and high particle density embedded on a flowerlike Al_2O_3 matrix was fabricated via an in situ reduction of a hierarchical $\text{Ni}^{\text{II}}\text{Al}^{\text{III}}\text{-LDH}$ precursor (denoted H-LDH) (Scheme 1), which exhibits excellent catalytic activity as well as

Scheme 1. Illustration of the Formation of Ni Nanoparticles with High Dispersion and High Density on a Hierarchical Flowerlike Al_2O_3 Matrix via an in Situ Reduction Process of the $\text{Ni}^{\text{II}}\text{Al}^{\text{III}}\text{-LDH}$ Precursor



stability for CO_2 methanation. HRTEM, HAADF-STEM, positron annihilation spectroscopy, and extended X-ray absorption fine structure (EXAFS) measurements demonstrate that the abundant surface vacancy clusters exist on the surface of Ni nanoparticles serving as active sites, accounting for the significantly enhanced low-temperature activity of the supported Ni nanocatalyst. In addition, the anchoring effect from the support gives rise to a high reaction stability for long-term employment. Our approach holds significant promise for the design and fabrication of supported metal nanocatalysts in which activity and stability can be guaranteed at the same time.

EXPERIMENTAL SECTION

Materials. Chemical reagents, including $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, urea $[\text{CO}(\text{NH}_2)_2]$, sodium tartrate, and NH_4NO_3 , were obtained from Beijing Chemical Co., Ltd., and used without further purification. Deionized and decarbonated water was used in all the experimental processes.

Preparation of the H-LDH Precursor. First, amorphous Al_2O_3 microspheres were prepared by the hydrothermal method reported previously.¹⁴ The hierarchical H-LDH was prepared by an in situ growth technique similar to that from a previous report by our group.¹⁵ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) and NH_4NO_3 (0.06 mol) were dissolved in deionized water (100 mL), and a 3% ammonia solution was then slowly added until the pH reached 6.5. The amorphous Al_2O_3 microspheres were placed in the solution described above in an autoclave at 75°C for 36 h. Finally, the H-LDH was separated by centrifugation, rinsed with ethanol, and dried at room temperature.

Preparation of $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(400)$ and $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(500)$. Supported Ni nanoparticles on a hierarchical flowerlike Al_2O_3 matrix

were obtained via an in situ reduction process of the H-LDH precursor at reduction temperatures of 400 and 500°C [denoted as $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(400)$ and $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(500)$, respectively]. In a typical procedure, 1.5 g of H-LDH was reduced in a H_2/N_2 (50/50, v/v) stream at different reduction temperatures (400 or 500°C) for 5 h, with a heating rate of $2^\circ\text{C}/\text{min}$. The reduction process results in the phase transformation of the H-LDH to $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(400)$ and $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(500)$ (Ni loading of ~ 20 wt %). The resulting products were slowly cooled to the reaction temperature in a N_2 stream for subsequent catalytic evaluation.

Preparation of $\text{Ni}/\text{Al}_2\text{O}_3$. The comparison catalyst, $\text{Ni}/\text{Al}_2\text{O}_3$, was prepared by a conventional impregnation method. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was first dissolved in distilled water, followed by the addition of amorphous Al_2O_3 microspheres. The slurry was stirred at room temperature for 8 h, aged for 24 h, and then dried at 100°C for 6 h. The solid sample was calcined in air at 450°C for 5 h, with a heating rate of $2^\circ\text{C}/\text{min}$. Finally, it was reduced in a H_2/N_2 (50/50, v/v) stream at 500°C for 6 h, with a heating rate of $2^\circ\text{C}/\text{min}$. The resulting product (Ni loading of ~ 20 wt %) was slowly cooled to the reaction temperature in a N_2 stream for subsequent catalytic evaluation.

Evaluation of the Catalytic Performance in CO_2 Methanation. The catalytic activity in CO_2 methanation was evaluated by using a quartz tube reactor (8 mm in diameter) at atmospheric pressure. Brooks mass flow controllers were used to control the gas flow rate. To eliminate temperature and concentration gradients, 1.0 g of the catalyst was mixed with 0.3 mL of SiC (40–60 mesh) and then packed in the reactor. The temperature of the reactor was controlled by three thermocouples (located near the entrance, at the middle, and near the exit of the bed). The catalyst bed length was 3 cm. After the catalyst pretreatment, the reaction gas (CO_2 and H_2 , 1/4, v/v) was mixed with Ar (25%, v/v), a 60 standard cubic centimeters per minute (sccm) total flow rate was introduced to the reactor, and the CO_2 conversion was measured over an elevated temperature range of $200\text{--}410^\circ\text{C}$. The weight hourly space velocity (WHSV) was maintained at $2400\text{ mL g}_{\text{cat}}^{-1}\text{ h}^{-1}$. At each temperature, the conversion reached a constant value in ~ 3 h. To obtain the turnover frequency (TOF) of the catalysts, steady-state experiments were also conducted at approximately the low reaction temperature (220°C), a low level of CO_2 conversion ($<10\%$), and a high WHSV ($9600\text{ mL g}_{\text{cat}}^{-1}\text{ h}^{-1}$), to minimize the effect of transport and water inhibition. TOF is defined as the number of methane molecules produced per surface Ni atom of the catalyst per second according to hydrogen temperature-programmed desorption ($\text{H}_2\text{-TPD}$) results of as-prepared catalysts and the FID signal of CH_4 . The product gas stream was analyzed on line by gas chromatography (GC) (Shimadzu, 2014C) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The CO_2 conversion and selectivity were calculated on the basis of the CO_2 , CO, H_2 , and CH_4 mole fractions in the products.

Characterization. Powder X-ray diffraction (XRD) patterns of the samples were collected using a Shimadzu XRD-6000 diffractometer using a $\text{Cu K}\alpha$ source, with a scan step of 0.02° and a 2θ scan range between 5° and 80° . The morphology of $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(400)$, $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(500)$, and $\text{Ni}/\text{Al}_2\text{O}_3$ samples was investigated using a Zeiss Supra 55 scanning electron microscope (SEM) with an accelerating voltage of 20 kV. A FEI Cs-corrected Titan 80–300 microscope operated at 300 kV was employed to conduct structural investigations by using TEM, HRTEM, and STEM modes. For detection of the Ni nanoparticles dispersed on the $\text{Ni}/\text{H}-\text{Al}_2\text{O}_3(400)$ nanoflakes and estimation of particle size distribution, high-angle annular dark field imaging (HAADF) and elemental maps were used in the STEM mode. The specific surface area was determined by Brunauer–Emmett–Teller (BET) methods using a Quantachrome Autosorb-1C-VP analyzer. Positron annihilation measurements were taken with a fast–slow coincidence ORTEC system with a time resolution of 187 ps for the full width at half-maximum. A 5×10^5 Bq source of ^{22}Na was sandwiched between two identical samples. The Ni K-edge XANES measurements were performed at beamline IW1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS).

Hydrogen temperature-programmed reduction (H_2 -TPR) was conducted in a quartz tube reactor on a Micromeritics AutoChem II 2920 instrument with a thermal conductivity detector (TCD). In a typical process, 100 mg of a sample was sealed in the reactor, and then a gaseous mixture of H_2 and Ar (1/9, v/v) was fed into the reactor at a rate of 40 mL/min. The temperature was increased to 900 °C at a heating rate of 10 °C/min. Hydrogen temperature-programmed desorption (H_2 -TPD) was used for the measurement of nickel surface area and dispersion of the catalyst, after H_2 chemisorption, by removing the prior chemisorbed hydrogen with an argon stream at a rate of 40 mL/min in the temperature range of 298–823 K on a Micromeritics AutoChem II 2920 instrument.

RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of the H-LDH precursor, which can be indexed to a pristine NiAl-LDH phase.^{9a} SEM

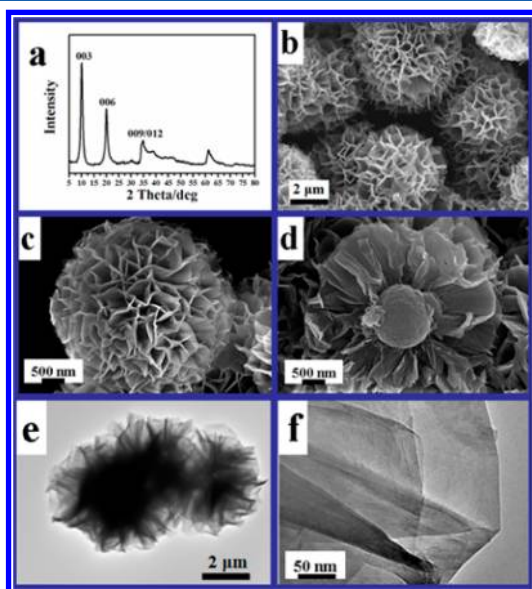


Figure 1. (a) XRD pattern of the as-prepared H-LDH precursor. (b and c) SEM images of the as-prepared H-LDH at (b) low magnification and (c) high magnification. (d) SEM sectional image of a single microsphere exhibiting the structure of LDH flowerlike shell/ Al_2O_3 core. (e and f) TEM images of (e) the H-LDH microspheres and (f) a single LDH nanoflake selected from panel e.

images (Figure 1b,c) show that the as-synthesized H-LDH sample is composed of numerous frizzy nanoflakes ($\sim 1.5 \mu m$ in width and ~ 30 nm in thickness) intercrossing with each other. The sectional image of an H-LDH microsphere (Figure 1d) confirms that the LDH flowerlike shell ($\sim 1.5 \mu m$ in height) is grafted to the amorphous Al_2O_3 core. TEM images show that a single LDH microsphere consists of a flowerlike shell and a solid core (Figure 1e), and an individual nanoflake exhibits a smooth and frizzy surface (Figure 1f). The in situ crystallization technique involves direct growth of LDH crystallites on the Al_2O_3 microsphere with their *ab*-facet perpendicular to the substrate surface. This can be explained by a homogeneous nucleation mechanism as described in our previous work,¹⁵ in which chemical bonding ensures a strong adhesion of the LDH nanoflakes to the substrate.

Supported Ni nanoparticles were subsequently obtained by an in situ reduction of the H-LDH microspheres (see Scheme S1 of the Supporting Information and the corresponding detailed discussion). Panels a and b of Figure S1 of the Supporting Information illustrate the XRD patterns of the

products obtained at reduction temperatures of 400 and 500 °C, respectively [denoted as Ni/H- Al_2O_3 (400) and Ni/H- Al_2O_3 (500), respectively], both of which can be indexed to the face-centered cubic (fcc) Ni phase (JCPDS 7440-02-0). For the purpose of comparison, Figure S1c of the Supporting Information shows the XRD pattern of a Ni/ Al_2O_3 material prepared via the traditional impregnation method followed by reduction at 500 °C. The TEM image of Ni/H- Al_2O_3 (400) (Figure 2a) displays well-dispersed Ni nanoparticles with a

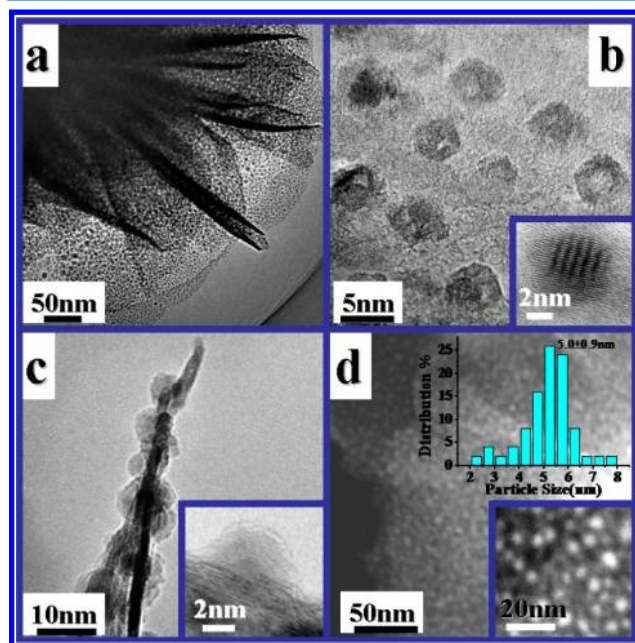


Figure 2. HRTEM images of Ni/H- Al_2O_3 (400): (a) an overall image, (b) one nanoflake with Ni nanoparticles embedded onto its surface (inset, a single-crystalline Ni nanoparticle), (c) a cross-sectional image of one nanoflake with Ni nanoparticles embedded on both sides of the substrate (inset, a cross section of a single-crystalline Ni nanoparticle), and (d) STEM image of the Ni nanoparticles dispersed on the nanoflakes (inset, a portion of the nanoflake and the size distribution based on more than 200 nanoparticles counted).

rather high density on the nanoflake substrate. The high-magnification TEM image (Figure 2b) of a nanoflake reveals that polyhedral Ni nanoparticles with a uniform size (~ 5.0 nm) are immobilized within the nanoflake substrate with a high dispersion. A single Ni nanoparticle with a clearly observed lattice interplanar spacing of 0.202 nm is shown in the inset of Figure 2b, corresponding to the (111) plane of a fcc Ni phase. The cross-sectional TEM image of a nanoflake (Figure 2c) shows that the Ni nanoparticles are grafted onto both sides of the nanoflake, with the lattice fringe of Ni superimposed on the substrate (Figure 2c, inset).¹⁶ In addition, the STEM image (Figure 2d) reveals that the supported Ni nanoparticles possess a uniform size distribution (5.0 ± 0.9 nm) and extremely high density ($\sim 2.4 \times 10^{16}$ particles/ m^2), far exceeding the densities of metal nanoparticles reported previously.¹⁷ Ni/H- Al_2O_3 (500) (Figure S2a,b of the Supporting Information) displays a similar architecture but has a larger Ni particle size (7.2 ± 1.5 nm) and lower density ($\sim 7.8 \times 10^{15}$ particles/ m^2), indicating that the higher reduction temperature leads to an increase in particle size. In marked contrast, the Ni/ Al_2O_3 sample prepared by the traditional method was characterized by a random packing of Ni nanoparticles with irregular

morphology and very broad particle size distribution (14.0 ± 3.5 nm) as well as low density ($\sim 3.5 \times 10^{15}$ particles/m²) (Figure S2c,d of the Supporting Information). In addition, the average particle sizes of Ni/H–Al₂O₃(400), Ni/H–Al₂O₃(500), and Ni/Al₂O₃, determined by using the Scherrer formula, are 4.6, 6.8, and 14.3 nm, respectively, in approximate agreement with the TEM observations.

The chemical compositions of Ni/H–Al₂O₃(400), Ni/H–Al₂O₃(500), and Ni/Al₂O₃ were studied by energy dispersive X-ray spectroscopy (EDS) (Figure S3 of the Supporting Information), which indicate that the three samples possess similar element components and content. Furthermore, the loading of Ni nanoparticles in these samples was found to be ~ 20 wt % by means of inductively coupled plasma–atomic emission spectroscopy (ICP–AES). In addition, the nitrogen adsorption–desorption isotherms of the three samples all display a type IV isotherm with a type H3 hysteresis loop, with a pore size distribution of 2–5 nm (see Figure S4 of the Supporting Information and the corresponding discussion). The specific surface areas of Ni/H–Al₂O₃(400), Ni/H–Al₂O₃(500), and Ni/Al₂O₃ were 143, 152, and 135 m²/g, respectively (Table S1 of the Supporting Information).

The catalytic activity of the three samples toward the reaction of CO₂ methanation was studied. Figure 3A displays the CO₂

however, the level of CO₂ conversion exceeded 90% at 265 °C and reached the maximal value (99%) at 300 °C, which is far superior to the catalytic activity of supported Ru, Pd, Ni, and Ni/Ru catalysts reported previously.^{11,18–21} It should be noted that both Ni/H–Al₂O₃(400) and Ni/H–Al₂O₃(500) have very satisfactory selectivity toward CH₄ (>99%) over the whole temperature range, much higher than that of Ni/Al₂O₃ (95%). The results clearly show that the Ni/H–Al₂O₃(400) catalyst exhibits the highest activity toward the reaction of CO₂ methanation.

To establish the structure–activity relationship, the turnover frequency (TOF) toward CO₂ methanation of the three catalysts was evaluated at a low reaction temperature (220 °C), a low level of CO₂ conversion (<10%) and a high WHSV (9600 mL g_{cat}^{−1} h^{−1}), to minimize the effect of transport and water inhibition. Figure S5 of the Supporting Information shows that the methane production rate increased along with Ni surface area, indicating a strong correlation between the activity and Ni surface area. It was found that Ni/H–Al₂O₃(400) exhibits a Ni surface area of 39.5 m²/g_{cat}, much larger than those of Ni/H–Al₂O₃(500) (30.3 m²/g_{cat}) and Ni/Al₂O₃ (14.7 m²/g_{cat}). The TOF value as a function of Ni dispersion for the three samples (Figure 3B) shows a linear correlation, indicative of a structure-sensitive reaction. Table S2 of the Supporting Information lists the TOF values of the three catalysts toward CO₂ methanation that decrease in the following order: Ni/H–Al₂O₃(400) (2.4×10^{-3} s^{−1}) > Ni/H–Al₂O₃(500) (1.2×10^{-3} s^{−1}) > Ni/Al₂O₃ (5.0×10^{-4} s^{−1}).

STEM and Cs-HRTEM measurements (Figure 4) were performed to investigate the correlation between the microstructure and excellent low-temperature activity of Ni/H–Al₂O₃(400) toward CO₂ methanation. Panels a-1 and a-2 of

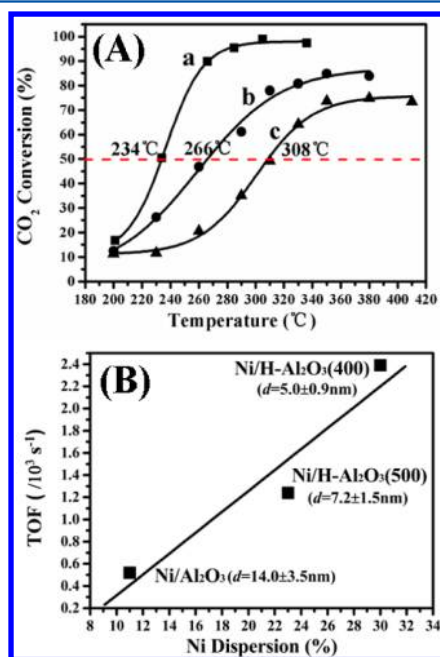


Figure 3. (A) Profiles of CO₂ conversion vs temperature for CO₂ methanation in the presence of (a) Ni/H–Al₂O₃(400), (b) Ni/H–Al₂O₃(500), and (c) Ni/Al₂O₃ (reaction conditions of 200–410 °C and a WHSV of 2400 mL g_{cat}^{−1} h^{−1}). (B) Relationship between the TOF value and Ni dispersion (reaction conditions of 220 °C, a WHSV of 9600 mL g_{cat}^{−1} h^{−1}, and <10% CO₂ conversion).

conversion as a function of temperature. The value of T_{50} , corresponding to the temperature at which 50% conversion is obtained, was 234, 266, and 308 °C for Ni/H–Al₂O₃(400), Ni/H–Al₂O₃(500), and Ni/Al₂O₃, respectively. Ni/H–Al₂O₃(400) thus clearly possesses a significantly enhanced low-temperature activity for CO₂ methanation. Moreover, it was found that the maximal levels of CO₂ conversion in the presence of Ni/H–Al₂O₃(500) and Ni/Al₂O₃ were only 85.3 and 75.1%, respectively, at 350 °C. In the case of Ni/H–Al₂O₃(400),

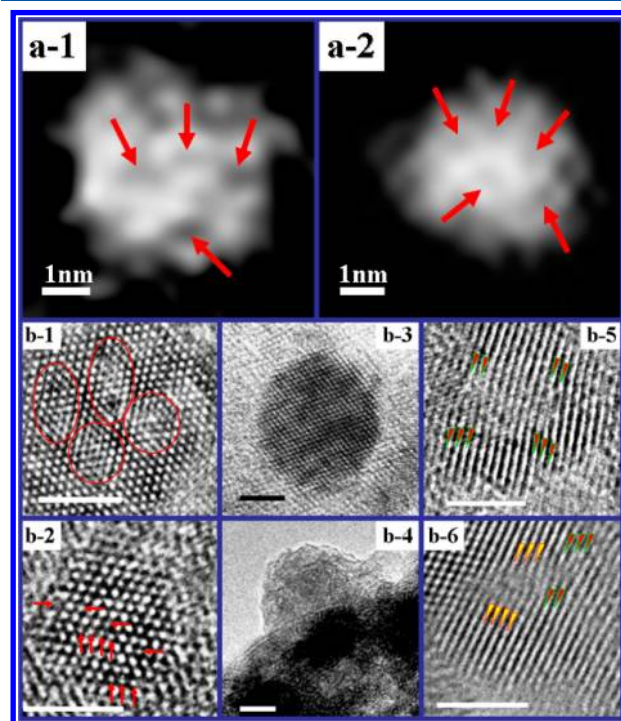


Figure 4. (a-1 and a-2) High-angle annular dark field (HAADF) STEM images of Ni nanoparticles in the sample of Ni/H–Al₂O₃(400). (b-1–b-6) HRTEM images of Ni nanoparticles selected from the Ni/H–Al₂O₃(400) sample (the scale bar is 2 nm).

Table 1. Positron Lifetimes and Relative Intensities for Ni/H–Al₂O₃(400), Ni/H–Al₂O₃(500), Ni/Al₂O₃, and Pristine Al₂O₃

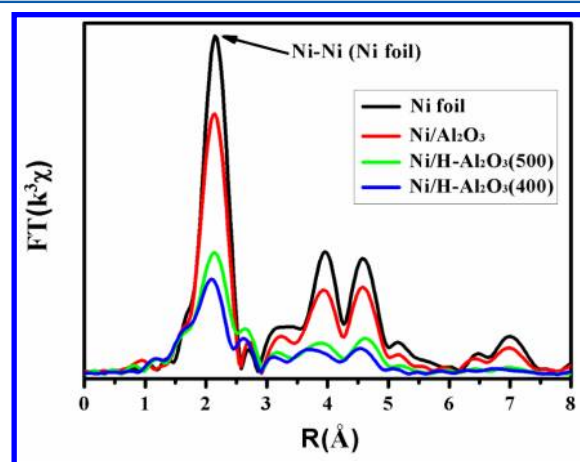
sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	I_2/I_1
amorphous Al ₂ O ₃	255.5	592.0	1.979	58.5	37.0	4.47	0.63
Ni/H–Al ₂ O ₃ (400)	219.1	398.5	2.033	40.5	56.3	3.18	1.39
Ni/H–Al ₂ O ₃ (500)	227.4	418.0	1.982	47.1	48.3	4.61	1.03
Ni/Al ₂ O ₃	215.3	455.0	2.411	52.6	44.7	2.69	0.85

Figure 4 show HAADF-STEM images of Ni nanoparticles selected from the Ni/H–Al₂O₃(400) sample. Several “dark pits” (~1 nm) can be found on the surface of the Ni nanoparticle, which is probably indicative of Ni vacancy clusters. Panels b-1 and b-2 of Figure 4 display a high density of elongated or aggregated dark spots in the images of Ni nanoparticles grafted on the Al₂O₃ substrate, which can be attributed to linear Ni vacancies or Ni vacancy clusters on the surface.^{2a,22–24} Several dark pits (Figure 4b-3) as well as steps and ledges (Figure 4b-4) on the surface of Ni nanoparticles are observed. This shows that the Ni nanoparticles possess a very rough surface, suggesting the occurrence of surface reconstruction that results in Ni vacancy clusters.^{24–27} Moreover, it is clearly observed from panels b-5 and b-6 of Figure 4 that the Ni nanoparticles exhibit a distortion of lattice fringes (including bending and dislocation), demonstrating the presence of abundant surface defect sites. It is widely accepted that the surface defect of catalysts plays a decisive role in the adsorption and reactivity in many heterogeneous catalytic processes. Therefore, it is proposed that these defect sites are responsible for the excellent low-temperature activity of Ni/H–Al₂O₃(400).

Positron annihilation spectroscopy (PAS) is well-recognized as a powerful tool for studying defects in solids,²⁸ which can provide information about the size, type, and relative density of various defects and/or vacancies. The electronic environment and positron annihilation mechanism of the trapping center are usually characterized by the parameters S and W , the values of which reflect the relative contributions to positron annihilation of the lower- and higher-momentum core electrons, respectively.^{28b,29} Figure S6 of the Supporting Information shows a plot of S versus W for the three supported Ni samples as well as for pristine Al₂O₃. The three supported Ni samples fall on a single line, indicating they have identical trapping centers, e.g., Ni vacancies on the surface of the samples. However, the position of pristine Al₂O₃ deviates from this line significantly, suggesting that a different positron annihilation mechanism and trapping center is involved. Table 1 lists the positron lifetime components (τ_1 , τ_2 , and τ_3) and corresponding relative intensities (I_1 , I_2 , and I_3) for the three supported Ni samples and pristine Al₂O₃. The longest-lived component (τ_3) for all these samples is probably caused by the annihilation of orthopositronium atoms formed in the large voids present in the material.³⁰ The shortest one (τ_1) can be attributed to small size defects, e.g., monovacancies mainly in the bulk section of nanoparticles,³¹ accounting for the similar τ_1 values for the three supported Ni samples. It was found that the τ_1 value of Al₂O₃ is much larger than those of the three supported Ni samples. This indicates that the trapping centers in the supported Ni samples mainly originate from Ni rather than the Al₂O₃ substrate, in accordance with the results of the S – W plot. The intermediate component τ_2 arises from positrons trapped by large size defects (e.g., vacancy clusters, such as dimers, trimers, or larger species), which tend to be located on the surface, boundary, and interface of the nanoparticles.^{27,31a,32}

In addition, the I_2/I_1 ratio represents the relative concentration proportion of larger size defects (Ni vacancy clusters) to small size defects (Ni monovacancies) and decreases in the following order: Ni/H–Al₂O₃(400) > Ni/H–Al₂O₃(500) > Ni/Al₂O₃. This confirms that Ni/H–Al₂O₃(400) possesses the highest relative concentration of Ni vacancy clusters on its surface and suggests that this may be the reason for the highest catalytic activity toward CO₂ methanation.

EXAFS spectroscopy was further applied to confirm the relationship between Ni vacancy clusters and catalytic activity by elucidating the local coordination environment of Ni atoms (Figure 5). The fitting parameters (Table 2) show that the Ni–

**Figure 5.** Fourier transforms of EXAFS spectra for Ni foil (black), Ni/Al₂O₃ (red), Ni/H–Al₂O₃(500) (green), and Ni/H–Al₂O₃(400) (blue).**Table 2.** EXAFS Fitting Parameters of Ni Foil, Ni/Al₂O₃, Ni/H–Al₂O₃(500), and Ni/H–Al₂O₃(400)^a

sample	N	R (Å)
Ni foil	12	2.50
Ni/Al ₂ O ₃	11.1	2.49
Ni/H–Al ₂ O ₃ (500)	8.5	2.49
Ni/H–Al ₂ O ₃ (400)	7.3	2.49

^a N is the coordination number. Error bounds (accuracies) characterizing the structural parameters obtained by EXAFS spectroscopy are estimated as follows: $\pm 20\%$ for N and ± 0.02 Å for R .

Ni coordination number in the three supported Ni samples is lower than that of Ni foil (12) and decreases in the following order: Ni/Al₂O₃ > Ni/H–Al₂O₃(500) > Ni/H–Al₂O₃(400). This indicates that the Ni/H–Al₂O₃(400) sample possesses the highest level of unsaturation of Ni–Ni coordination, in accordance with the highest concentration of surface Ni vacancy clusters on its surface revealed by PAS. It has been reported that the reactivity of catalysts is often dominated by low-coordinated atoms such as surface defect sites.³³ Therefore, we can conclude that the abundant vacancy clusters on the surface of Ni/H–Al₂O₃(400) serve as active sites, accounting

for its significantly enhanced low-temperature reactivity in CO₂ methanation.

Although CO₂ methanation is a comparatively simple reaction, the reaction mechanism is rather controversial. There are two main opinions about the nature of the intermediate and the methane formation process. The first one involves the conversion of CO₂ to CO with the formation of formate through a carbonate species, followed by the subsequent reaction as CO methanation.^{34a–c} In this route, formation of CO and CO dissociation (C–O bond breaking) are two key steps for the CO₂ methanation process. The second describes the direct hydrogenation of CO₂ to methane without a CO intermediate.^{34d,e} In terms of this work, it is proposed that the presence of Ni vacancy clusters is favorable for H₂ dissociation, CO dissociation, and its interaction with hydrogen, because of a marked decrease in the reaction barrier at the defects.^{2a,35} Furthermore, the supported Ni nanocatalyst with a high dispersion and large particle density may facilitate the cooperative effect of active sites and basic sites for CO formation, which is a key intermediate in CO₂ methanation.

The long-term catalytic stability and thermal stability of Ni/H–Al₂O₃(400) were also investigated. As shown in Figure 6A,

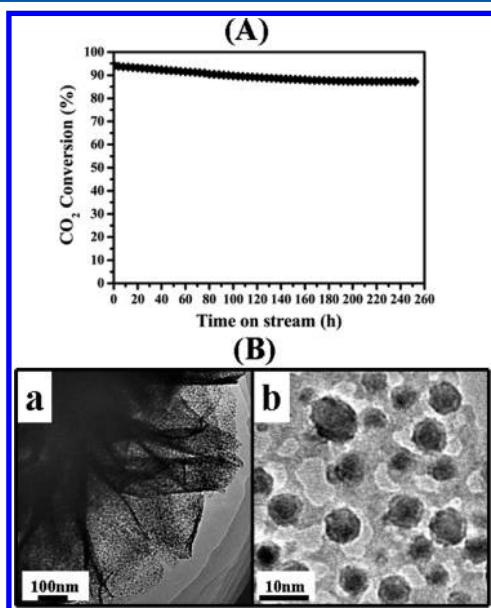


Figure 6. (A) Plot of CO₂ conversion vs reaction time at 290 °C for the Ni/H–Al₂O₃(400) catalyst. (B) TEM images of the Ni/H–Al₂O₃(400) catalyst after reaction for 252 h: (a) low and (b) high magnification.

the level of CO₂ conversion decreases slowly in the first 180 h and then remains almost constant, with a total decrease of 7% over 252 h. No obvious aggregation or sintering of Ni nanoparticles was observed for the Ni/H–Al₂O₃(400) catalyst after 252 h on stream (Figure 6B). Moreover, the control of thermal sintering is critical for maintaining the activity, which requires a stable support and effective method to prevent particle migration and coalescence.³⁶ The thermal stability of the Ni/H–Al₂O₃(400) catalyst was studied in the reaction gas (4/1 H₂/CO₂, 400 °C, 1 atm) for 500 h, and the relative diameter of the nickel particle ($d_{\text{Ni},t}/d_{\text{Ni},0}$) was plotted as a function of time on stream (Figure S7A of the Supporting Information). It was found that the relative diameter of Ni nanoparticles increases slowly with time. In addition, no

obvious morphological change was observed after 500 h (Figure S7B of the Supporting Information), except a small increase in the mean diameter of Ni nanoparticles (from ~5.0 to ~8.1 nm). The embedding of Ni nanoparticles onto the flowerlike Al₂O₃ matrix enhances the metal–support interaction and therefore prevents sintering and/or aggregation of the active species. This shows that by virtue of being embedded in the hierarchical matrix via an in situ reduction approach, the Ni nanoparticles exhibit a high degree of dispersion and high stability, which guarantees their high activity during long-term use.

CONCLUSIONS

In summary, a supported Ni nanocatalyst embedded onto a hierarchical substrate with a high particle density and high dispersion was fabricated by in situ reduction of a NiAl-LDH precursor. The catalyst shows excellent low-temperature activity and stability in carbon dioxide methanation. The high degree of Ni^{II} dispersion in the LDH precursor induces a good distribution of Ni nanoparticles and prevents their aggregation; the intrinsic topotactic phase transformation from the LDH matrix to supported Ni nanoparticles ensures a strong anchoring effect. By virtue of the wide versatility of LDH composition and architecture, the control over reactivity and stability of supported Ni nanoparticles demonstrated in this work offers a promising strategy for the fabrication of other metal nanocatalysts with significantly enhanced catalytic behavior.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S7, Scheme S1, and Tables S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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