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Self-assembly of flower-like LaNiAlO_3 -supported nickel catalysts for CO methanation

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Abstract

A series of supported Ni nanoparticles on a flower-like porous $\text{LaNi}_{0.6}\text{Al}_{0.4}\text{O}_3$ (LNAO) perovskite carrier ($z\text{Ni/LNAO}$; $z = 5, 10$ and 15 wt%) were successfully synthesized using a controlled self-assembly sol-gel method. The experimental results showed that the presence of Ni nanoparticles markedly enhanced the reaction rate of CO conversion, namely from 12.4 $\text{mmol}/(\text{g}_{\text{cat}} \text{ h})$ over LNAO to 244 $\text{mmol}/(\text{g}_{\text{cat}} \text{ h})$ over 10 wt% Ni/LNAO. The porous LNAO perovskite support provides both a large surface area to well disperse Ni nanoparticles and active sites for the methanation reaction, thus resulting in a catalyst with activity (per gram of catalyst basis) at least comparable to other nickel metal-based supported catalysts reported so far and with very good stability. Reaction rates calculated based on Ni exposed surface and total Ni amount revealed that Ni active sites in the Ni nanoparticles and bulk perovskite were distinct.

Keywords: Self-assembly; Flower-like porous material; Al-substituted lanthanum nickelate; Perovskite-supported Ni catalyst; CO methanation.

1. Introduction

Conversion of carbon monoxide to methane through hydrogenation, which is named CO methanation, is an effective technology for energy applications. Recently, attention has been paid on CO methanation as a practical technology and an operative methodology for fuel gas clean up [1, 2]. Synthetic natural gas (SNG) is produced via gasification of coal [3] and biomass [4, 5], which then can generate synthetic gas (syngas, a mixture of CO/H₂) via steam reforming (SMR) and WGS reaction processes [6-8]. The product gas stream from the latter processes contains 1–20 % CO and the rest is H₂. One of the common methods for removing CO from the reformat gas (pure hydrogen production) is preferential oxidation of CO (PROX) [9]. Methanation of CO ($\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$, $\Delta H^\circ = -206 \text{ kJ/mol}$) is another pathway to reduce the CO content in reformat gas [1]. Compared with the PROX process, methanation of CO has the advantage of no air (or O₂) addition to the reformat gas stream, which prevents from safety issues [10]. Fe, Co, Ni, and Ru show sufficiently high activities for the hydrogenation of carbon monoxide [11-13].

Although noble metal-based catalysts have been widely investigated to inhibit coking as compared to Ni-based catalysts, some disadvantages (e.g. easy agglomeration and high cost) limit their wide application [14]. For this reason, research on developing highly active and selective Ni-based catalysts with less coke deposition is of great importance [15, 16]. Several studies have categorized the type of carbon deposited on Ni-based catalysts [17-19]. Recently, Vasiliades et al. [18, 19] extended the knowledge in this field (carbon deposition via CH₄ and CO dissociation) and enabled understanding of the actual redox-promotional role of reducible metal oxide supports through a series of steady-state isotopic transient kinetic analysis (SSITKA) experiments.

An attractive alternative is to use Ni as active phase together with other transition metals to form perovskite-type oxides (ABO₃). Replacement of part of A or B ions with other cations brings about modifications on catalytic activity, selectivity and stability of an ABO₃ at comparatively high temperatures (700–900 °C) with relatively less deactivation (i.e. sintering

and chemical degradation) [20] by adjusting the metal oxidation states, structural defects and oxygen lattice mobility [21]. Additionally, ABO_3 after hydrogen reduction treatment allows to obtain small particles, in which high metal dispersion can reduce coke deposition on the surface of the catalyst. Such a high metal dispersion could also lead to suppression of coke formation and good resistance to environmental pollution [22]. In the past years, several researchers have investigated preparation and physicochemical properties of ABO_3 . For instance, Khalesi et al. [23] reported that the catalytic activity of $\text{M}_x\text{La}_{1-x}\text{Ni}_{0.3}\text{Al}_{0.7}\text{O}_3$ ($\text{M} = \text{K}, \text{Na}, \text{and Li}$) for carbon dioxide reforming markedly increased by the tuning of highly basic Li, Na, and K, and coke formation was greatly suppressed over $\text{Li}_{0.2}\text{La}_{0.8}\text{Ni}_{0.3}\text{Al}_{0.7}\text{O}_{2.8}$ and $\text{Na}_{0.5}\text{La}_{0.5}\text{Ni}_{0.3}\text{Al}_{0.7}\text{O}_{2.5}$ displayed high yield of the desired product, and $\text{K}_{0.5}\text{La}_{0.5}\text{Ni}_{0.3}\text{Al}_{0.7}\text{O}_{2.5}$ showed an H_2/CO ratio close to one in a broad temperature range.

Working on the characterization of $\text{LaNi}_x\text{Al}_{1-x}\text{O}_3$ ($0.1 \leq x \leq 0.9$), Parvary et al. [24] found that the gradual substitution of Ni by Al could induce the reduction of LaNiO_3 to La_2NiO_5 and $\text{Ni/La}_2\text{O}_3$. Furthermore, addition of Al to the LaNiO_3 perovskite structure changed the Ni reduction temperature and the stability of the catalyst under reduction conditions that could limit the migration of the active Ni [23]. Over the past several years, our group has investigated several physicochemical and catalytic properties of the porous or micro/nanostructured materials with well-defined morphologies (e.g., $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ [25-27], $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ [28], $\text{LaNi}_x\text{Fe}_{1-x}\text{O}_3$ [29], $\text{La}_{0.4}\text{M}_{0.6}\text{Al}_{0.2}\text{Ni}_{0.8}\text{O}_3$ ($\text{M} = \text{Pt}, \text{Pd}, \text{Ir}, \text{Rh}, \text{Ru}$) [30], and NiCo_2O_4 [31, 32]). It was found that most of the porous materials performed well for the catalytic oxidation of hydrocarbons and/or methanation reactions. Nevertheless, no detailed works on the synthesis and catalytic applications for the CO methanation over $\text{LaNi}_x\text{Al}_{1-x}\text{O}_3$ ($x = 0.1, 0.4, 0.6, \text{and } 0.9$) appeared so far. It might be expected that the strong interaction between Ni and $\text{LaNi}_x\text{Al}_{1-x}\text{O}_3$ could enhance catalytic activity.

Herein, we report the synthesis, physicochemical characterization and catalytic activities of flower-like porous Ni substituted LaAlO_3 perovskite-supported Ni using a

controlled self-assembly sol-gel method for the CO methanation reaction. After primary investigation, the Ni/Al molar ratio was fixed to the value 6/4 ($\text{LaNi}_{0.6}\text{Al}_{0.4}\text{O}_3$) due to the optimal catalytic performance for CO methanation as depicted in Fig. S1 (ESI). Ni nanoparticles (NPs) loading on the porous $\text{LaNi}_{0.6}\text{Al}_{0.4}\text{O}_3$ (LNAO) support significantly improved the CO methanation activity. Important physicochemical properties of the $z\text{Ni/LNAO}$ ($z = 5, 10, \text{ and } 15 \text{ wt\%}$) catalysts were characterized and attempts were made to correlate these properties with their catalytic behaviour. The active sites of Ni present on the surface of Ni NPs and LNAO perovskite support have also been investigated.

2. Experimental

Details of catalysts synthesis (Scheme S1 and Fig. S2) are described in the Electronic Supplementary Information (ESI). The CO methanation activity evaluation over the various catalysts investigated was conducted according to the procedures described in ESI (Section 2.7, Fig. S3). All of the catalysts were characterized by N_2 adsorption-desorption (Brunauer–Emmett–Teller, BET), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), powder X-ray diffraction (XRD), temperature-programmed desorption of carbon monoxide (CO-TPD), and H_2 temperature-programmed reduction (H_2 -TPR), and these characterization procedures are described in the ESI (see Sections 2.1-2.6).

3. Results and discussion

The LNAO and Ni/LNAO samples were successfully synthesized by a controlled sol-gel strategy, which provided small-sized Ni NPs and uniformly dispersed on the surface of the flower-like porous LNAO (Scheme S1, ESI). Structures and morphologies of the catalytic samples were observed by the SEM and TEM techniques (Fig. 1a-c, Fig. S4-8). As shown in Fig. 1a and Fig. S4a, the LNAO contains a number of sheets forming a flower-like porous

morphology. The irregular sheets of 300–800 nm in length and 30–50 nm in thickness were densely packed. Having a closer observation of Fig. S4b, one can see that the flower-structure in the hole depicted exhibits more loose-packed morphology than the structure on the surface. The SEM images (Fig. S4b–d) imply that different Ni loadings (5, 10 and 15 wt%) on the LNAO support did not change the overall flower-like porous morphology. The EDS elemental mapping profiles visualized the elemental composition and dispersion of the 10 wt% Ni/LNAO sample (Fig. S4e–j). It can be observed that La, Ni, Al and O elements were evenly distributed within the nanostructures, confirming the formation of a uniform LNAO perovskite material and a good dispersion of Ni NPs on the support (ca. 10 wt% Ni/LNAO (Fig. 1a)).

To identify the structural morphology of Ni NPs, TEM characterization was also conducted. Fig. 1b–c and Fig. S5 show TEM images obtained for the LNAO and γ -Ni/LNAO samples. It should be noted that after the fragmentation of the flower-like porous LNAO by the power density of ultrasound in ethanol solution (sample pre-treatment before TEM observation), pieces of nanosheets were detected in the TEM images. A number of macrostructures with mesopores were recorded in the LNAO nanosheets with average pore sizes in the range of 20–50 nm (Fig. S5). Highly dispersed and uniformly sized Ni NPs were observed on the surface of LNAO, as indicated in the 5 and 10 wt% Ni/LNAO samples, where the average particle size is estimated to be ~ 10 nm (Figs. S6–S8). When Ni loading increased to 15 wt%, agglomeration of Ni NPs appeared, and the average particle size increased to ~ 12 nm. From HR-TEM images obtained for the 15 wt% Ni/LNAO, an inter-planar spacing (d value) of 0.26 nm corresponding to the (110) plane of the standard LaNiO_3 sample (JCPDS PDF# 50-0308) was estimated. The nanosheets forming the flower-like morphology might be derived from the cetyltrimethylammonium bromide (CTAB) added during the preparation process of LNAO. The CTAB-mediated route resulted in a high-quality mesoporous structure

(as illustrated by the arrows of Fig. 1b) and prevented the morphological structure against conglomeration.

Further evidence of the porous structure of prepared supports arises from the N₂ adsorption-desorption isotherms, in which all of the samples exhibited a similar type-II isotherm and type H2 ($p/p_0 = 0.3-0.7$) and H3 ($p/p_0 = 0.7-1.0$) hysteresis loops, indicating the presence of macropores and mesopores in the LNAO samples. The LNAO-supported Ni samples showed larger hysteresis loops than that of the LNAO support, demonstrating that introduction of Ni NPs consequently modifies the porous structure (pore size and distribution) of LNAO (Fig. S9a). The BET surface areas of the LNAO and γ -Ni/LNAO samples are provided in Table 1. The BET surface area (21.1–25.4 m²/g) of the γ -Ni/LNAO samples is found to be larger than that of the LNAO support alone (9.1 m²/g), which might be caused by surface modifications from the impregnation process using nickel nitrate, thus leading to the variation of surface roughness.

The powder XRD patterns of the LNAO and γ -Ni/LNAO samples are shown in Fig. S9b. All of the samples were highly crystalline. The characteristic diffraction peaks at $2\theta = 22.3^\circ, 32.8^\circ, 40.6^\circ, 47.3^\circ, 53.5^\circ, 59.1^\circ, 69.6^\circ, 79.4^\circ, 84.1^\circ$, and 89.1° correspond to the (012), (110), (202), (024), (116), (300), (220), (306), (134), and (226) lattice crystal planes of the rhombohedral LaAlO₃ perovskite phase (JCPDS PDF# 50-0308), respectively. The characteristic powder XRD peaks of Ni phases (Ni⁰ and/or NiO) were very weak to be identified by XRD.

Fig. 1. (a) SEM image of 10 wt% Ni/LNAO, (b) TEM image of 5 wt% Ni/LNAO, (c) TEM image of 15 wt% Ni/LNAO, (d) H₂-TPR profiles and (e) CO-TPD profiles of samples.

The reducibility of the as-prepared samples was studied using the H₂-TPR technique, and the obtained results are presented in Fig. 1d. It should be noted that La and Al had no reduction responses under the applied H₂-TPR conditions, since La and Al oxides were irreducible below 1000 °C. Thus, the TPR peaks were due to the several reduction steps of Ni with different oxidation states. The reduction of Ni ions in LNAO and *z*Ni/LNAO takes place according to a two-step process: (i) the reduction peak in the temperature range 250-300 °C is related to the reduction of Ni³⁺ to Ni²⁺, and (ii) the reduction peak in the higher temperature range of 430-500 °C is associated with the reduction of Ni²⁺ to metallic nickel (Ni⁰) [33]. As the Ni loading increases the relative intensity of the high-temperature peak in H₂-TPR profiles increases. It can be suggested that the increase in Ni content gradually increases the amount (per gram) of nickel species in the catalyst support. The estimated H₂ consumption in the 250-300 °C range is nearly the same as the H₂ amount needed for the reduction of Ni³⁺ to Ni²⁺ [23].

The H₂ consumption in the 430–500 °C range also supports the view that the peak in this higher temperature range is due to the reduction of Ni²⁺ to Ni⁰. It can be observed that the reduction peak associated with the first reduction step of Ni ions in the γ Ni/LNAO samples slightly shifted towards lower temperatures (from 391 to 247 °C), and reduction peaks associated with the second reduction step shifted towards higher temperatures (from 420 to 504 °C) with the increase of Ni loading. This result indicates that oxidized Ni in the presence of nanoparticles on the support is more likely to be reduced than oxidized Ni in the crystal lattice of the perovskite structure (LaNi_{0.6}Al_{0.4}O₃). The large peak area of the peaks at higher temperatures (from 420 to 504 °C) for Ni loading samples also suggests a large amount of Ni²⁺ species present in the nickel nanoparticles.

The CO-TPD experiment was performed in order to investigate the adsorption types of CO species on the surface of LNAO and γ Ni/LNAO catalysts. Two peaks were observed for each catalyst composition (Fig. 1e). The low-temperature desorption peak recorded at 40–50 °C is ascribed to CO molecules weakly bonded to the catalyst surface, whereas the high-temperature desorption peak recorded at 700–826 °C is assigned to a very strongly chemisorbed CO species. However, the possibility that part of this high-T desorbed CO might be the result of recombination of C-s and O-s after CO dissociation at lower T's during the experiment cannot be excluded. The characteristic profiles were practically very similar to those previously reported [2]. Upon the loading of Ni NPs, the intensity of the low-temperature desorption peak increased significantly, while the high-temperature peak gradually shifted to lower temperatures and its intensity is obviously enhanced. This result indicates that the loading of Ni NPs has modified the CO chemisorptive and dissociation abilities of the LNAO catalyst surface. Among the catalysts investigated 10 wt% Ni/LNAO showed the largest amount of high-T desorbed CO (ca. 720 °C) and a small peak at ca. 50 °C, suggesting an improved CO adsorption ability in terms of concentration (mols/g_{cat}).

The methanation of CO was carried out in a fixed-bed microreactor in the range of 200–300 °C. Fig. S10 illustrates that the CO methanation activity is largely improved by introducing Ni NPs when compared to the pure LNAO support. More precisely, a 30-50 °C lower temperature is obtained for 50% CO conversion compared to the pure LNAO support (268 °C). Reaction CH₄-selectivity results are shown in Fig. S11. These results demonstrate the significant promotional effect of Ni NPs towards CH₄ selectivity. In particular, CH₄ selectivity nearly 100% is observed over the 10 wt% Ni/LNAO, while that of LNAO is only 60% at 220 °C. During CO methanation reaction at 220 °C, a small concentration of CO₂ was detected as a by-product over the 5 wt% Ni/LNAO and 10 wt% Ni/LNAO catalysts. Based on some proposed mechanisms [34, 35] for the CO methanation reaction, the step of CO dissociation is a slower step than others. At low reaction temperatures, where the rate of methanation reaction is small (there is not enough energy to effectively dissociate adsorbed CO followed by hydrogenation of derived C-s species), the probability for CO disproportionation reaction only ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) increases (ca. ~ 100 °C, [36]).

The activity results (Fig. 2) suggest that Ni on the surface of LNAO perovskite and nickel NPs serve as active sites for CO methanation. To distinguish their activation ability, the reaction rate of CO conversion, normalized by the catalyst mass (mmol/g_{cat} /h), the surface Ni (Ni_s) in NPs (mol/mol_{Ni,s} /h) and the Ni total molar amount (mol/mol_{Ni total} /h), was calculated for comparison. As shown in Fig. 2 and Table 1, the reaction rate per gram of catalyst follows the same trend as the CO conversion vs temperature profile, decreasing in the order: 10 wt% Ni/LNAO (244 mmol/g_{cat} /h) > 5 wt% Ni/LNAO (238 mmol/g_{cat} /h) > 15 wt% Ni/LNAO (4.81 mmol/g_{cat} /h) > LNAO (12.4 mmol/g_{cat} /h). The reaction rate of 10 wt% Ni/LNAO is about 20 times higher than that obtained over pure LNAO, demonstrating the outstanding activity of Ni active sites in NPs.

The reaction rate calculated on the basis of surface Ni in the NPs (279 mol/mol_{Ni,s} /h) and of the total Ni in the sample (72.1 mol/mol_{Ni total} /h) is the highest for the 5 wt% Ni/LNAO

among the other samples. These results suggest an optimal Ni loading of 5 wt% Ni that exhibits practically the best reaction rate of CO conversion at 220 °C when the latter is expressed per unit mass of catalyst or per surface Ni sites (TOF, h⁻¹).

The factors which influence the activity of supported catalysts mainly include: the nature of support and loaded active metal, the particle size and dispersion of metal and the metal-support interactions [11]. Comparing the reaction rate based on the surface Ni sites (TOF, h⁻¹, Table 1), it can be concluded that the homogeneous dispersion and moderate metal-support interactions developed between the 5 wt% Ni and the LNAO support result in the best activity for CO methanation. A comparison of CO methanation rate (mols CO/g_{cat}/h) over several heterogeneous very active catalysts is summarized in Table S1. Obviously, the catalytic activity over γ -Ni/LNAO (Table 1) is at least comparable to that exhibited by alumina-supported and other nickel metal catalysts, where the former showed the highest catalytic performance.

To evaluate the stability of the best-performing catalyst, a long-term CO methanation reaction at 225 °C (CO conversion < 100%) was conducted over the 10 wt% Ni/LNAO catalyst. As shown in Fig. S12, the 10 wt% Ni/LNAO sample exhibits a very good catalytic stability, with a slight only activity drop (< 10%) after 60 h on time-of-stream. The possibility for coke formation was also investigated by TPO analysis on the aged 10 wt% Ni/LNAO sample after the 60-h stability test. The result obtained is presented in Fig. S13. No obvious coke formation can be seen.

Table 1. BET surface areas, catalytic activities (CO conversion rate at 220 °C per g_{cat}, per mol_{Ni,s} and per mol_{Ni total}) of the 5 wt% Ni/LNAO, 10 wt% Ni/LNAO, 15 wt% Ni/LNAO and LNAO samples.

Sample	BET surface area	CO conversion rate at 220 °C		
	(m ² /g)	mmol/g _{cat} /h	mol/mol _{Ni,s} /h	mol/mol _{Ni total} /h
LNAO	9.1	4.81		1.86
5 wt% Ni/LNAO	21.1	238	279	72.1
10 wt% Ni/LNAO	21.5	244	143	60.6
15 wt% Ni/LNAO	25.4	12.4	4.83	2.61

Fig. 2 CO conversion rate normalized by catalyst mass (black bar, mmol/g_{cat} /h), Ni surface sites in NPs (red bar, mol/mol_{Ni,s} /h) and Ni total molar weight (blue bar, mol/mol_{Ni total} /h) of LNAO, 5 wt% Ni/LNAO, 10 wt% Ni/LNAO and 15 wt% Ni/LNAO.

4. Conclusions

In summary, Ni/LNAO samples (Ni loading 5-15 wt%) with a flower-like porous morphology was synthesized using a simple sol-gel method. It was found that the loading of Ni NPs on the surface of LNAO support modified the catalytic activity towards CO methanation of the catalysts. The outstanding reaction rate over the Ni-loaded LNAO catalysts was found to be largely due to Ni active sites on the surface of Ni NPs which possessed higher intrinsic activity than the Ni sites on the surface of LNAO for the CO methanation. The appropriate Ni dispersion and metal-support interactions developed in the 5 wt% Ni/LNAO catalyst resulted in the excellent catalytic performance when compared to other active Ni-based supported metal catalysts reported in the open literature.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2018.XX.XXX>.

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Graphical Abstract

Highlights

- Flower-like LaNiAl complexes are self-assembled using the template-free strategy;
- LaNiAl-supported Ni catalysts are synthesized;
- The loading of Ni nanoparticles improves the catalytic activity for CO methanation;
- The 10 wt% Ni/LaNiAl catalyst shows an excellent activity in CO methanation.