Supporting Information

Investigation on mesoporous NiAl₂O₄/MO_x (M=La, Ce, Ca, Mg)– γ -Al₂O₃ nanocomposites for dry reforming of methane

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1. Measurement and estimation of turnover frequency (TOF)

TOF is defined as the number of converted CH_4 or CO_2 molecules per surface Ni atom and second. Taking into account the reaction stability of the present catalysts, the molar number of surface Ni atoms on the catalyst surface was estimated on the basis of the Ni crystallite sizes after 100-h DRM reaction.

In order to precisely determine the intrinsic reaction rate on the metal active sites, the reforming reaction was carried out at a very high gas hourly space velocity (GHSV) without channeling in the catalyst bed, where the possibility of the external and internal diffusion limitations were almost completely eliminated by the experiments of varying the catalyst particle sizes and GHSV. For this, 10 mg catalyst powder diluted with 190 mg of quartz powder was used for the reaction. After stabilized for the 100-h DRM reaction under the reaction conditions: GHSV = 1.8×10^5 mL/g_{cat} h, CO₂/CH₄ = 1, 1 atm, and 750 °C, the GHSVs were adjusted to 1.8×10^6 mL/g_{cat} h to obtain the low CH₄ and CO₂conversions. At this time, the DRM reaction was believed to be governed by chemical kinetics and the effect of the backward reactions was negligible.

On the assumption that all Ni ions were reduced to form spherical particles with a diameter (d_{TEM}) from Table 3 in the manuscript, and the distance between metal atoms in Ni particles was assumed to be 0.249 nm.

(1) The mole number of surface Ni atoms:

$$N_{Ni,surf.} = N_{Ni} \times \left(\frac{d_{TEM}^{3} - (d_{TEM} - 0.498)^{3}}{d_{TEM}^{3}} \right)$$

Where N_{Ni} : the mole number of Ni in 10 mg Ni/(MO_x)- γ -Al₂O₃ catalysts, 2.23 × 10⁻⁵ mol; d_{TEM} : the average size of Ni particles by TEM after the 100-h DRM reaction shown in Table 3.

(2) TOF was calculated by the equation as follows:

$$\text{TOF} = \left(\frac{N_{in}}{N_{Ni,surf.}} \times X\right) \, \text{s}^{-1}$$

Where N_{in} : the molar flow rate of CH₄ or CO₂ in the feed, 1.12×10^{-4} mol/s; *X*: the CH₄ or CO₂ conversions under the reaction conditions: GHSV = 1.8×10^{6} mL/g_{cat} h, CO₂/CH₄ = 1, 750 °C, 1atm.

Supporting Tables and Figures

Table S1 Thermodynamic equilibrium values calculated by HSC software under the reaction conditions of $CO_2/CH_4 = 1$ and 1 atm, assuming that methane thermal cracking and Boudouard reactions were negligible.

Reaction temperature (°C)	CO ₂ conversion (%)	CH ₄ conversion (%)	H ₂ /CO
550	36.9	25.6	0.64
575	45.2	32.9	0.68
600	53.6	40.7	0.72
625	61.9	49.0	0.76
650	69.6	57.4	0.81
675	76.5	65.3	0.84
700	82.3	72.5	0.87
725	86.9	78.5	0.90
750	90.3	83.4	0.92
775	93.0	87.3	0.94
800	94.9	90.3	0.95

sample	Ni particle size (nm) by		
	XRD	TEM	
Ni/γ - Al_2O_3	15.9	15.7±2.4	
Ni/La ₂ O ₃	16.7	16.5±2.7	
Ni/CeO ₂	15.6	15.7±2.5	
Ni/CaO	14.9	14.3±2.4	
Ni/MgO-\gamma-Al ₂ O ₃	16.3	17.0±2.6	
Ni/La ₂ O ₃ /γ-Al ₂ O ₃ -imp	18.9	19.7±2.8	

Table S2 Ni particle sizes of Ni/(MO_x)- γ -Al₂O₃ catalysts.



Fig. S1. CH₄ conversion as a function of gas hourly space velocity (GHSV) for the DRM reaction over the Ni/La₂O₃- γ -Al₂O₃. Reaction conditions: CO₂/CH₄ = 1, 750 °C, 1atm.



Fig. S2. STEM images and corresponding elemental analysis for $NiAl_2O_4/La_2O_3-\gamma-Al_2O_3$.

High angle annular dark field scanning transmission electron microscopy (HAADF–STEM) was employed to characterize the detailed morphology of catalysts. EDS mapping data were collected using an acceleration voltage of 200 kV, a collection time of 180 s, and a 1.0-nm-diameter probe.



Fig. S3. XRD patterns of (1) the fresh samples, (2) the samples after H₂ reduction at 800 °C for 2 h, (a) NiAl₂O₄/ γ -Al₂O₃, (b) NiAl₂O₄/La₂O₃- γ -Al₂O₃, (c) NiAl₂O₄/CeO₂- γ -Al₂O₃, (d) NiAl₂O₄/CaO- γ -Al₂O₃, and (e) NiAl₂O₄/MgO- γ -Al₂O₃.

We have previously verified that the NiAl₂O₄ spinel was successfully formed in NiAl₂O₄/ γ -Al₂O₃ after 800 °C calcination by identifying the variations in the relative intensities and slight shifts of the diffraction peaks for spinel compared with γ -Al₂O₃.¹ Under high calcination temperature, Ni ions possessed high-surface energies could overcome the surface barrier of γ -Al₂O₃ to embed into the lattice, and the incorporation of Ni²⁺ ions into the oxide cubic close packed array would enlarge the lattice parameters, shift the diffraction peaks to lower 2 θ values.^{2,3} Therefore, the three strong diffraction peaks at 2 θ values of ca. 37°, 45°, 66° for all the fresh samples in Fig. S3 (1) could be attributed to NiAl₂O₄ spinel (JCPDS 10-0339). This revealed that addition of La, Ce, Ca, and Mg would not change the crystalline phases of the materials. The relative intensities of the diffraction peaks for NiAl₂O₄/MgO- γ -Al₂O₃ were stronger than those for other catalysts, this might be due to the formation of part MgAl₂O₄ (JCPDS 21-1152).

Subsequently, all the calcined samples were reduced with H₂ under the *in-situ* prereduction condition for DRM, and the characteristic diffraction peaks of the metallic Ni (JCPDS 87-0712) at 2θ = 44.5°, 51.8° and 76.4° were clearly observed in Fig. S3 (2). The shift of the diffraction peaks for NiAl₂O₄ phase to the higher 2 θ values corresponding to pure γ -Al₂O₃ also illustrated that the NiAl₂O₄ precursor was reduced, and γ -alumina-supported Ni catalyst was concomitantly formed.



Fig. S4. XRD patterns of (a) NiAl₂O₄/La₂O₃/ γ -Al₂O₃-imp, (b) Ni/La₂O₃/ γ -Al₂O₃-imp reduced at 800 °C, and (c) Ni/La₂O₃/ γ -Al₂O₃-imp–*S235*. Reaction conditions: GHSV = 1.8 × 10⁵ mL/g_{cat} h (STP), CO₂/CH₄ = 1, 750 °C, 1atm.



Fig. S5 (a) Nitrogen adsorption-desorption isotherms, and (b) BJH pore size distributions of the reduced Ni/(MO_x)– γ -Al₂O₃ catalysts.

The N₂ adsorption-desorption isotherms and pore size distributions illustrated in Fig. S5 (a) and (b) were used to investigate the morphologies and textural properties of the reduced samples, and the quantificational data were summarized in Table 3. The isotherms with apparent hysteresis loops of the Ni/(MO_x)– γ -Al₂O₃ samples were attributed to characteristic type IV curves, and the pore size distributions evaluated from the desorption branches of N₂ isotherms by BJH method showed main peaks in the range of 4.0–6.0 nm, which indicated that uniform mesopores had formed in the frameworks according to the IUPA classification.^{4,5}

The Ni/ γ -Al₂O₃ and La, Ce, Ca doped catalysts possessed the similar BET surface areas (S_{BET}) around 150 m₂/g and pore volumes (V_p) around ca. 0.23 cm³/g in Table 3. However, those of Mg doped catalyst significantly decreased to 114 m²/g and 0.19 cm³/g. This was one of the reasons for its relatively low catalytic activities, due to providing less attachment points for active sites.⁶



Fig. S6. TEM images and corresponding Ni particle size distributions of the reduced samples. (a) Ni/ γ -Al₂O₃, (b) Ni/La₂O₃- γ -Al₂O₃, (c) Ni/CeO₂- γ -Al₂O₃, (d) Ni/CaO- γ -Al₂O₃, (e) Ni/MgO- γ -Al₂O₃, and (f) Ni/La₂O₃/ γ -Al₂O₃-imp.



Fig. S7 TEM and SEM images of the various spent catalysts. Reaction conditions: GHSV = $1.8 \times 10^5 \text{ mL/g}_{cat} \text{ h}$ (STP), CO₂/CH₄ = 1, 750 °C, 1atm.

Fig. S7 illustrated the TEM and SEM images and the corresponding Ni particle size distributions of the used catalysts after long-term reaction. Highly dispersed Ni particles with relatively narrow particle size distributions were clearly observed on the Ni/ γ -Al₂O₃ and Ni/MO_x- γ -Al₂O₃ after 100 h and 400 h reaction, respectively, which was profited from the strong metal–support interaction derived from the reduction of NiAl₂O₃ precursor. However, Ni/La₂O₃/ γ -Al₂O₃-imp–*S235* displayed severe agglomeration of Ni crystallites and

inhomogeneous particle size distribution, which was consistent with the XRD results in Fig. S4.

References

- L. Zhang, X. G. Wang, X. F. Shang, M. W. Tan, W. Z. Ding and X. G. Lu, Journal of Energy Chemistry, 2017, 26, 93–100.
- L. Zhou, L. D. Li, N. N. Wei, J. Li and J. M. Basset, *ChemCatChem*, 2015, 7, 2508– 2516.
- 3 G. Garbarino, C. Y. Wang, I. Valsamakis, S. Chitsazan, P. Riani, E. Finocchio, M. Flytzani-Stephanopoulos and G. Busca, *Appl. Catal. B*, 2015, **174–175**, 21–34.
- 4 X. P. Yu, F. B. Zhang and W. Chu, RSC Adv., 2016, 6, 70537–70546.
- 5 Y. Cao, H. R. Li, J. P. Zhang, L. Y. Shi and D. S. Zhang, *RSC Adv.*, 2016, **6**, 112215–112225.
- 6 F. Guo, J. Q. Xu and W. Chu, Catal. Today, 2015, 256, 124-129.