

Supplementary Information for

Facile one-step preparation of ordered mesoporous Ni-M-Al (M = K, Mg,
Y, and Ce) oxide catalysts for methane dry reforming

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Synthesis of ordered mesoporous catalysts

Preparation of ordered mesoporous NiO-Al₂O₃ catalyst

In a typical synthesis procedure, 1.0 g of P123 was dissolved in 20 mL of anhydrous ethanol under vigorously magnetic stirring at room temperature for 4 h. Then, 1.6 mL of 66 wt.% HNO₃, 9.5 mmol of aluminum isopropoxide, and 0.5 mmol of Ni(NO₃)₂·6H₂O were sequentially added into the above solution under continuous stirring for 5 h [1]. The mixed solution was transferred into a drying oven at 60 °C to evaporate the solvent for 2 days. The as-obtained solid was calcined at 800 °C for 5 h with a linear ramping rate of 1 °C/min in air flow (30 mL/min). Hence, the catalyst was designed as NA.

Preparation of ordered mesoporous Ni-M-Al (M = K, Mg, Y, and Ce) oxide catalysts

Similarly, 1.0 g of P123 was dissolved in 20 mL of anhydrous ethanol under vigorously magnetic stirring at room temperature for 4 h. Then, 1.6 mL of 66 wt.% HNO₃, x mmol of aluminum isopropoxide, y mmol of Ni(NO₃)₂·6H₂O, and z mmol of M (M = KNO₃, Mg(NO₃)₂·6H₂O, Y(NO₃)₃·6H₂O, and Ce(NO₃)₂·6H₂O; $x + y + z = 10$) were sequentially added into the above solution under continuous stirring for 5 h. The mixed solution was transferred into a drying oven at 60 °C to evaporate the solvent for 2 days. The as-obtained solid was calcined at 800 °C for 5 h with a linear ramping rate of 1 °C/min in air flow (30 mL/min). Hence, the promoted catalysts were denoted as NMA (M = K, Mg, Y, and Ce).

Sample characterization

ICP: Ni and M (M = K, Mg, Y, and Ce) contents were measured by a Thermo Icap6300 element analyzer. 10 mg of sample was dissolved in HCl (3 mol/L) at 50 °C for 2h [2].

O₂-TPD: 100 mg of sample was pretreated with pure Ar (40 mL/min) at 500 °C for 1 h, followed by O₂ adsorption at 50 °C for 1 h. The sample was then purged with Ar (40 mL/min) to remove the physically adsorption of O₂, followed by heating the sample from 50 to 1000 °C at a linear heating rate of 10 °C/min in the Ar flow (40 mL/min). The O₂ signal was recorded by a Pfeiffer Omnistar GSD 320 mass spectrometer.

CO₂-TPD: 100 mg of sample was pretreated with pure Ar (40 mL/min) at 500 °C for 1 h, followed by CO₂ adsorption at 50 °C for 1 h. The sample was then purged with Ar (40 mL/min) to remove the physically adsorption of CO₂, followed by heating the sample from 50 to 1000 °C at a linear heating rate of 10 °C/min in the Ar flow (40 mL/min). The CO₂ signal was recorded by a Pfeiffer Omnistar GSD 320 mass spectrometer.

NH₃-TPD: 100 mg of sample was pretreated with pure Ar (40 mL/min) at 500 °C for 1 h, followed by NH₃ adsorption at 50 °C for 1 h. The sample was then purged with Ar (40 mL/min) to remove the physically adsorption of NH₃, followed by heating the sample from 50 to 1000 °C at a linear heating rate of 10 °C/min in the Ar flow (40 mL/min). The NH₃ signal was measured by a Pfeiffer Omnistar GSD 320 mass spectrometer.

H₂-TPR: 50 mg of sample was pretreated at 500 °C for 1 h in the pure Ar (40 mL/min) flow to remove any adsorbed impurities. After cooling down to the room temperature, the sample was reduced from 50 to 1000 °C at a linear heating rate of 10 °C/min in 5 vol.% H₂/Ar (40 mL/min) flow. The H₂ consumption was analyzed using a Micromeritics ASAP-2920 instrument.

CO chemisorption: Ni dispersion was carried out using a static volume Micromeritics ASAP-2920 instrument. The catalyst was reduced in at 800 °C with a 25 vol.% H₂/Ar (80 mL/min) for 2 h, then purged with pure Ar at this temperature for 2 h

and cooled under vacuum to 40 °C for CO chemisorption measurement [3].

TG: The amount of carbon deposition was quantitatively by a Rigake TG instrument. 10 mg of coked sample was heated from 50 °C to 750 °C at a heating speed of 10 °C/min in flowing air (30 mL/min).

Results and discussion

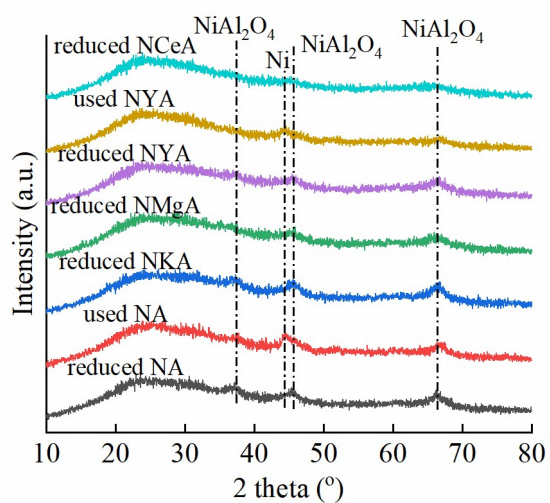


Figure S1. XRD patterns of the reduced and used catalysts.

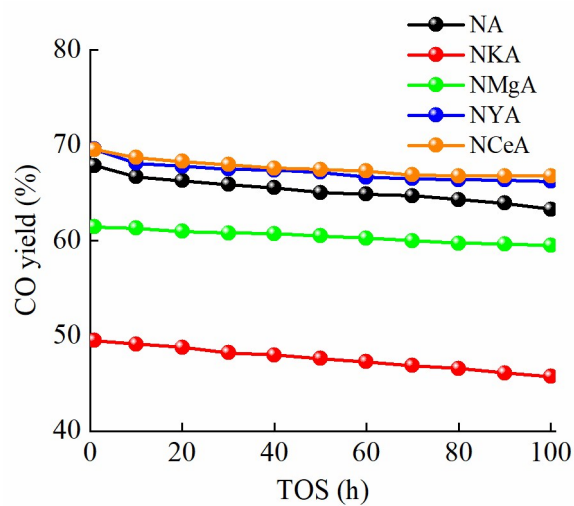


Figure S2. CO yield as a function of TOS over the NMA for 100 h (reaction conditions: 700 °C, 1 atm, GHSV = 48 L/g/h, and CH₄:CO₂ = 1)

References

- [1] L. Xu, H. Song, L. Chou, *Catal. Sci. Technol.*, 2011, **1**, 1032-1042.
- [2] D. Alonso, J. Juan, M. Gómez, M. Martínez, *Appl. Catal. A, Gen.*, 2009, **371**, 54-59.
- [3] X. Huang, G. Xue, C. Wang, N. Zhao, N. Sun, W. Wei, Y. Sun, *Catal. Sci. Technol.*, 2016, **6**, 449-459.