

## Engineering the Interface and Interaction Structure on Highly Coke-Resistant Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Catalyst for Dry Reforming of Methane

Sha Li<sup>1</sup>, Xin Wang<sup>1</sup>, Min Cao<sup>1</sup>, Jingjun Lu<sup>1</sup>, Li Qiu<sup>1</sup> and Xiaoliang Yan<sup>1,2\*</sup>

<sup>1</sup>College of Chemical Engineering and Technology, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

<sup>2</sup>State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

\*Corresponding author. Email: yanxiaoliang@tyut.edu.cn

# SUPPORTING INFORMATION

**S** Chinese Journal of  
Structural Chemistry

**Table S1.** Textural Properties of NiO/Al<sub>2</sub>O<sub>3</sub> and NiO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

Catalyst	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )	D <sub>p</sub> (nm)
NiO/Al <sub>2</sub> O <sub>3</sub>	171	0.7	16.3
NiO/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	197	0.8	16.1

# SUPPORTING INFORMATION

**S** Chinese Journal of  
Structural Chemistry

**Table S2.** Results of H<sub>2</sub> Chemisorption for Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

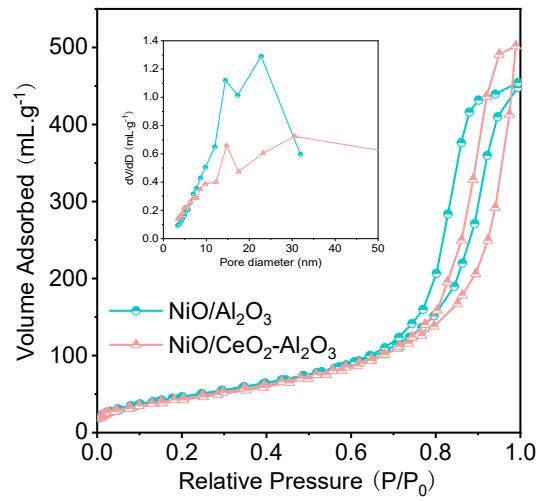
Catalyst	H <sub>2</sub> uptake (m <sup>3</sup> /g)	Dispersion (%)	S <sub>Ni</sub> (m <sup>2</sup> /g)	d <sub>Ni</sub> (nm)
Ni/Al <sub>2</sub> O <sub>3</sub>	1.10	6.5	54.8	7.7
Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	1.13	6.5	55.0	6.5

# SUPPORTING INFORMATION

**Table S3.** Comparison of CH<sub>4</sub> and CO<sub>2</sub> Conversions as Well as Coke Deposition Rate with Other Catalysts in DRM

Catalysts	Temperature (°C)	GHSV (mL g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )	Ratio of feed gases	CH <sub>4</sub> conversion (%)	CO <sub>2</sub> conversion (%)	Stability (h)	Coke deposition rate (mg <sub>c</sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ) <sup>a</sup>	Ref.
Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	500	24,000	CH <sub>4</sub> /CO <sub>2</sub> = 1/1	12	16	50	0.42	This work
NiFe/Al <sub>2</sub> O <sub>3</sub>	450	12,000	CH <sub>4</sub> /CO <sub>2</sub> = 1/1	9.6	14	20	1.18	1
Pt <sup>0.25</sup> -NiCe@SiO <sub>2</sub>	500	60,000	CH <sub>4</sub> /CO <sub>2</sub> /N <sub>2</sub> = 1/1/1	~6.5	~11.5	20	1.81	2
Ni-Co/La <sub>2</sub> O <sub>3</sub>	650	119,000	CH <sub>4</sub> /CO <sub>2</sub> /N <sub>2</sub> = 45/45/10	30	40	10	100	3
0.3PdNi/MCM-41	550	120,000	CH <sub>4</sub> /CO <sub>2</sub> /N <sub>2</sub> = 1/1/3	38	52	12	156.8	4
NMG-600	600	54,000	CH <sub>4</sub> /CO <sub>2</sub> /N <sub>2</sub> = 1/1/1	48	52	12	1.44	5
1Ni2Co/ZSM5	700	60,000	CH <sub>4</sub> /CO <sub>2</sub> /Ar = 1/1/3	69	60	12	28.69	6
0.5Ru@Ni-MCM-41	600	36,000	CH <sub>4</sub> /CO <sub>2</sub> /Ar = 1/1/1	35	38	4	485.29	7
Ni-Ce <sub>1-x</sub> Zr <sub>x</sub> O <sub>2</sub> _cp	600	60,000	CH <sub>4</sub> /CO <sub>2</sub> /Ar = 1/1/8	55	70	24	684	8
75Ni25Co-Al-5Ca	600	7,000	CH <sub>4</sub> /CO <sub>2</sub> /N <sub>2</sub> = 1/1/3	19	57	3.5	37.7	9
Ni@SBA-15-EG	750	7,500	CH <sub>4</sub> /CO <sub>2</sub> = 1/1	45	35	20	1.975	10

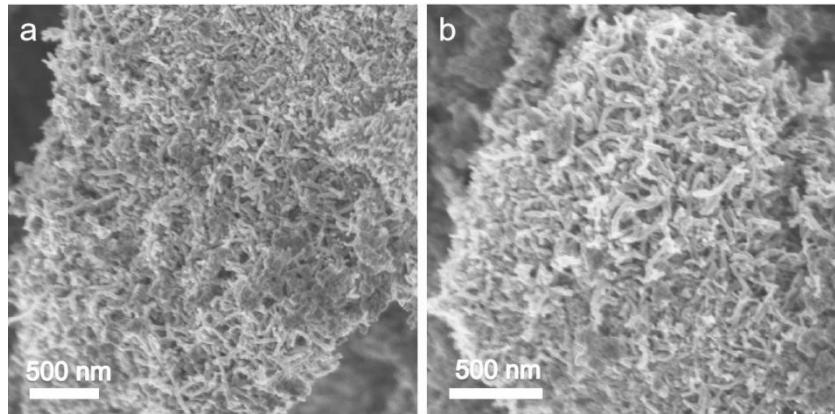
<sup>a</sup> carbon deposition rate:  $R_c = \frac{m_c}{m_{cat} \cdot \text{time (h)}}$ , where m<sub>c</sub> and m<sub>cat</sub> represent the amounts of carbon on the spent catalyst and the mass of catalyst, respectively.



**Figure S1.**  $\text{N}_2$  isotherms of fresh  $\text{NiO}/\text{Al}_2\text{O}_3$  and  $\text{NiO}/\text{CeO}_2\text{-}\text{Al}_2\text{O}_3$ .

# SUPPORTING INFORMATION

**S** Chinese Journal of  
Structural Chemistry



**Figure S2.** SEM images of the control NiO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst after stability test.

# SUPPORTING INFORMATION

**S** Chinese Journal of  
Structural Chemistry

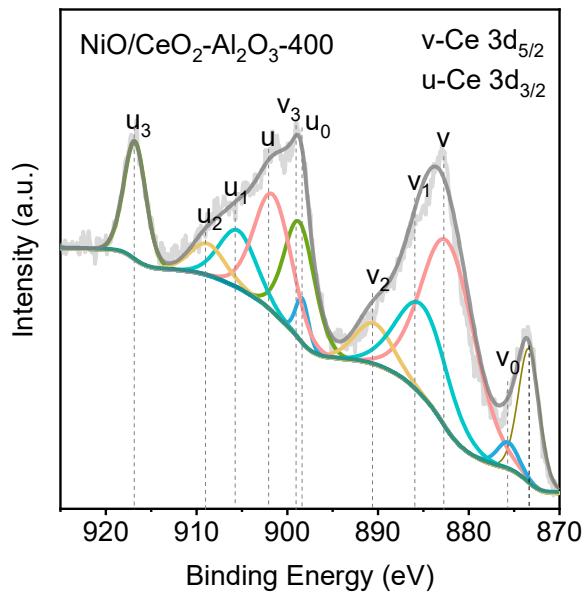


Figure S3. Ce 3d XPS spectra of the control NiO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

# SUPPORTING INFORMATION

## ■ REFERENCES

- (1) Song, Z. W.; Wang, Q. Q.; Guo, C.; Li, S.; Yan, W. J.; Jiao, W. Y.; Qiu, L.; Yan, X. L.; Li, R. F. Improved effect of Fe on the stable NiFe/Al<sub>2</sub>O<sub>3</sub> catalyst in low temperature dry reforming of methane. *Ind. Eng. Chem. Res.* **2020**, 59, 17250-17258.
- (2) Kim, S.; Lauterbach, J.; Sasmaz, E. Yolk-shell Pt-NiCe@SiO<sub>2</sub> single-atom-alloy catalysts for low temperature dry reforming of methane. *ACS Catal.* **2021**, 11, 8247-8260.
- (3) Tsoukalou, A.; Imtiaz, Q.; Kim, S. M.; Abdala, P. M.; Yoon, S.; Müller, C. R. Dry-reforming of methane over bimetallic Ni-M/La<sub>2</sub>O<sub>3</sub> (M = Co, Fe): the effect of the rate of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> formation and phase stability on the catalytic activity and stability. *J. Catal.* **2016**, 343, 208-214.
- (4) Damyanova, S.; Pawelec, B.; Arishtirova, K.; Fierro, J.; Sener, C.; Dogu, T. MCM-41 supported PdNi catalysts for dry reforming of methane. *Appl. Catal. B: Environ.* **2009**, 92, 250-261.
- (5) Kim, K. Y.; Lee, J. H.; Lee, H.; Noh, W. Y.; Kim, E. H.; Ra, E. C.; Kim, S. K.; An, K.; Lee, J. S. Layered double hydroxide-derived intermetallic Ni<sub>3</sub>GaC<sub>0.25</sub> catalysts for dry reforming of methane. *ACS Catal.* **2021**, 11, 11091-11102.
- (6) Estephane, J.; Aouad, S.; Hany, S.; El Khoury, B.; Gennequin, C.; El Zakhem, H.; El Nakat, J.; Aboukaïs, A.; Abi Aad, E. CO<sub>2</sub> reforming of methane over Ni-Co/ZSM5 catalysts. Aging and carbon deposition study. *Int. J. Hydrogen Energy* **2015**, 40, 9201-9208.
- (7) Yasyerli, S.; Filizgok, S.; Arbag, H.; Yasyerli, N.; Dogu, G. Ru incorporated Ni-MCM-41 mesoporous catalysts for dry reforming of methane: effects of Mg addition, feed composition and temperature. *Int. J. Hydrogen Energy* **2011**, 36, 4863-4874.
- (8) Wolfbeisser, A.; Sophiphun, O.; Bernardi, J.; Wittayakun, J.; Föttinger, K.; Rupprechter, G. Methane dry reforming over ceria-zirconia supported Ni catalysts. *Catal. Today* **2016**, 277, 234-245.
- (9) Sengupta, S.; Deo, G. Modifying alumina with CaO or MgO in supported Ni and Ni-Co catalysts and its effect on dry reforming of CH<sub>4</sub>. *J. CO<sub>2</sub> Util.* **2015**, 10, 67-77.
- (10) Xie, T.; Shi, L.; Zhang, J.; Zhang, D. Immobilizing Ni nanoparticles to mesoporous silica with size and location control via a polyol-assisted route for coking- and sintering-resistant dry reforming of methane. *Chem. Commun.* **2014**, 50, 7250-7253.