Oxygen Vacancy-Dependent Low-Temperature Performance of Ni/CeO_2 in CO_2 Methanation

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Content

S1 Characterization

The performance of the catalyst is significantly influenced by its pore structure. X-ray diffraction (XRD) was employed with Cu Kα radiation (λ = 1.5405 Å), scanning 2θ angles from 10 to 90° at a speed of 2°/min, using a 30 mA tube current and 40 kV tube voltage. Micromeritics ASAP-2020 surface area analyzer was utilized for catalyst surface area analysis. Prior to testing, catalyst samples were vacuum-degassed at 250 °C for 3 hours, followed by N_2 adsorption-desorption at -196 °C to obtain BET surface area and pore volume, with pore size distribution determined using the BJH method. Raman analysis, conducted on a Renishaw spectrometer with a laser wavelength of 532 nm, explored surface defects over a range of 200 to 900 cm^{-1}. CO_2-TPD, crucial for investigating catalyst surface basicity, was performed using a Micromeritics AutoChem 2920 chemisorption analyzer. XPS, based on the photoelectric effect, facilitated qualitative and semi-quantitative/quantitative elemental and chemical state analysis of solid surfaces, utilizing a PHI 5000 CESCA System with Al/Mg anode, operating at 14.0 kV and 250 W, with vacuum conditions better than 1×10-8 Torr. Binding energy was calibrated with C 1s = 284.6 eV as the reference. In-situ FTIR, crucial for

capturing intermediate species and elucidating reaction mechanisms, employed a Bruker instrument featuring a highly sensitive MCT detector. Prior to experimentation, samples underwent pretreatment at 300 °C in high-purity Ar, followed by cooling to 50 °C and background correction under Ar. Subsequently, a mixed gas (4% H_2, 1% CO_2, 95% Ar) was introduced for CO_2 hydrogenation testing, with a gas flow rate of 20 mL/min, ramping from 50 °C to 400 °C to monitor dynamic changes in intermediate species until reaching a steady state.

S2. Supplementary Figure

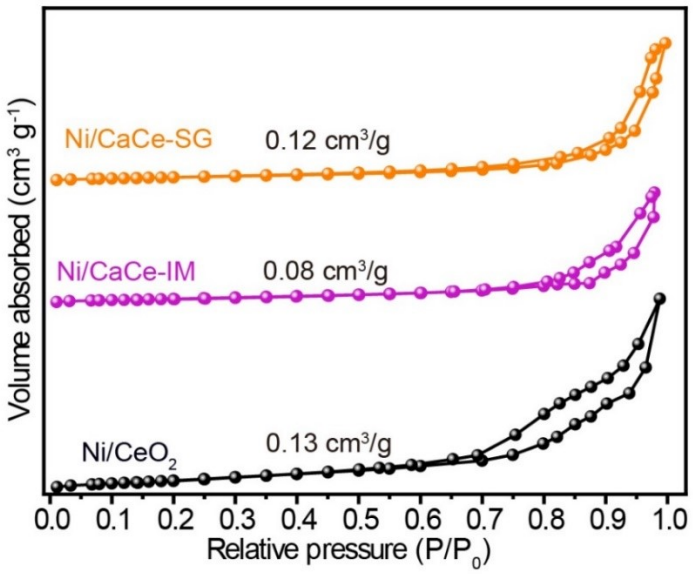

Figure S1. N_2 adsorption and desorption of the Ni/CaCe catalysts.

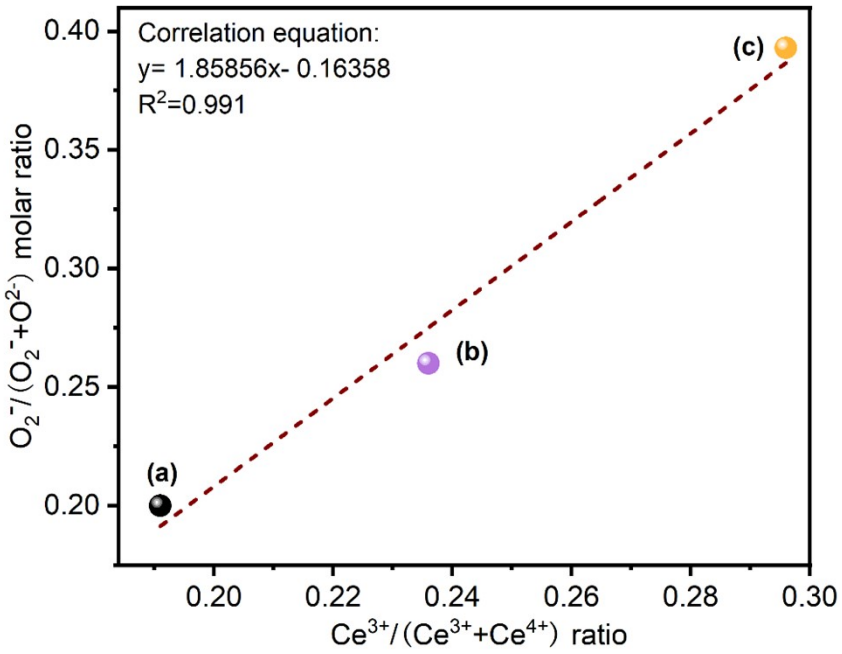

Figure S2. Surface $O_2^-/O_2^-+O^{2-}$) molar ratios versus $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ ratios on the Ni/CaCe catalysts. (a) Ni/CeO_2, (b)Ni/CaCe-IM, (c) Ni/CaCe-SG.

S3. Supplementary Table

Table S1 Quantitative results of O_2^- surface oxygen vacancies.

Supports	I_{570}/I_{460} ($\times10^{-2}$)	I_{1068}/I_{460} ($\times10^{-2}$)
CeO_2	0.8	1.2
CaCe-IM	1.2	1.5
CaCe-SG	4.6	4.4

Table S2 Quantitative results of XPS

Catalysts	Relative amount (%)			$O_2^-/(O_2^-+O^{2-})$ [a] (%)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$[a] (%)	M/(Ce+M) molar ratio [b]
	O_2^- [a]	CO_3^{2-} [a]	O^{2-} [a]			
Ni/CeO_2	17.5	14.4	68.1	20.3	19.1	-
Ni/CaCe-IM	16.3	35.3	48.4	26.0	23.6	0.096
Ni/CaCe-SG	28.1	24.6	47.3	39.3	29.6	0.091

[a] Measured by XPS.

[b] Measured by ICP.

Table S3 Quantitative results of the activation energy and reaction rate

Catalysts	R_w[a] (250 °C) [10^{-3} mmol $s^{-1}g^{-1}$]	R_S[b] (250 °C) [10^{-4} mmol s^{-1} m^{-2}]	E_a[c] [kJ mol^{-1}]
Ni/CeO_2	3.0	1.4	111
Ni/CaCe-IM	6.6	3.9	104
Ni/CaCe-SG	11.6	6.9	82

Table S4 Quantitative results of H_2-TPD

Catalysts	Ni contents (wt%) [a]	H_2 desorption amount (μmol g^{-1})	Metallic Ni surface area (m^2 g_{Ni}^{-1}) [b]	Dispersion (%) [b]	TOF $_{CO2}$ (s^{-1}) [c]
Ni/CeO_2	9.3	38.8	20.8	2.5	0.03
Ni/CaCe-IM	9.2	50.8	26.5	3.1	0.07
Ni/CaCe-SG	9.2	60.9	31.8	3.9	0.10

[a]Determined by ICP.

[b]Pt/Al_2O_3 (D = 34.5%) was used as the standard. Based on the cross-sectional area of one surface Ni atom, 8.24×10^{-20} m^2.

[c]Calculated based on the steady state CO_2 conversion at 250 °C.

Table S5 Quantitative results of CO_2-TPD

Catalysts	Weak alkaline site amount (μmol m^{-2})	Moderate alkaline site amount (μmol m^{-2})	Total amount below 450 °C (μmol m^{-2})
Ni/CeO_2	1.2	1.1	2.3
Ni/CaCe-IM	1.3	1.9	3.1
Ni/CaCe-SG	1.9	2.5	4.5

Table S6 A literature summary of Ni-based catalysts in CO_2 methanation

Entry	Catalysts	Ni% (wt%)	Reaction condition			GHSV	CO_2 conversion (%)	Ref
			S_{BET} (m^2/g)	T (^oC)	P (bar)	(mL/g_{cat} h)		
1	2Ni-2Co /CeO_2	2	-	290	1	12000	5	[1]
2	2Ni-2Mn/CeO_2	2	-	290	1	12000	4	[1]
3	Ni/CeO_2-10	10	27.9	275	1	30000	28	[2]
4	NiCe/ZrO_2	10	5.2	350	1	18000	48	[3]
5	NiLa/ZrO_2	10	6	350	1	18000	37	[3]
6	Ni/CeO_2	10	84	350	1	18000	55	[3]
10	NiO/CeO_2	10	-	300	1	36000	58	[4]
11	Ni/CeO_2-NR	8	72	300	1	16500	68	[5]
12	10NiCe	10	-	300	1	72000	71	[6]
13	Ni/CeO_2	2	31	275	1	30000	32	[7]
14	Ni/CeO_2-NR	8	72	275	1	30000	79	[8]
15	Ni/CaCe-SG	10	26	290	1	18000	77	This wok

S4. References

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