

Electronic Supplementary Information (ESI)

Mesoporous Ni/Ce_{1-x}Ni_xO_{2-y} Heterostructure as Efficient Catalyst for Converting Greenhouse Gas to H₂ and Syngas

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1. Supplementary data

Table S1 The dispersion, grain diameter, and surface density of surface Ni species of all samples before and after reaction.

Samples	Metal Surface area (m ² /g) ^a	Dispersion (%) ^a	Metal Particle Size (nm)	
			D ^b	D ^c
Ni/CeO ₂	1.82	7.9	10.1	12.7
Ni/ <i>n</i> -Ce _{1-x} Ni _x O _{2-y}	2.53	19.2	n.d	5.2
Ni/ <i>mp</i> -Ce _{1-x} Ni _x O _{2-y}	2.91	25.1	n.d	3.9
used Ni/CeO ₂	0.82	3.7	21.8	27.7
used Ni/ <i>n</i> -Ce _{1-x} Ni _x O _{2-y}	1.03	5.6	13.5	16.9
used Ni/ <i>mp</i> -Ce _{1-x} Ni _x O _{2-y}	3.09	16.9	n.d	5.8

^a Dispersion was calculated assuming $H_{ad}/Ni_{surf}=1$, and Ni metal particle shape was assumed to be spherical. ^b represents Ni NP diameter determined using XRD. ^c designates Ni NP diameter derived via H₂- chemisorption.

2. Reasons for selecting Ni/SBA-15 as the comparison test

As clearly displayed in the main paper, the significant difference between Ni/*n*-Ce_{1-x}Ni_xO_{2-y} and Ni/*mp*-Ce_{1-x}Ni_xO_{2-y} consists in the meso-structure; meanwhile, Ni/*mp*-Ce_{1-x}Ni_xO_{2-y} remarkably outperformed Ni/*n*-Ce_{1-x}Ni_xO_{2-y}. These results unambiguously signified that the mesostructure played a very significant role in enhancing the catalytic activity.

Actually, the mesostructure could impact the catalytic function in two main

manners. One is the pure steric or geometrical confinement effect for the heterogeneous catalysis process, with the mesoporous walls not participating in the hetero-catalysis process. Under this situation, the mesoporous channels normally either function as the nanospaces to accommodate the Ni NPs (further provide the physical diffusion barrier to inhibit the agglomeration and fusion of Ni NPs) or act as the nanoreactors to increase the density of reactants¹ (therefore create a locally higher pressure, and accelerate the dynamics, which will favour two greenhouse gases transformation into syngas and H₂ in current case).

The other effect is that the mesoporous walls can get involved in the catalysis process affecting the reaction mechanism. In this case, the support itself is the active phase for the reaction; and the mesostructure can significantly expose the more specific areas to increase the amounts of active sites accessible, and tightly contact the loaded metal NPs to reinforce the metal-support strong interaction. To verify whether the latter effect also notably occurs in the Ni/*mp*-Ce_{1-x}Ni_xO_{2-y} catalyst, a suitable reference test is necessary.

On the one hand, for dry reforming of CO₂-CH₄, SiO₂ is well known to be nearly regarded as an inert support which presents a negligible catalytic activity for CO₂ or CH₄ adsorption/activation, particularly in comparison with the active oxide carriers such as Fe₂O₃, TiO₂, ZrO₂, La₂O₃, and CeO₂. Thus, when silica is used as the supporting materials for CO₂-CH₄ reforming, it will impart the negligible impact upon the mechanic process.

On the other hand, similar to N₂-volumetry data on Ni/*mp*-Ce_{1-x}Ni_xO_{2-y}, the isotherm of SBA-15 has been unequivocally documented to exhibit the typical type-IV isotherm curve with H1-type hysteresis loop,² indicating that both Ni/*mp*-Ce_{1-x}Ni_xO_{2-y} and SBA-15 have the typical mesoporous structure with a typical cylindrical mesostructure.

Thus, the selected SBA-15 with the channel diameter of 7-8 nm (analogous to the averagely 8.5 nm pore size of Ni/*mp*-Ce_{1-x}Ni_xO_{2-y}) can be an ideal control support for loading the Ni NPs to examine whether the contribution to the improved catalytic properties from the geometrical effect of the mesoporous channels of the CeO₂ is exclusive. Since SBA-15 also has a similar cylindrical channel with a pore diameter of 7-8 nm, it can impart an analogous dimensional or steric confinement on the catalytic systems. In this sense, if the steric or geometrical effect of the channel structure on the unique catalytic function inside mesoporous Ce-Ni solid solution is mere or predominant, the mesoporous silica SBA-15-confined Ni NPs will yield a comparable or superior behavior to the Ni/*mp*-Ce_{1-x}Ni_xO_{2-y}. Especially considering the high rang-range

ordering and periodicity of the mesostructure in SBA-15, this dimensional confinement effect will become more notable. However, the obviously inferior activity results to Ni/*mp*-Ce_{1-x}Ni_xO_{2-y} (in Fig.6 and 7) clearly rule out the exclusive contribution of the geometrical confinement effect of the mesostructure upon the enhanced behavior inside the mesoporous CeO₂, suggesting that the mesoporous walls, actually, significantly facilitate the metal-support synergy and/or afford more active sites. This comparison experiment also offers the direct activity evidence for discussing the effect of defects in the surface and bulk for reaction mechanism.

References:

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2. N. Wang, X. Yu, K. Shen, W. Chu, W. Qian, *Int. J. Hydrogen Energy*, 2013, **38**, 9718-9731.