Supporting Information†

Heterosturcture NiO/Ce$_{1-x}$Ni$_x$O$_2$: Synthesis and synergistic effect of simultaneous surface modification and internal doping for creating superior catalytic performance

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Sample characterization

![Graph showing CO conversion at 150 °C for different samples](image)

**Fig.S1** CO oxidation activities at 150 °C (reaction temperature) of the samples (1-x) CeO$_2$-xNiO (0.05≤x≤0.7) after calcination at 600 °C.
Fig. S2 an amplified XRD patterns of the samples (1-x)CeO$_2$-xNiO, (a) at x=0 after calcination at 600 °C, x=0.1 after calcinations at (b) 400, (c) 500, (d) 600, (e) 700 °C, and (f) x=1 after calcination at 600 °C from 42 to 50 degree. Al was selected as an internal standard for peak position calibration.

Fig. S3 Amplified XRD patterns about CeO$_2$ (111) crystalline plane patterns of the samples (1-x)CeO$_2$-xNiO for x=0.1 after calcinations at (a) 400°C, (b) 500°C, (c) 600°C, (d) 700 °C and (e) x=0 after calcination at 600 °C. Al was selected as an internal standard for peak position calibration.
**Fig. S4** Amplified Raman spectrum over a frequency range from 420 to 500 cm\(^{-1}\) for the samples \((1-x)\) CeO\(_2\)-xNiO at \(x=0.1\) after calcinations at (a) 400, (b) 500, and (c) 700 °C, and (d) at \(x=0\) after calcination at 600 °C.

**Fig. S5** Amplified XRD patterns of the sample \((1-x)\)CeO\(_2\)-xNiO at (a) \(x=0.1\), (b) \(x=0.2\), and (c) \(x=1\) before calcinations.

Fig. S5 shows the XRD patterns of the samples \((1-x)\)CeO\(_2\)-xNiO \((x=0.1, 0.2, 1)\) before calcination prepared by hydrothermal method. For further confirm phase composition of the \((1-x)\)CeO\(_2\)-xNiO \((x=0.1)\) catalyst before calcination, the XRD results of (1-x)
CeO$_2$-xNiO (x=0.2, 1) samples are together presented as reference. The diffraction peaks of only $\beta$-Ni(OH)$_2$ (space group P-3m1, JCPDS, No.14-0117) were observed for (1-x)CeO$_2$-xNiO (x=1) sample before calcination. For x=0.1 and 0.2, it is found that strong diffraction peaks are attributed to CeO$_2$ (space group Fm-3m, JCPDS, No.65-5923) and another two weak diffraction peaks presented in XRD patterns are attributed to $\beta$-Ni(OH)$_2$, the peaks position of which is consistent with pure (1-x)CeO$_2$-xNiO (x=1). The intensity of $\beta$-Ni(OH)$_2$ is increasing with Ni content.

![Fig.S6](image)

**Fig.S6** SEM micrographs of the sample (1-x)CeO$_2$-xNiO prepared at x=0.1 after calcination at (a) 400, (b) 500, (c) 600, and 700 °C.

From the SEM images of Fig. S6, it can be seen that the shape of (1-x) CeO$_2$-xNiO sample (x=0.1) after calcination is irregular, which is caused by small nanoparticle aggregation after calcination treatment. With the increment of calcination temperature, more nanoparticles aggregate into the bulk together.
Fig. S7. In-situ DRIFT spectra 2050-2250 cm$^{-1}$ of (1-x)CeO$_2$:xNiO catalysts was exposed to 1% CO/He at 160 oC at (a) x=0 after calcination at 600 oC. (b) x=1 after calcination at 600 oC, x=0.1 after calcinations at (c) 400 oC, (d) 500 oC, (e) 600 oC, (f) 700 oC.

The In-situ DRIFT spectra obtained upon exposure of the (1-x)CeO$_2$:xNiO catalysts to 1% CO/He gas stream at 160 oC were shown in Fig. S7. The twin bands at 2117 and 2172 cm$^{-1}$ are resulted from the P-branch and R-branch of gaseous CO.$^{[1]}$ As shown in Fig. S7b, for pure NiO, the band at 2182 cm$^{-1}$ is attributed to CO adsorbed on nickel species. $^{[2]}$ For the samples at x=0.1 calcined at different temperatures, since the amount of surface NiO is less, it is difficult to observe CO adsorption on Ni species as calcination temperature increases.


Fig. S8 CO oxidation activities of the samples (1-x)CeO$_2$·xNiO for x=0 after calcination at (a) 400°C (b)500°C (c)600°C and (d)700°C.

Fig. S9 CH$_4$ oxidation activities of the samples (1-x)CeO$_2$·xNiO for x=0.1 after calcination at (a) 400°C (b)500°C (c)600°C and (d)700°C.