Electronic Supplementary Information for

Fabrication of Oxygen Vacancies through Assembling Amorphous Titanate Overlayer on Titanium Oxide for Catalytic Water-Gas Shift Reaction

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Table S1 Contents of Ni and Na for 1-Ni-R350 and 1-Ni-Na-350 measured by ICP-OES.

	1-Ni-R350	**1-Ni-Na-R350**
Ni	1.35%	1.23%
Na	-	2.48%

Table S2 Crystal structure parameters of TiO_2 and Na_2TiO_3.[1, 2]

Crystal Structure	Crystal system	Lattice parameter（Å）	Density（g/cm^3）	Ti-O bond length of（Å）
Rutile	Tetragonal	a = b = 4.584 c = 2.953	4.25	1.946 1.983
Anatase	Tetragonal	a = b = 3.782 c = 9.502	3.89	1.937 1.966
α-Na_2TiO_3	Cubic	a = b = c = 4.510	-	2.255

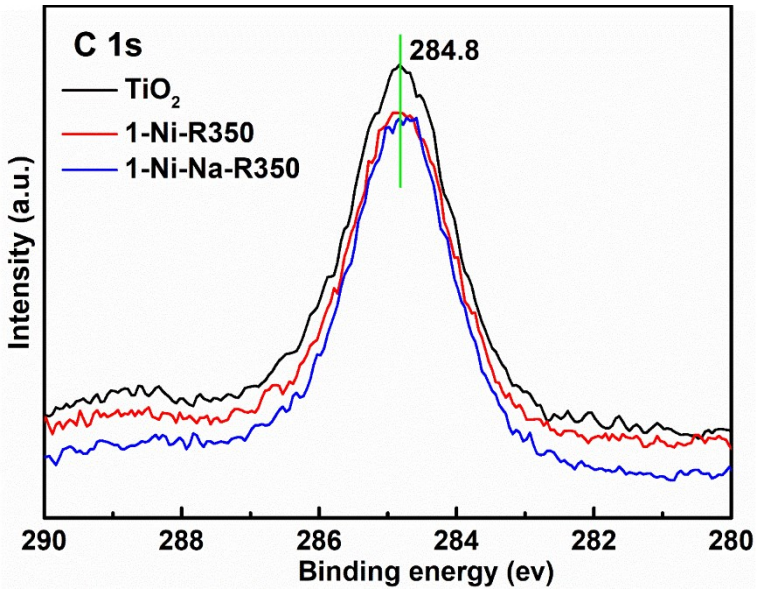

Fig. S1 XPS spectra of C 1s in 1-Ni-R350 and 1-Ni-Na-R350 samples.

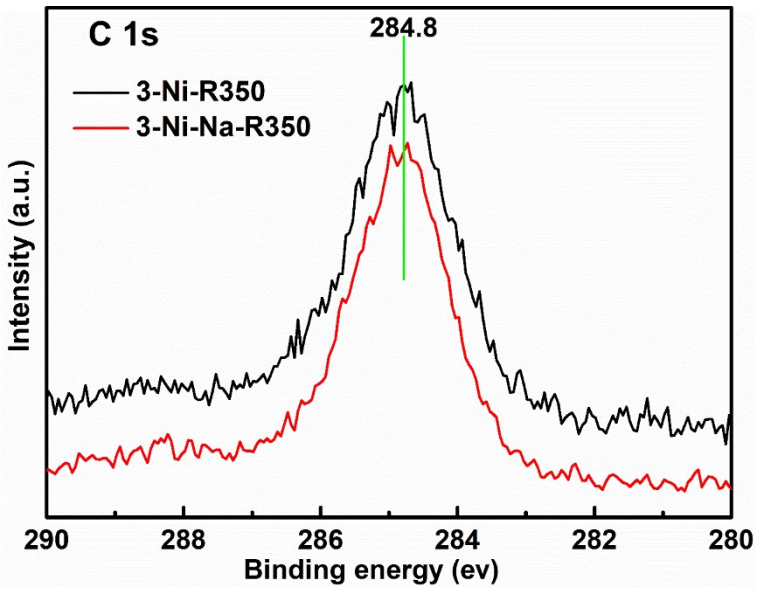

Fig. S2 XPS spectra of C 1s in 3-Ni-R350 and 3-Ni-Na-R350 samples.

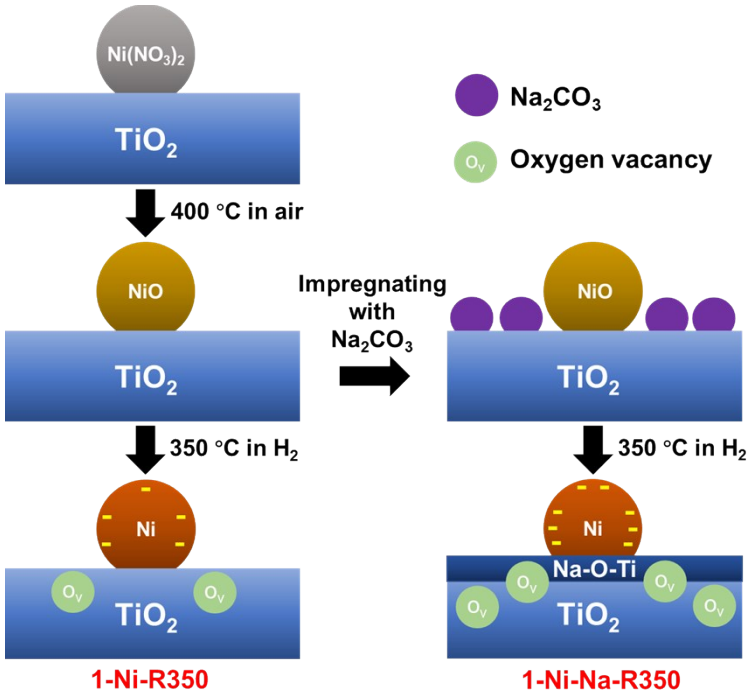

Fig. S3 Preparation process of 1-Ni-R350 and 1-Ni-Na-R350 catalysts.

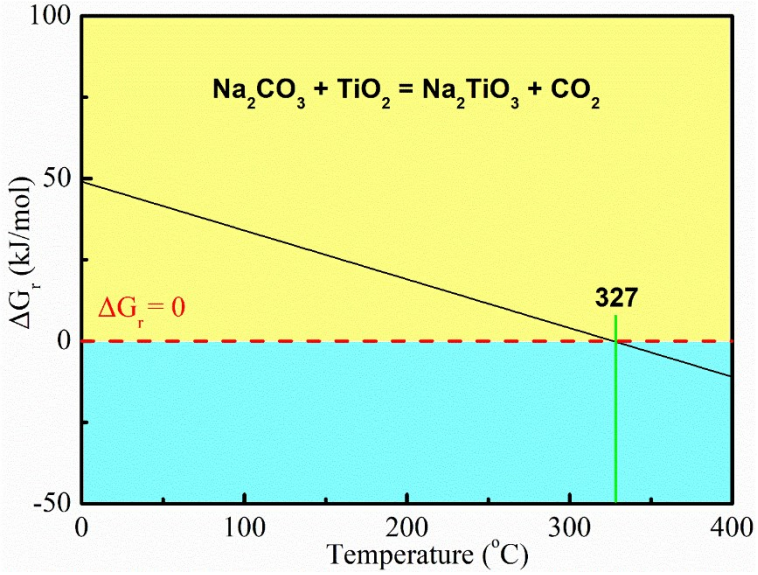

Fig. S4 Thermodynamic analysis of the reactions between Na_2CO_3 and TiO_2 to form Na_2TiO_3.

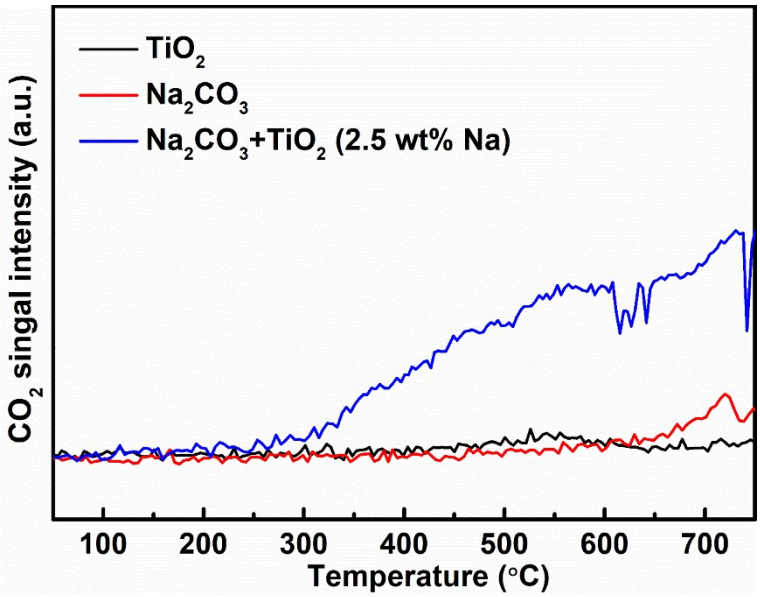

Fig. S5 Temperature-programmed reaction of TiO_2, Na_2CO_3 and the mixture of TiO_2-Na_2CO_3 in Ar flow. CO_2 (m/z = 44) is monitored on-line by MS.

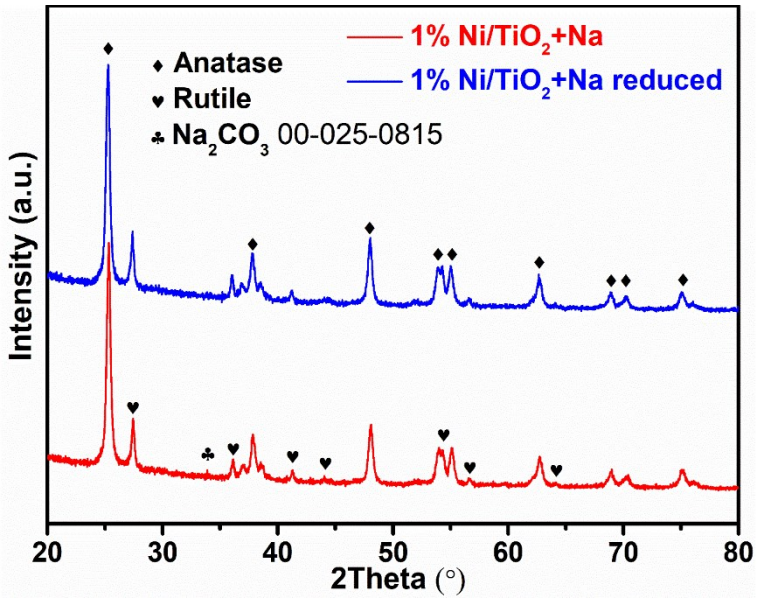

Fig. S6 XRD patterns of 1% Ni/TiO_2+Na samples before or after reduction. Small diffraction peak of Na_2CO_3 can be detected from Na_2CO_3-doped Ni/TiO_2. However, no Na_2CO_3 can be observed after heat treatment, indicating the occurrence of reaction between TiO_2 and Na_2CO_3.

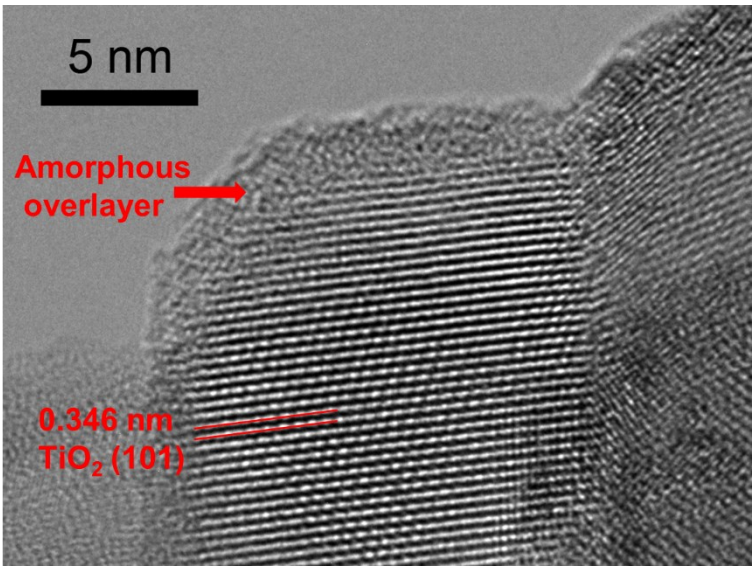

Fig. S7 HRTEM image of 1-Ni-Na-R350 catalyst. An amorphous titanate overlayer on TiO_2 surface was clearly observed.

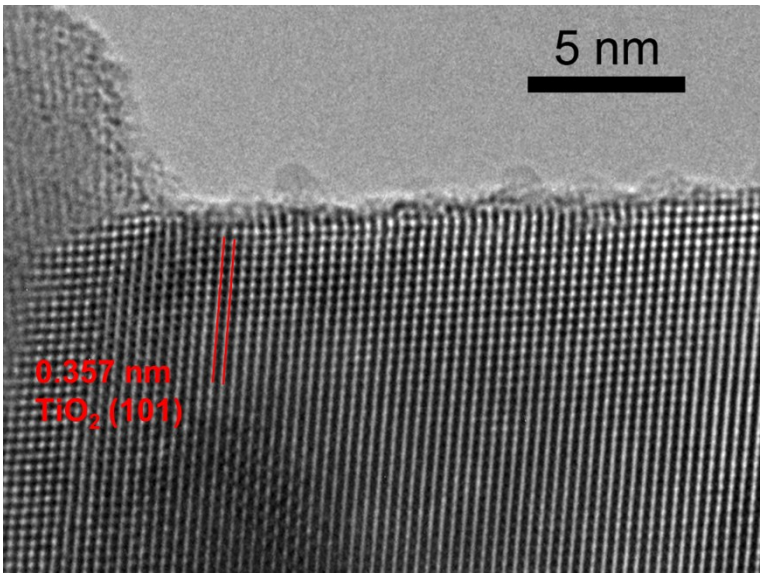

Fig. S8 HRTEM image of 1-Ni-R350 catalyst.

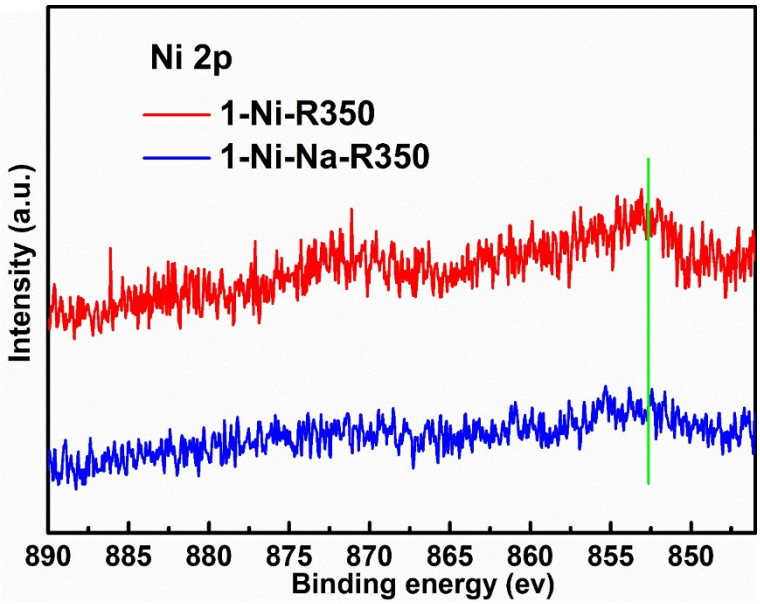

Fig. S9 XPS spectra of Ni 2p in 1-Ni-R350 and 1-Ni-Na-R350 samples.

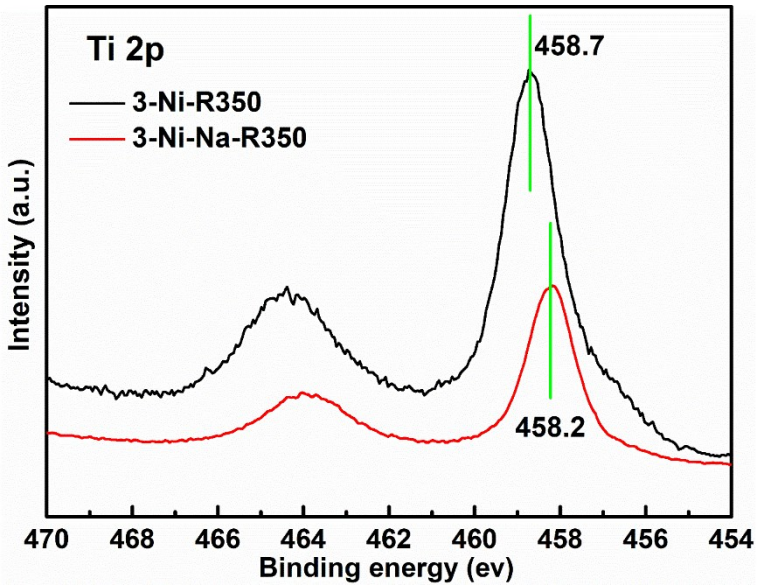

Fig. S10 XPS spectra of Ti 2p in 3-Ni-R350 and 3-Ni-Na-R350 samples.

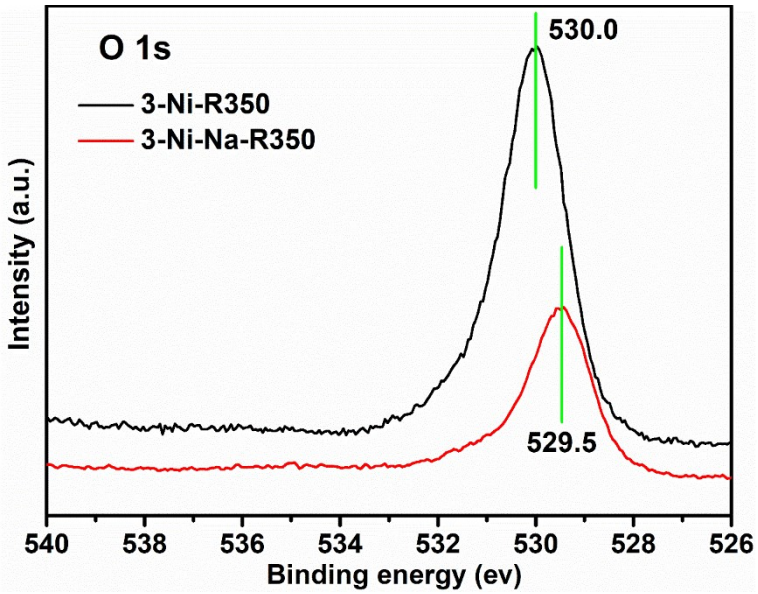

Fig. S11 XPS spectra of O 1s in 3-Ni-R350 and 3-Ni-Na-R350 samples.

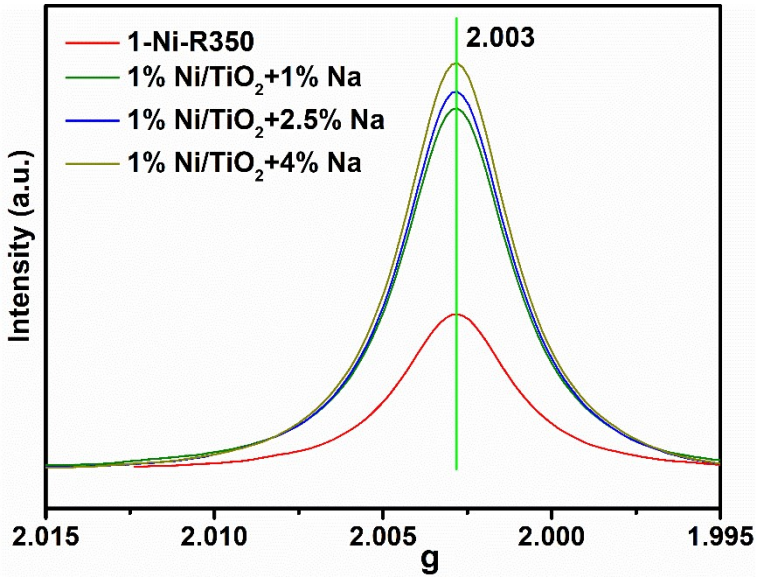

Fig. S12 Integral EPR spectra of 1% Ni/TiO_2 samples doped by different weight ratios of sodium in the range of g from 1.995 to 2.015.

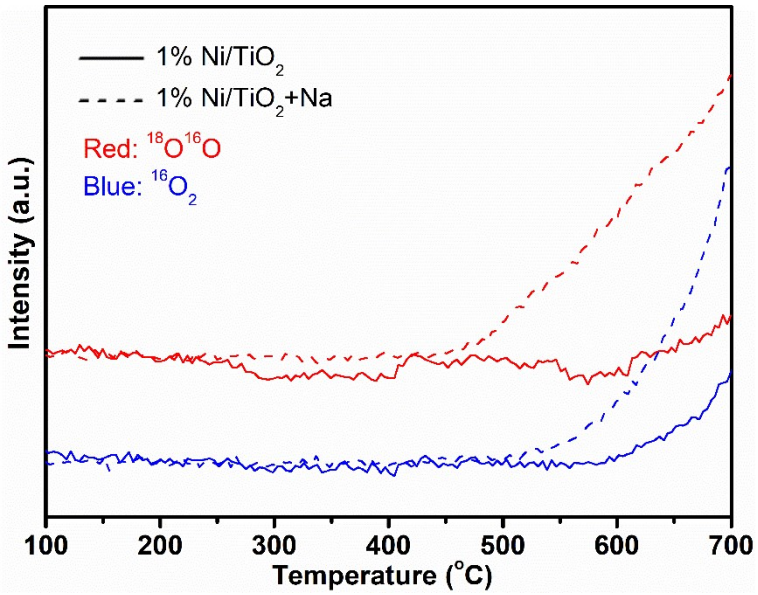

Fig. S13 Isotopic oxygen analyses of 1% Ni/TiO_2 and sodium-doped 1% Ni/TiO_2 samples in $^{18}O_2$ flow at temperature programmed reaction. ($^{18}O^{16}O$: m/z = 34 and $^{16}O_2$: m/z = 32).

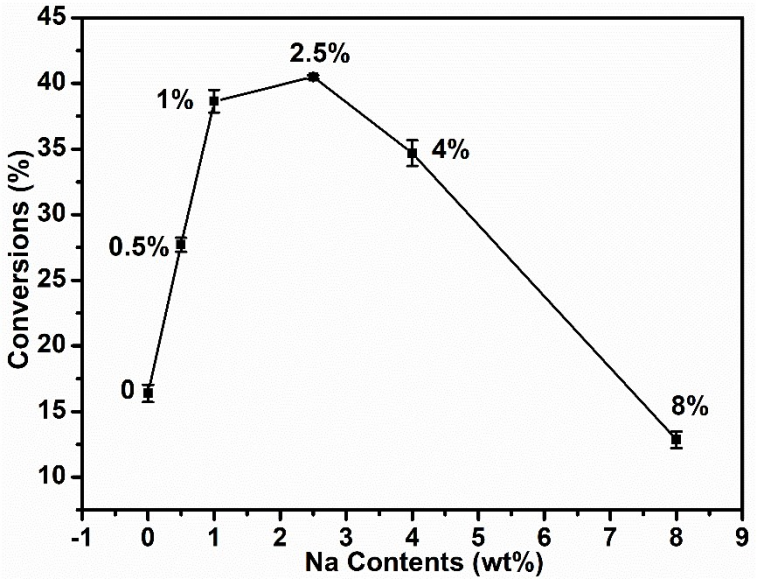

Fig. S14 Catalytic performance of 1% Ni/TiO_2 catalysts doped with different amount of sodium at 350 °C, WHSV=100,000 $mL \cdot g^{-1} \cdot h^{-1}$.

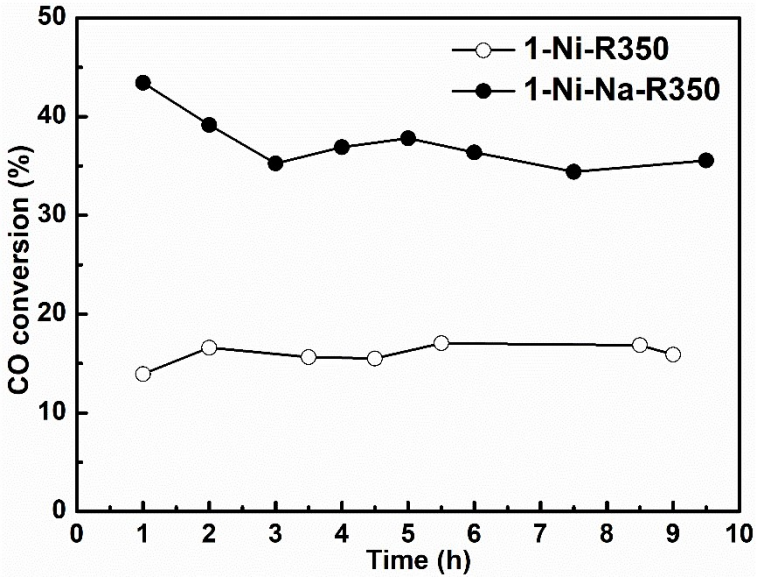

Fig. S15 Stability evaluation of 1-Ni-R350 and 1-Ni-Na-R350 catalysts at 350 °C,

WHSV=100,000 $mL \cdot g^{-1} \cdot h^{-1}$.

Notes and references

1 U. Diebold, *Surf. Sci. Rep.*, 2003, **48**, 53-229.

2 W. Antony Hill, A. R. Moon and G. Higginbotham, *J. Am. Ceram. Soc.*, 1985, **68**, C-266-C-267.