Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary material

Roles of highly ordered mesopore structures of Fe-Ni bimetal oxide for an enhanced high temperature water-gas shift reaction activity

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Table S1. Summarized results of XRD analysis of the m-FeNi catalysts such as the crystalline and strain natures derived from Rietvelt and Williamson-Hall plot method

Catalyst	Main peak (104) position (2θ)	Crystallite size (nm)[a]	Microstrain (%)[a]	Strain of lattice (%)[b]
m-FeNi(0)	33.19	16.4	0.20	-
m-FeNi(0.1)	33.17	11.5	0.16	0.18
m-FeNi(0.2)	33.16	10.1	0.07	0.22
m-FeNi(0.5)	33.15	11.7	0.30	0.15
m-FeNi(1)	33.10	12.2	0.40	0.18

[a]The data was obtained after the refinement of Fe_2O_3 spectra from raw XRD data by Rietvelt's method. The crystallite sizes and microstrains were derived by a Williamson-Hall plot method and by plotting all Fe_2O_3 peaks in the range of $2\theta = 24$ to 89^o.

[b]The strains of lattice were calculated by a direct linear plot method from the characteristic Fe_2O_3 peaks in the range of $2\theta = 24$ to 89^o with the assumption of the stretched lattice of the m-FeNi based on that of the reference m-Fe_2O_3 (m-FeNi(0)).

Table S2. Summarized catalytic performance and deactivation rate of WGS reaction on the m-FeNi catalysts[a]

Catalyst	CO conversion (mol%)	CO_2 selectivity (mol%)	CH_4 selectivity (mol%)	Deactivation rate (mol%/h)
m-FeNi(0)	12.5	88.5	11.5	0.37
m-FeNi(0.1)	70.6	82.1	7.9	0.16
m-FeNi(0.2)	74.7	96.0	4.0	0.01
m-FeNi(0.5)	72.5	91.3	8.7	0.37
m-FeNi(1)	72.4	72.7	27.3	0.74

[a]The catalytic activity such as CO conversion and selectivity of CO_2 and CH_4 was measured at T = 400 ^{o}C, P = 0.1 MPa, weight hour space velocity (SV) of syngas with 5200 (ml/(g_{cat}·h)) and a feed gas composition of N_2/CO/H_2/H_2O/CH_4/CO_2 = 4/6.3/46.4/28.2/5.5/9.7 (H_2O/CO molar ratio of 4.5 with a typical composition of the reformate after steam reforming of propane. The deactivation rate (mol%/h) was represented by the average CO conversion between an initial value of 1 – 5 h and that of a steady-state of 16 – 20 h.

Table S3. Summarized XPS results of the fresh and used m-FeNi catalysts[a]

Catalyst	Surface ratios of the representative chemical species (fresh / used)[a]			
	Fe^{3+}/Fe^{2+}	Ni^{3+}/Ni^{2+}	$S(I_{Ni}/I_{Fe})$	$S(I_{Ni}/I_{Fe})/B(I_{Ni}/I_{Fe})$
m-FeNi(0)	0.87 / 2.26	- / -	0 / 0	0 / 0
m-FeNi(0.1)	0.97 / 1.93	- / 1.29	0.21 / 0.10	1.66 / 0.82
m-FeNi(0.2)	0.79 / 1.98	0.90 / 2.07	0.49 / 0.34	1.94 / 1.36
m-FeNi(0.5)	0.84 / 1.84	1.34 / 1.87	0.81 / 0.46	1.62 / 0.92
m-FeNi(1)	0.86 / 1.97	1.37 / 1.73	1.31 / 0.91	1.31 / 0.91

[a]Surface composition ratios of the Fe^{3+}/Fe^{2+} and Ni^{3+}/Ni^{2+} were calculated by integrating the peak intensity of Fe $2p_{3/2}$ assigned to Fe^{3+} (~712 eV, Fe_2O_3 hematite) and Fe^{2+} (~710.8 eV, Fe_3O_4 magnetite and FeO) as well as Ni $2p_{3/2}$ appeared at ~857 eV for Ni^{2+} (NiO) and ~855 eV for Ni^{3+} (Ni_2O_3) on the fresh and used m-FeNi catalysts. The surface to bulk composition ratio of $S(I_{Ni}/I_{Fe})/B(I_{Ni}/I_{Fe})$ was calculated by using the peak intensity ratio of the surface $S(I_{Ni}/I_{Fe})$ ratio measured by surface sensitive XPS analysis to the bulk intensity $B(I_{Ni}/I_{Fe})$ ratio measured by XRF analysis on the fresh and used m-FeNi catalysts.

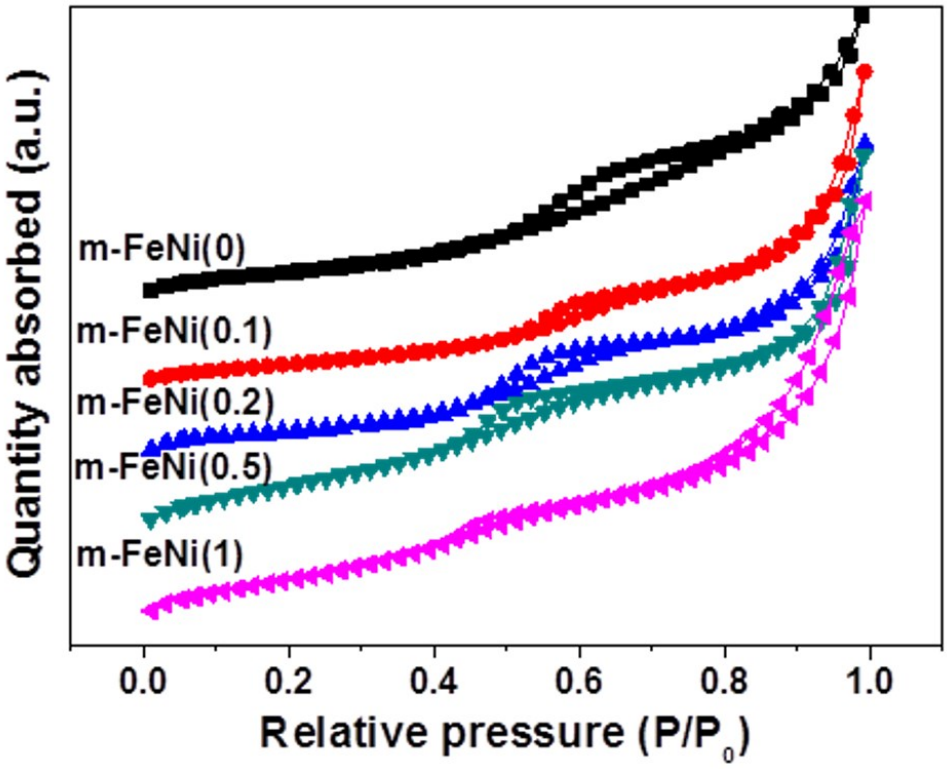

Figure S1. N_2 adsorption-desorption isotherms of the as-synthesized fresh m-FeNi catalysts

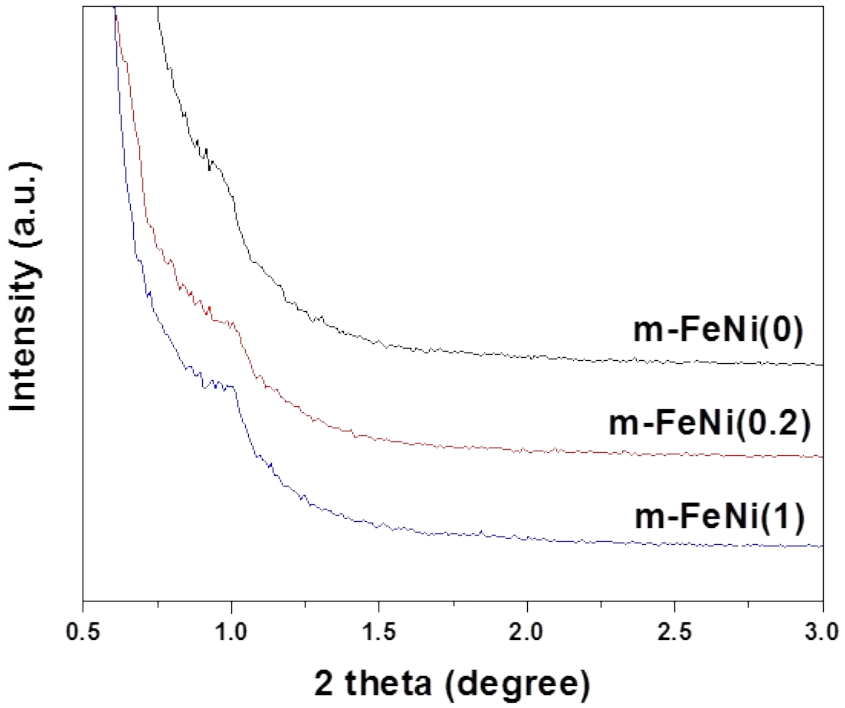

Figure S2. Small-angle X-ray scattering (SAXS) spectra of the as-synthesized m-FeNi catalysts

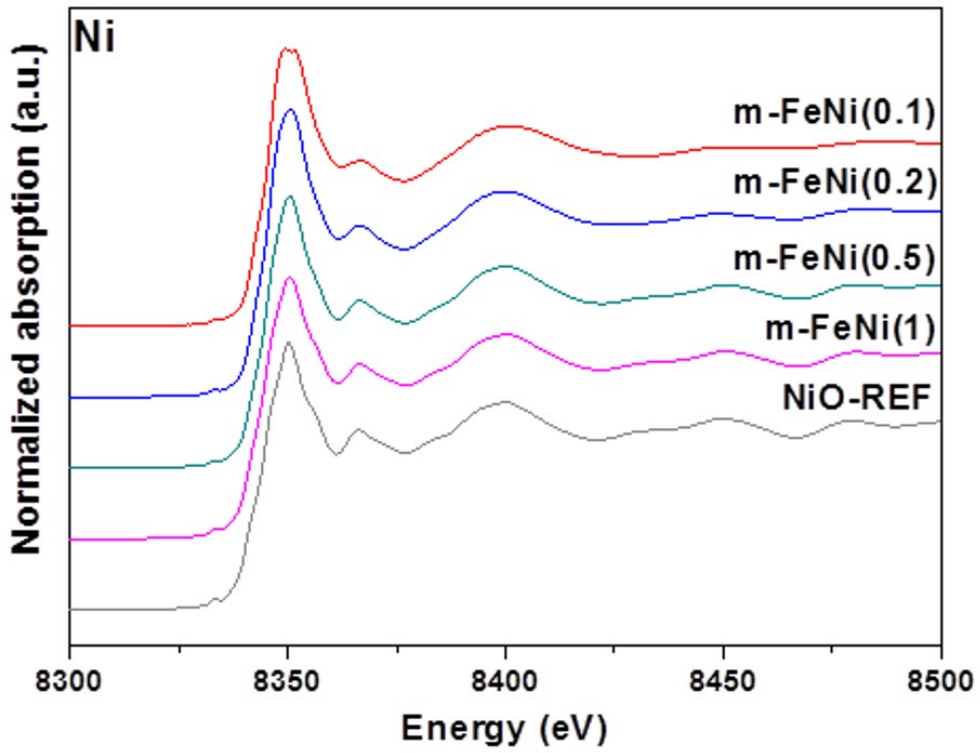

Figure S3. X-ray absorption fine structures (XAFS) spectra of Ni K-edge from the as-synthesized fresh m-FeNi catalysts

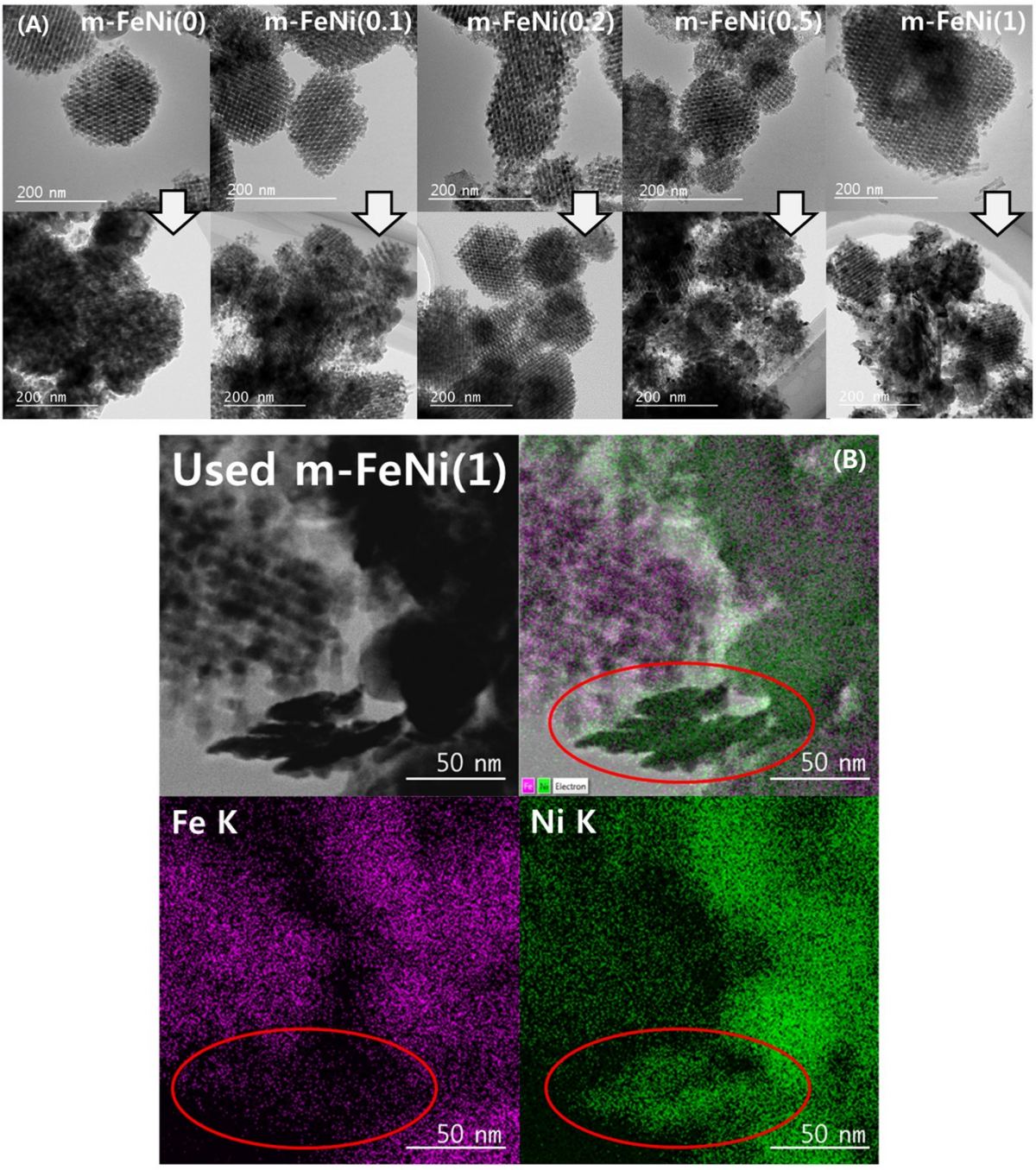

Figure S4. (A) TEM images of the fresh (upper figure) and used (bottom figure) m-FeNi catalysts with (B) EDS mapping images

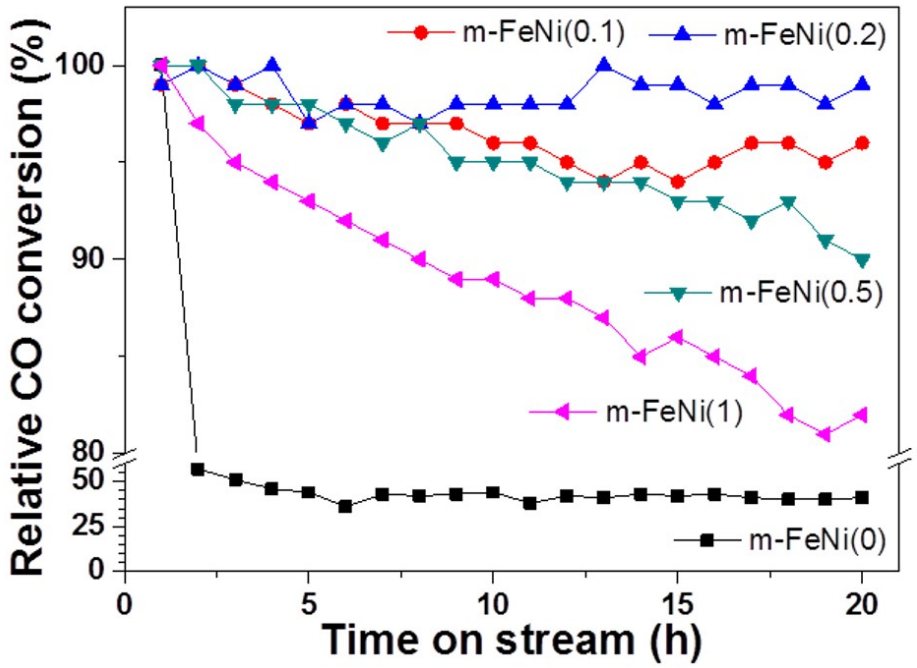

Figure S5. Relative CO conversion (based on the 100% CO conversion on the most active point for each catalyst) with time on stream (h) on the m-FeNi catalysts under the HT-WGS reaction conditions such as weight hourly space velocity (SV) of syngas (composition of $N_2/CH_4/CO/CO_2/H_2$ = 5.5/7.7/8.7/13.5/64.6 mol%, typical composition of reformate after steam reforming of propane) with 5200 (ml/g_{cat}·h), H_2O/CO molar ratio of 4.5, T = 400 °C and ambient pressure

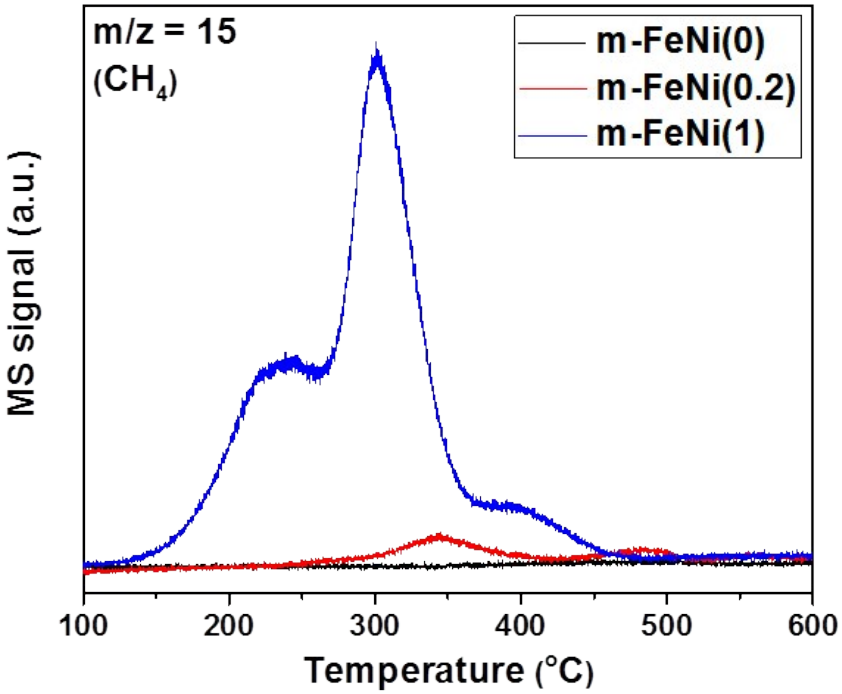

Figure S6. Spectra of temperature-programmed surface reaction with H_2 (H_2-TPSR) with mass spectrometer to measure CH_4 fragment (m/z =15) on the used m-FeNi(0), m-FeNi(0.2) and m-FeNi(1)

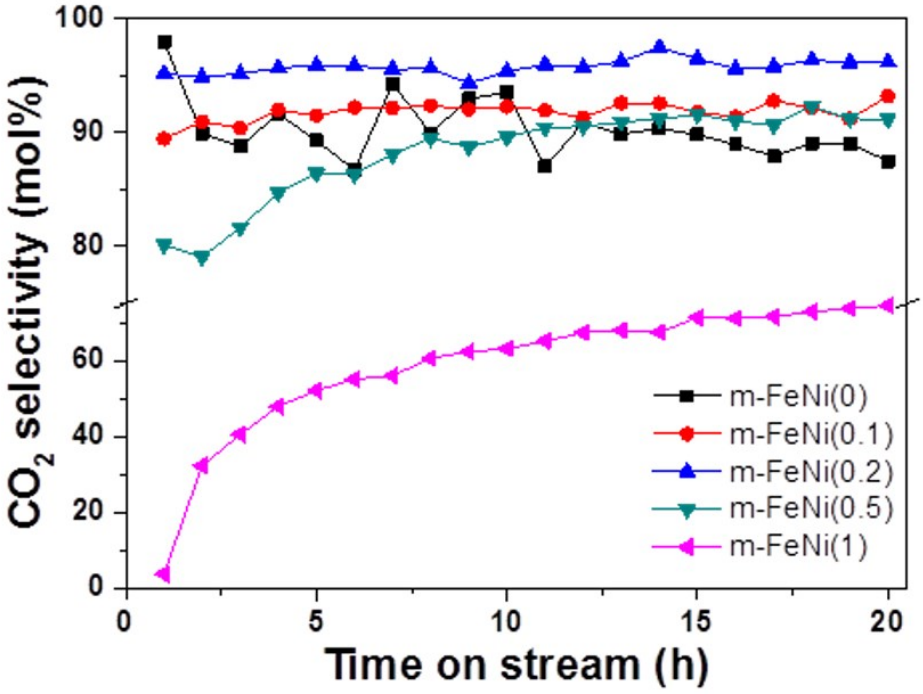

Figure S7. CO_2 selectivity with time on stream (h) of the m-FeNi catalysts under HT-WGS reaction conditions such as weight hourly space velocity (SV) of syngas (composition of $N_2/CH_4/CO/CO_2/H_2$ = 5.5/7.7/8.7/13.5/64.6 mol%, typical composition of reformate after steam reforming of propane) with 5200 (ml/g_{cat}·h), H_2O/CO molar ratio of 4.5, T = 400 °C and ambient pressure

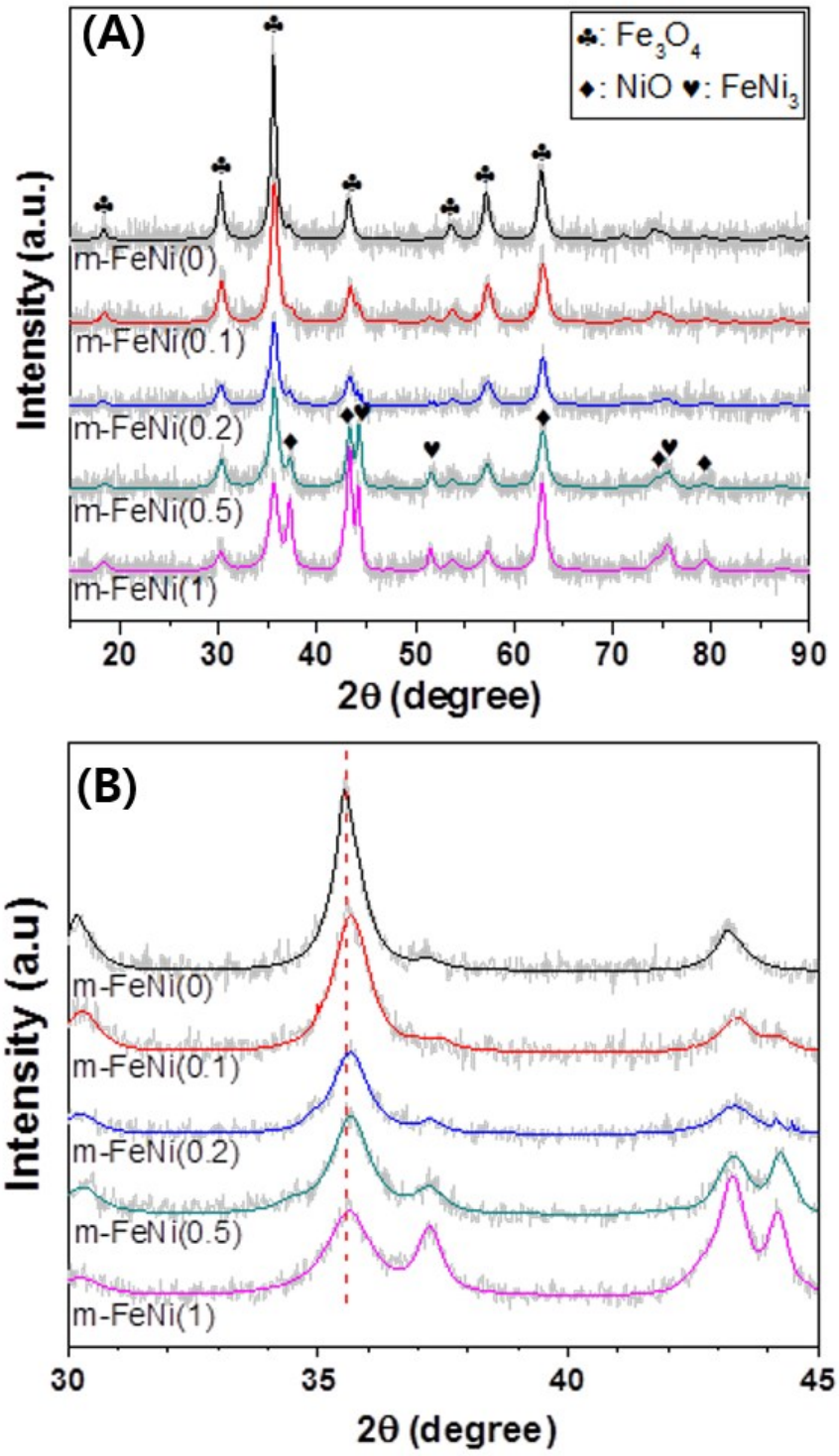

Figure S8. XRD patterns of the used m-FeNi catalysts; (A) wide angle XRD patterns for all crystalline phases and (B) XRD patterns in the range of 30 – 45^{o} for phase confirmations

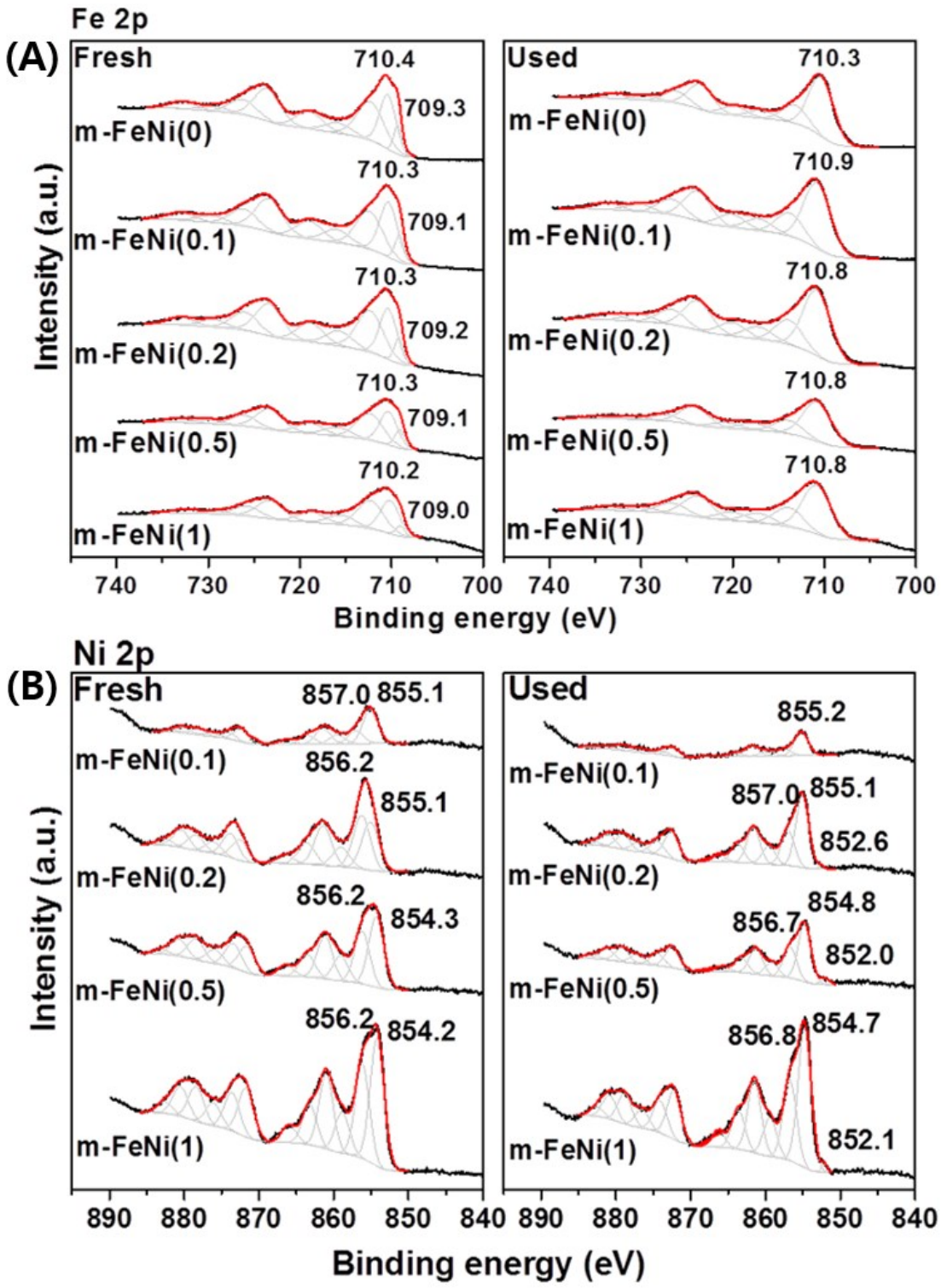

Figure S9. XPS spectra of the fresh (left) and used (right) m-FeNi catalysts; (A) Fe 2p spectra and (B) Ni 2p spectra with their characteristic binding energy (BE)