Hierarchical Fe-modified $MgAl_2O_4$ as Ni-catalyst support for methane dry reforming

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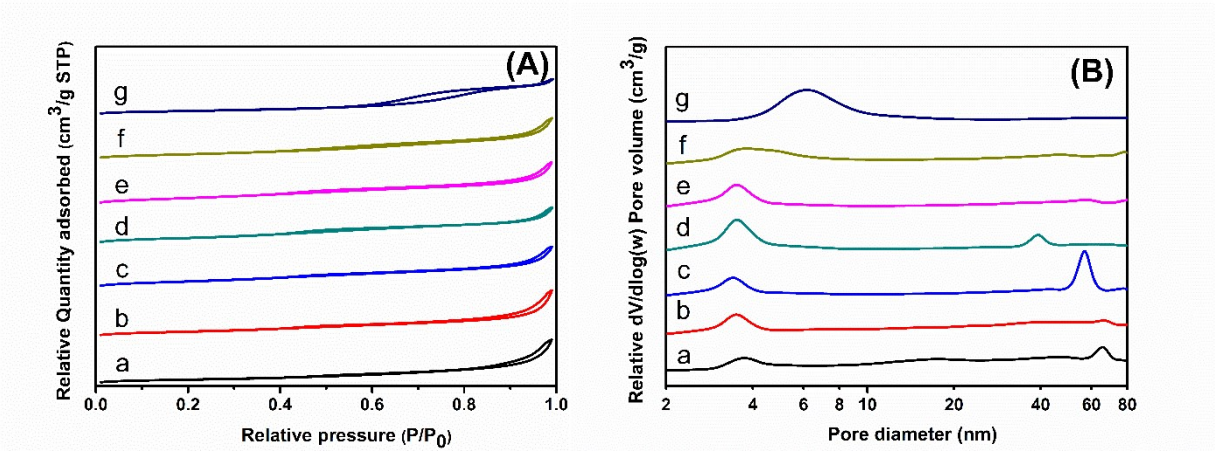

Supplementary figures

Fig. S1. (A) N_2 adsorption-desorption isotherms and (B) corresponding pore size distributions of support materials calcined at 800 °C for 4 h. (a) Al_2O_3, (b) Mg-0.25, (c) Mg-0.5, (d) Mg-1.0, (e) FeMg-0.75, (f) FeMg-6.0, (g) $MgAl_2O_4$

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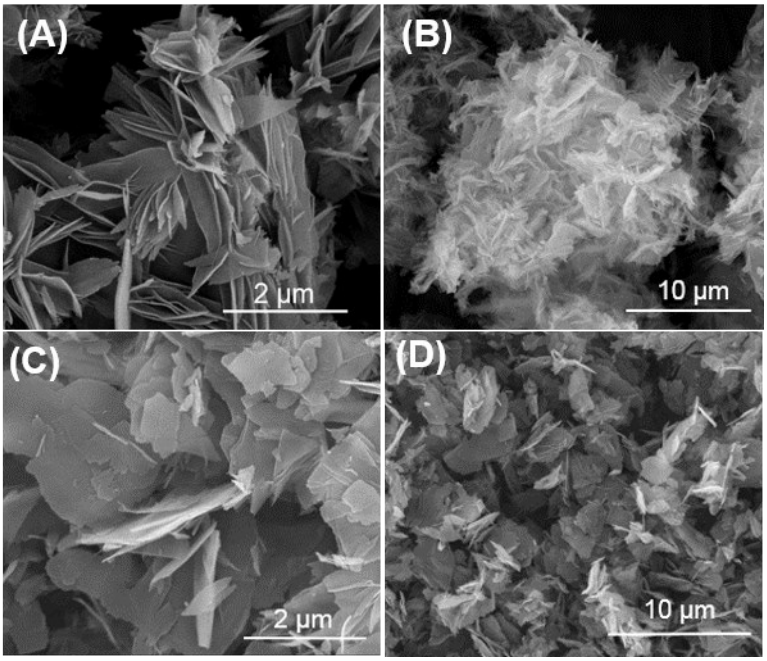

Fig. S2. SEM images of samples calcined at 800 °C for 4 h. (A) Mg-0.25, (B) Mg-0.5, (C) (D) Mg-1.0.

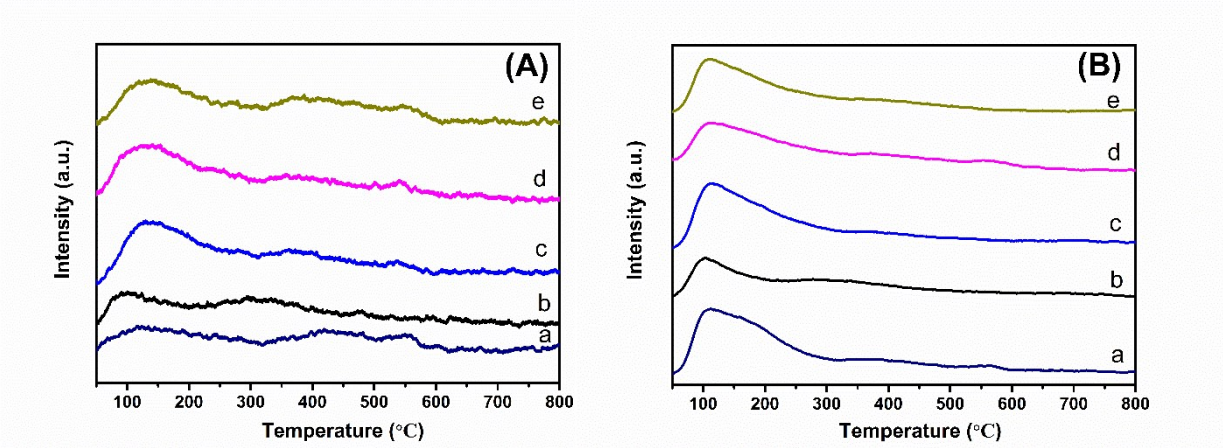

Fig. S3. (A) CO_2-TPD profiles and (B) NH_3-TPD profiles during thermal treatment of calcined support materials at 800 °C for 4 h. (a) $MgAl_2O_4$, (b) Al_2O_3, (c) Mg-0.5, (d) FeMg-0.75, (e) FeMg-6.0. Respective pre-treatments: 60 ml/min 4% NH_3/He or 100% CO_2 at room temperature for 1 h.

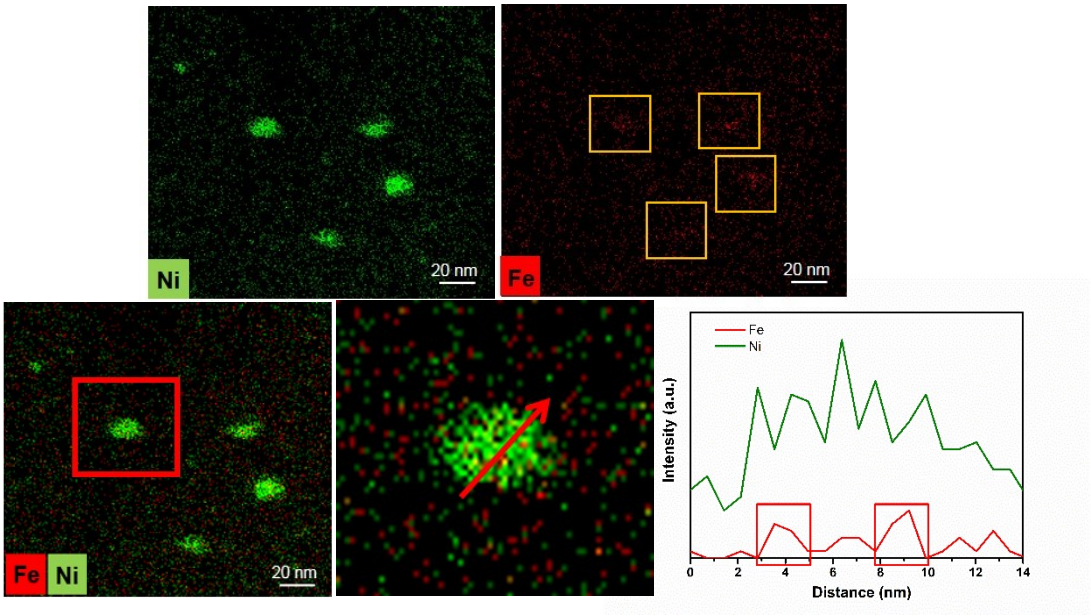

Fig. S4. EDX mapping and line scan of reduced Ni/FeMg-0.75.

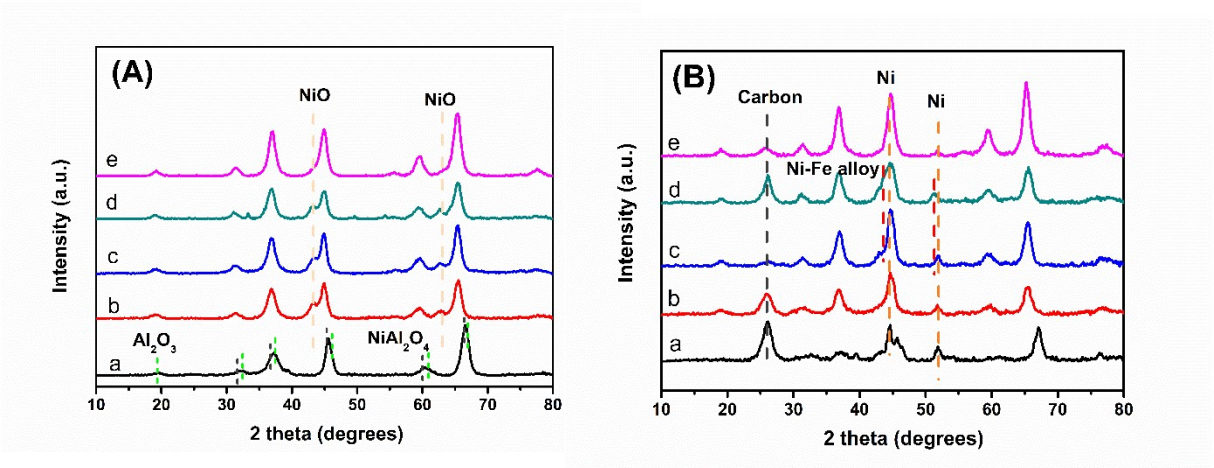

Fig. S5. XRD scans of (A) calcined catalysts and (B) spent catalysts after DRM 750 °C for 12 h (200 ml/min CH_4:CO_2:Ar with volumetric ratio of 1:1:3, 111.3 kPa, W_{Ni}/F^0_{CH4} = 0.33 kg_{Ni} . s . mol_{CH4}^{-1}). (a) Ni/Al_2O_3, (b) Ni/Mg-0.5, (c) Ni/FeMg-0.75, (d) Ni/FeMg-6.0, (e) Ni/$MgAl_2O_4$.

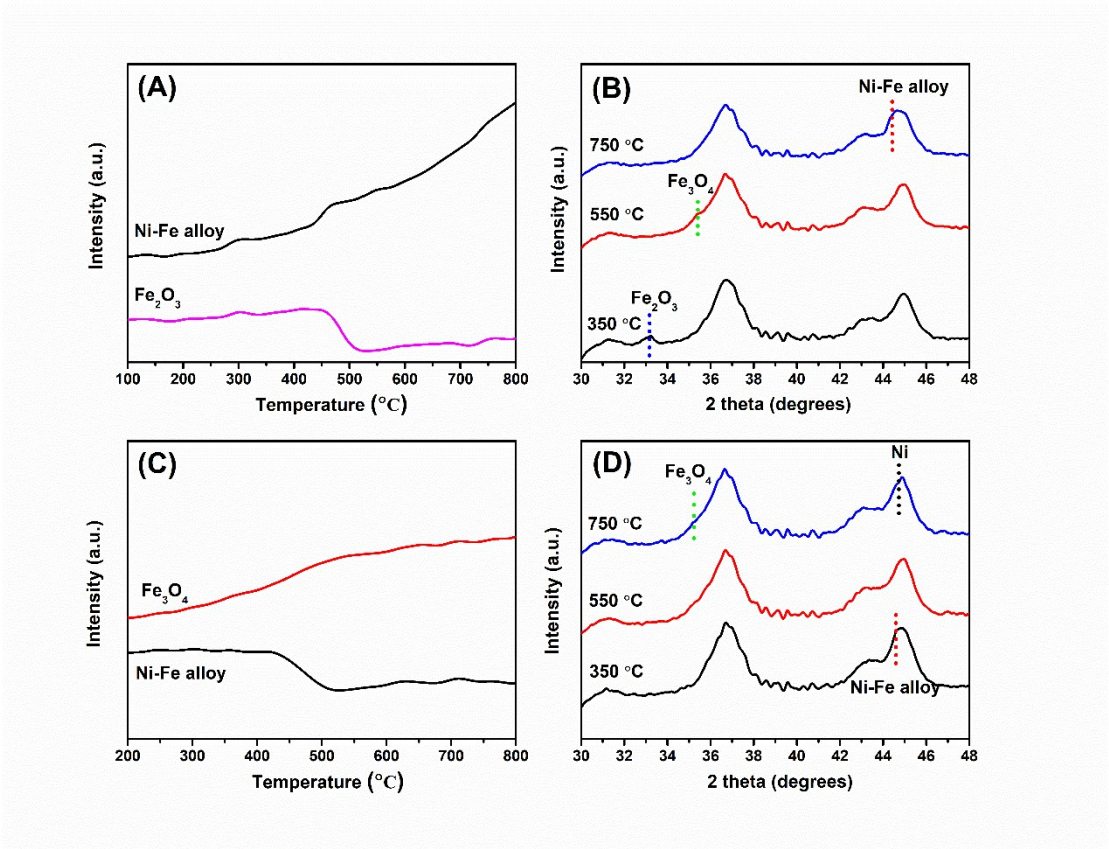

Fig. S6. In situ XRD for Ni/FeMg-6.0. (A) integral intensity variation during H_2-TPR for diffraction areas 32.5−33.5° (Fe_2O_3) and 43.7−44.2° (Fe-Ni alloy); (B) diffraction peaks at different temperature during H_2-TPR; (C) integral intensity variation during CO_2-TPO for diffraction areas 35−36° (Fe_3O_4) and 43.7−44.2° (Fe-Ni alloy); (D) diffraction peaks at different temperature during CO_2-TPO.

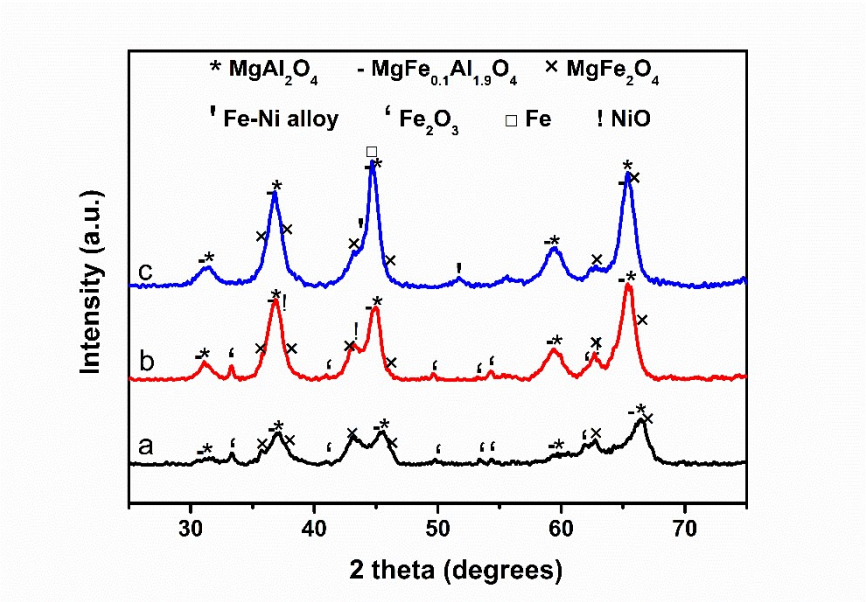

Fig. S7. XRD scans of Ni/FeMg-6.0 sample in different states. (a) FeMg-6.0 support, (b) calcined catalyst, (c) reduced catalyst.

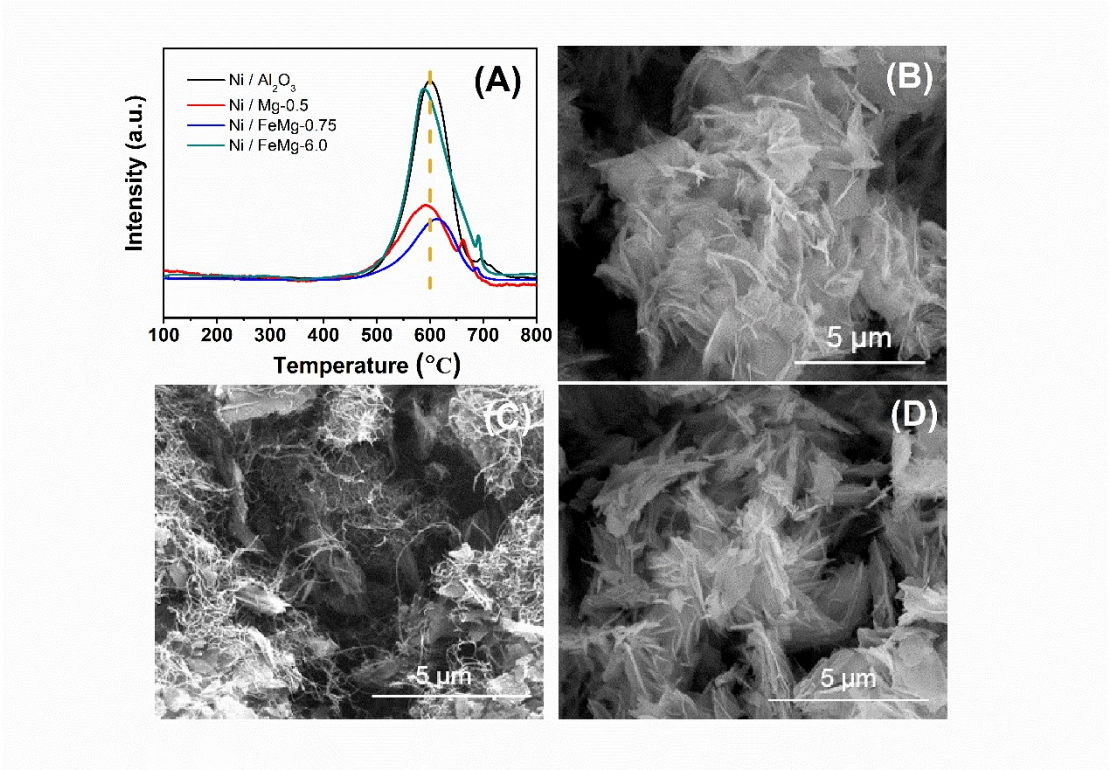

Fig. S8. (A) O_2-TPO profiles for spent hierarchical catalysts and SEM images for Ni/FeMg-0.75 sample in different stages: (B) before reaction, (C) after reaction, (D) after O_2-TPO.

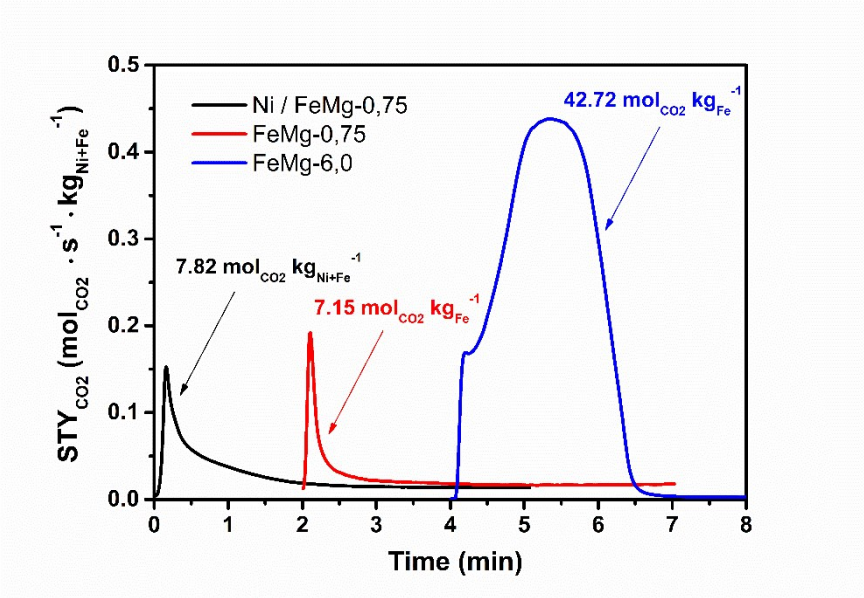

Fig. S9. CO_2 space-time yield (STY, $mol_{CO2} \cdot s^{-1} \cdot kg_{Ni+Fe}^{-1}$) upon O_2 oxidation of deposited carbon for the three different spent materials (using a 2 min offset for the different curves).