## Supplementary materials

# Natural Fe-based catalysts for the production of hydrogen and carbon nanomaterials via methane decomposition 

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XRD analysis
The crystalline structures of the materials were characterized by X-ray diffraction using a diffractometer Bruker D8 Advance Series 2 with a $\mathrm{Cu}(\lambda=0.154 \mathrm{~nm})$ anode and a secondary graphite monochromator. The diffractometer was operated with a range of $20-80^{\circ}$, using a counting step of $0.05^{\circ}$ and a counting time per step of 3 s . The powder XRD patterns were further processed using the accompanying DIFRAC PLUS EVA 8.0 and TOPAS software for some qualitative and quantitative analysis by applying Rietveld refinement method. GC analysis

The composition of the product gases was collected in gas sampling bags for 5 min every 10 min in the first hour and every 20 min after that. Then, the gases were examined by a micro GC (HP Varian CP 4900) equipped with two packed columns (Q-Porapak and molecular sieve MS5) and a thermal conductivity detector (TCD). The $\mathrm{H}_{2}$ and $\mathrm{CH}_{4}$ concentration were obtained by GC analysis using a calibration curve previously constructed with known concentrations of $\mathrm{H}_{2}$ and $\mathrm{CH}_{4}$ samples.

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Figure S1- $\mathrm{H}_{2}$ concentration and $\mathrm{CH}_{4}$ conversion evolutions for Tierga- $\mathrm{CH}_{4}$ in the CDM reaction at $850^{\circ} \mathrm{C}$ and different WHSVs for 3 h .


Figure S2 - XRD patterns of spent Tierga catalysts after the CDM reaction: (a) Tierga treated with $\mathrm{H}_{2}$ and (b) Tierga treated with $\mathrm{CH}_{4}$.


Figure S3 - Raman spectra of the spent Tierga catalysts.


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