

Supporting Information

Methane coupling over magnesium oxide: how doping can work

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1. Experimental Details

1.1. Catalyst synthesis

Fe-MgO: Two Teflon autoclaves with a volume of 100 mL were filled each with 3 g MgO (Alfa Aesar 99.998 m.b. (ID#14564, batch number 24686) suspended in 69.5 mL distilled water. Subsequently, 0.537 mL of a 0.05 M $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (99+, Sigma-Aldrich) solution was added. The suspension was heated to 483 K for 3 hours in a microwave oven (Speedwave MWS-3+, Berghof Products + Instruments GmbH) at a pressure of 10 bar. The resulting material was isolated by filtration, washed with distilled water, and dried at 393 K in air for 12 h. For thermal treatment, the dried product was placed into a quartz crucible, which was located inside a quartz tube, and annealed in flowing Ar (150 mL/min) at 1173 K (heating rate 10 K/min) for 3 hours using a tube furnace (Carbolite). To remove segregated iron oxide particles, the resulting solid was washed in a mixture of 5 mL 0.1 M HNO_3 and 25 mL H_2O by stirring at 293 K for 1 hour. The washed and dried product was annealed again in flowing Ar (150 mL/min) at 1123 K (heating rate 5 K/min) for 3 hours.

Au-MgO: Two Teflon autoclaves with a volume of 100 mL were filled each with 3 g MgO (Alfa Aesar 99.998 m.b. (ID#14564, batch number 24686) suspended in 69.5 mL distilled water. Subsequently, 0.51 mL of a 0.015 M $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (50% Au basis, Sigma-Aldrich) solution was added. The suspension was heated to 483 K for 3 hours in a microwave oven (Speedwave MWS-3+, Berghof Products + Instruments GmbH) at a pressure of 10 bar. The resulting material was isolated by filtration, washed with distilled water, and dried at 393 K in air for 12 h. For thermal treatment, the dried product was placed into a quartz crucible, which was located inside a quartz tube, and annealed in flowing Ar (150 mL/min) at 1173 K (heating rate 10 K/min) for 3 hours using a tube furnace (Carbolite). To remove segregated Au particles, the resulting solid was washed in a mixture of 5 mL 0.1 M *aqua regia* and 25 mL H_2O by stirring at 293 K for 1 hour. The washed and dried product was annealed again in flowing Ar (150 mL/min) at 1123 K (heating rate 5 K/min) for 3 hours. The resulting catalyst was stored under argon and freshly pre-treated before analysis or catalysis.

Au-Fe-MgO: Two Teflon autoclaves with a volume of 100 mL were filled each with 3 g MgO (Alfa Aesar 99.998 m.b. (ID#14564, batch number 24686) suspended in 69 mL distilled water. Subsequently, 0.508 mL of a 0.015 M $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (50% Au basis, Sigma-Aldrich) solution, and 0.538 mL of 0.05 M $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (99+, Sigma-Aldrich) solution were added. The suspension was heated to 483 K for 3 hours in a microwave oven (Speedwave MWS-3+, Berghof Products + Instruments GmbH) at a pressure of 10 bar. The resulting material was isolated by filtration, washed with distilled water, and dried at 393 K in air for 12 h. For thermal treatment, the dried product was placed into a quartz crucible, which was located inside a quartz tube, and annealed in flowing Ar (150 mL/min) at 1173 K (heating rate 10 K/min) for 3 hours using a tube furnace (Carbolite). To remove segregated iron oxide and Au particles, the resulting solid was washed in a mixture of 10 mL 0.1 M *aqua regia* and 20 mL H_2O by stirring at 293 K for 1 hour. The washed and dried product was annealed again in flowing Ar (150 mL/min) at 1123 K (heating rate 5 K/min) for 3 hours. The resulting catalyst was stored under argon and freshly pre-treated before analysis or catalysis.

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1.2. X-ray diffraction

XRD was measured on a STOE STADI-P transmission diffractometer with a focusing primary Ge(111) monochromator and a linear PSD applying $\text{Cu K}\alpha_1$ radiation ($\lambda=1.5406 \text{ \AA}$).

The XRD data were analyzed by full pattern fitting using the TOPAS software (version 3, copyright 1999, 200 Bruker AXS).

1.3. Nitrogen adsorption

The surface area determination was carried out in a volumetric N_2 physisorption set-up (Autosorb-6-B, Quantachrome) at the temperature of liquid nitrogen. The sample was degassed in dynamic vacuum at a temperature of 473 K for 2 h prior to adsorption. The relative N_2 pressure was varied ($p/p_0=0.05-0.3$), and 11 data points were measured. The linear range of the adsorption isotherm was considered to calculate the specific surface area according to the BET method.

1.4. Atomic Absorption Spectroscopy (AAS)

The iron content was determined by Atomic Absorption Spectroscopy (AAS). Experiments were performed on a Perkin Elmer AAS 4100 spectrometer using a N_2O -acetylene flame and a wavelength of 271.9 nm. 250 mg of the catalyst were dissolved in 25 mL HNO_3 (65 % p.a.) and backfilled to 250 mL with distilled H_2O . Zero, 50 and 100 μg iron were added to 25 mL of this solution, respectively, and backfilled to 50 mL with a solution of 5% HNO_3 in water.

1.5. Diffuse reflectance spectroscopy (DRS)

The *in situ* UV-VIS experiments were performed in the range between 200 and 800 nm using a Perkin Elmer Lambda 650 spectrometer equipped with a diffuse reflectance accessory (Praying Mantis, Harrick) complete with an environmental chamber attachment (Harrick HVC-VUV-4) using Spectralon® as white standard. The catalysts were pretreated *in situ* at 923 K for 30 min in flowing Ar (20 mL/min), and measured in the same argon flow at room temperature.

1.6. Electron Paramagnetic Resonance (EPR)

EPR spectra were recorded at liquid nitrogen temperature on a Bruker ESR 300 E spectrometer equipped with a microwave bridge Bruker ER 042 MRH E. A Bruker ER 4116 DM resonator operating in the TE 102 mode (resonance frequency ≈ 9.5 GHz) was used. The spectra were recorded with a modulation frequency of 100 kHz and a microwave power of 2 mW. The frequency and g values were calibrated using the signal of Mn^{2+} ions ($g = 2.0007$, $A = -244$ MHz, $a = 55$ MHz)^[S1a] present as impurity in MgO (3 ppm as determined by ICP-OES analysis). A small signal assigned to Cr^{3+} can also be observed with a g tensor of 1.98 (0.2 ppm as determined by ICP-OES analysis).^[S1b] The samples were placed in a quartz cell equipped with Teflon Duran® valves and connected to a vacuum system that allows the dosing of gases. Before the EPR measurements, the MgO samples were activated at 1073 K under dynamic vacuum ($10^{-6} - 10^{-7}$ mbar) for 3 hours.

[S1] a) W. Low, *Physical Review* **1957**, *105*, 793-800; b) S. Eidels-Dubovich, V. Beltran-Lopez, *J. Magnet. Res.* **1987**, *74*, 94-104.

1.7. Temperature-Programmed-Reduction-Oxidation (TPR-O) experiments

Temperature-programmed oxidation and reduction experiments were performed in a fixed-bed quartz reactor placed inside a tube furnace (Carbolite). The position of the catalyst inside the reactor was fixed applying a frit. The temperature was measured in the catalyst bed using a thermocouple (K-type). The feed was composed of 0.5 % O_2 or H_2 , respectively, in He and Ar, respectively. A flow rate of $90 \text{ mL} \cdot \text{min}^{-1}$ was applied. A sieved fraction (grain size 200 – 300 μm) of 600 mg catalyst was diluted with 3 g SiC (grain size 200 – 300 μm) in order to improve the thermal conductivity in the catalyst bed. The measurements were performed applying a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$. Hydrogen concentration in the gas phase was analyzed using a TCD detector (Rosemount Analytical) after the off-gas passed a molecular sieve trap to remove water. Before measurements, the catalysts were pretreated in $90 \text{ mL} \cdot \text{min}^{-1}$ Ar at 1073 K with a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ for 1 h to remove adsorbed water molecules and other adsorbates.

1.8. Catalytic measurements

The catalytic measurements were carried out in a laboratory quartz U-tube fixed bed reactor (4 mm inner diameter, 6 mm outer diameter, 26 cm length) applying reaction conditions as indicated in the main text. The inner diameter of the tube downstream the catalyst bed is reduced to 1 mm in order to minimize the influence of gas phase reactions. The reactor is heated using a tube furnace (Carbolite®). An axial K-Type thermocouple inserted in a ceramic jacket was placed just above the catalyst bed for measurement of input gas temperature. To avoid condensation of products (e.g. water) the reactor, part of the gas delivery system and the gas sampling system are placed in a heating cabinet that is usually kept at 353 K. N_2 , O_2 , and methane are mixed outside of the heating cabinet via mass flow controllers (EL-FLOW, Bronkhorst). Gas analysis is performed online by gas chromatography (gas chromatograph 6890A, Agilent) equipped with two channels. A combination of two capillary columns (GS-Carbonplot (length 30 m, 0.53 mm inner diameter, 40 μm film thickness), and Plot Molesieve 5A (length 30 m, 0.53 mm inner diameter, 25 μm film thickness)) in connection with a thermal conductivity detector (TCD) is used to analyze the permanent gases CO_2 , O_2 , N_2 , and CO. A combination of two capillary columns (HP-FFAP (length 30 m, 0.53 mm inner diameter, 1 μm film thickness), and HP Plot Q (length 30 m, 0.53 mm inner diameter, 40 μm film thickness)) connected to a flame ionization detector (FID) is used to analyze alkanes, olefins, and oxygenates. Nitrogen was used as internal standard to account for volume effects due to the high temperature. Selectivity was calculated including the number of carbon atoms, rather than stoichiometric coefficients.

1.9. Electron microscopy

Electron microscopy was carried out using a Cs-corrected FEI Titan 80-300 instrument operating at 300 kV in bright field high-resolution transmission electron microscopy (HRTEM) and high angle annular dark field scanning transmission electron microscopy (HAADF STEM) mode, respectively.

2. Diffuse reflectance spectroscopy

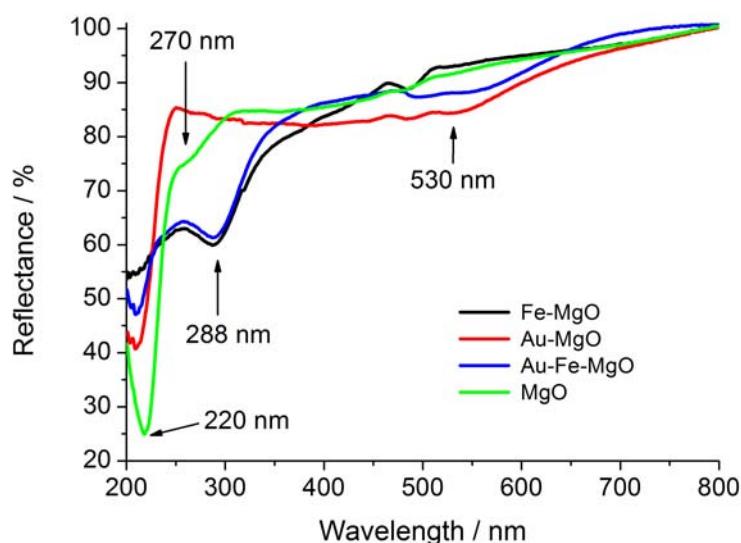


Fig. S1. UV-vis spectra of the doped catalysts measured in Ar at 293 K after pretreatment of the catalysts in Ar at 923 K.

3. EPR spectroscopy

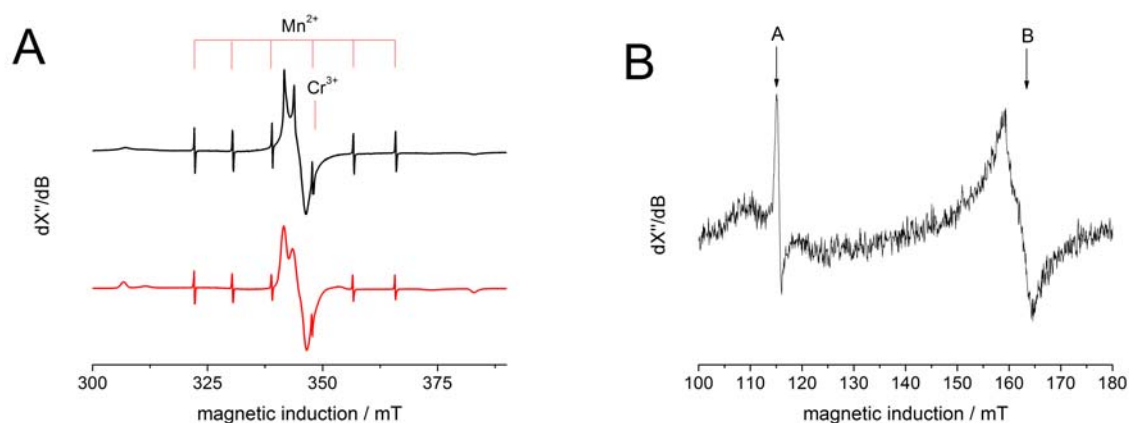


Fig. S2. EPR spectrum of Au-Fe-MgO after pretreatment at 1073 K under high vacuum, measured at 77 K, A) Experimental (black line) and simulated^[S2] spectrum (red line). B) Experimental spectra of Fe³⁺ at lower magnetic field. Both spectra are measured at a frequency of 9.63637 GHz.

The experimental signal (Fig. S2 A, black line) at $g=2.0037$ is attributed to Fe³⁺ ions present in a cubic symmetry field,^[S3] which is also well reflected by the simulation of the spectrum ($g=2.0037$, $a=640$ MHz, $lwpp=1$ mT, and $D=-100$ MHz) using the Easyspin package in MATLAB.^[S2] The species A and B at low fields (Fig. S2 B) are assigned to Fe³⁺ ions in a coordination geometry of lower symmetry. These signals are usually assigned to Fe³⁺ in orthorhombic or tetragonal symmetry sites in MgO.^[S4] No sign of point defect can be found in the Au-Fe-MgO sample by EPR.^[S5]

[S2] S. Stoll, A. Schweiger, *Journal of Magnetic Resonance* **2006**, 178, 42-55.

[S3] a) V. Beltrán-López, J. Castro-Tello, *Journal of Magnetic Resonance* (1969) **1980**, 39, 437-460; b) J. H. Lunsford, *The Journal of Chemical Physics* **1965**, 42, 2617-2618.

[S4] J. T. Castner, G. S. Newell, W. C. Holton, C. P. Slichter, *The Journal of Chemical Physics* **1960**, 32, 668-673.

[S5] a) R. S. d. Biasi, *Journal of Physics C: Solid State Physics* **1981**, 14, 4885; b) R. S. De Biasi, A. Caldas, *J. Phys. C: Solid State Phys.* **1977**, 10, 107-111.

4. Temperature-programmed- reduction-oxidation (TPR-TPO)

Table S1: Hydrogen consumption in TPR (H₂ evolution during activation (negative values)).

	Hydrogen consumption (evolution) / $\mu\text{mol}(\text{H}_2)/(\text{s}\cdot\text{g}_{\text{cat}})$	Fraction of total Fe /%
Au-Fe-MgO Fe content*: 7.20 $\mu\text{mol/g}$		
Activation	- 0.25	-
TPR1	0.13	1.8
TPR2	0.48	6.7
TPR3	0.48	6.7
Fe-MgO Fe content*: 11.71 $\mu\text{mol/g}$		
Activation	- 0.56	-
TPR1	0.81	6.9
TPR2	0.75	6.4
TPR3	0.74	6.3

* Analyzed by AAS.

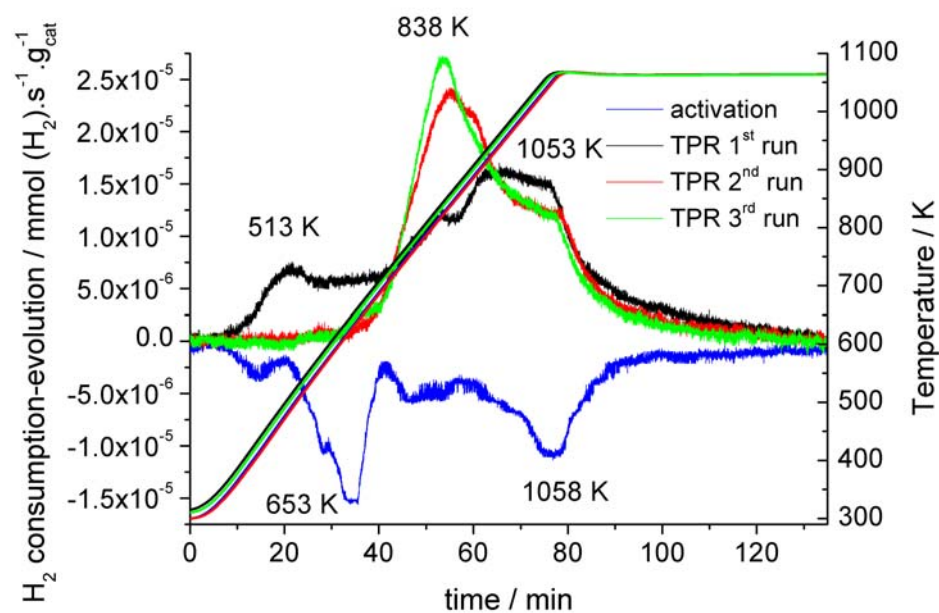


Fig. S3. TPR-O of Fe-MgO. The blue line was measured during pretreatment of the catalyst in $90 \text{ mL} \cdot \text{min}^{-1}$ Ar applying a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$.

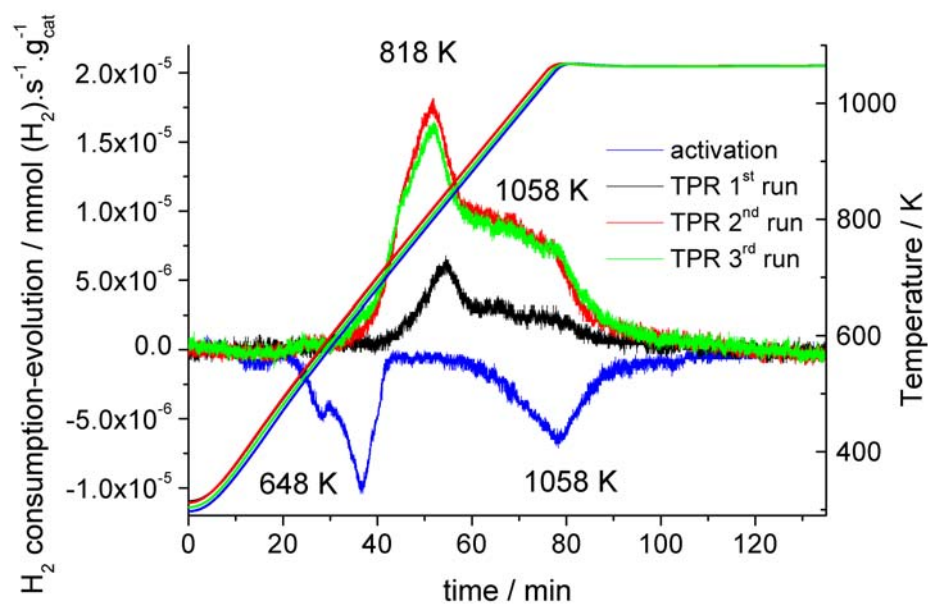


Fig. S4. TPR-O of Au-Fe-MgO. The blue line was measured during pretreatment of the catalyst in $90 \text{ mL} \cdot \text{min}^{-1}$ Ar applying a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$.

5. Oxidative coupling of methane

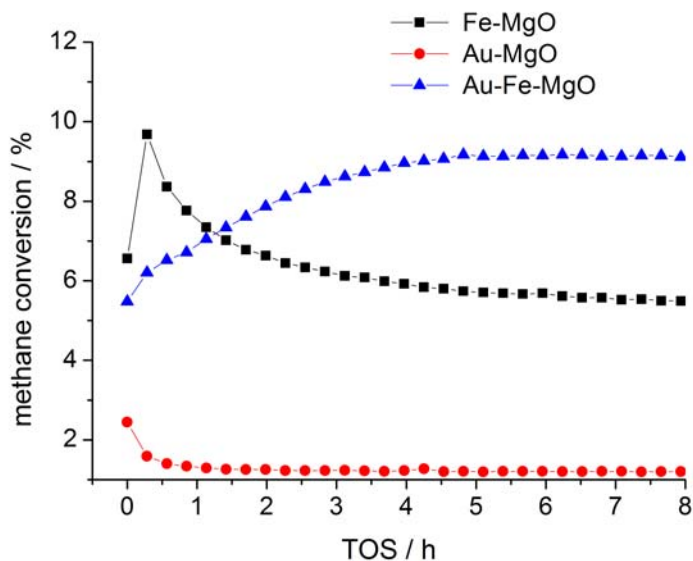


Fig. S5 Methane conversion in the oxidative coupling of methane as a function of time on stream (TOS) at $T=1023\text{ K}$; $W/F=0.0167\text{ g}\cdot\text{s}\cdot\text{ml}^{-1}$; $\text{CH}_4/\text{O}_2/\text{N}_2=3/1/1$.

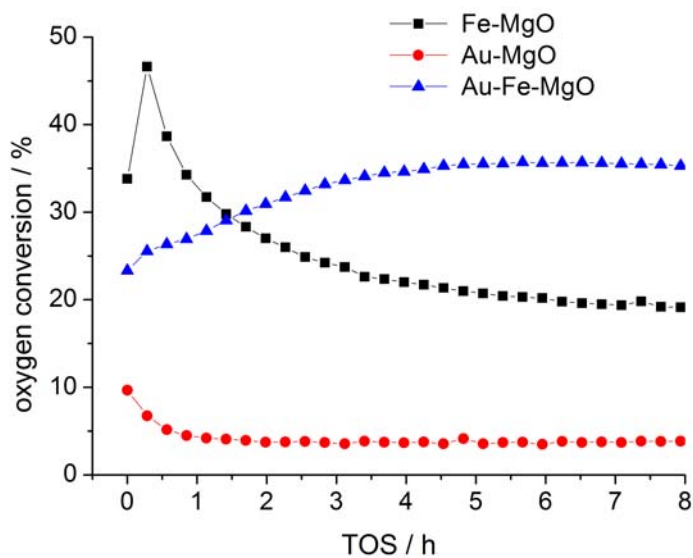


Fig. S6 Oxygen conversion in the oxidative coupling of methane as a function of time on stream (TOS) at $T=1023\text{ K}$; $W/F=0.0167\text{ g}\cdot\text{s}\cdot\text{ml}^{-1}$; $\text{CH}_4/\text{O}_2/\text{N}_2=3/1/1$.

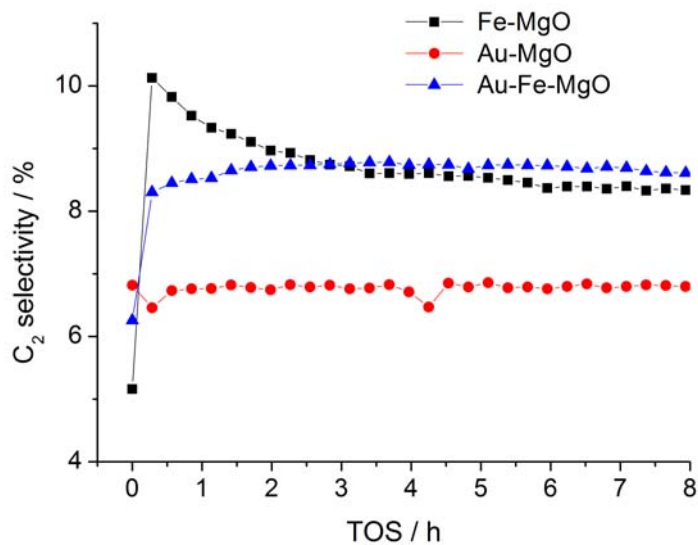


Fig. S7 Selectivity of the sum of ethane and ethene (C₂) in the oxidative coupling of methane as a function of time on stream (TOS) at T=1023 K; W/F= 0.0167 g·s·ml⁻¹; CH₄/O₂ /N₂=3/1/1.

6. Electron microscopy

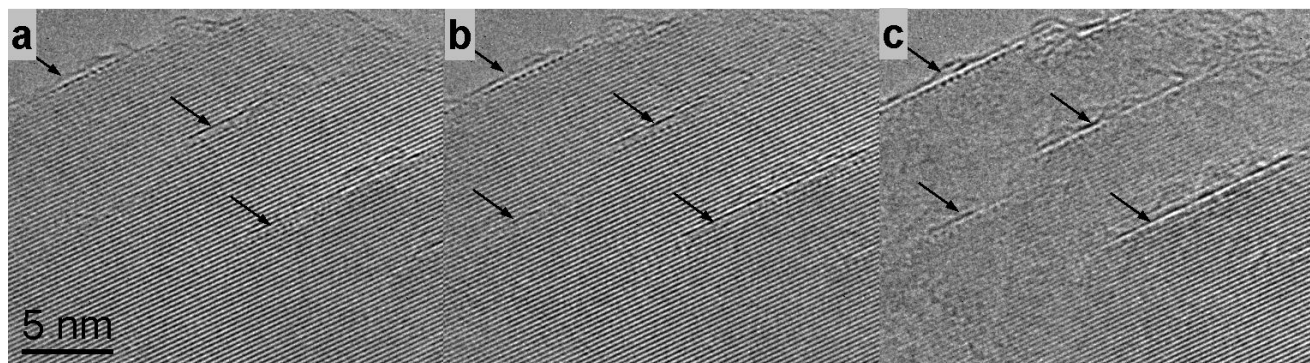


Fig. S8. Series of HRTEM images recorded at different defocus reveal the presence of strongly scattering atoms located at the steps in the Au-Fe-MgO catalyst after catalysis.