SUPPORTING INFORMATION

What makes Fe-modified $MgAl_2O_4$ an active catalyst support? Insight from X-ray Raman Scattering.

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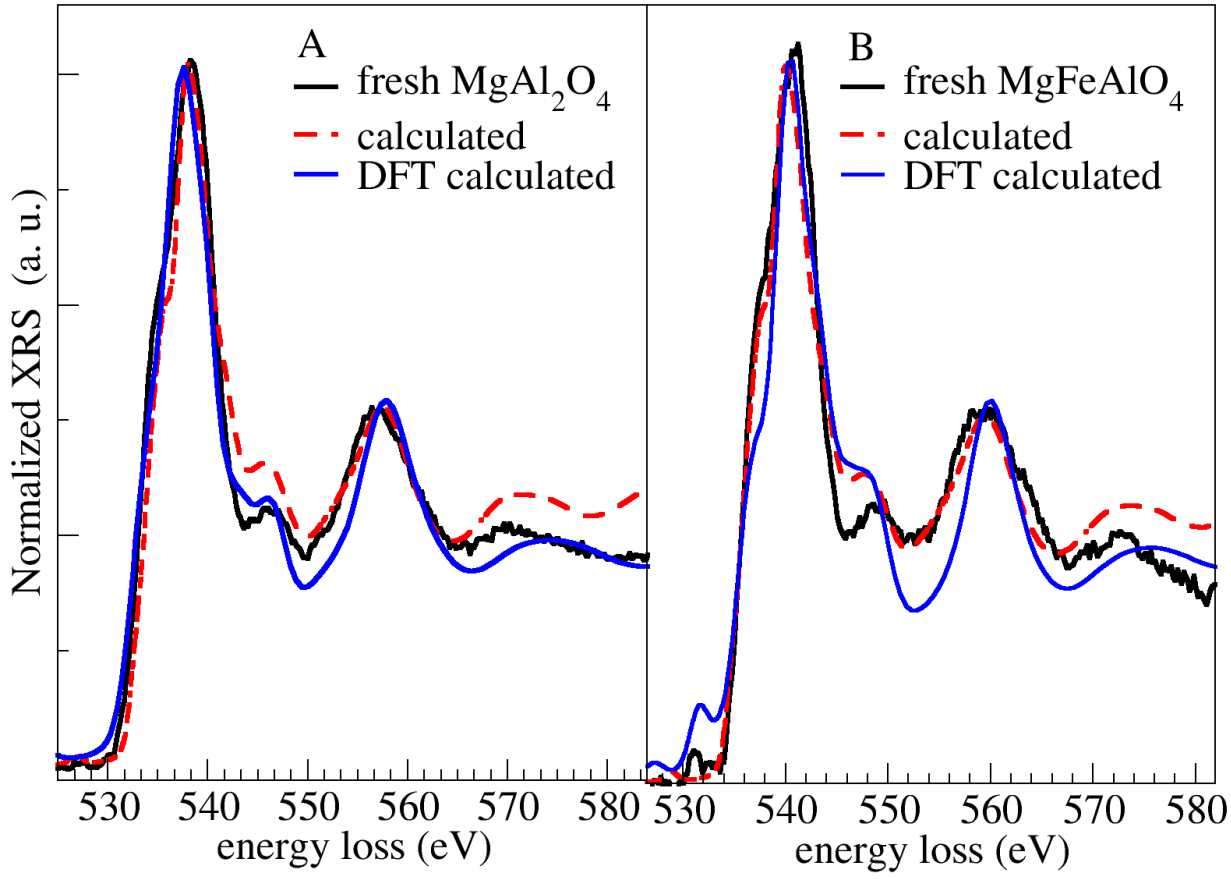

Figure S1: comparison of the XRS data with FDMNES (red) and DFT (VASP) (blue) calculations, for A: fresh $MgAl_2O_4$ and B: fresh $MgFeAlO_4$, respectively. Computational details for the DFT calculations can be found at the end of the Supporting Information.

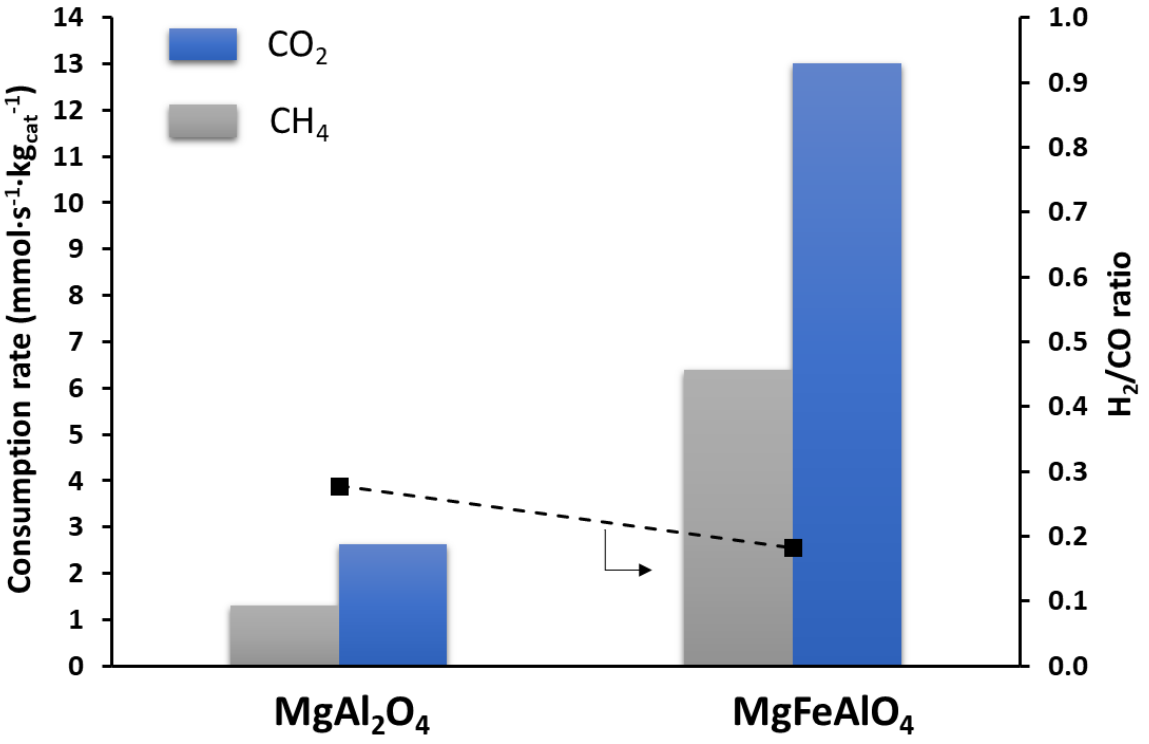

Figure S2: Consumption rate of CO_2 and CH_4 for $MgAl_2O_4$ and $MgFeAlO_4$ after 30 min of DRM (1023 K, 111.3 kPa and CH_4/CO_2~1). The secondary axis shows the H_2/CO product ratio. $MgAl_2O_4$: X_{CH4}= 0.7%; X_{CO2}= 1.4%. $MgFeAlO_4$: X_{CH4}= 3.4%; X_{CO2}= 6.8%.

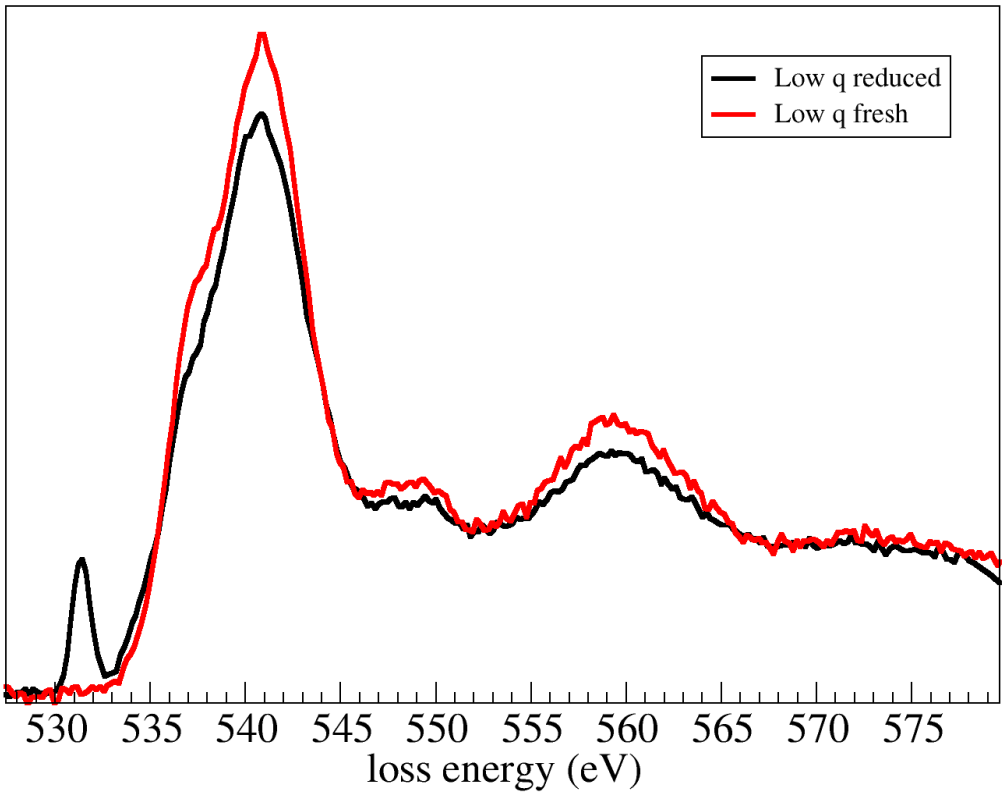

Figure S3: O K edge data measured at low q scattering angle for fresh and reduced $MgAl_2O_4$.

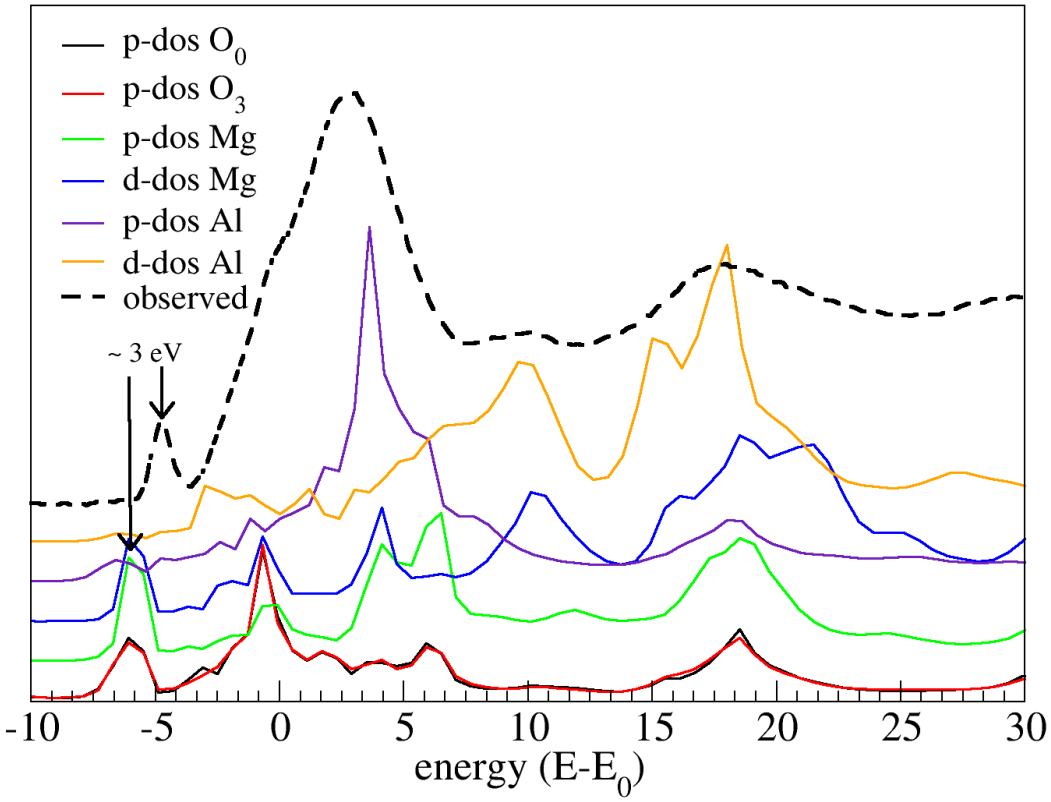

Figure S4: O K edge spectrum for reduced $MgAl_2O_4$ with *p*- and *d*-projected Density of States (DOS) for regular $MgAl_2O_4$, calculated using the *Feff9* code. Both adsorbed oxygen (black solid line) and oxygen from the spinel lattice (red line) are shown at the bottom.

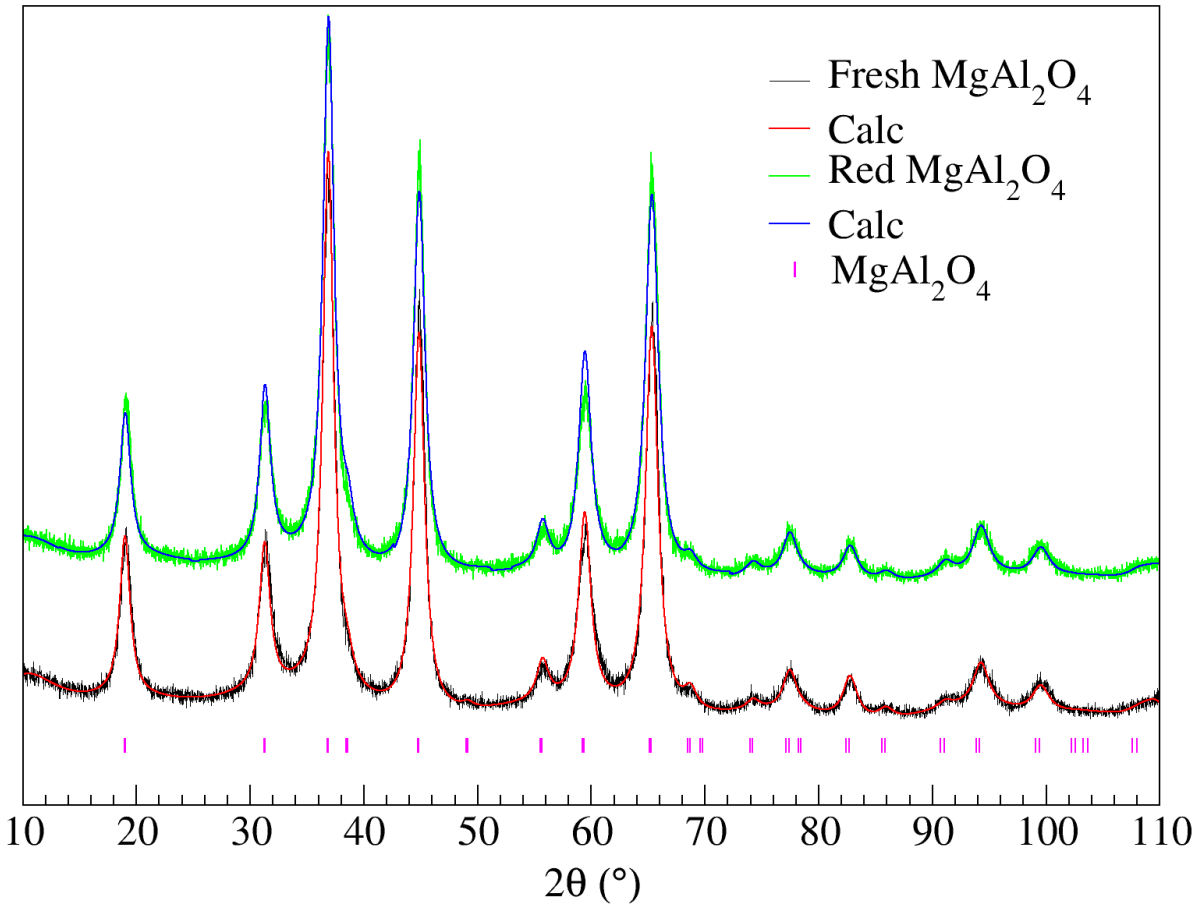

Figure S5: Comparison between fresh (black-red) and reduced $MgAl_2O_4$ (green-blue) with corresponding Rietveld analysis.

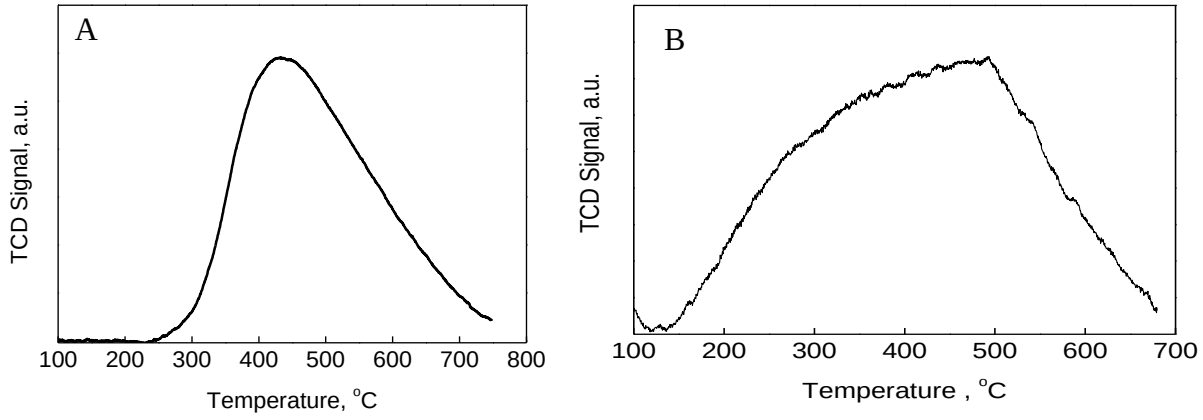

Figure S6: O_2-TPD measurement performed on A: $MgAl_2O_4$, B: $MgFeAlO_4$ after H_2-reduction (5 vol.% H_2/He at 700°C) and air exposure at room temperature; both signals show oxygen evolution, though less for $MgFeAlO_4$, given the higher noise level.

Simulation details for Fe $M_{2,3}$ edges

Slater-Condon parameters for the direct Coulomb repulsion and the Coulomb exchange interaction, respectively, were set to 80% of their atomic values, which was empirically found to be reasonable for transition metals and agrees well with literature[1]. The crystal field splitting parameter 10Dq, defined as the energy gap between the t_{2g} and e_g states in the particular case of the Oh symmetry, was set to 1.2 eV. Furthermore, a scaling factor for the spin-orbit coupling for core and valence electrons was considered. The calculated transition patterns were convoluted with a Lorentzian function (FWHM of 0.2 eV) and a Gaussian function (FWHM of 1.2 eV) to simulate the peak broadening due to the finite core-hole life-time and a realistic experimental resolution, respectively.

Computational details for the DFT optimization of the bulk structures

The DFT-optimized geometries for both structures have been obtained using the Vienna ab initio simulation package (VASP 5.3.3)[2], with the PBE functional. Plane-wave basis sets with the projector augmented wave method (PAW)[3-4] were used with an energy cutoff of 500 eV. Gaussian smearing is applied to describe the partial occupancies close to the Fermi level, using a smearing width of 0.2 eV. Brillouin-zone integration is done on a 5×5×5 Monkhorst-Pack grid[5]. The electronic convergence criterion is 10^{-8} eV, while the geometry is considered converged for energy differences below 10^{-7} eV. All calculations allow for spin polarization; there is no spin in the non-substituted $MgAl_2O_4$ and one unpaired electron per unit cell for the Fe-substituted structure. The optimized lattice parameters amount to 8.1599 Å for the unsubstituted and 8.1689 Å for the Fe-substituted structure.

References

1 Stavitski, E., de Groot, F.M.F. *The CTM4XAS program for EELS and XAS spectral shape analysis of transition metal L edges.* Micron, 2010, **41**(7) p687 – 694.

2 Kresse, G., Furthmuller, J., *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set.* Physical Review B, 1996. **54**(16) p11169-11186.

3 Kresse, G., Joubert, D., *From ultrasoft pseudopotentials to the projector augmented-wave method.* Physical Review B, 1999. **59**(3) p1758-1775.

4 Blochl, P.E., *Projector augmented-wave method.* Physical Review B, 1994. **50**(24) p17953-17979.

5 Monkhorst, H.J., Pack, J.D., *Special Points for Brillouin-Zone Integrations.* Physical Review B, 1976. **13**(12) p5188-5192.