Supporting information

Structure sensitivity of the oxidative activation of methane over MgO model

catalysts: II. Nature of active sites and reaction mechanism

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1. Adsorption of methane



Fig. S1. Adsorption of 100 Pa CH₄ at T=77 K at the surface of C-MgO dehydroxylated at 1073 K(black line); Red line: after evacuation up to $5 \cdot 10^{-4}$ Pa.

2. Diffuse Reflectance Spectroscopy



Fig. S2. UV-vis spectrum of C-MgO measured at 313K after evacuation at 923 K for 30 minutes.

3. Photoluminescence spectroscopy



Fig. S3. 2D photoluminescence of fresh S-MgO (ID: 12817) recorded at 300 K in dynamic vacuum after activation at 1073 K in vacuum.



Fig. S4. 2D photoluminescence of used S-MgO (ID: 12992) recorded at 300 K in dynamic vacuum after activation at 1073 K in vacuum.



Fig. S5. 2D photoluminescence of fresh SG-MgO (ID: 12342) recorded at 300 K in dynamic vacuum after activation at 1073 K in vacuum.



Fig. S6. 2D photoluminescence of fresh HT-MgO (ID: 12498) recorded at 300 K in dynamic vacuum after activation at 1073 K in vacuum.

4. Deconvolution of infrared spectra

For a semi-quantitative analysis of the IR spectroscopy of adsorbed CO on the MgO surface, the spectra were fitted by gaussian shaped curves. For this purpose the wavenumber of five bands at 2188, 2165, 2155, 2146, 2134 cm⁻¹ described in the literature were kept fixed. The assignment of these bands is reported in the main text of this article. The spectra used for deconvolution have been measured at a CO coverage of 15 %.



Fig. S7. Spectrum of CO adsorbed on S-MgO at T=77 K and a coverage of θ =0.15. Black curve: experimental data, red curve: resultant, green curves: individual Gaussian component.



Fig. S8. Spectrum of CO adsorbed on C-MgO at T=77 K and a coverage of θ =0.15. Black curve: experimental data, red curve: resultant, green curves: individual Gaussian component.



Fig. S9. Spectrum of CO adsorbed on SG-MgO at T=77 K and a coverage of θ =0.15. Black curve: experimental data, red curve: resultant, green curves: individual Gaussian component.



Fig. S10. Spectrum of CO adsorbed on MW-MgO at T=77 K and a coverage of θ =0.15. Black curve: experimental data, red curve: resultant, green curves: individual Gaussian component.



Fig. S11. Spectrum of CO adsorbed on HT-MgO at T=77 K and a coverage of θ =0.15. Black curve: experimental data, red curve: resultant, green curves: individual Gaussian component.



Fig. S12. Comparison of the fitted Gaussian component at 2146 cm⁻¹ for the five MgO catalysts.

Table S1

Integration of the Gaussian components in arbitrary units.

	2146 cm ⁻¹	2155 cm ⁻¹	2165 cm ⁻¹
S-MgO	0,01207	0,03393	0,02362
C-MgO	0,09284	0,09345	0,11258
SG-MgO	0,10808	0,17251	0,07613
MW-MgO	0,11382	0,26707	0,07008
HT-MgO	0,07122	0,21813	0,13682