Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Mechanistic Insights into the selective Oxidation of 5-(Hydroxymethyl)furfural over Silver-based Catalysts

- Supporting Information -

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Analysis of reaction products

Samples were taken before and after the catalytic reactions for HPLC analysis. The measurements were carried out on a Hitachi Primaide instrument (Bio-Rad Aminex HPX-87H column, solvent 5 mM H_2SO_4, Hitachi Chromaster 5450 refractive index detector, Hitachi 1430 diode array detector), which was calibrated by reference solutions of HMF, BHMF, HFCA, FDCA, DFF and FFCA in five different concentrations as external standards.

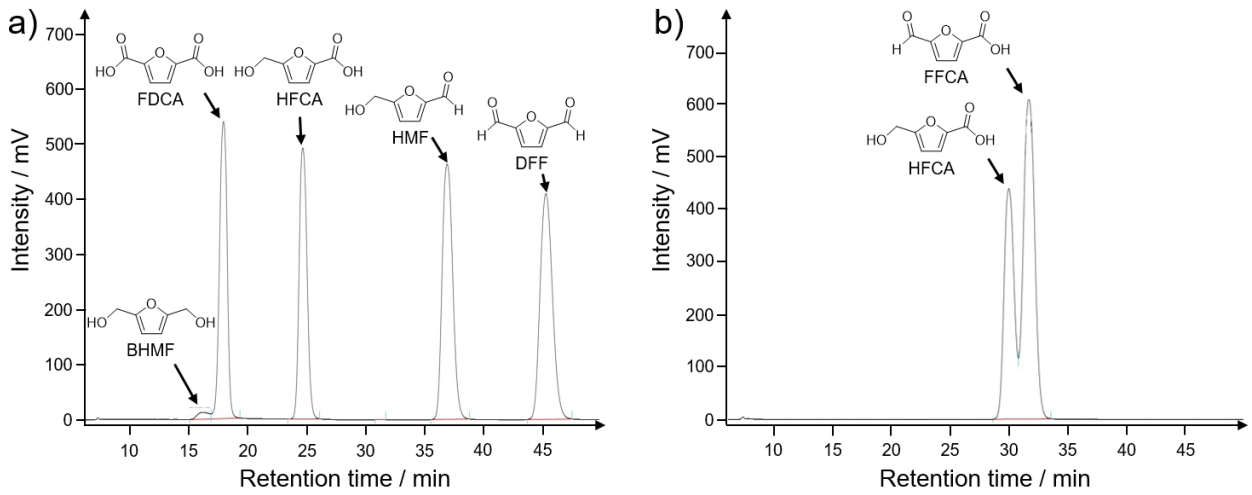

Figure S1: Representative HPLC chromatograms of calibrated reference compounds (a) at 50 °C and (b) 25 °C.

Measurements were performed at 50 °C for the analysis of HMF, BHMF, HFCA, FDCA and DFF (Figure S1a) and 25 °C for the separation of HFCA and FFCA (Figure S1b). The concentrations in the reaction solutions were derived from the peak areas of the respective compounds to estimate HMF conversion (1), product yields (2) and selectivities (3) according to:

$$X(HMF) = \frac{n(HMF)_0 - n(HMF)_t}{n(HMF)_0} \quad (1)$$

$$Y(x) = \frac{n(x)_t}{n(HMF)_0} \quad (2)$$

$$S(x) = \frac{n(x)_t}{n(HMF)_0 - n(HMF)_t} \quad (3)$$

Ex situ Characterization of the used Catalysts

XRD:

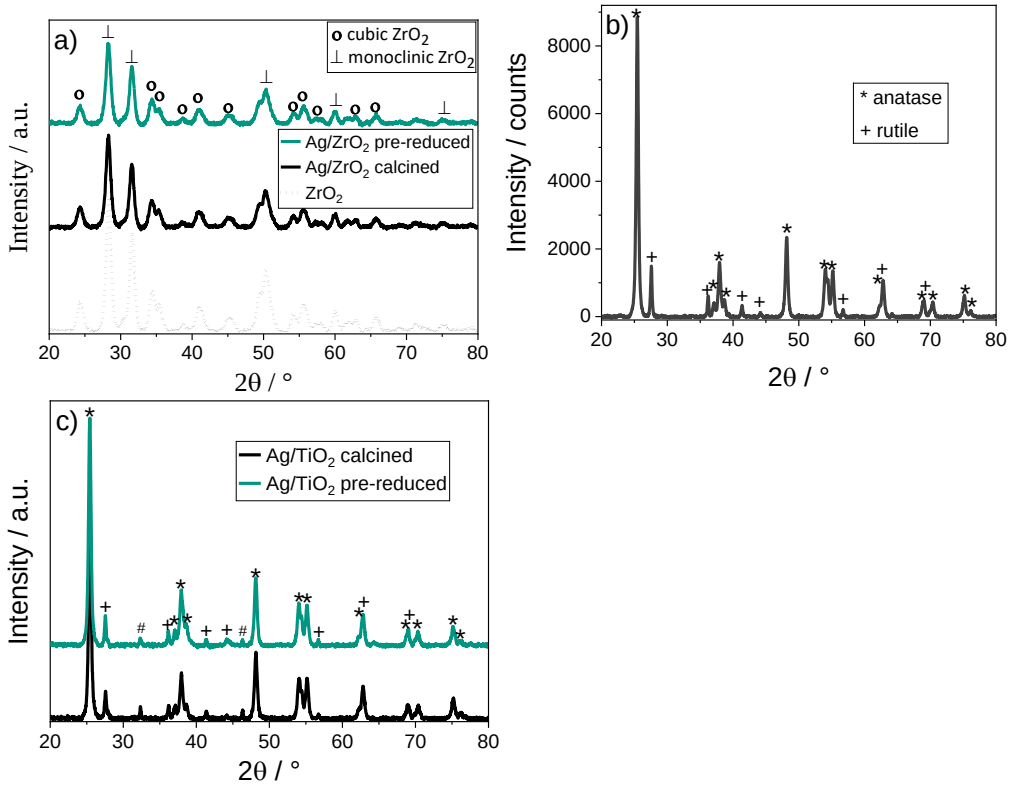

Figure S2: XRD patterns of (a) the used ZrO_2 and the Ag/ZrO_2 catalyst after different stages of preparation, (b) the used TiO_2 support material and (c) the Ag/TiO_2 catalyst after different stages of preparation.

XAS:

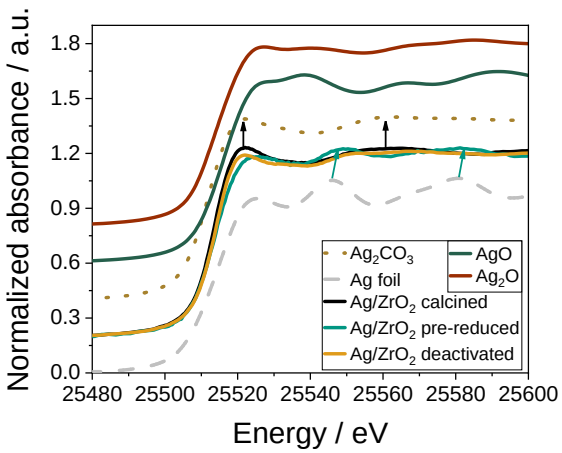

Figure S3: X-ray absorption near edge structure (XANES) spectra of Ag/ZrO_2 after the different stages of preparation i.e. calcination in air and pre-reduction in hydrogen. Deactivated Ag/ZrO_2 refers to a catalyst that was stored for one year in air, which led to a decreasing catalytic activity in HMF oxidation (see main publication: The decrease in catalytic activity was observed within four weeks of storage in air and did not change with extended storage time). The assignment of features corresponding to the

reference spectra is indicated by arrows. Re-emerging features and an edge shift show that Ag_2CO_3 is formed in air. In line with these findings, the degree of reduction drops to 11 % based on LCF (89 % Ag_2CO_3).

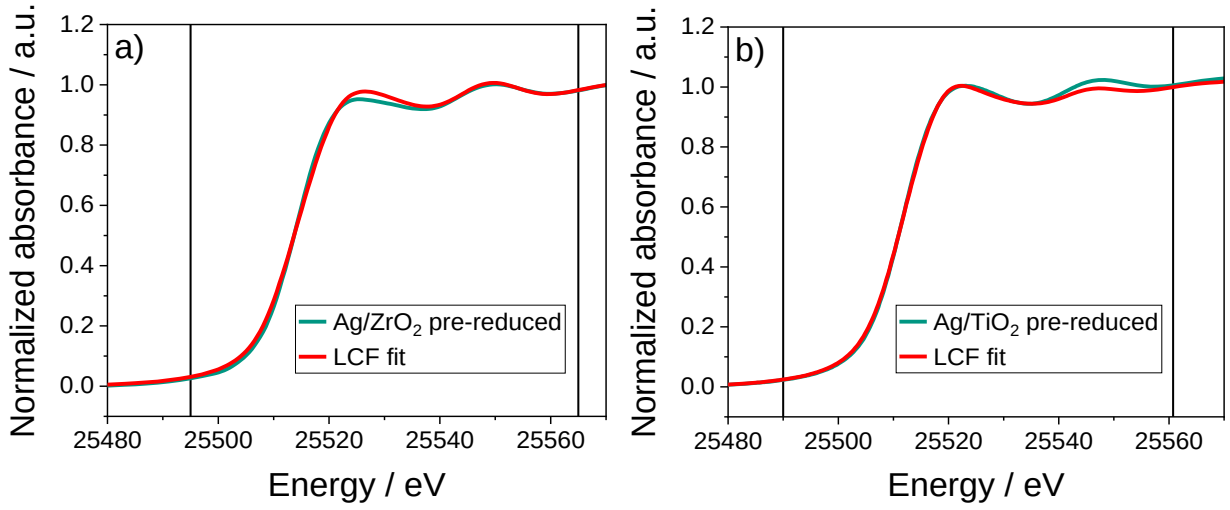

Figure S4: Linear combination fittings to Ag foil and Ag_2CO_3 in the X-ray absorption near edge structure (XANES) spectra of pre-reduced (a) Ag/ZrO_2 and (b) Ag/TiO_2 catalysts.

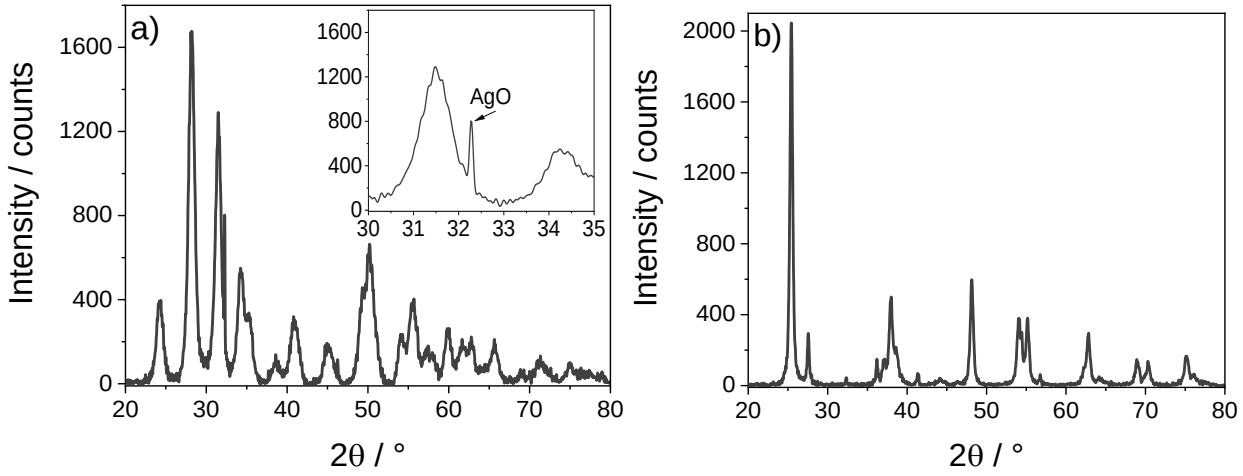

Figure S5: X-Ray diffraction patterns of the spent (a) Ag/ZrO_2 and (b) Ag/TiO_2 catalysts after the reactions in a HMF solution without NaOH.

For Ag/ZrO_2 (Figure S4 a), an emerging reflection indicates particle growth. Since the catalyst pellets were exposed to air after the spectroscopic reactions, a reflection of AgO rather than Ag is observed.

Additional *in situ* XAS experiments

In situ XAS of pre-reduced Ag/ZrO_2 in pure water

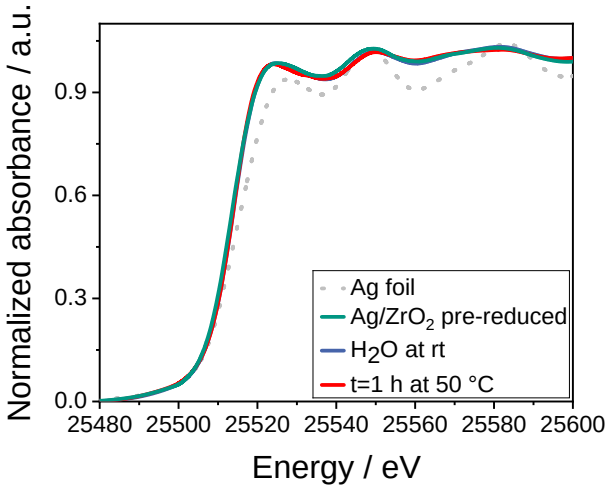

Figure S6: *In situ* XANES spectra of pre-reduced Ag/ZrO_2 in water. Reaction conditions: 50 °C, 10 bar air, 1 h.

In situ XAS of pre-reduced Ag/TiO_2 in the absence of air

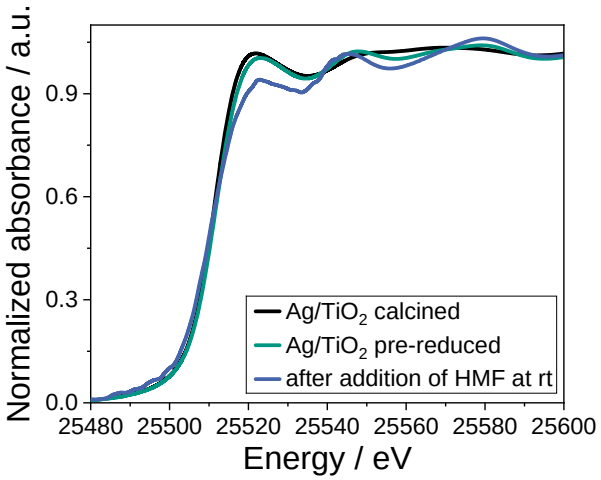

Figure S7: *In situ* XANES spectra of pre-reduced Ag/TiO_2 in a basic HMF solution under nitrogen. Reaction conditions: rt, 10 bar N_2, HMF:NaOH:Ag 1:1:25.

In situ XAS of calcined Ag/ZrO_2 under optimized conditions

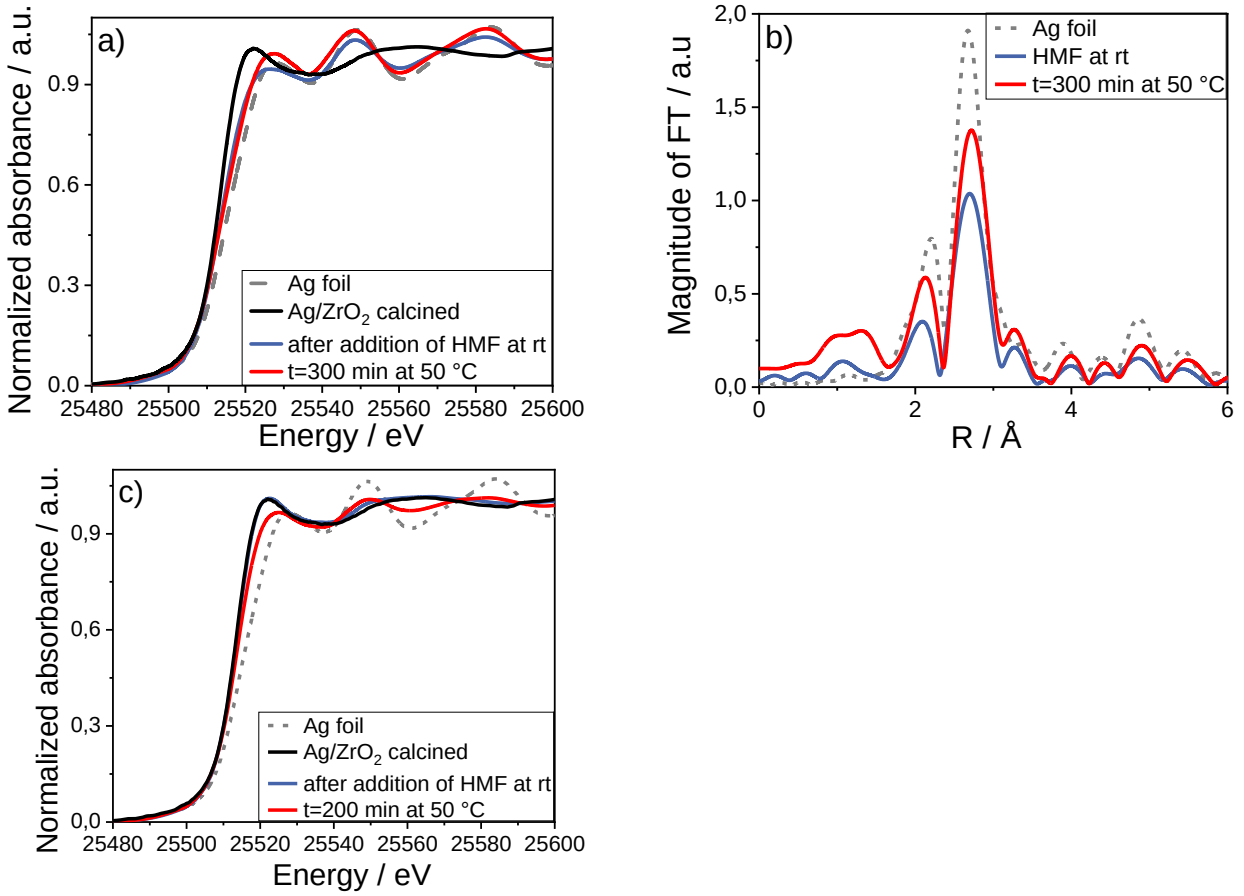

Figure S8: *In situ* X-ray absorption near edge and FT EXAFS spectra of the calcined Ag/ZrO_2 during the oxidation of HMF. This reaction was also performed using a catalyst powder (c) instead of a pellet. Reaction conditions: 50 °C, 10 bar air, HMF:NaOH:Ag 1:1:21, 345 min (a), 240 min (c).

To investigate whether also catalysts in a more oxidized state were reduced by the reaction mixture, the calcined Ag/ZrO_2 catalyst was studied under the optimized reaction conditions of 50 °C in the presence of one equivalent of NaOH at 10 bar air pressure. Using a catalyst pellet in the spectroscopic batch reactor, HFCA was produced in 76 % yield at 96 % conversion of HMF. Even in this reaction, reduction of Ag was observed as indicated by XANES (Figure S4 a, 82 % based on LCF) and FT EXAFS spectra (Figure S4 b). Thus, even the calcined catalyst got reduced and activated by the mixture. Therefore, the comparable yield to using the more active pre-

reduced catalyst can again be attributed to using a catalyst pellet. After the rapid reduction, both catalysts perform similarly as the reaction takes place on the outside of the catalyst pellet. The EXAFS oscillations of metallic silver enhanced upon heating to 50 °C again indicating reduction or ordering, which can also be observed from the FT EXAFS spectra in which the amplitude of the Ag-Ag scattering peaks enhanced significantly at 50 °C. EXAFS revealed a coordination number of Ag-Ag (2.86 Å) of 8.3±1.2 at room temperature and a higher coordination number of 11.4±2.7 at 50 °C (Table S4). As a model, this reaction was also performed using a catalyst powder instead of a catalyst pellet as it was used in all other spectroscopic reactions. Reduction was also observed in the XANES spectra (Figure S4 c), however, the changes took much longer compared to the catalyst pellet. This can be explained by the fact that a rather low stirring speed was applied to prevent the formation of a slurry, which would affect the spectroscopic results. On the other hand, this led to a dense powder filling in the sample chamber, which resulted in a slow diffusion of the reaction mixture into the catalyst filling. Therefore, the changes were observed on a longer time scale. On the basis of this observation and the fact that HMF might polymerize before being converted on the catalyst surface, the spectroscopic reactions were performed using a catalyst pellet.

In situ XAS of calcined Ag/TiO_2 in the absence of NaOH

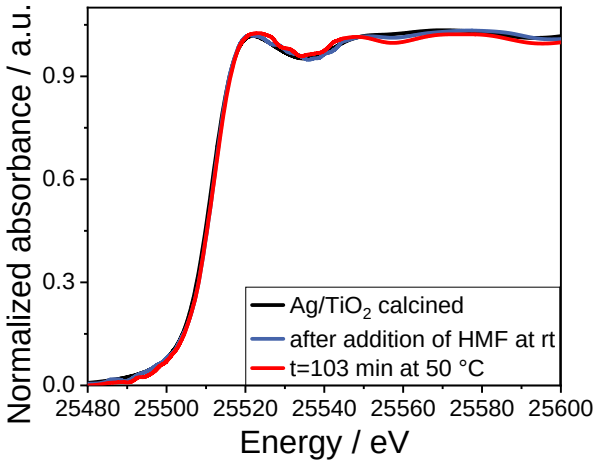

Figure S9: *In situ* XANES spectra of the calcined Ag/TiO_2 catalyst in a HMF solution without NaOH. Reaction conditions: 50 °C, 10 bar air, HMF:NaOH:Ag 1:0:25, 103 min.

In one reaction, calcined Ag/TiO_2 was used in the base-free reaction to study the effect of the degree of reduction on the leaching behavior. Here, no HMF conversion and no reduction of Ag was observed (Figure S7). This shows that the reduction strength of the solution was not sufficient to reduce and with that activate this catalyst. As in the previous base-free reactions over pre-reduced catalysts, leaching of 14 % of Ag was confirmed by ICP-OES, which is indeed higher than for the pre-reduced catalysts. Hence, the higher degree of Ag leaching in this reaction can be explained by the presence of a more oxidized Ag species and the rather low pH, both of which lead to an oxidative dissolution of Ag.[1-3]

Degree of reduction in the *in situ* XAS experiments on Ag/ZrO_2

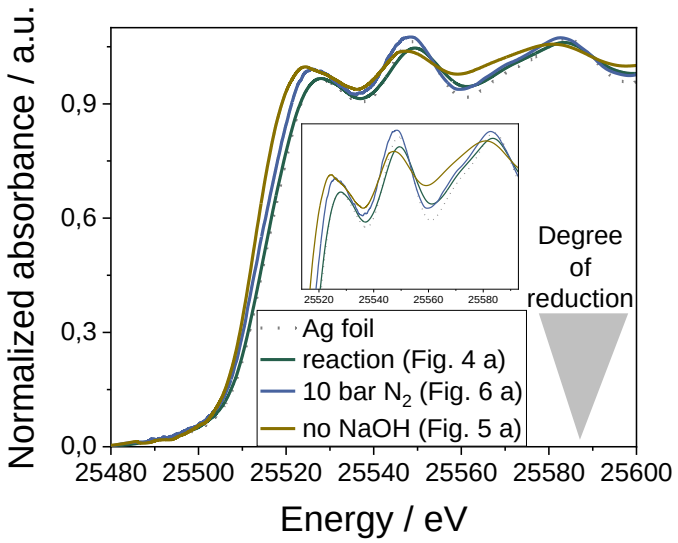

Figure S10: Comparison of the i*n situ* XANES spectra of the pre-reduced Ag/ZrO_2 catalyst at 50 °C in different reaction solutions. The inset shows a zoom into the spectra.

Comparison of the *in situ* XANES spectra of Ag/ZrO_2 under different reaction conditions clearly shows that the degree of reduction is dependent on the reaction solution by comparing white line intensities and the edge shift. In the reaction conditions that were previously optimized in the lab reactors, the catalyst is highly reduced. However, the degree of reduction is comparatively low in the absence of oxygen and even lower in the absence of NaOH. Thus, the degree of reduction follows the trend: reaction conditions > nitrogen (with base) > no NaOH.

Summary of the spectroscopic reactions on Ag/ZrO_2

Table S1: Reaction conditions and degrees of reduction for the spectroscopic reactions performed on Ag/ZrO_2.

Conditions	Ag/ZrO_2 reduced	Ag/ZrO_2 calcined
rt/50 °C, water	No change/reduction*	-
rt, 10 bar air, HMF:NaOH:Ag 1:1:20	Degree of reduction 82 % based on LCF*	Degree of reduction 73 % based on LCF* (increase of CN_{Ag-Ag})#
50 °C, 10 bar air, HMF:NaOH:Ag 1:1:20	Degree of reduction 92 % based on LCF*	Degree of reduction 82 % based on LCF*
rt, 10 bar air, HMF:NaOH:Ag 1:0:25	Degree of reduction 28 % based on LCF*	-
50 °C, 10 bar air, HMF:NaOH:Ag 1:0:25	Degree of reduction 47 % based on LCF*	-
rt, 10 bar N_2, HMF:NaOH:Ag 1:1:24	Degree of reduction 89 % based on LCF*	-
50 °C, 10 bar N_2, HMF:NaOH:Ag 1:1:24	Degree of reduction 96 % based on LCF* (increase of CN_{Ag-Ag})#	-

*Interpretation from XANES, #Interpretation from EXAFS

Summary of the spectroscopic reactions on Ag/TiO_2

Table S2: Reaction conditions and degrees of reduction for the spectroscopic reactions performed on Ag/TiO_2.

Conditions	Ag/TiO_2 reduced	Ag/TiO_2 calcined
rt, 10 bar air, HMF:NaOH:Ag 1:1:20	Degree of reduction 86 % based on LCF* (increase of CN_{Ag-Ag})#	-
50 °C, 10 bar air, HMF:NaOH:Ag 1:1:20	Degree of reduction 96 % based on LCF*	-
rt, 10 bar air, HMF:NaOH:Ag 1:0:20	Degree of reduction 39 % based on LCF* (comparatively smaller increase of CN_{Ag-Ag})#	Slightly reduced*§
50 °C, 10 bar air, HMF:NaOH:Ag 1:0:20	Degree of reduction 47 % based on LCF* (increase in particle size)#	Slightly reduced*§
rt, 10 bar N_2, HMF:NaOH:Ag 1:1:20	Reduced*§	-
50 °C, 10 bar N_2, HMF:NaOH:Ag 1:1:20	Reduced*§	-

*Interpretation from XANES, #Interpretation from EXAFS, §LCF analysis not possible due to data quality (small edge step).

EXAFS data and EXAFS fits

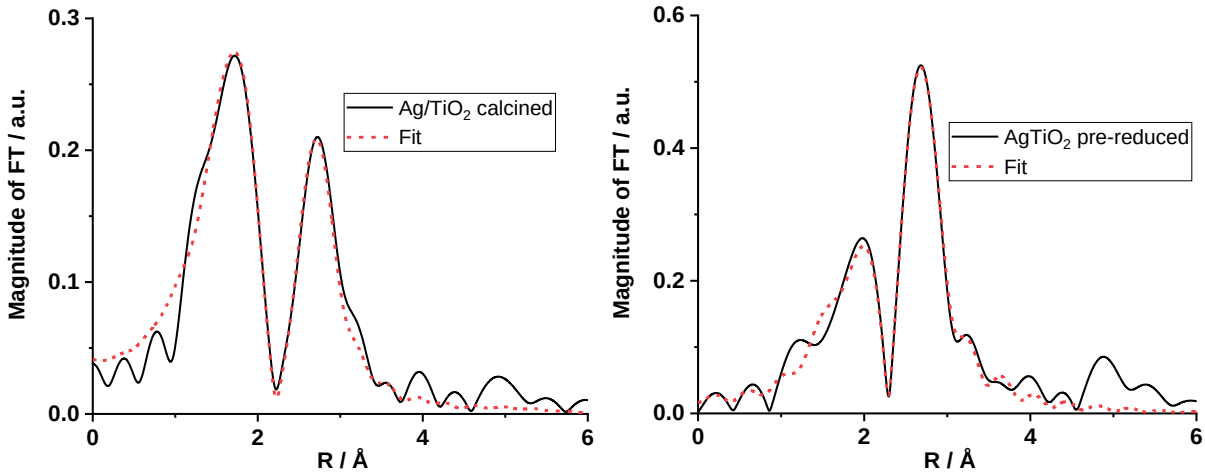

Figure S11: EXAFS fits of Ag/TiO_2 after different stages of preparation (left: calcined, right: pre-reduced).

Table S3: EXAFS fits of Ag/TiO_2 after different stages of preparation.

Catalyst	Ag-O			Ag-Ag			χ_ν^2	E0
	R / Å	CN	DW factor	R / Å	CN	DW factor		
Ag/TiO_2 calcined	2.30	2.8 ± 0.4	0.0153 ± 0.0028	2.85	2.8 ± 0.5	0.0154 ± 0.0019	29	3.2±0.8
Ag/TiO_2 reduced	2.30	2.4 ± 0.7	0.0146 ± 0.0049	2.85	5.0 ± 0.5	0.0122 ± 0.0008	54	0.6±0.2

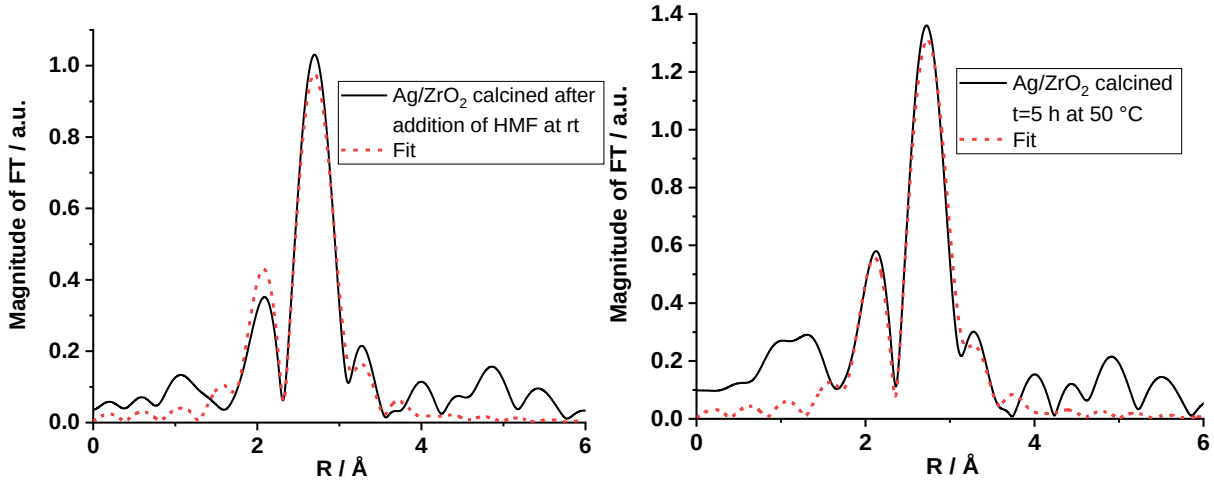

Figure S12: EXAFS fits of calcined Ag/ZrO_2 during the oxidation of HMF (left: after addition of HMF at room temperature, right: after 5 h at 50 °C). Reaction conditions: 50 °C, 10 bar air, HMF:NaOH:Ag 1:1:21, 345 min.

Table S4: EXAFS fits of calcined Ag/ZrO_2 during the oxidation of HMF. Reaction conditions: 50 °C, 10 bar air, HMF:NaOH:Ag 1:1:21, 345 min.

Temperature	Ag-Ag			χ_v^2	E0
	R / Å	CN	DW factor		
rt	2.86	8.3 ± 1.3	0.0114 ± 0.0016	219	0.9±0.5
50 °C	2.86	11.4 ± 2.7	0.0119 ± 0.0025	628	3.3±1.5

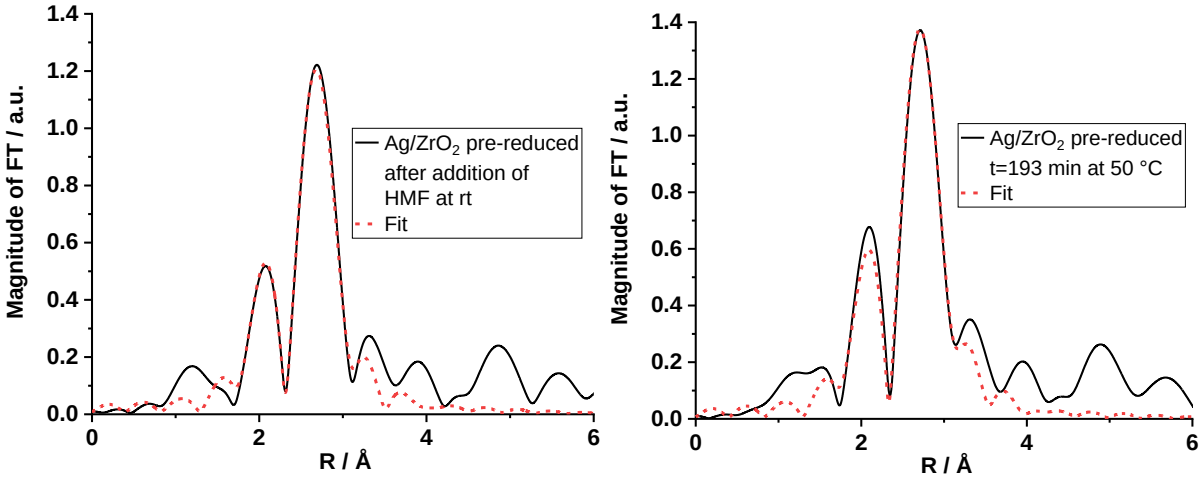

Figure S13: EXAFS fits of pre-reduced Ag/ZrO_2 in an alkaline HMF solution under nitrogen (left: after addition of HMF at room temperature, right: after 193 min at 50 °C). Reaction conditions: 50 °C, 10 bar N_2, HMF:NaOH:Ag 1:1:24, 193 min.

Table S5: EXAFS fits of reduced Ag/ZrO_2 in an alkaline HMF solution under nitrogen (left: after addition of HMF at room temperature, right: after 193 min at 50 °C). Reaction conditions: 50 °C, 10 bar N_2, HMF:NaOH:Ag 1:1:24, 193 min.

Temperature	Ag-Ag			χ_v^2	E0
	R / Å	CN	DW factor		
rt	2.85	9.2 ± 1.2	0.0104 ± 0.0012	6	0.8±0.6
50 °C	2.85	11.2 ± 1.4	0.0112 ± 0.0013	9	2.8±0.8

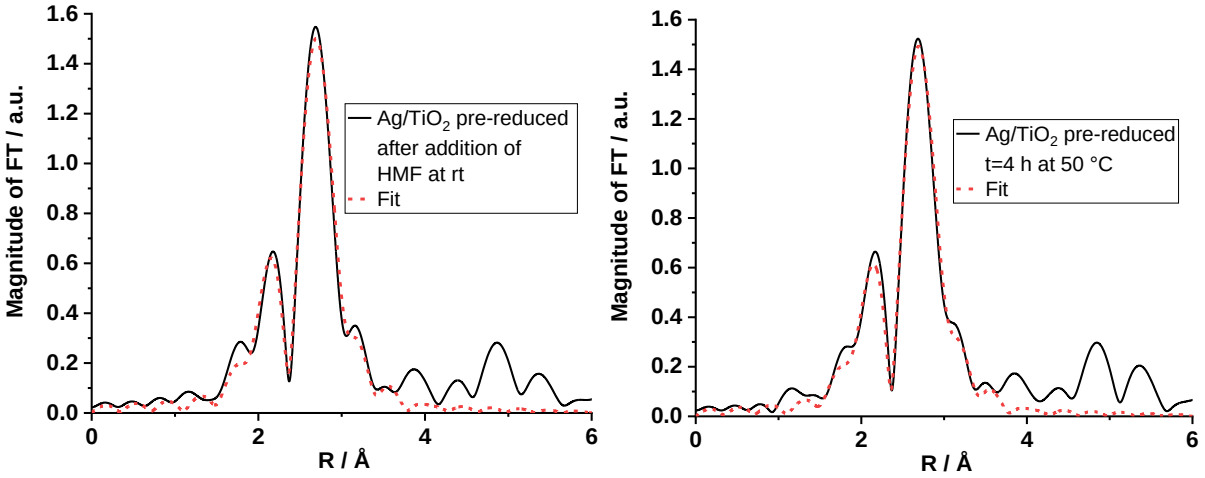

Figure S14: EXAFS fits of pre-reduced Ag/TiO_2 during the oxidation of HMF (left: after addition of HMF at room temperature, right: after 4 h at 50 °C). Reaction conditions: 50 °C, 10 bar air, HMF:NaOH:Ag 1:1:20, 4 h.

Table S6: EXAFS fits of reduced Ag/TiO_2 during the oxidation of HMF (left: after addition of HMF at room temperature, right: after 4 h at 50 °C). Reaction conditions: 50 °C, 10 bar air, HMF:NaOH:Ag 1:1:20, 4 h.

Temperature	Ag-Ag			χ_ν^2	E0
	R / Å	CN	DW factor		
rt	2.87	10.5 ± 0.8	0.0102 ± 0.0007	42	1.7±0.5
50 °C	2.86	11.4 ± 0.9	0.0110 ± 0.0007	46	1.7±0.5

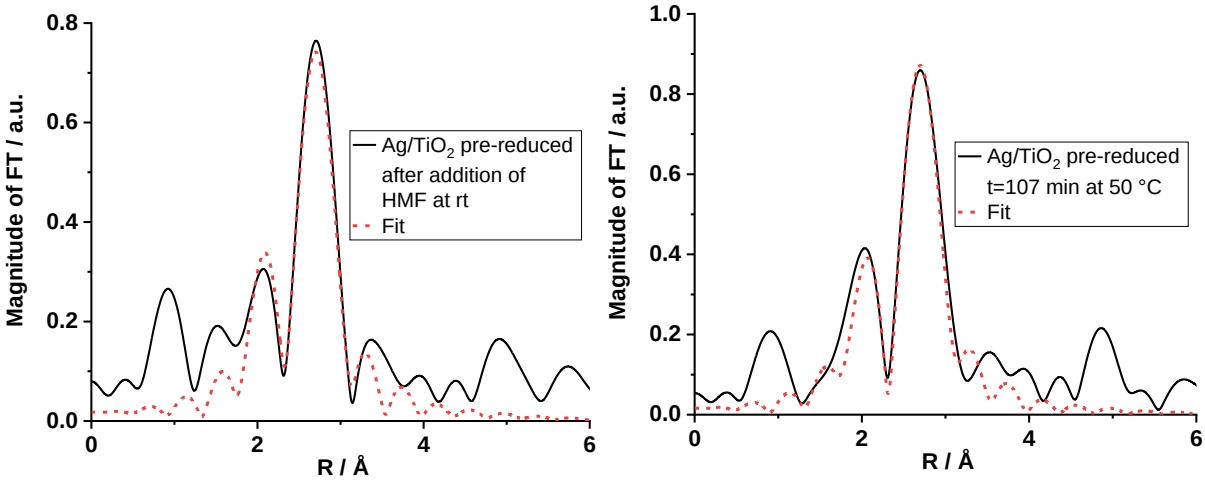

Figure S15: EXAFS fits of pre-reduced Ag/TiO_2 in a HMF solution without NaOH (left: ater addition of HMF at room temperature, right: after 107 min at 50 °C). Reaction conditions: 50 °C, 10 bar air, HMF:NaOH:Ag 1:0:6, 107 min.

References

[1] G. A. Sotiriou, A. Meyer, J. T. Knijnenburg, S. Panke, S. E. Pratsinis, *Quantifying the origin of released Ag^+ ions from nanosilver*, *Langmuir* **2012**, *28*, 15929-15936.

[2] B. Molleman, T. Hiemstra, *Surface structure of silver nanoparticles as a model for understanding the oxidative dissolution of silver ions*, *Langmuir* **2015**, *31*, 13361-13372.

[3] B. Molleman, T. Hiemstra, *Time, pH, and size dependency of silver nanoparticle dissolution: the road to equilibrium*, *Environmental Science: Nano* **2017**, *4*, 1314-1327.