catalysts

Aerobic Methanol Oxidation over Unsupported Nanoporous Gold: The Influence of an Added Base

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Supporting Information

$$A_{\mathrm{spec}} = \frac{A_{\mathrm{m}}}{m_{\mathrm{npAu}}} = \frac{IE}{v \cdot Q_{\mathrm{ref}} \cdot m_{\mathrm{npAu}}}$$

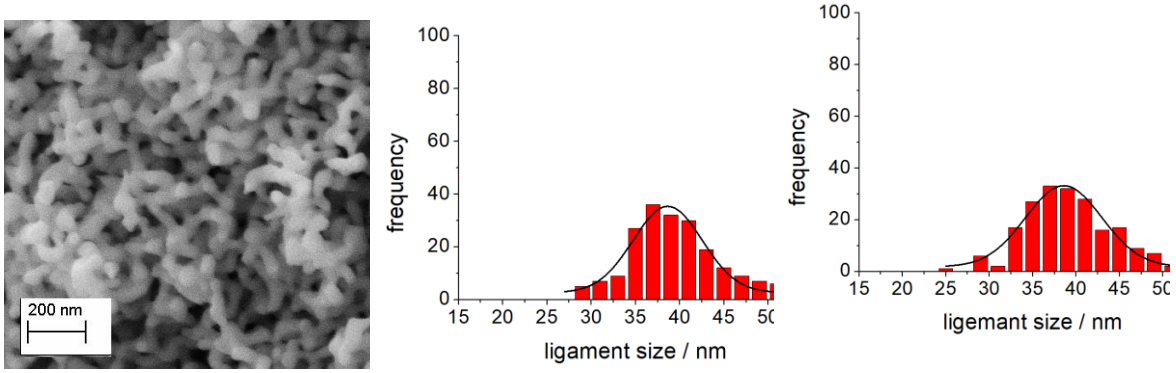
A_m: microscopic surface of npAu / m^2
m_{npAu}: weight of npAu / g
IE: integration of the reduction peak / AV
v: speed velocity / V/s
Q_{ref}: electric charge of the Au-O_x monolayer (400 µC/cm)[1]

Equation S-1: Determination of the specific surface of npAu A_{spec} from cyclic voltammograms.

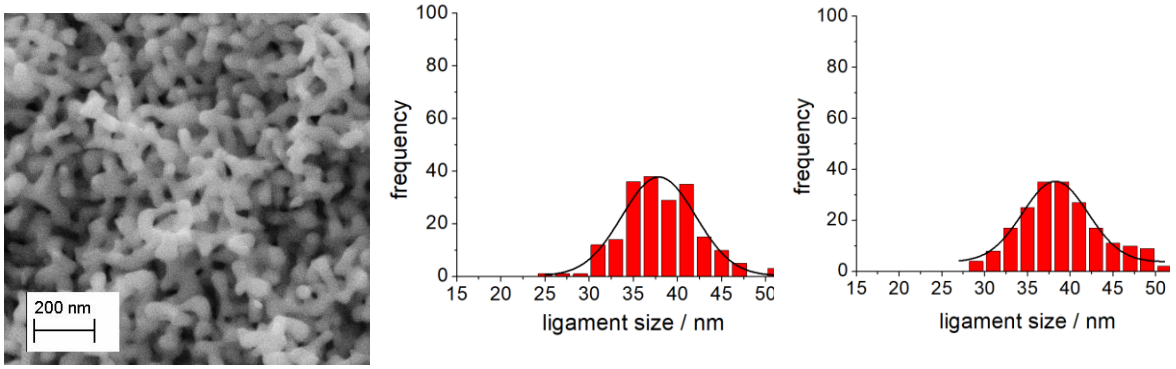
ESI-1: npAu characterization

bottom **center**

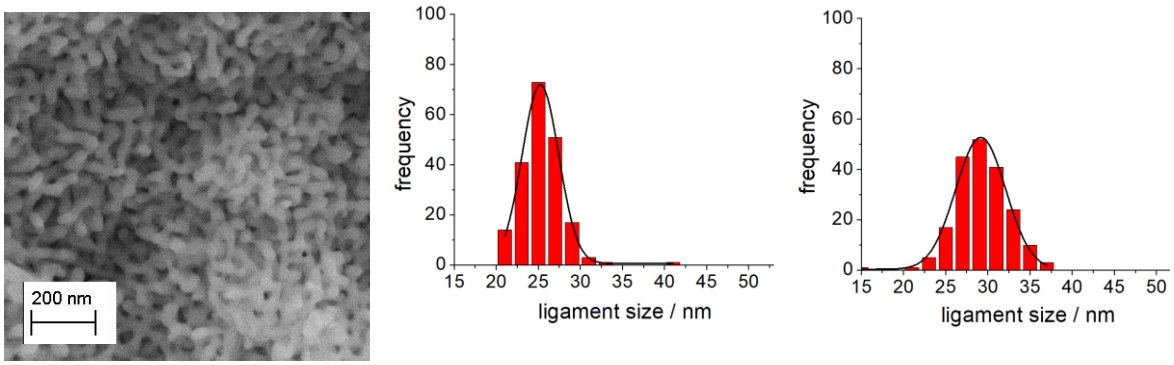
a) FC, $Au_{25}Ag_{75}$



b) FC, $Au_{30}Ag_{70}$



c) GCD, $Au_{25}Ag_{75}$



d) GCD, $Au_{30}Ag_{70}$

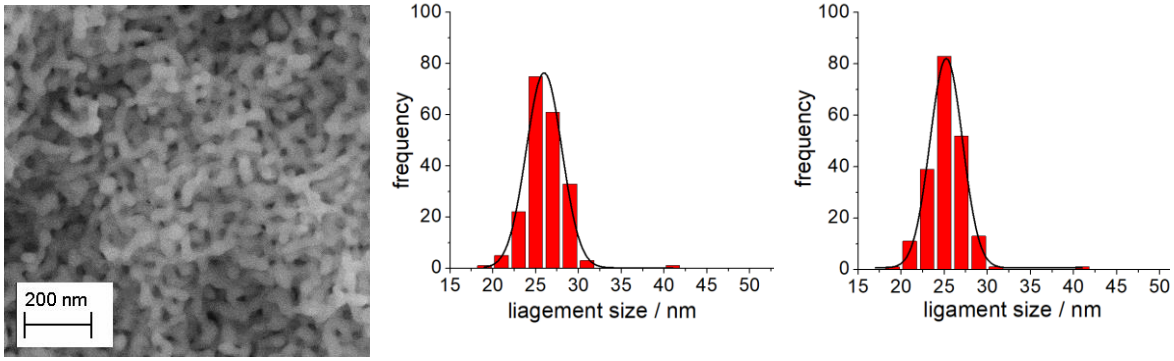


Fig. S1: Representative SEM images and corresponding histograms characterized for positions on bottom and center in cross section of npAu containing less than 1 at % Ag after preparation using free corrosion (FC) and galvanodynamically controlled dealloying (GCD) from $Au_{25}Ag_{75}$ and $Au_{30}Ag_{70}$.

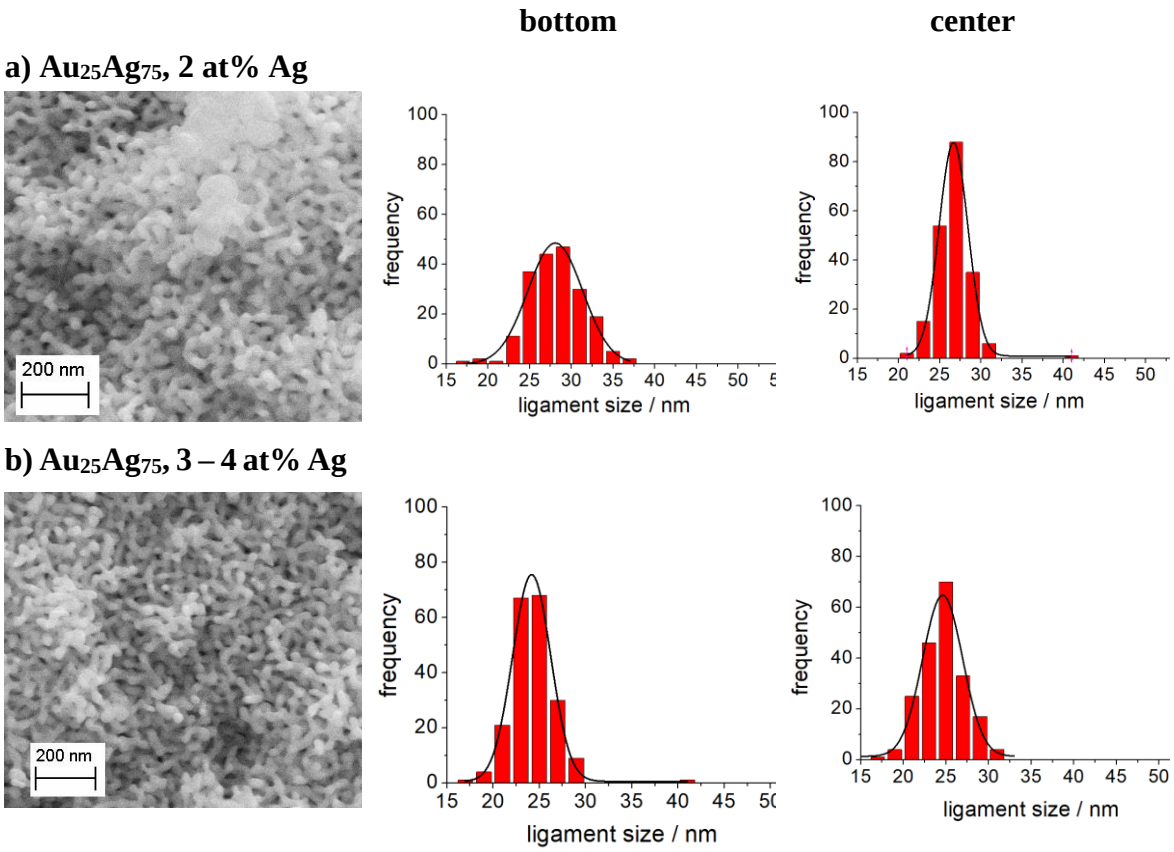


Fig. S2: Representative SEM images and corresponding histograms characterized for positions on bottom and center in cross section of npAu containing various residual Ag content after preparation by GCD from $Au_{25}Ag_{75}$.

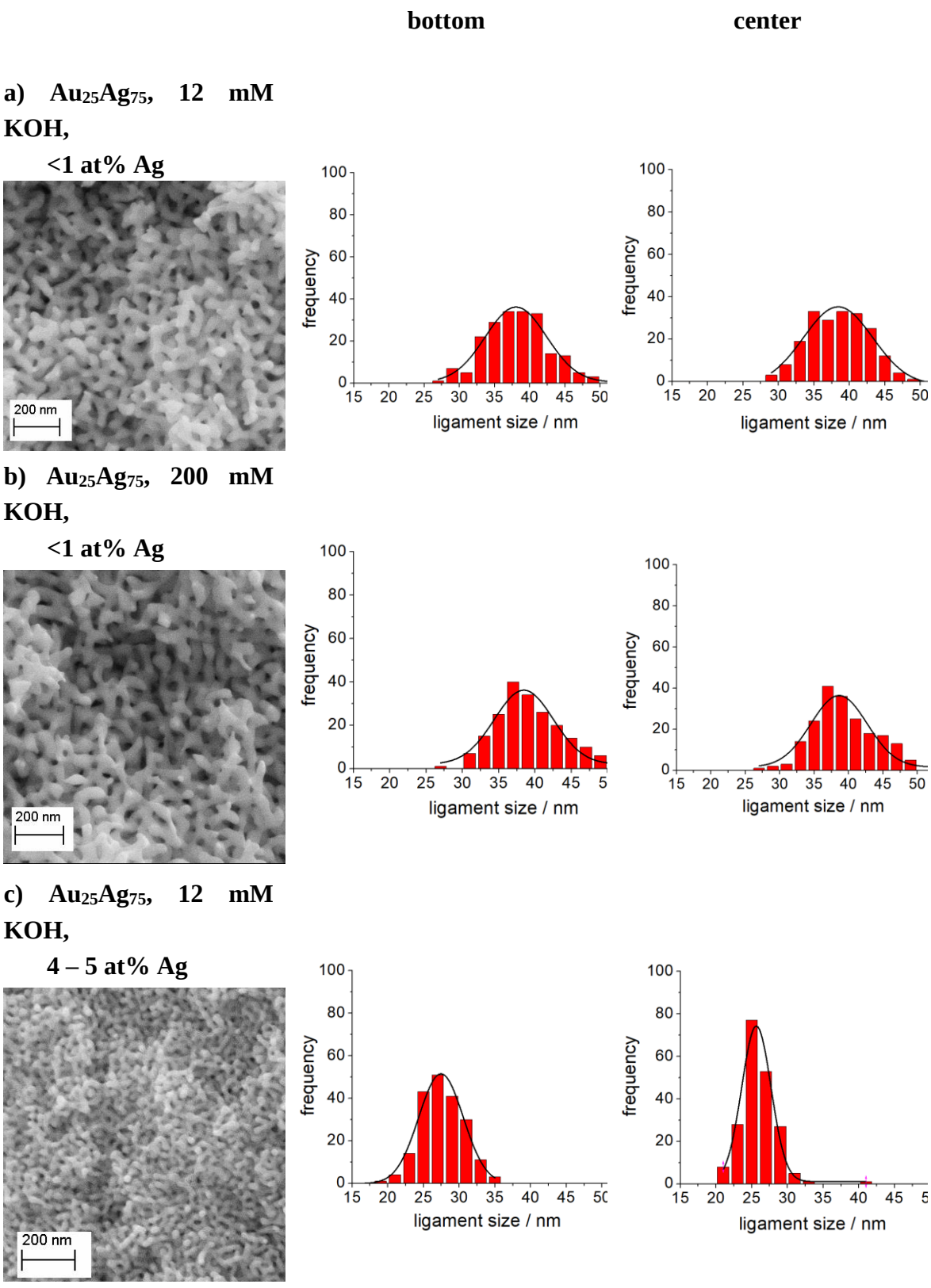


Fig. S3: Representative SEM images and corresponding histograms characterized for positions on bottom and center in cross section of npAu samples after catalysis. Methanol oxidation experiments were performed a) of 12 mM and b) 200 mM KOH in methanol at 60 °C and 3 bar O_2 for 24 h over unsupported npAu samples containing less than 1 at % Ag prepared by FC from $Au_{25}Ag_{75}$, and c) of 12 mM KOH in methanol at the same reaction

conditions over npAu sample containing residual Ag content of 4 – 5 at% prepared by GCD from $Au_{25}Ag_{75}$.

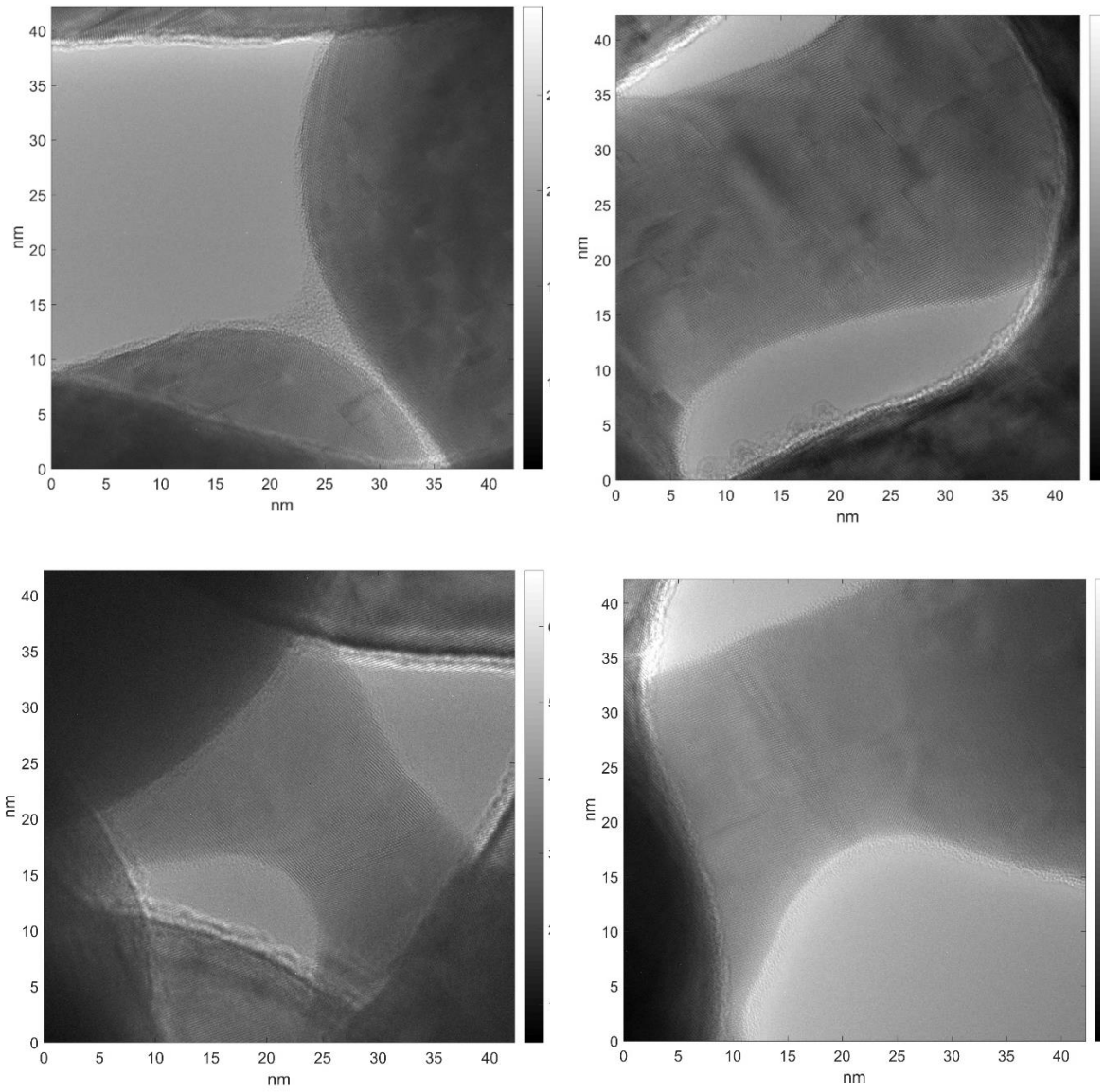


Fig. S4: TEM images from a lamella cut from the center of the npAu disk after catalysis. Catalytic experiments were performed of 12 mM KOH in methanol at 60 °C and 3 bar O_2 over unsupported npAu containing less than 1 at% Ag from $Au_{25}Ag_{75}$ fabricated by FC for 24 h.

ESI-2: Catalytic investigations

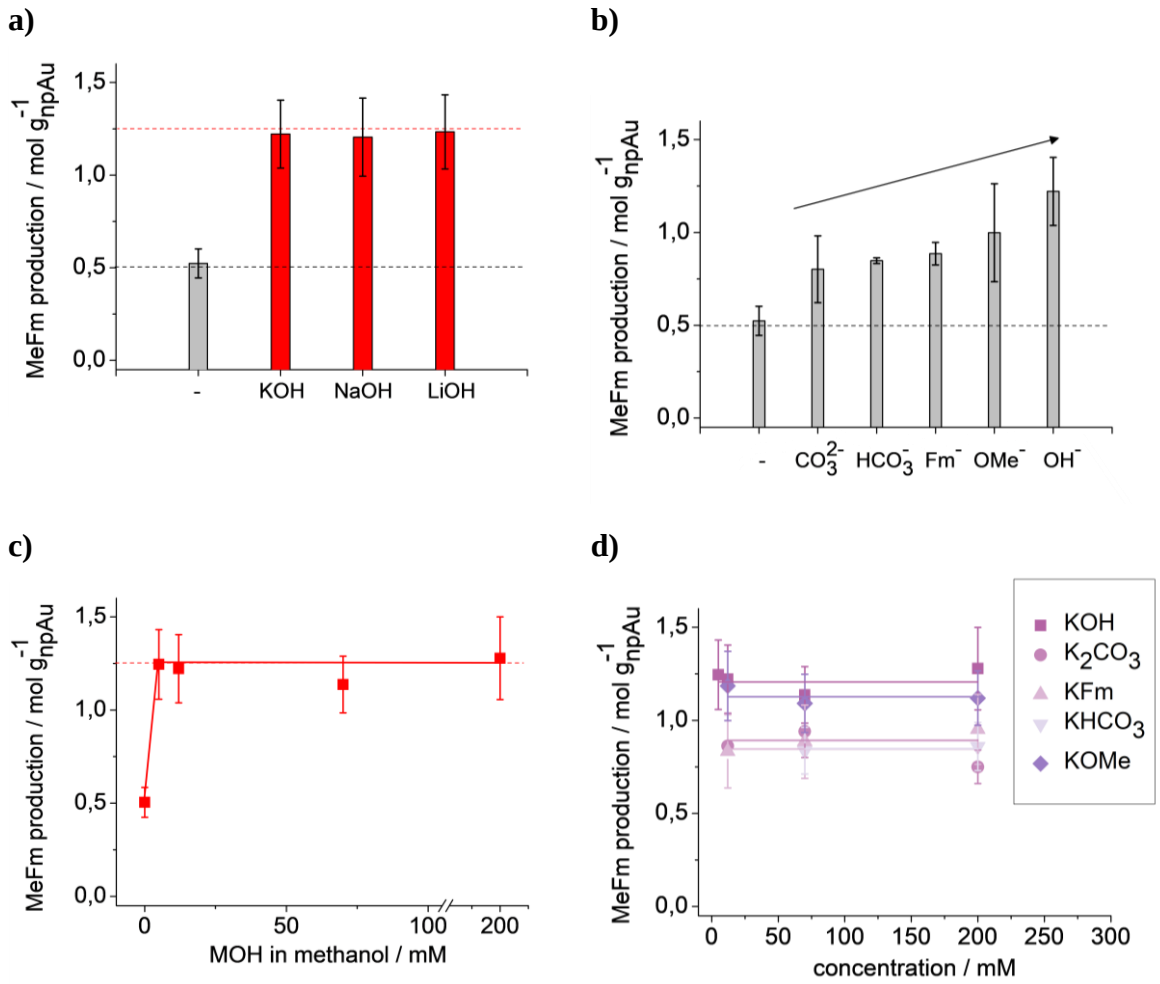


Fig. S5: a) MeFm production over npAu samples containing less than 1 at% Ag using no additional base (-) and different alkali hydroxides MOH to clarify that there is no difference in catalysis (M = K, Na, Li). MeFm production at different basic conditions using various potassium-based bases b) of 12 mM and c-d) at different concentrations in methanol. Catalytic experiments were performed under neutral (-) and basic conditions over unsupported npAu containing less than 1 at% Ag residues at 60 °C and 3 bar O_2 after 24 h.

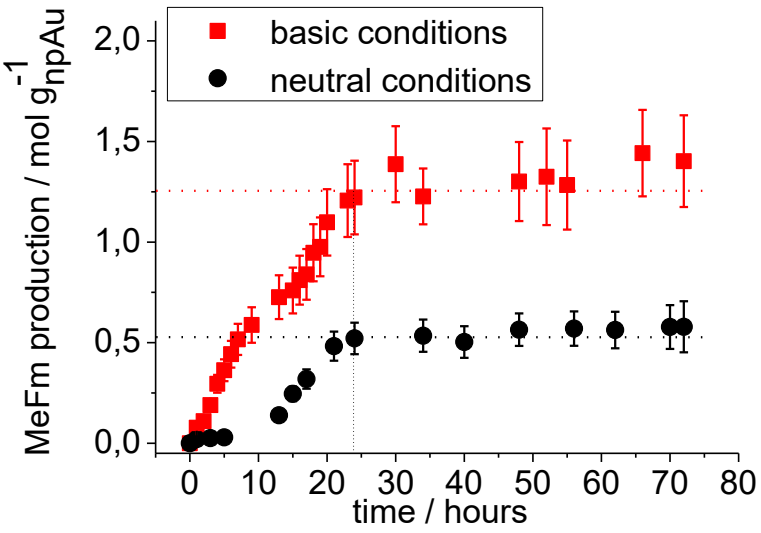


Fig. S6: MeFm production as a function of time comparing the rates under neutral (empty squares) and basic (filled squares) conditions. Catalytic experiments were performed at 60 °C and 3 bar O_2 under neutral and basic (12 mM MOH in methanol) conditions over unsupported npAu containing less than 1 at% Ag.

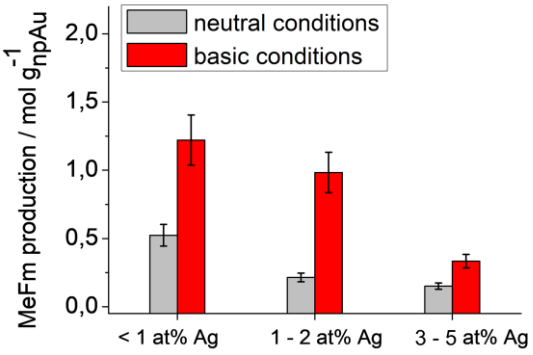


Fig. S7: MeFm production over npAu with various residual Ag content under basic conditions (12 mM MOH in methanol). Catalytic experiments were performed at 3 bar O_2 at 60 °C for 24 h. For samples containing more than 2 at% Ag the observed conversion was constant (within the error bars).

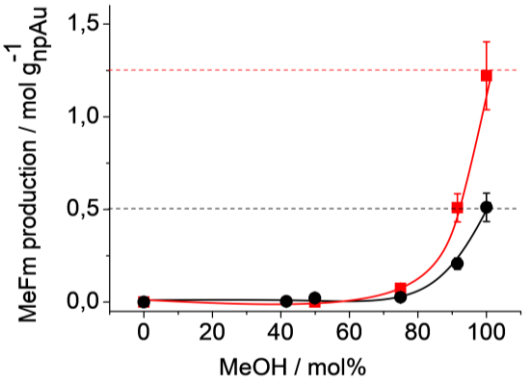


Fig. S8: MeFm production as a function of MeOH content dilution with water. Catalytic experiments were performed under neutral (given in black) and basic (12 mM MOH in methanol, given in red) conditions. Catalytic experiments were performed under neutral (-) and basic conditions over unsupported npAu containing less than 1 at% Ag residues at 60 °C and 3 bar O_2 after 24 h.

Table S1: MeFm production and corresponding turnover frequencies (TOF) over unsupported npAu containing less than 1 at% Ag residues at 60 °C and 3 bar O_2 after 24 h under neutral and basic condtions (12 mM MOH).

	Neutral conditions		**Basic conditions**	
T / °C	**MeFm / mol g_{npAu}^{-1}**	**TOF / h^{-1}**	**MeFm / mol g_{npAu}^{-1}**	**TOF / h^{-1}**
40	0.83 ± 0.01	32 ± 5	0.59 ± 0.09	95 ± 14
50	1.66 ± 0.02	79 ± 12	0.97 ± 0.15	165 ± 25
60	0.51± 0.08	190 ± 28	1.22 ± 0.18	210 ±31
70	0.71 ± 0.11	271 ± 40	1.54 ±0.23	261 ± 40
80	1.99 ± 0.15	378 ± 55	1.66 ±0.25	282 ± 42

$$TOF = \frac{amount\ of\ MeFm}{amount\ of\ catalytic\ sites} \cdot \frac{1}{t} = \frac{n_{\mathrm{Pro}}}{\left(\frac{\rho_{\mathrm{Au(111)}}}{N_{\mathrm{A}}} \cdot m_{\mathrm{npAu}} \cdot A_{\mathrm{spec}}\right)} \cdot \frac{1}{t}$$

t: time / h (t_2-t_1; specific time range was regarded from t_1 to t_2)

n_{pro}: formed amount of MeFm from in the regarded time range / mol

$\varrho_{Au(111)}$: density of Au(111)-surface (1,4 x 10^{19} atoms m^{-3})

N_A: Avogadro constant (6,023 x 10^{23} atoms mol^{-1})

m_{npAu}: weight of npAu / g

A_{spec}: specific surface of npAu / m^2 g^{-1} (14 ± 2 m^2 g^{-1})[2]

Equation S-2: Determination of the turnover frequency TOF from obtained MeFm production as function of time.

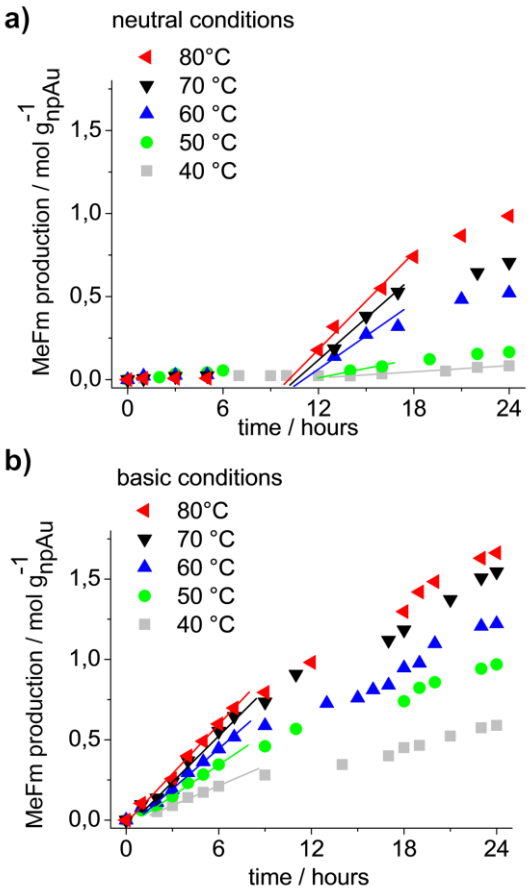


Fig. S9: MeFm production as a function of time at different temperatures under a) neutral and b) basic conditions (12 mM MOH in methanol). Catalytic experiments were performed at 60 °C and 3 bar O_2 over unsupported npAu containing less than 1 at% Ag. The slopes after activation period were used to determine the highest turnover frequency TOF.

Uncategorized References

[1] S. Cherevko, A. A. Topalov, I. Katsounaros, K. J. J. Mayrhofer, *Electrochem Commun* **2013**, *28*, 44-46.

[2] A. Lackmann, C. Mahr, M. Schowalter, L. Fitzek, J. Weissmüller, A. Rosenauer, A. Wittstock, *J Catal* **2017**, *353*, 99-106.