

Supporting Information

Titanium-anchored gold on silica for enhanced catalytic activity in aqueous ethanol oxidation

Sotiria Mostrou,[†] Mark A. Newton,[†] Andreas Tarcewski,[†] Andreas Nagl,[‡] Karin
Föttinger,[‡] and Jeroen A. van Bokhoven^{*,†,¶}

[†]*Institute for Chemical and Bioengineering, Department of Chemistry and Applied
Biosciences, ETH Zürich, 8093 Zurich, Switzerland*

[‡]*Institute of Material Chemistry, Division Physical Chemistry, TU Wien, 1060 Vienna,
Austria*

[¶]*Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, 5232
Villigen, Switzerland*

E-mail: jeroen.vanbokhoven@chem.ethz.ch

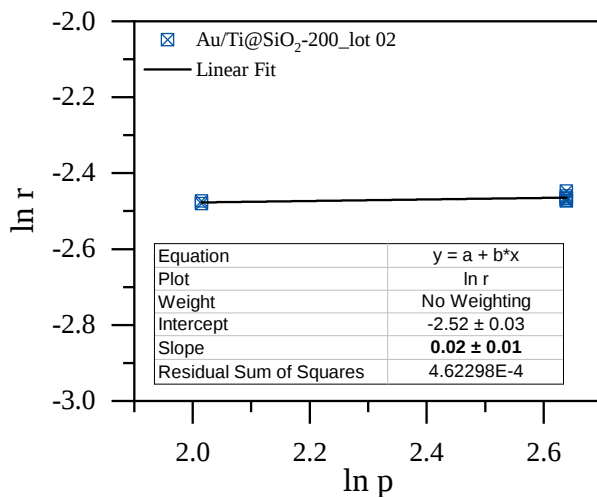


Figure S1: Reaction rate dependency on oxygen pressure. The linear fit indicates a zero order oxygen dependency. Reaction conditions: 423 K, 1:1 catalyst:SiC dilution, 5 wt.% EtOH/H₂O, 0.06 volumetric flow ratio of EtOH_aq.:O₂.

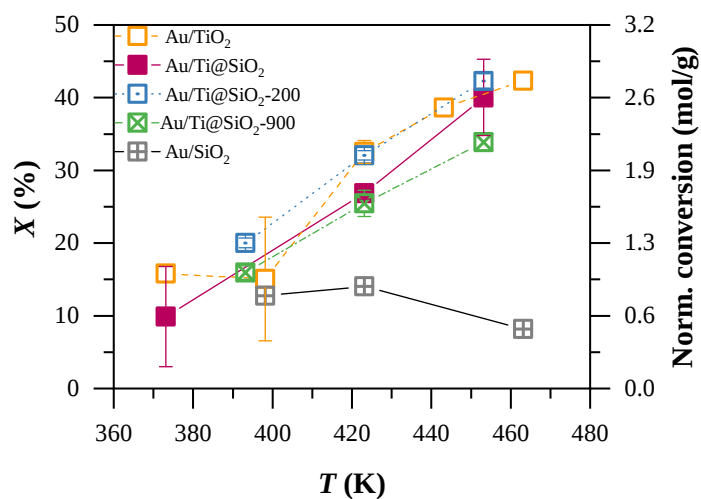


Figure S2: Moles of converted ethanoil per catalyst mass. Reaction conditions: 18 bar, 5 ml/min O₂, 0.3 ml/min 5 wt.% EtOH/H₂O, 0.15 g catalyst, 1:1 SiC dilution.

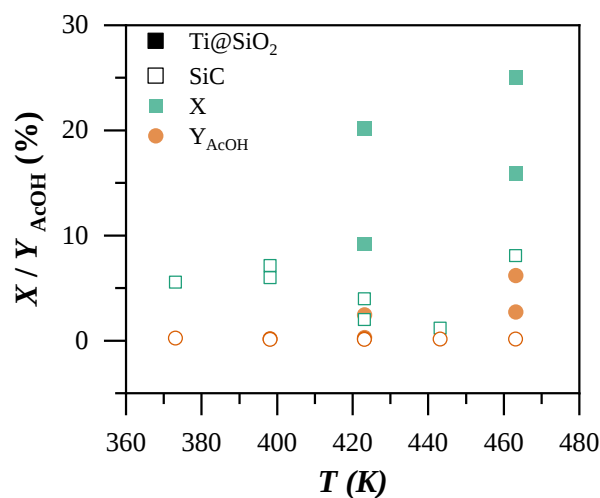


Figure S3: Ethanol conversion (X) and acetic acid yield (Y) over temperature of the support Au/Ti@SiO₂ and the inert SiC. Reaction conditions: 18 bar, 5 ml/min O₂, 0.3 ml/min 5 wt.% EtOH/H₂O, 0.15 g catalyst, 1:1 SiC dilution.

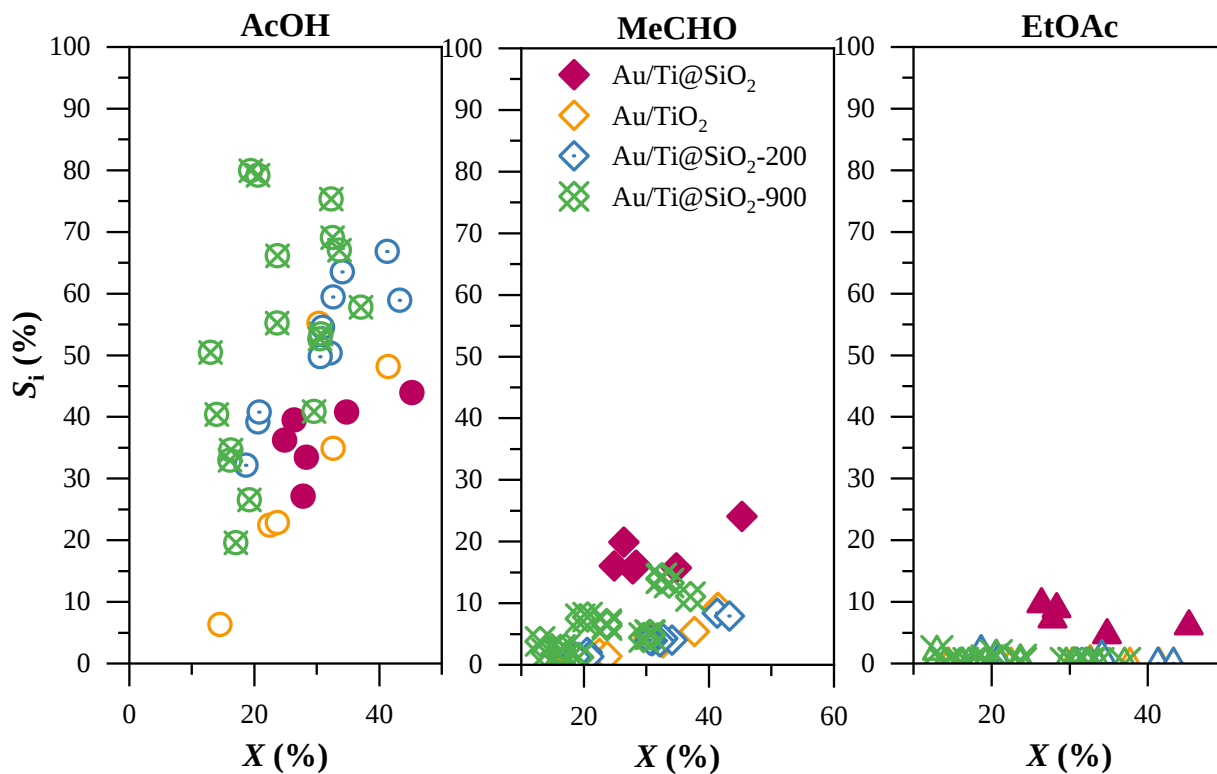


Figure S4: Product selectivity as a function of conversion over Au/TiO₂ and the Au/Ti@SiO₂-based catalysts. Reaction conditions: 400-443 K, 17±1 bar, 1:1 catalyst:SiC dilution, 5 wt.% EtOH/H₂O, 0.06 volumetric flow ratio of EtOH_{aq}:O₂.

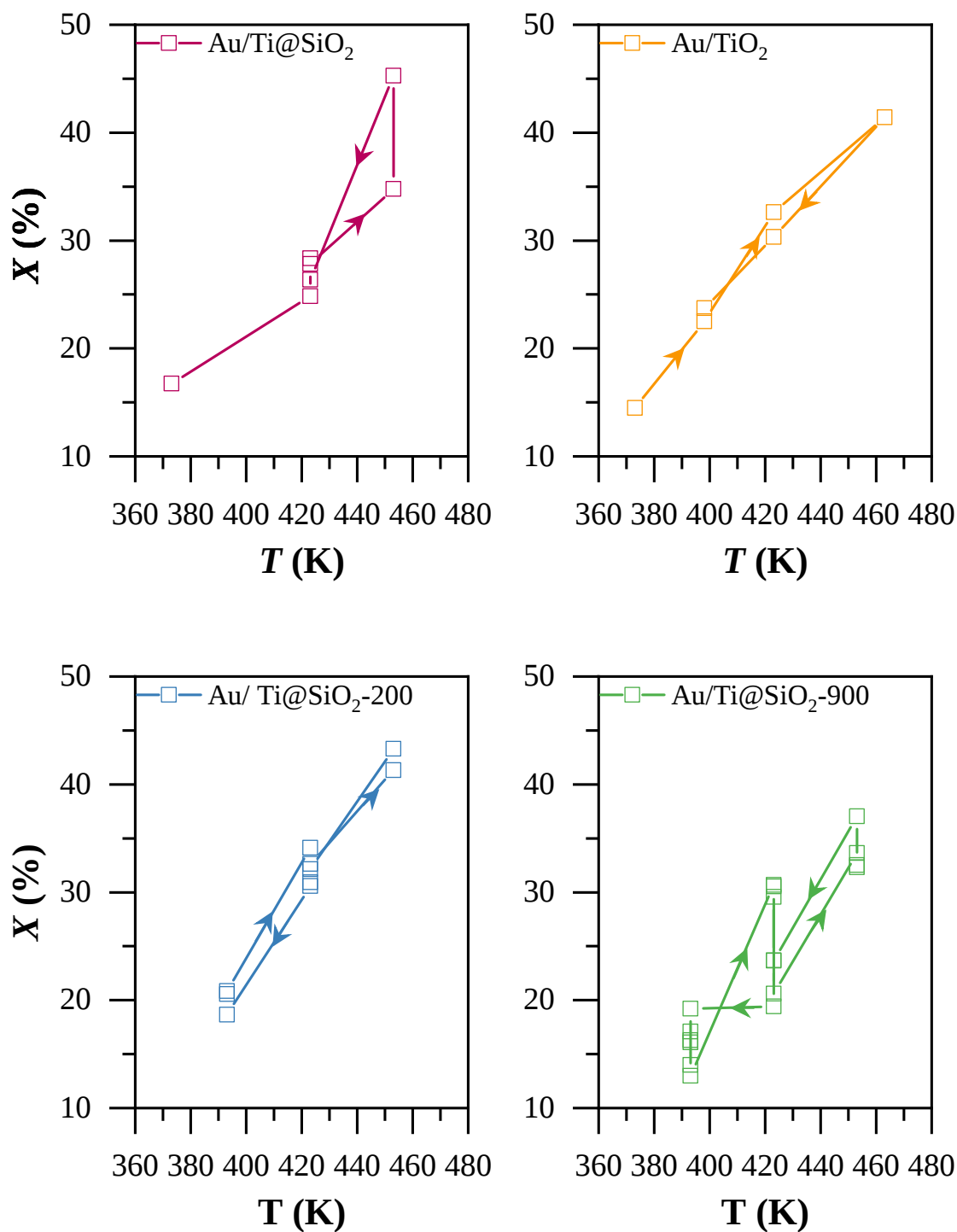


Figure S5: Ethanol conversion over the Au/Ti@SiO₂-based as a function of temperature, during subsequent heating and cooling. Reaction conditions: 18 bar, 5 ml/min O₂, 0.3 ml/min 5% EtOH/H₂O, 0.15 g catalyst, 1:1 SiC dilution.

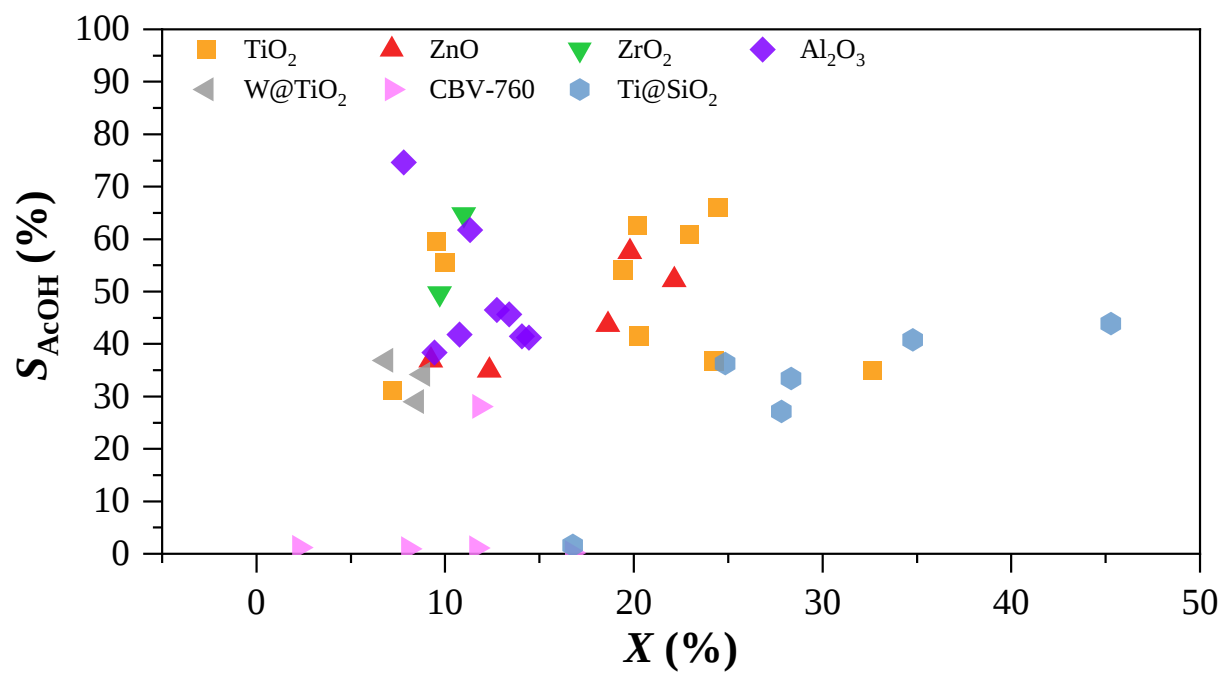


Figure S6: Distribution of conversion and selectivity to acetic acid over gold catalysts supported on different metal oxides. Reaction conditions: 400-443 K, 17 ± 1 bar, 1:1 catalyst:SiC dilution, 5 wt.% EtOH/H₂O, 0.06 volumetric flow ratio of EtOH_{aq}:O₂.

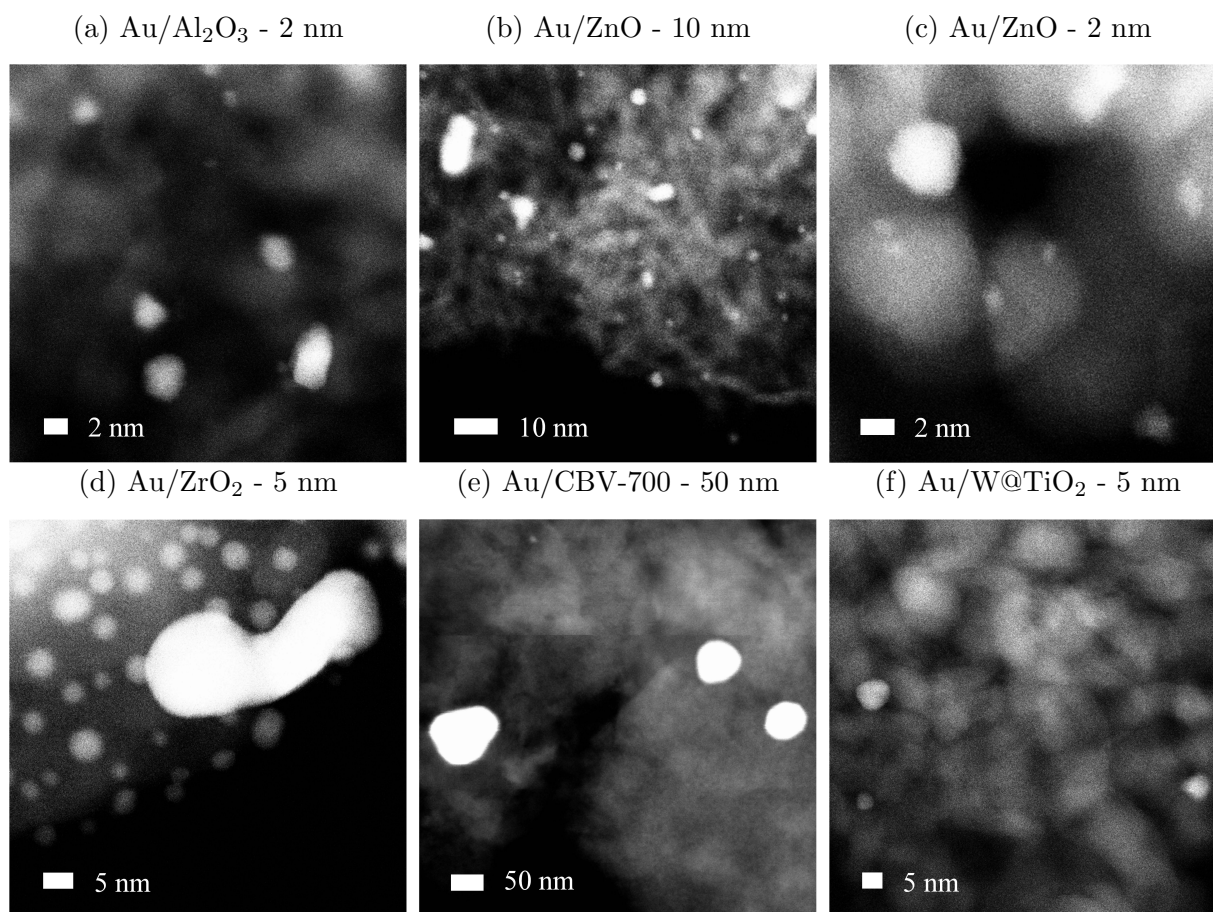


Figure S7: HAADF-STEM images of gold catalysts supported over different metal oxides, namely Au/Al₂O₃ - 2 nm (a), Au/ZnO - 10 nm (b), Au/ZnO - 2 nm (c), Au/ZrO₂ - 5 nm (d), Au/CBV-700 - 50 nm (e), and Au/W@TiO₂ - 5 nm (f). Gold appears brighter than the supports, due to the larger atomic number of gold.

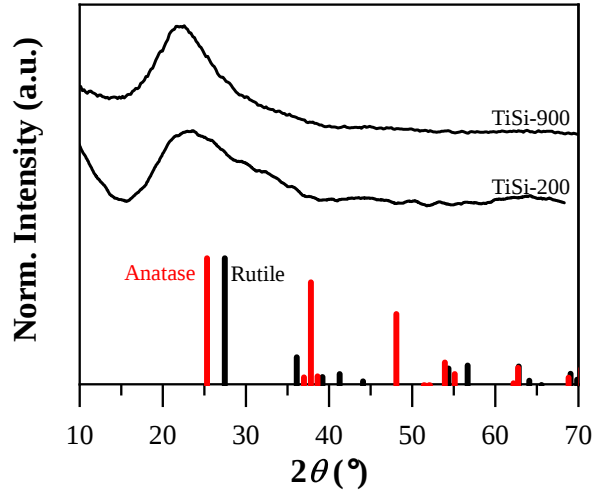


Figure S8: XRD patterns of the Ti@SiO₂ supports before gold deposition. The provided references are titania rutile (ICSD: 16636), anatase (ICSD: 9852), and metallic gold (ICSD: 52700).

Table S1: EXAFS of Au/Ti@SiO₂ fitting results.

Fit	Scatterer	N	R (Å)	DW	EF	R(%)	Chi
Au/Ti@SiO₂; Parameters: Kmin = 3, Kmax = 13, AFAC = 0.9							
OSi	O	4.3	1.89	0.021	5.1	39	5.13
	Si	0.125	3.26	0.011			
OAu	O	4.2	1.89	0.021	4.3	33.9	4.59
	Au	3.1	3.09	0.027			
OAuTi	O	4.5	1.89	0.022	4	30.5	4.16
	Ti	1.3	3.08	0.02			
	Au	1.5	3.05	0.025			
OTi	O	4.3	1.89	0.021	4	32.1	4.27
	Ti	1.5	3.06	0.017			
OTi ^{sp}	O	4	1.88	0.02	4.8	32.9	4.49
	Ti	1	3.054	0.011			
Au/Ti@SiO₂; Parameters: Kmin = 3, Kmax = 14, AFAC = 0.8							
OTiSi	O	2.5	1.863	0.011	34.1	1.92	3.87
	O	2.2	1.971	0.017			
	Ti	2.0	3.076	0.018			
	Si	3.4	3.576	0.037			
OTi	O	2.9	1.868	0.014	37.95	2.951	4.52
	O	2.1	1.967	0.021			
	Ti	1.8	3.073	0.017			
TiO₂ Rutile; Parameters: Kmin = 3, Kmax = 14, AFAC = 0.8							
OTi	O	4	1.99	0.011	42.76	6	8.845
	O	2	1.844	0.017			
	Ti	2	2.961	0.018			

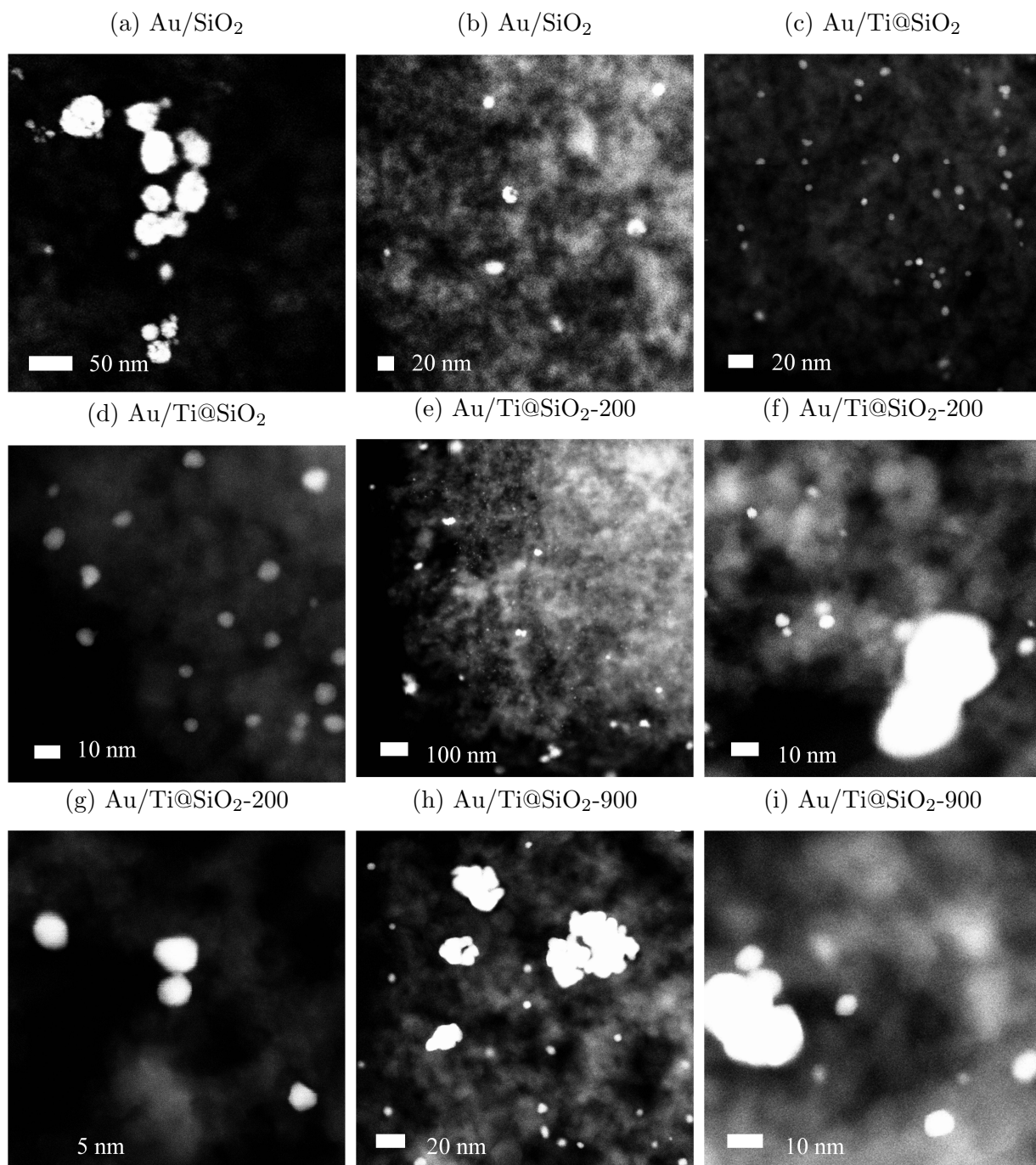
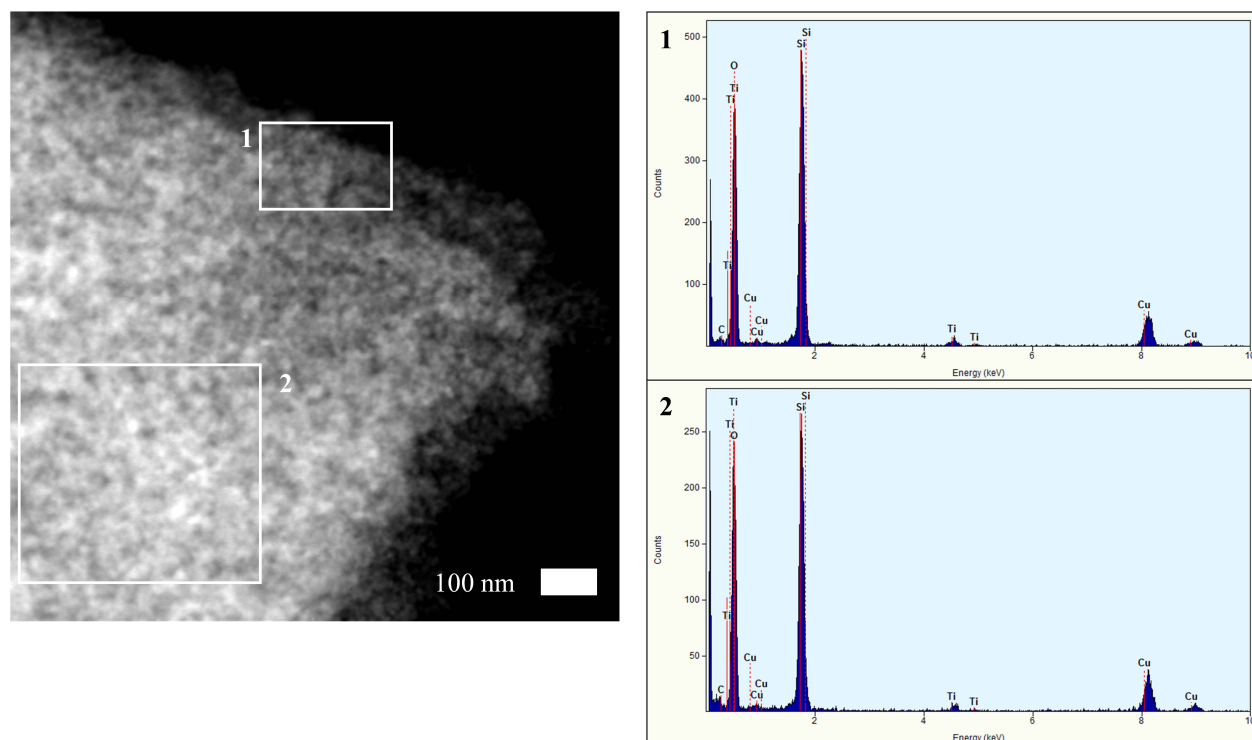


Figure S9: HAADF-STEM images of the titania-silica supported gold catalysts, namely Au/SiO₂ (a and b), Au/Ti@SiO₂ (c and d), Au/Ti@SiO₂-200 (e-g), and Au/Ti@SiO₂-900 (h and i). Gold appears brighter than the supports, due to the larger atomic number of gold.

(a) Ti@SiO₂



(b) Ti@TiO₂-200

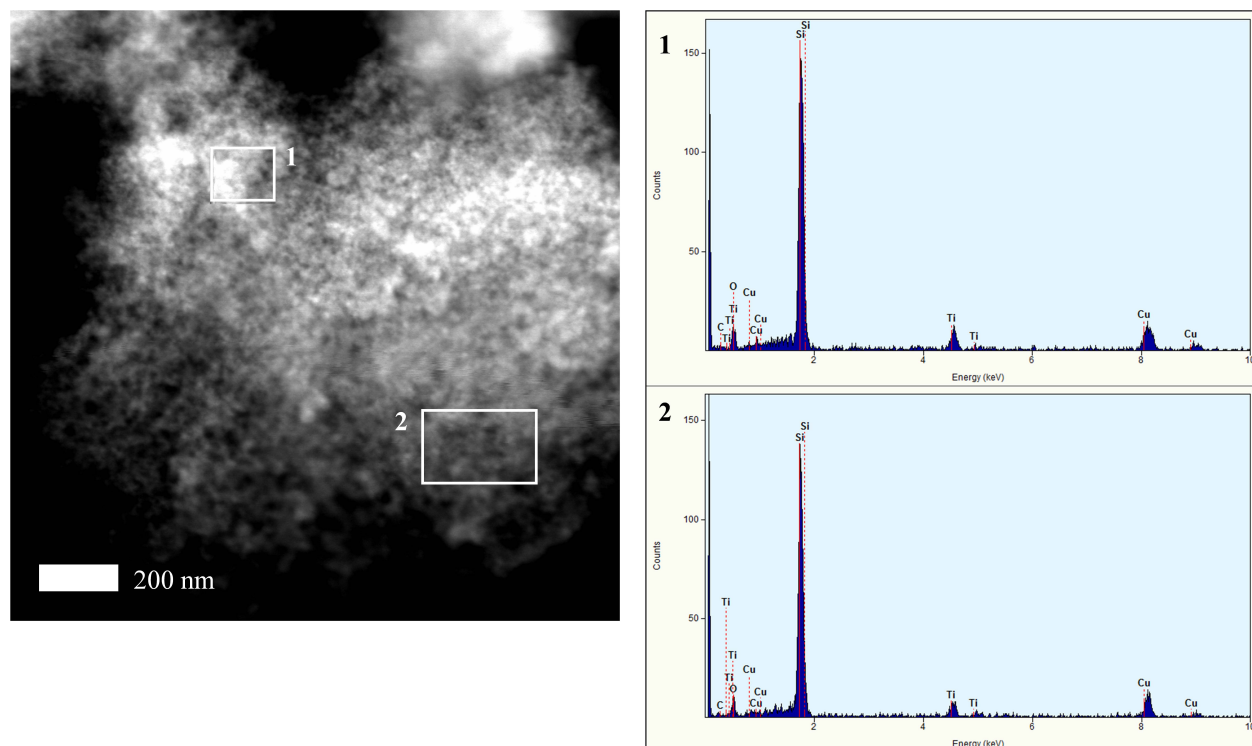
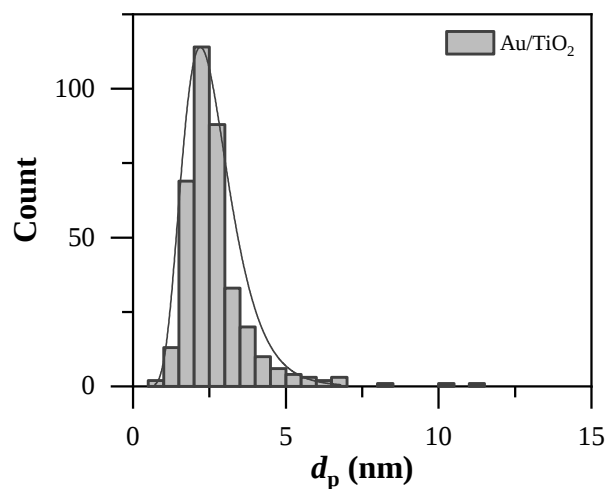
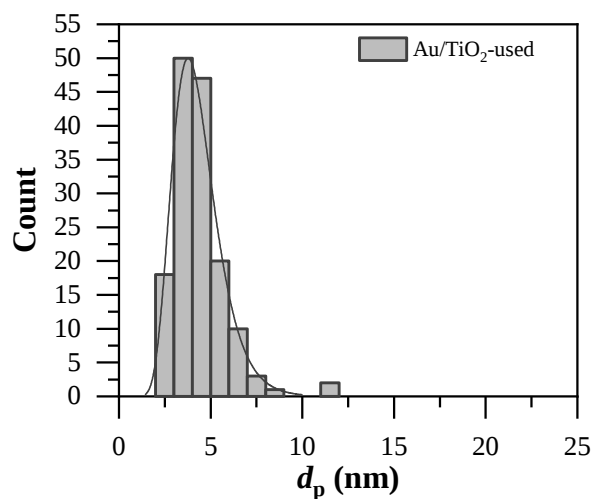


Figure S10: EDX spectra of Ti@SiO₂ (a) and Ti@SiO₂-200 (b).

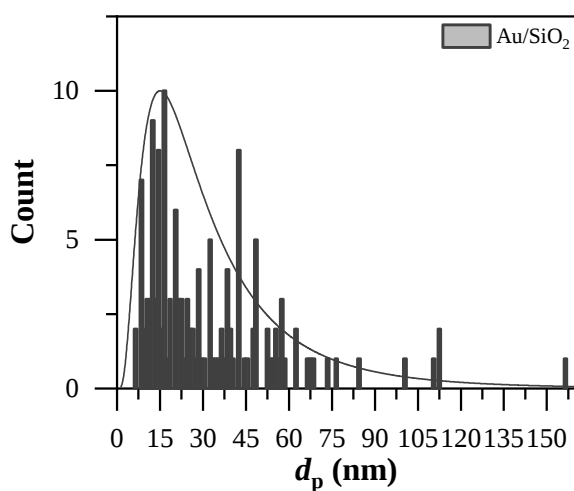
(a) Fresh Au/TiO₂



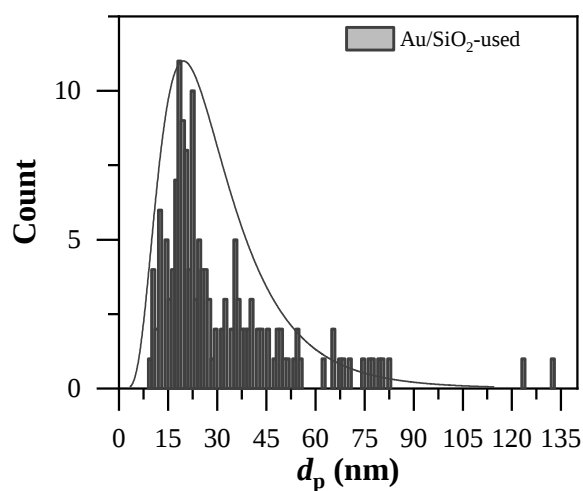
(b) Used Au/TiO₂



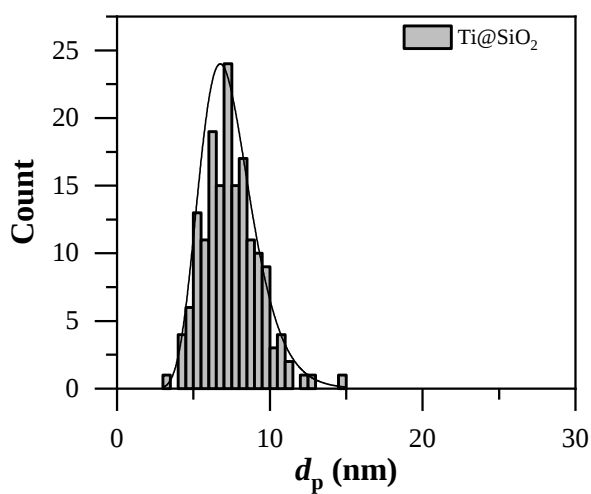
(c) Fresh Au/SiO₂



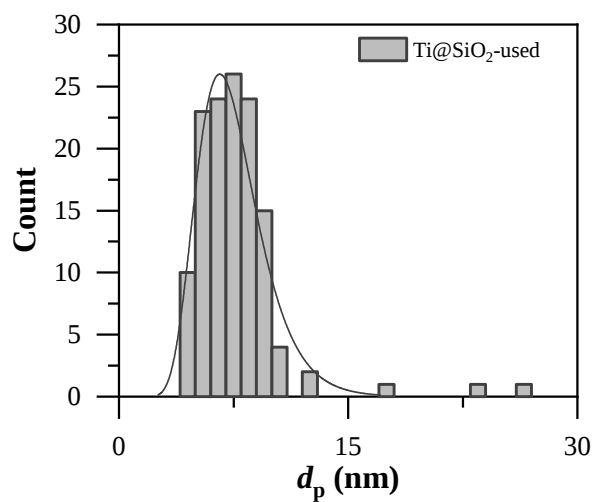
(d) Used Au/SiO₂



(e) Fresh Au/Ti@SiO₂



(f) Used Au/Ti@SiO₂



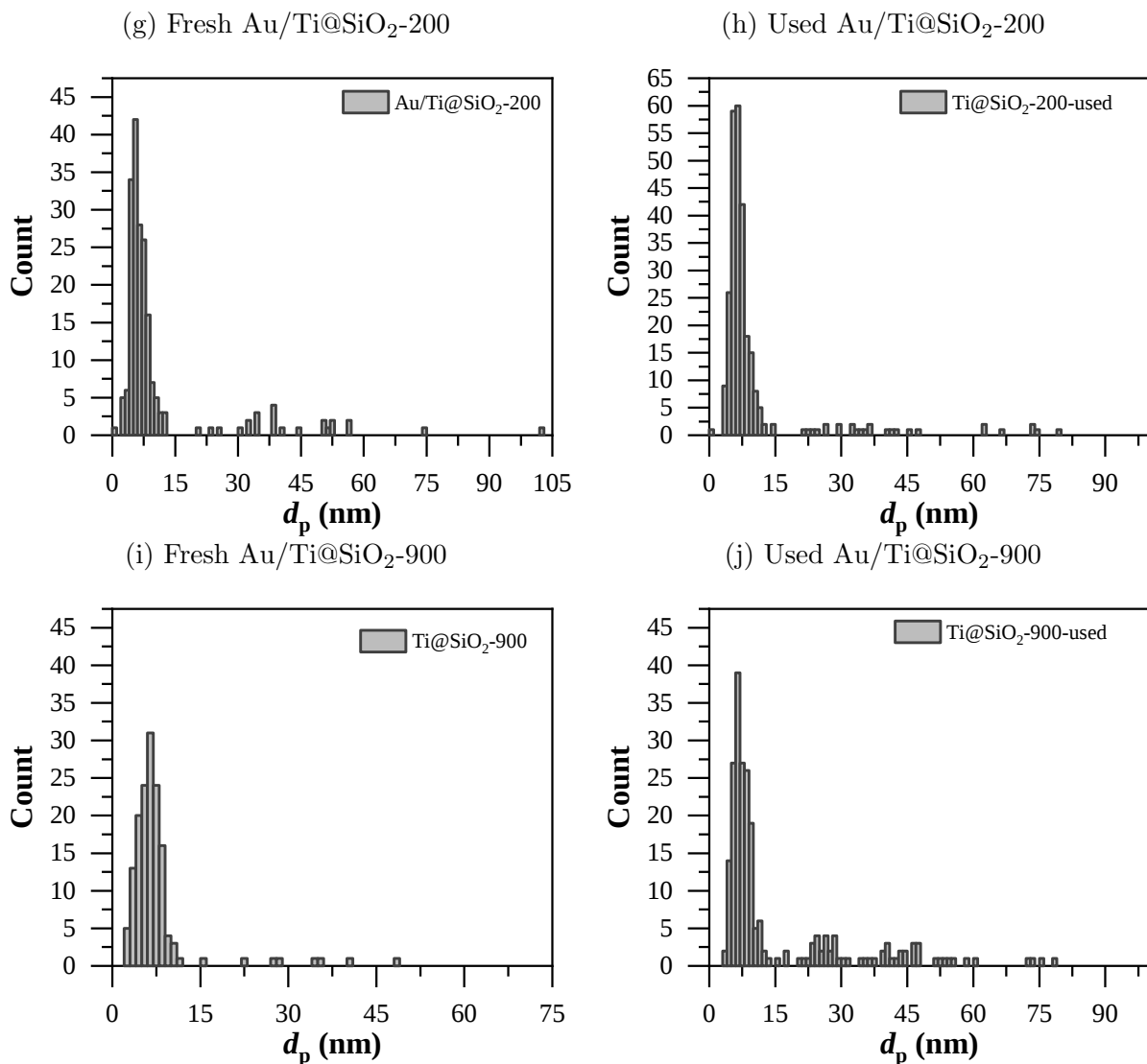
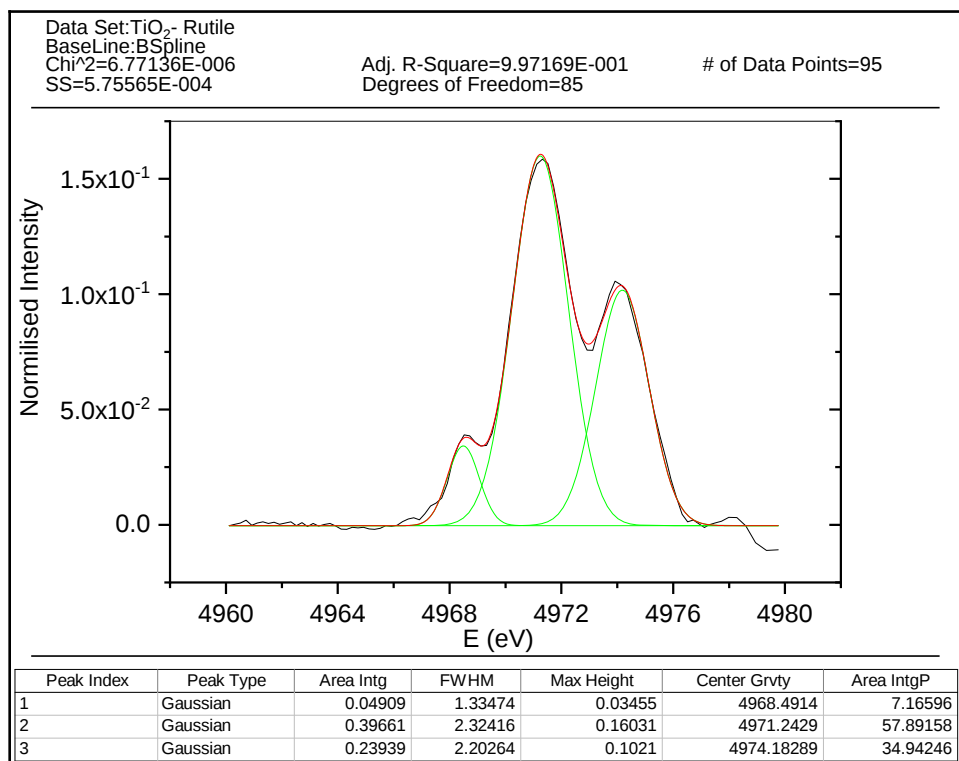


Figure S11: Gold particle size distribution of the tested catalyst before and after catalytic testing. Namely Fresh Au/TiO₂ (a), Used Au/TiO₂ (b), Fresh Au/SiO₂ (c), Used Au/SiO₂ (d), Fresh Au/Ti@SiO₂ (e), Used Au/Ti@SiO₂ (f), Fresh Au/Ti@SiO₂-200 (g), Used Au/Ti@SiO₂-200 (h), Fresh Au/Ti@SiO₂-900 (i), and Used Au/Ti@SiO₂-900 (j).

(a) Fresh TiO_2 Rutile



(b) Au/Ti@SiO_2

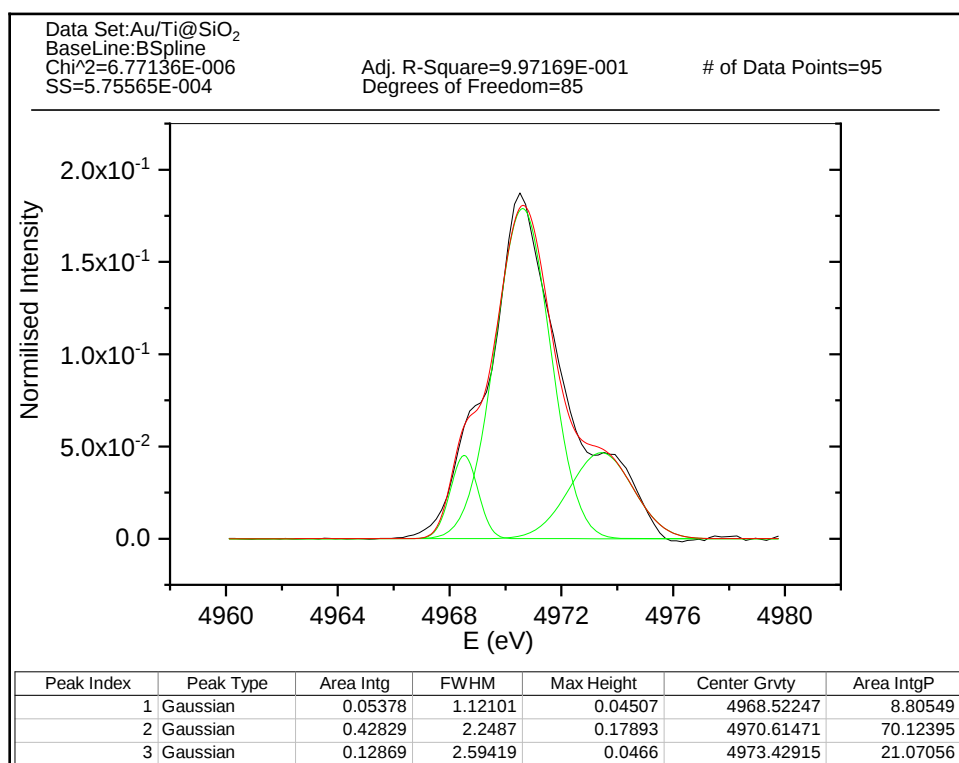


Figure S12: Peak analysis of the XAS pre-edge spectra of titania rutile (a) and Au/Ti@SiO_2 (b). The analysis was performed after subtraction of the edge jump, by Gaussian fit.

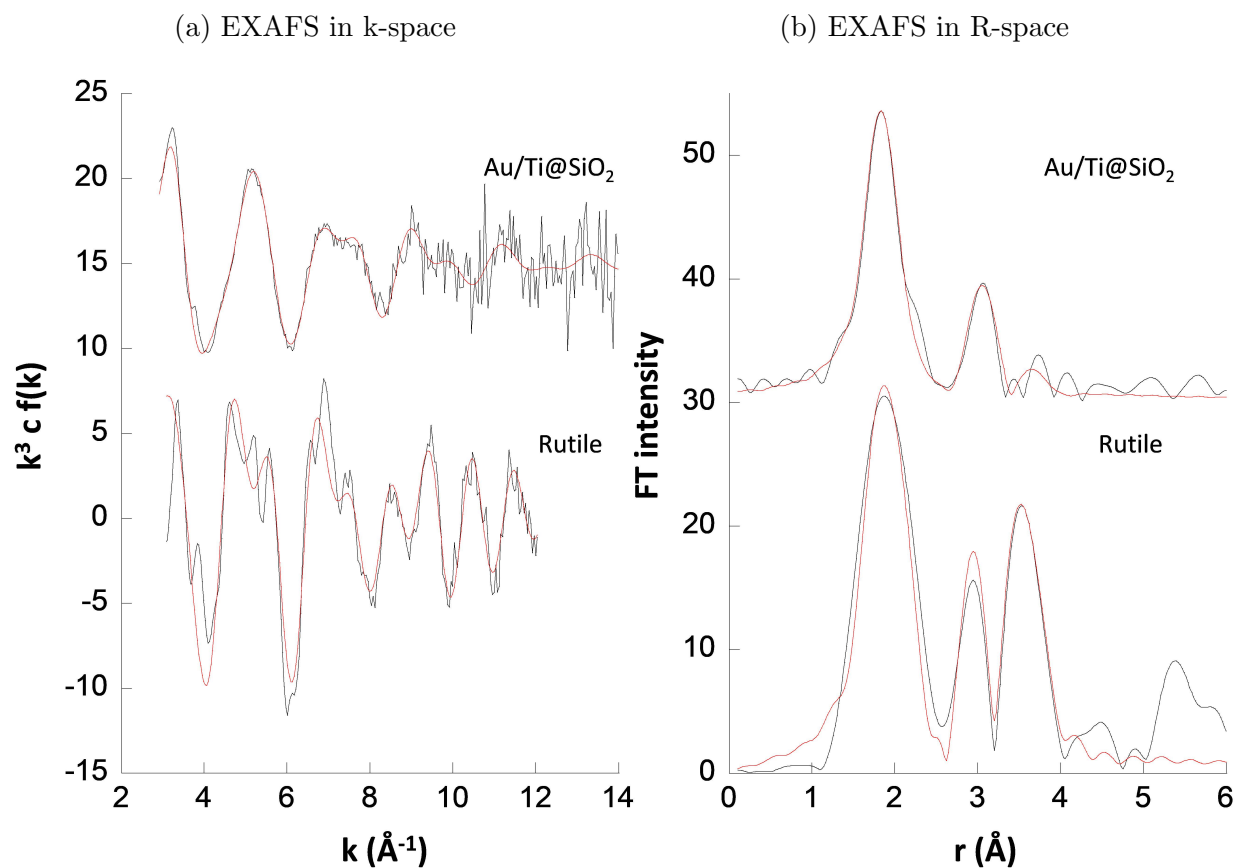


Figure S13: Ti K edge EXAFS, plotted in k-space (a) and R-space (b), of TiO_2 rutile and Au/TiO_2 (black) compared with fitted (red) spectra of Au/Ti@SiO_2 and TiO_2 rutile. Fitting parameters: $K_{\min} = 3$, $K_{\max} = 14$, $\text{AFAC} = 0.8$