Supporting Information

Temperature-driven evolution of Ceria-Zirconia supported AuPd and AuRu bimetallic catalysts under different atmospheres: Insights from IL-STEM studies

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Table S1. Energy-dispersive X-ray spectroscopy analysis of the atomic percentages of Au and Pd of AuPdCZ catalyst of different areas contrasted before versus after thermal treatments, R700 and O700. The set of IL-HAADF-STEM-XEDS maps are shown in Figure 2, 3 and S3 of supporting information.

AuPdCZ				**AuPdCZ-R700**			
Area	Normalized atomic content (%)		Au:Pd atomic ratio	Area	Normalized atomic content (%)		Au:Pd atomic ratio
	Au	Pd			Au	Pd	
1[a]	3.2	7.6	1:2.4	1 R700[a]	3.7	7.6	1:2.1
2	3.8	8.4	1:2.2	2 R700	1.8	8.3	1:4.6
3	3.8	7.7	1:2.0	3 R700	1.7	7.2	1:4.2
4	3.1	8.9	1:2.9	4 R700	1.6	8.7	1:5.4
5	2.7	5.5	1:2.0	5 R700	1.2	5.2	1:4.3
Average	3.3	7.6	1:2.3	Average	2.0	7.4	1:3.7
AuPdCZ				**AuPdCZ-O700**			
1[b]	2.5	4.9	1:2.0	1 O700[b]	0.5	5.0	1:10.0
2	3.2	5.4	1:1.7	2 O700	0.7	4.8	1:6.9
3	2.8	8.5	1:3.0	3 O700	1.3	6.7	1:5.2
4	3.3	8.6	1:2.6	4 O700	0.7	7.1	1:10.1
5	3.6	9.4	1:2.6	5 O700	0.7	6.6	1:9.4
Average	3.2	7.5	1:2.4	Average	0.8	6.0	1:7.7

(a) Quantitative results from XEDS maps 2c-d. (b) Quantitative results from XEDS maps 3c-d.

Table S2. Energy-dispersive X-ray spectroscopy analysis of the atomic percentages of Au and Ru of AuRuCZ catalyst of different areas contrasted before versus after sequentially R700-O700 treatments. The set of IL-HAADF-STEM-XEDS maps are shown in Figure 7 and S6.

	AuRuCZ			AuRuCZ-R700			AuRuCZ-O700		
Area	Atomic content (%)		Au:Ru ratio	Atomic content (%)		Au:Ru ratio	Atomic content (%)		Au:Ru ratio
	Au	Ru		Au	Ru		Au	Ru	
1[a]	0.3	2.4	1:8.0	0.4	2.2	1:5.5	0.4	1.7	1:4.2
2	0.4	1.5	1:3.8	0.5	1.9	1:3.8	0.3	0.9	1:3
3	1.6	1.7	1:1.1	1.1	1.9	1:1.7	1.2	0.9	1:0.8
4	0.4	1.8	1:4.5	0.4	2.3	1:5.8	0.7	1.0	1:2.1
5	1.4	3.2	1:2.3	1.3	3.1	1:2.4	1.9	1.6	1:0.8
Av	0.8	2.1	1:2.7	0.7	2.3	1:3.3	0.9	1.2	1:1.4

(a) Quantitative results from XEDS maps represented in Fig 6

Table S3. Chemical composition of the AuPdCZ catalysts before and after O700

Catalyst	Metal loading (wt %)[a]		Atomic ratio Au:X	Gold content (%) - balanced to X
	Au	Second metal		
AuPdCZ	2.4	1.6	1:1.2	44.8
AuPdCZ-O700	2.0	1.7	1:1.7	37.0

[a] Atomic ratio was calculated directly from ICP-AES analysis

Table S4. Energy-dispersive X-ray spectroscopy analysis of the atomic percentages of Au and Pd of AuPdCZ catalyst of different areas contrasted after R700 and after aging at room temperature. The set of IL-HAADF-STEM-XEDS maps are shown in Figure 6 and Fig S5 of supporting information.

AuPdCZ-R700				**AuPdCZ-R700-RT (30 months)**			
Area	Normalized atomic content (%)		Au:Pd atomic ratio	Area	Normalized atomic content (%)		Au:Pd atomic ratio
	Au	Pd			Au	Pd	
1	1.8	8.2	1:4.6	1	1.8	5.9	1:3.3
2	1.7	7.2	1:4.2	2	1.7	4.6	1:2.7
3	1.6	8.7	1:5.4	3	1.3	5.6	1:4.3
4	2.5	7.0	1:2.8	4	1.3	2.3	1:1.8
Average	1.9	7.8	1:2.3	Average	1.5	4.6	1:3.0

(a) Quantitative results from XEDS maps 6b (b) Quantitative results from XEDS maps 6c

Figure S1. Representative Identical Location HAADF-STEM images of gold catalysts at (a) original versus after R700; (b) original versus after O700. In the set of images after O700 only one Au particle marked by arrow was found.

Figure S2. HAADF –STEM images of AuCZ after O700. (a) Representative image of CZ support aggregate in the absence of Au nanoparticles; (b) agglomerated Au particle attached to CZ support, (c) isolated Au nanoparticle found in the grid membrane and (d) the corresponding XED spectrum. (e - h) examples of single Au particles observed into the grid membrane after O700.

Figure S3. Representative Identical Location HAADF-STEM -XEDS composition maps of AuPdCZ catalysts (a) before and after R700; (b) before and after O700. The maps are represented by signals extracted from Au-L (red), Pd-L (green), and Ce-L (blue).

Figure S4. Figure S4. HAADF –STEM images of AuPdCZ showing gold-rich particles found in the grid membrane along with the corresponding XEDS spectrum and the relative atomic gold content balanced Pd. Besides Au and Pd, the spectrum presents some signals unrelated to the sample, as for example, Cu peaks appear due to scattering caused by the copper security clip of the TEM grid. The spectrum at the top shows additionally Ca and Ni signals, which correspond to traces of contamination. The signals of these elements do not overlap with those of the two metals of interest. Therefore, the quantitative analysis of Au and Pd remains reliable.

Figure S5. Comparison of representative Identical Location HAADF-STEM -XEDS composition maps of AuPdCZ catalysts at three different stages: initial, after R700 and after 30-month of storage under air at room temperature. The maps are represented by signals extracted from Au-L (red), Pd-L (green), and Ce-L (blue).

Figure S6. Comparison of representative Identical Location HAADF-STEM -XEDS composition maps of AuRuCZ catalysts at three different stages: before, after R700 and after O700. The maps are represented by signals extracted from Au-L (red), Ru-L (green), and Ce-L (blue).

Figure S7. Representative Identical Location HAADF-STEM images of gold catalysts at (a) R700 and (b) after O700.

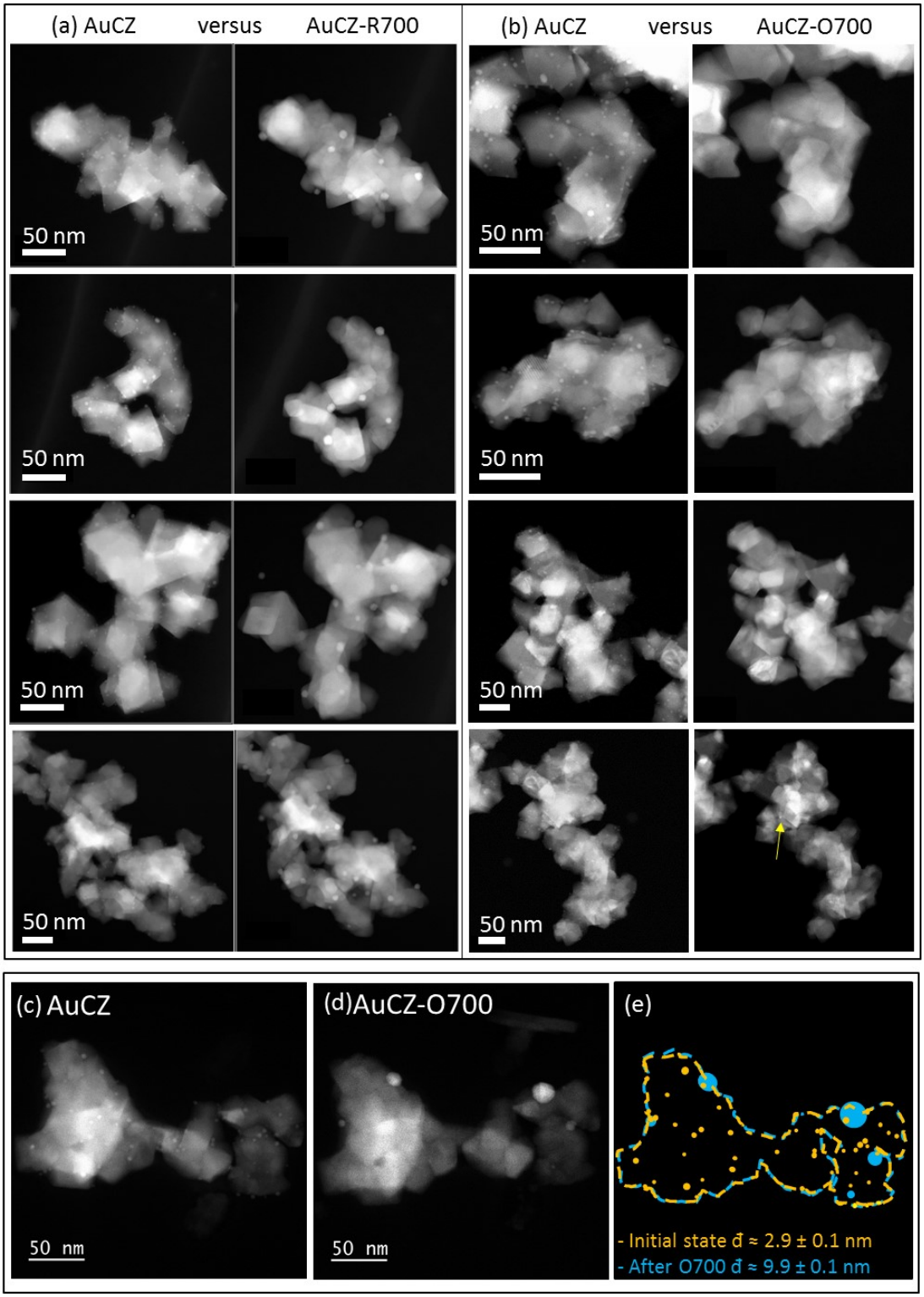

Figure S1. Representative Identical Location HAADF-STEM images of gold catalysts at (a) original versus after R700; (b) original versus after O700. In the set of images after O700 only one Au particle marked by arrow was found. (c) Identical Location area after O700 showing sign of Au particle growth

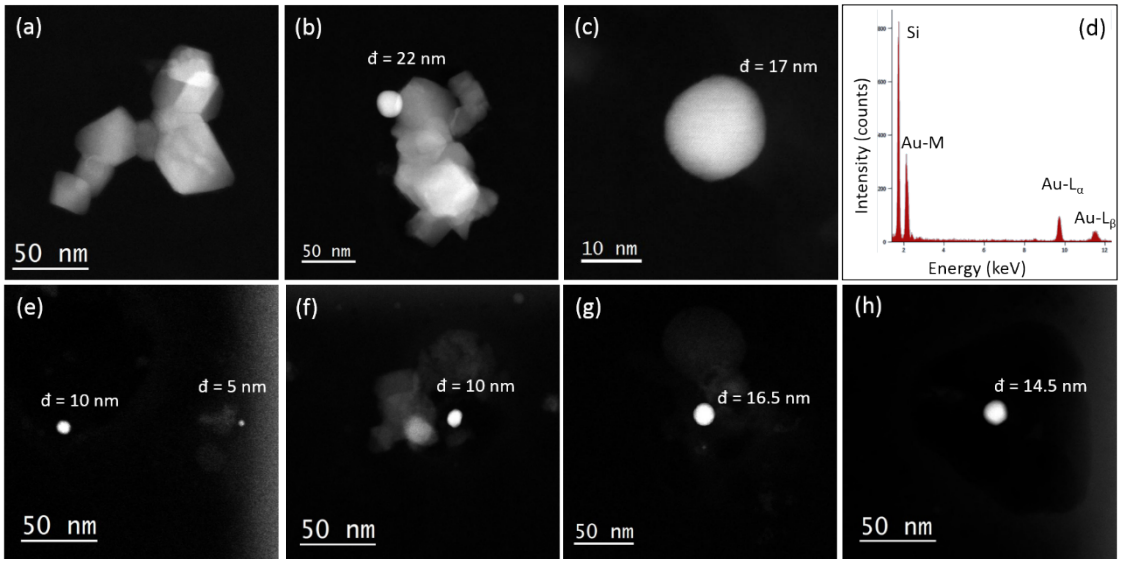

Figure S2 HAADF –STEM images of AuCZ after O700. (a) Representative image of CZ support aggregate in the absence of Au nanoparticles; (b) agglomerated Au particle attached to CZ support, (c) isolated Au nanoparticle found in the grid membrane and (d) the corresponding XED spectrum. (e - h) examples of single Au particles observed into the grid membrane after O700.

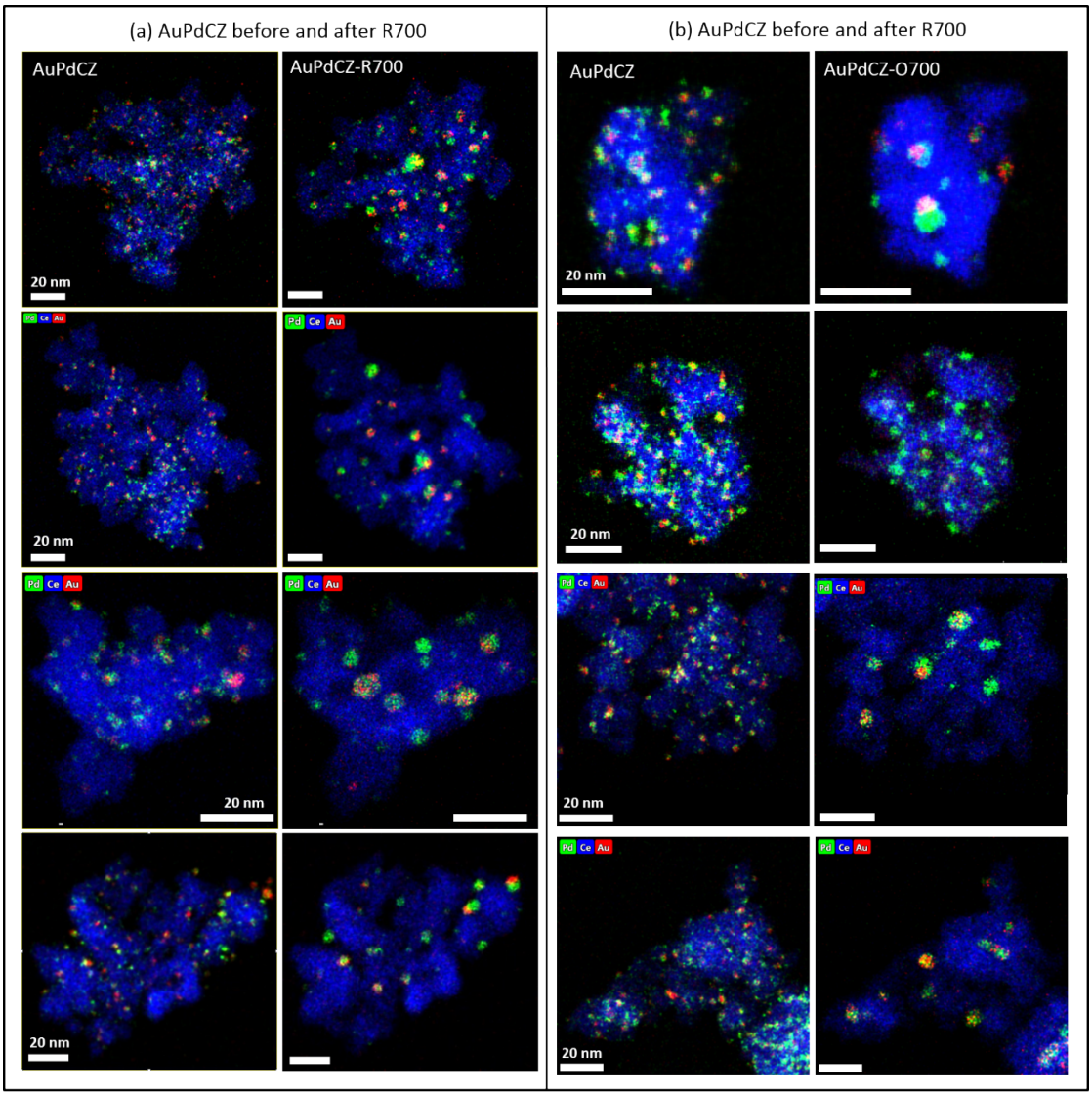

Figure S3 Representative Identical Location HAADF-STEM -XEDS composition maps of AuPdCZ catalysts (a) before and after R700; (b) before and after O700. The maps are represented by signals extracted from Au-L (red), Pd-L (green), and Ce-L (blue).

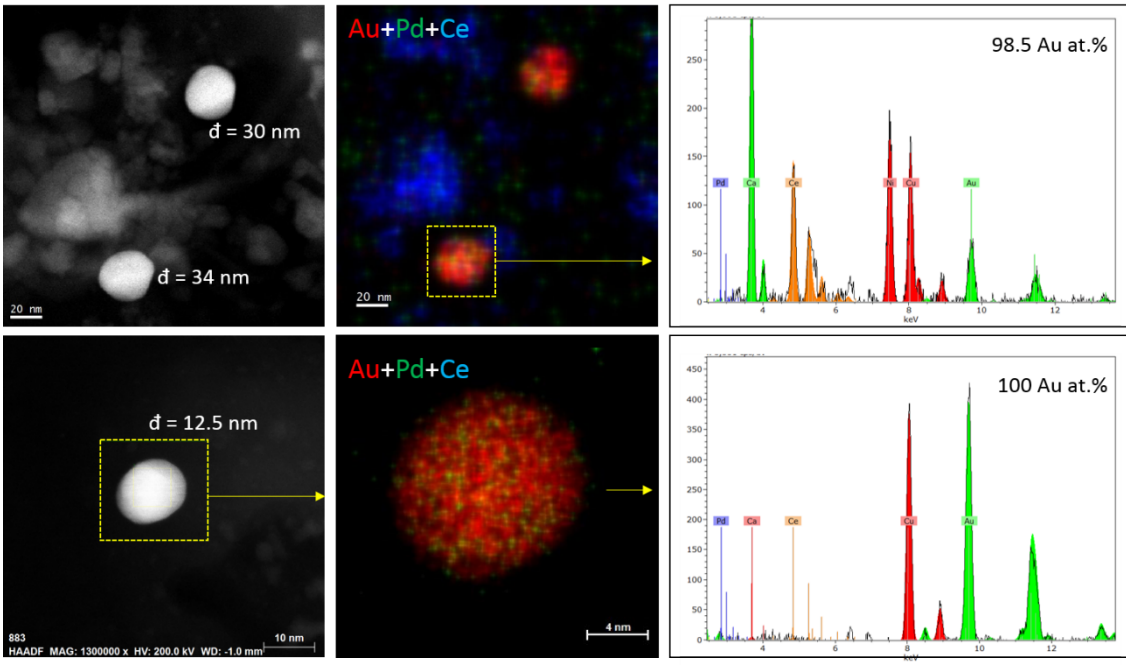

Figure S4. HAADF –STEM images of AuPdCZ showing gold-rich particles found in the grid membrane along with the corresponding XEDS spectrum and the relative atomic gold content balanced Pd. Besides Au and Pd, the spectra present some signals unrelated to the sample, as for example, Cu peaks appear due to scattering caused by the copper security clip of the TEM grid. The spectrum at the top shows additionally Ca and Ni signals, which correspond to traces of contamination. The signals of these elements do not overlap with those of the two metals of interest. Therefore, the quantitative analysis of Au and Pd remains reliable.

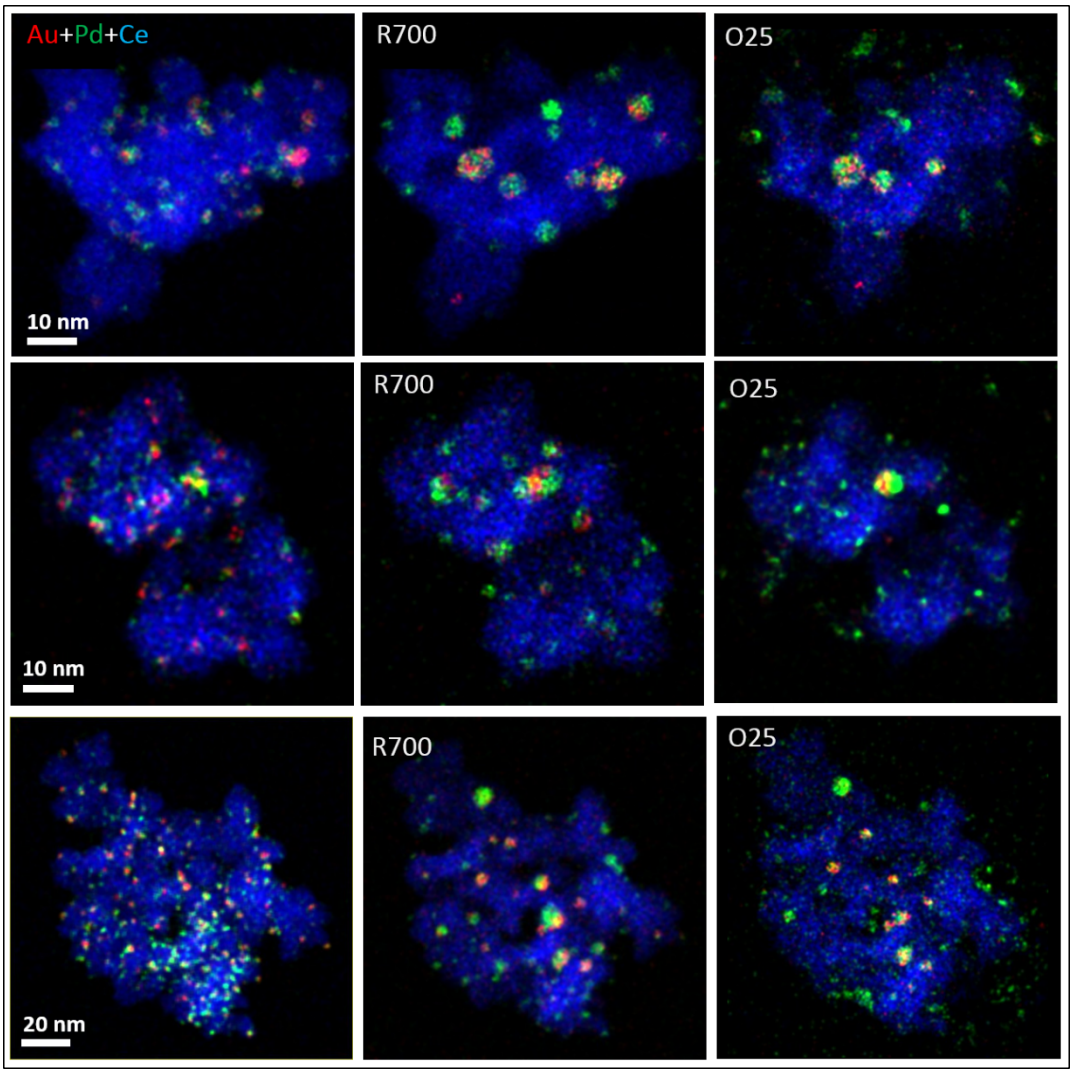

Figure S5. Comparison of representative Identical Location HAADF-STEM -XEDS composition maps of AuPdCZ catalysts at three different stages: initial, after R700 and after 30-month of storage under air at room temperature. The maps are represented by signals extracted from Au-L (red), Pd-L (green), and Ce-L (blue).

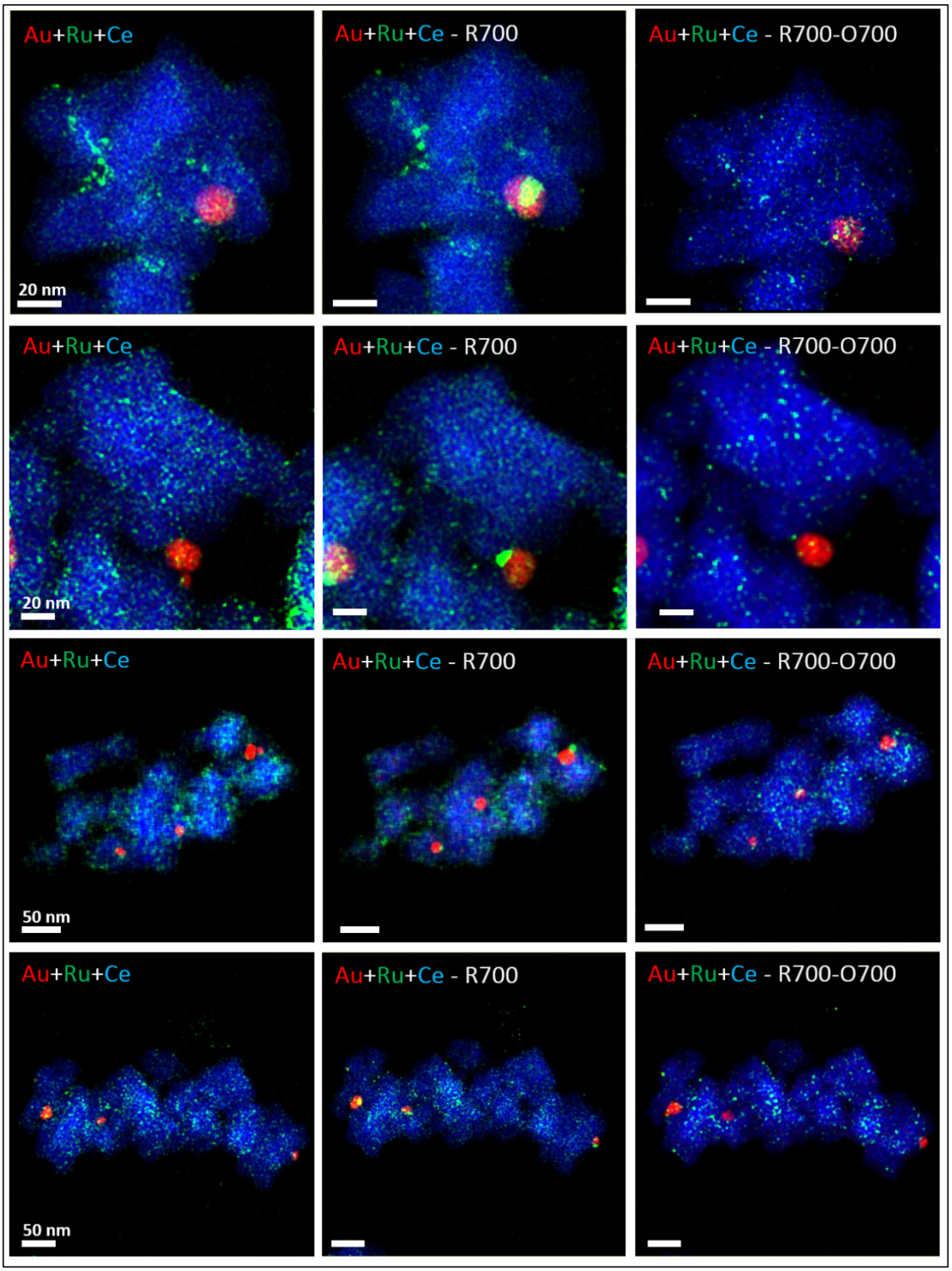

Figure S6. Comparison of representative Identical Location HAADF-STEM -XEDS composition maps of AuRuCZ catalysts at three different stages: before, after R700 and after O700. The maps are represented by signals extracted from Au-L (red), Ru-L (green), and Ce-L (blue).

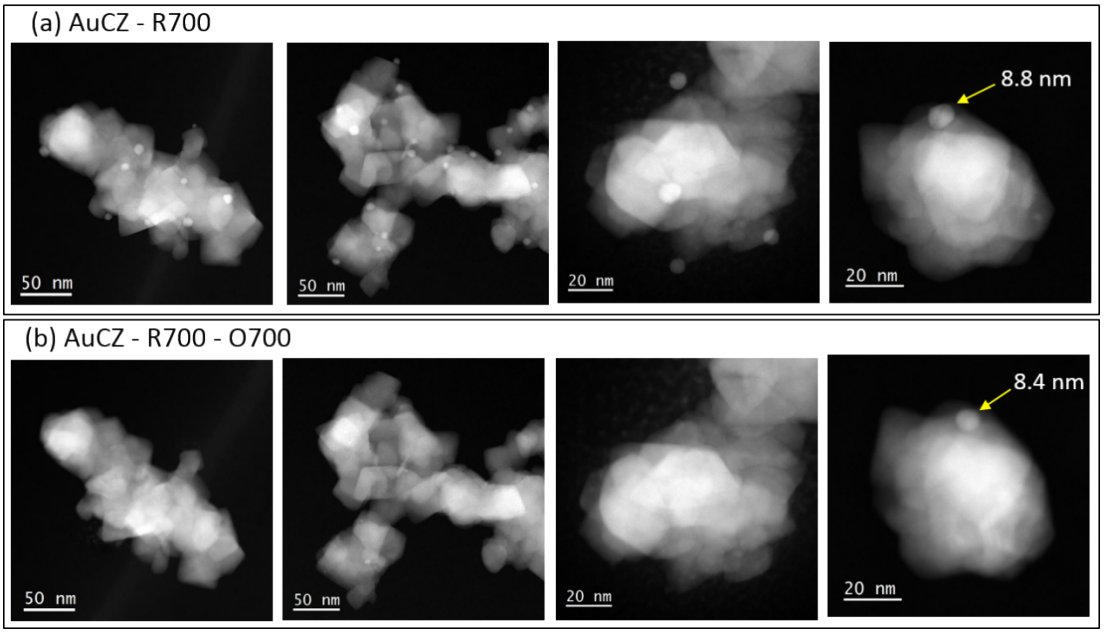

Figure S7. Representative Identical Location HAADF-STEM images of gold catalysts at (a) R700 and (b) after O700.