

Gold-based catalysts for complete formaldehyde oxidation: insights into the role of support composition

Lyuba Ilieva ¹, Dimitar Dimitrov ², Elitsa Kolentsova ², Anna Maria Venezia ³, Daniela Karashanova ⁴, Georgi Avdeev ⁵, Petya Petrova ¹, Razvan State ⁶ and Tatyana Tabakova ^{1,*}

¹Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria;

²Department of Chemistry and Phytopharmacy, Agricultural University, 4000 Plovdiv, Bulgaria

³Istituto per lo Studio dei Materiali Nanostrutturati, CNR, 90146, Palermo, Italy

⁴Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

⁵Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria;

⁶“Ilie Murgulescu” Institute of Physical Chemistry, Romanian Academy, 060021, Bucharest, Romania

*Correspondence: tabakova@ic.bas.bg

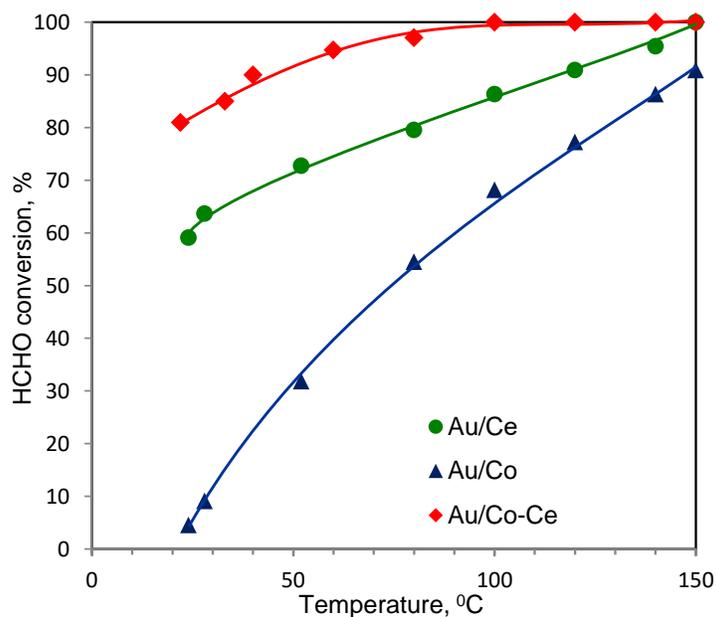


Figure S1. Comparison of HCHO conversion over Au/Ce, Au/Co, and Au/Co-Ce samples.

Table S1. HCHO conversion over the most active sample developed in this study compared with HCHO conversion over Co₃O₄-CeO₂-supported Au-based catalysts reported in the literature.

Catalyst	Au ¹ amount (wt.%)	Preparation method ²	WHSV (mL h ⁻¹ g ⁻¹)	[HCHO] _{inlet} concentration	T (°C)	HCHO conversion (%)	Ref. ³
Au/35%Co ₃ O ₄ - 5%CeO ₂ /50%Al ₂ O ₃ -b	3	mechanochemical mixing	20,000	120 ppm	25 40	95 100	This study
Au/2DCo ₃ O ₄ -CeO ₂ (Co/Ce=7:3)	1	nanocasting using 2D SBA-15 as hard template	24,000	200 ppm	25	50	[5]
Au/3DCeO ₂ -Co ₃ O ₄ (Co/Ce=1:2.5)	1	precursor thermal decomposition-assisted colloidal crystal templating method	15,000	8 ppm	25 100	<10 100	[25]
Au/3DCeO ₂ -Co ₃ O ₄ (Co/Ce=1:2.5)	2	precursor thermal decomposition-assisted colloidal crystal templating method	15,000	8 ppm	25 70	35 100	[25]
Au/3DCeO ₂ -Co ₃ O ₄ (Co/Ce=1:2.5)	3	precursor thermal decomposition-assisted colloidal crystal templating method	15,000	8 ppm	25 39	61 100	[25]
Au/3DCeO ₂ -Co ₃ O ₄ (Co/Ce=1:2.5)	4	precursor thermal decomposition-assisted colloidal crystal templating method	15,000	8 ppm	25 60	50 100	[25]
Au-Ce ₃ Co/GA (Co/Ce=1:3) GA - graphene aerogel	1	one-step method using SBA-15- OH as a hard template, mixing with GO	20,000	50 ppm	30 135	15 100	[27]
Au-Ce ₃ Co/GA (Co/Ce=1:3)	2	one-step method using SBA-15- OH as a hard template, mixing with GO	20,000	50 ppm	30 105	30 100	[27]
Au-Ce ₃ Co/GA (Co/Ce=1:3)	3	one-step method using SBA-15- OH as a hard template, mixing with GO	20,000	50 ppm	30 60	55 100	[27]
Au-Ce ₃ Co/GA (Co/Ce=1:3)	4	one-step method using SBA-15- OH as a hard template, mixing with GO	20,000	50 ppm	30 75	50 100	[27]
Au/CeCo ₉ (Co mol.%=9)	1.5	hydrothermal method	30,000	100 ppmv	30 100	80 100	[28]
Au/CeCo ₉ (Co mol.%=9)	3	hydrothermal method	30,000	100 ppmv	30 100	>90 100	[28]

¹ Gold content presented as nominal wt.%

² Method of preparation of Co₃O₄-CeO₂

³ Reference numbers refer to citations in the paper.

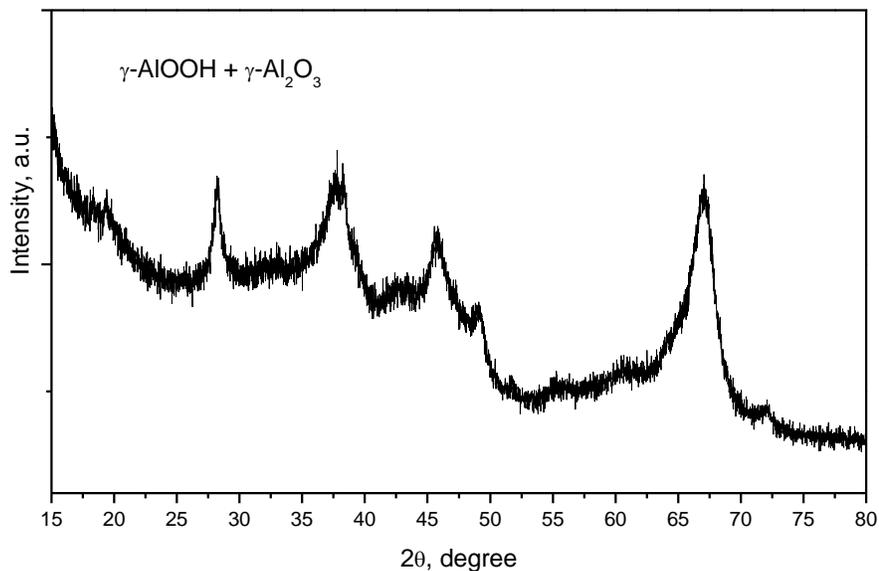
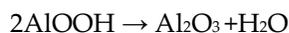


Figure S2. XRD pattern of $\gamma\text{-Al}_2\text{O}_3$ used for preparation of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Al}_2\text{O}_3$ support.

XRD analysis showed a mixed phase of $\gamma\text{-Al}_2\text{O}_3$ (ICSD-PDF 01-079-1558) and boehmite $\gamma\text{-AlOOH}$ (ICSD-PDF 01-073-6509). For correct determination of $\gamma\text{-AlOOH}$ amount a combined DTA/TG analysis was performed. The amount of absorbed water and associated OH groups in the structure of boehmite was evaluated. The first step, ambient temperature to endothermic peak at 122 °C, was due to dehydration of $\gamma\text{-AlOOH}$ and finished at about 260 °C. The next endothermic effect was observed at about 270 °C. It was ascribed to decomposition of by-products of the synthesis reaction [B. Sathyaseelan, I. Baskaran, K. Sivakumar, Phase Transition Behavior of Nanocrystalline Al_2O_3 Powders, *Soft Nanoscience Letters*, 2013, 3, 69-74]. Total weight loss at about 400 °C was nearly 13 %. The final step above 400–450 °C ended after 925 °C. It was related to the formation of $\gamma\text{-Al}_2\text{O}_3$ with a weight loss of about 5 %. According to Földvári calculated amount of $\gamma\text{-AlOOH}$ was 33.33 % [M. Földvári, Handbook of thermogravimetric system of minerals and its use in geological practice, Budapest, vol. 213, 2011, Published by the Geological Institute of Hungary].



$$119.98 \rightarrow 101.96 + 18 \quad f = 119.98 / 18 = 6.65 \text{ (stoichiometric factor)}$$

$$6.65 \times 5 (\%) = 33.33 \%$$

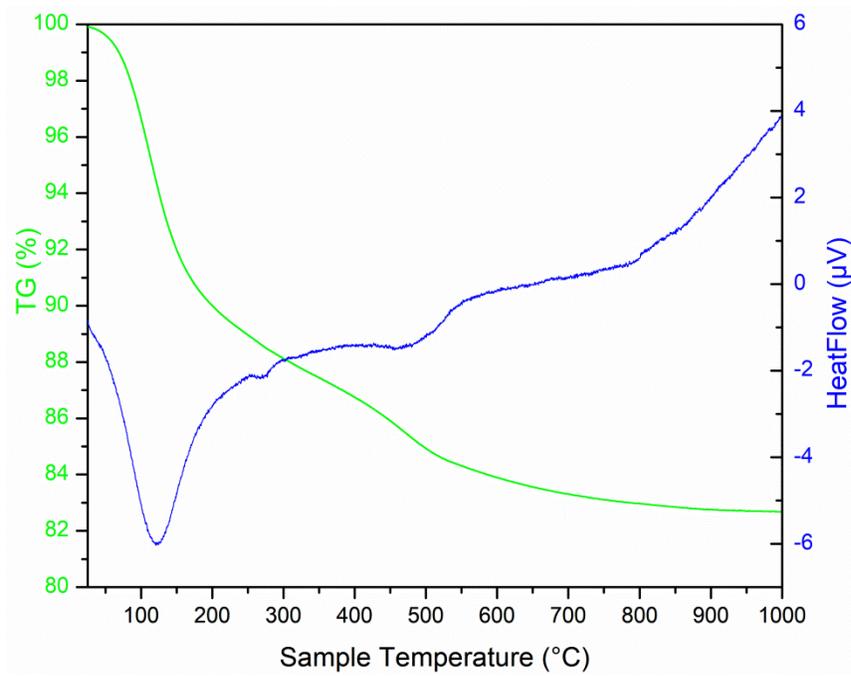


Figure S3. DTA/TG analysis of γ -Al₂O₃.