SUPPLEMENTARY INFORMATION

The structure and catalytic properties of Rh-doped CeO₂ catalysts

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Gas analysis procedure for TPR CO+O₂

The only product of CO oxidation is CO_2 . For an analysis of reaction gases (CO, CO_2 and O_2) the quadrupole mass spectrometer (Stanford Research Systems QMS200 gas analyzer) was used. The

 $P_i = \sum_{j=1}^m A_{ij}C_j$, signal from ions with a mass *i* was recorded as with mass *i*, the sensitivity coefficient for ion with mass *i* for a compound *j*, C_j – concentration of the *j* compound. When A_{ij} matrix elements are known, the concentrations of gas components are determined by a minimization of the sum of squared differences between measured and calculated

partial pressures $\sum_{i=1}^{n} (y_i - p_i)^2 \rightarrow \min$, where pi is a calculated signal for ions with mass i, yi – the measured signal for ions with mass i.

During the experiment the partial pressure for masses 12, 20, 28, 29, 32, 44 were detected, which then were transformed into the concentrations of CO, O_2 and CO_2 according to prior calibrations. Inert gas neon (that was present in all experiments as inert reference gas) was used to normalize the intensity of the registrated masses: $I^{rel}_{X} = I_X / I_{40}$ is the measured intensity of the m/z = X peak in the QMS normalized by the m/z = 20 intensity of Ne.

Name	Rh, % _{wt.}	Tcalc, °C	S_{BET} , m/g ²	a, Å	D, nm	e ₀
1Rh-CeO ₂	1.1	450	145	5.412(1)	7.9(2)	0.21(1)
		600	130	5.411(1)	8.0(2)	0.17(1)
		800	48	5.409(1)	14.8(3)	0.047(5)
		900	22	5.411(1)	24.3(5)	0.0095(3)
		1000	9	5.4122(1)	49(1)	0.004(1)
5Rh-CeO ₂	5.5	450	138	5.406(1)	8.7(3)	0.28(1)
		600	114	5.405(1)	8.3(3)	0.25(1)
		800	61	5.407(1)	11.1(3)	0.23(1)
		900	37	5.411(1)	13.9(4)	0.162(7)

Table S1. Characterization of the synthesized Rh-CeO₂ samples with different Rh content (1-17% wt) and calcination temperature $450 \div 1000$ °C

		1000	9	5.414(1)	45.5(8)	0.007(1)
8Rh-CeO ₂	8.13	450	126	5.403(1)	10.2(3)	0.29(1)
		800	46	5.406(1)	11.7(3)	0.247(9)
		1000	8.2	5.4139(1)	42.7(7)	0.014(2)
		450	113	5.401(1)	10.0(3)	0.25(1)
13Rh-CeO ₂	13.3	800	36	5.408(1)	12.5(4)	0.188(8)
		1000	5.5	5.4135(2)	40.6(8)	0.012(2)
		450	92	5.403(1)	7.1(4)	0.17(2)
17Rh-CeO ₂	17.3	800	27	5.409(2)	10.1(3)	0.12(1)
		1000	4	5.414(1)	40.7(9)	0.010(2)



Fig. S1. XRD patterns for the 1Rh-CeO₂ (a), 5Rh-CeO₂ (b), 13Rh-CeO₂(c) and 17Rh-CeO₂ (d) samples calcined at different temperatures.



Fig. S2. Calculated, experimental and difference curves for the 17Rh-CeO₂-450 sample after introduction of the additional diffuse scattering (diffuse peak at $2\theta = 31^{\circ}$) from the amorphous phase to the Rietveld calculation. R_{wp} =5.1



Fig. S3. The changes in the Rh3d spectra for the 1-Rh-CeO2-450 sample in the course of the XPS signal acquisition (1) 1 scan, (2) 30 scans, (3) 100 scans





For sample with low Rh content (1wt.%) the accumulation of Rh3d signal required a considerable amount of time and, consequently, a long-term exposure to X-ray radiation, which in turn caused the reduction of rhodium species on the surface. The initial spectrum of Rh3d might be approximated with only one doublet (curves (1)) related to the Rh³⁺ species. Under the exposure of X-ray radiation, the additional component related to the reduced rhodium species appears in the Rh3d spectrum and its intensity might reach up to 33 % (curves (3)).

Table S2. The values of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied samples with different statements of binding energy for the $Rh3d_{5/2}$ line for all the studied statements of binding energy for the $Rh3d_{5/2}$ line for all the studied statements of binding e	rent
rhodium content calcined at T=450-1000°C	

Tcalc, °C	1.1%	5.5%	8.13%	13.3%	17.3%
450	309.4	309.2	309.1	309.1	309.1
800	309.3	309.2	309.0	309.0	308.8
1000	309.0	309.0	308.9	308.7	308.7



Fig. S5. The enlarged PDF peak area showing the shift of the interatomic distances of Rh-doped CeO_2 catalysts in comparison to pristine CeO_2