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Effect of Ruthenium Addition to Palladium-Rhodium Nanoalloys on Their Catalytic Performance in CO Oxidation

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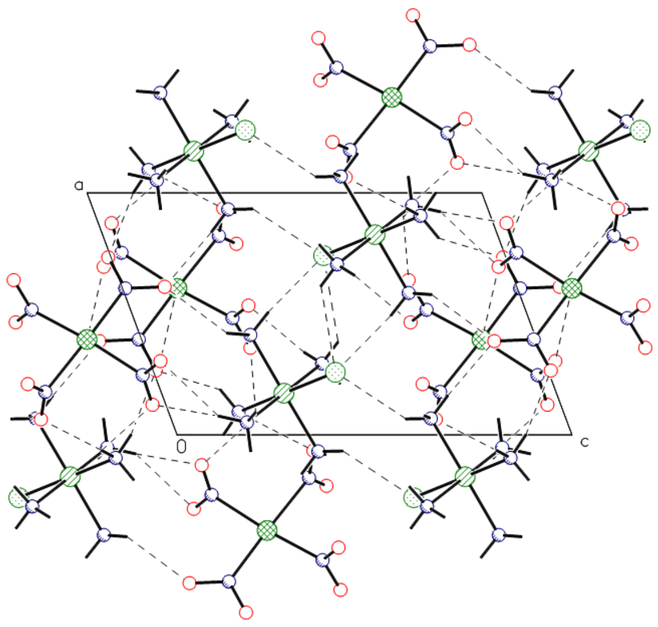
Three-way catalysts used for the purification of automotive exhaust gases from CO, unburnt hydrocarbons, and nitrogen oxides contain platinum group metals (Pt, Pd, and Rh) as active components. Thermal decomposition of the double complex salts (DCS) deposited on the support allows these metals to be obtained in an alloy (solid solution) state. The partial replacement of rhodium with the third metal additionally enhances the properties and reduces the cost of the catalytic composition. In the present work, alumina-supported trimetallic catalysts containing Rh, Ru and Pd in their composition were synthesized and studied in comparison with bimetallic Pd-Rh/Al_2O_3 reference sample.

Synthesis of DCS and their solid solutions

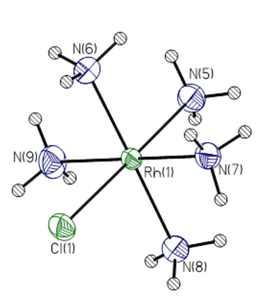
$$x[Rh(NH_3)_5Cl]Cl_2 + 1\text{-}x[Ru(NH_3)_5Cl]Cl_2 + K_2[Pd(NO_2)_4] \rightarrow [Rh(NH_3)_5Cl]_x[Ru(NH_3)_5Cl]_{1-x}[Pd(NO_2)_4]\downarrow + 2KCl$$

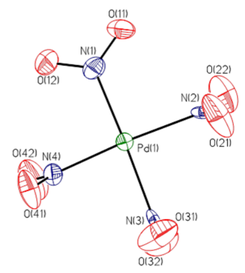
C ($[M(NH_3)_5Cl]Cl_2$) = 0,01-0,05 M, *C* ($K_2[Pd(NO_2)_4]$) = 0,07-0,1 M, x = 0÷1, T = 20°C. Yields: 70-75%



$[Rh(NH_3)_5Cl][Pd(NO_2)_4]$

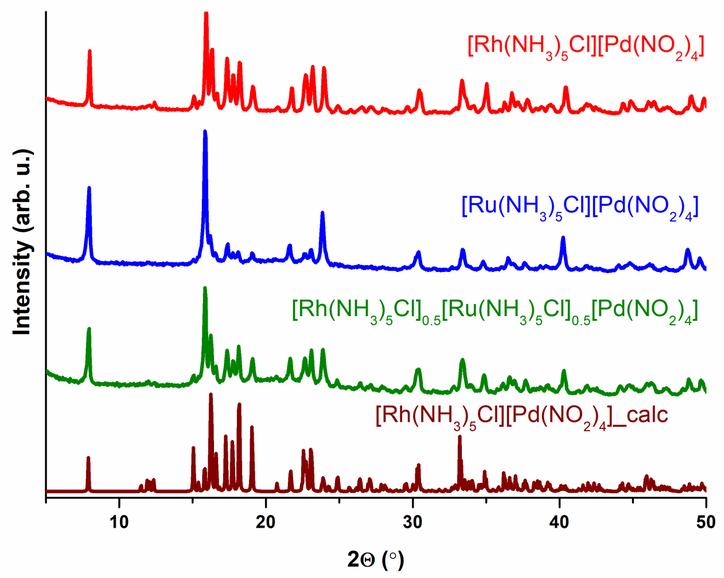
Space group *P-1, Z=2, V*= 698,67(6)Å^3
a **= 7,8724(3), *b* = 7,9777(4), *c* = 12,1530(6)Å,**
α **= 100,572(2)°, *β* = 108,6330(10)°, *γ* = 96,5410(10)°**





	ν (NH$_3$)	σ_a (HNH)	ν$_s$ (NO$_2$)	σ_a (HNH)	σ_s (HNH)	δ (ONO)
$[Rh(NH_3)_5Cl][Pd(NO_2)_4]$	3296 3205	1624	1394	1334	1272	828
$[Ru(NH_3)_5Cl][Pd(NO_2)_4]$	3309 3191	1622	1392	1334	1273	828
$[Ru_{0.5}Rh_{0.5}(NH_3)_5Cl][Pd(NO_2)_4]$	3300 3190	1624	1392	1334	1271	828

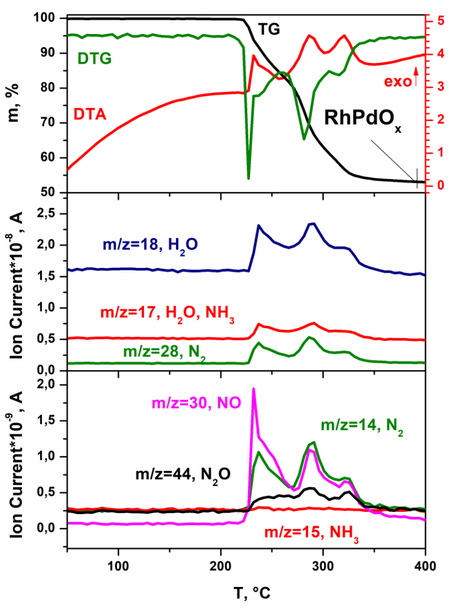
Vibrational Frequencies (cm–1) of Main IR Bands



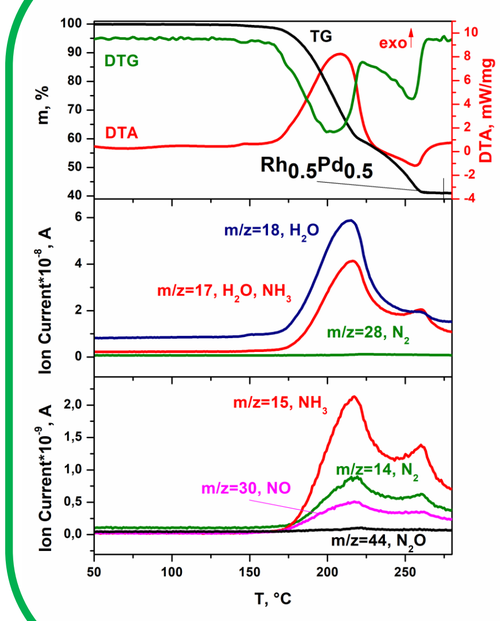
XRD data

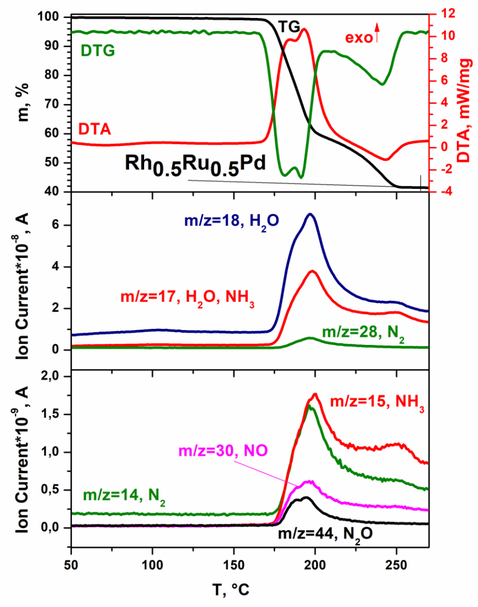
Thermal properties

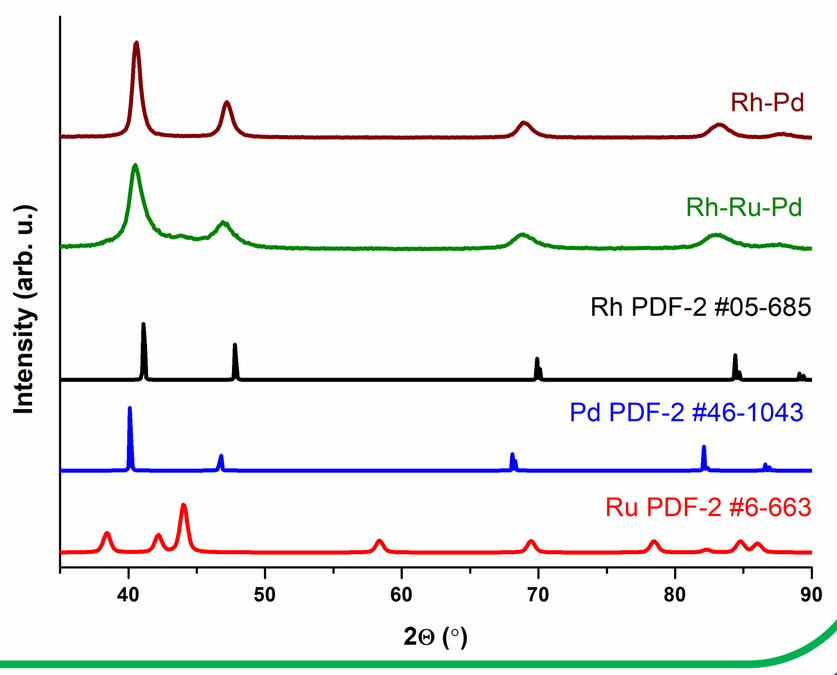
in a synthetic air atmosphere



in a hydrogen atmosphere







Catalytic tests

γ-Al_2O_3

↓

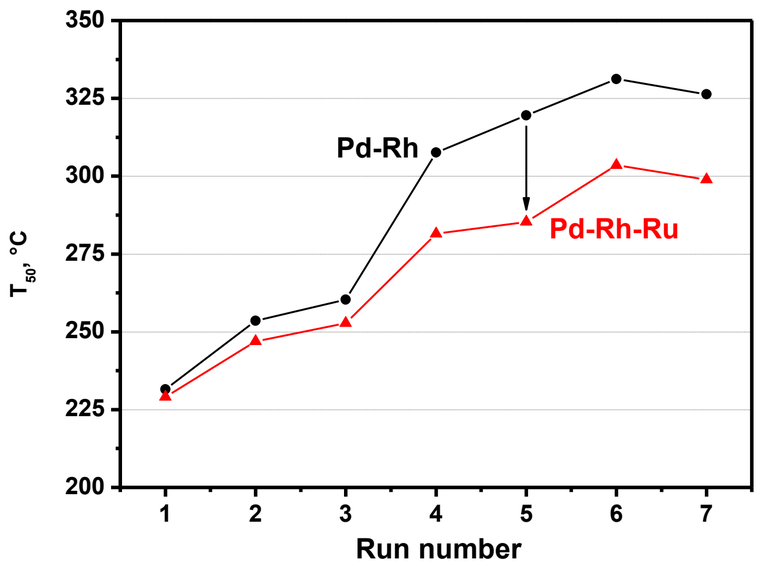
Impregnation with DCS solution
$[Rh(NH_3)_5Cl]_x[Ru(NH_3)_5Cl]_{1-x}[Pd(NO_2)_4]$

↓

$Rh(NH_3)_5Cl]_x[Ru(NH_3)_5Cl]_{1-x}[Pd(NO_2)_4]/\gamma$-Al2O3

↓ 300 °C, H_2, 1 h
or 550 °C, Air, 1 h

$Rh_xRu_{1-x}Pd/\gamma$-Al_2O_3
(ΣM=0.2 %)



The activity and stability of the catalyst compositions obtained were examined in CO oxidation reaction carried out under prompt thermal aging conditions. The addition of ruthenium only slightly improves the initial activity of the catalytic system but significantly increases its thermal stability.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation, No. 121031700315-2.