Effect of CeO_2 reductive pretreatment on the formation of bimetallic particles in Ag-doped Pt/CeO_2 catalysts for 4-nitrophenol reduction

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INTRODUCTION

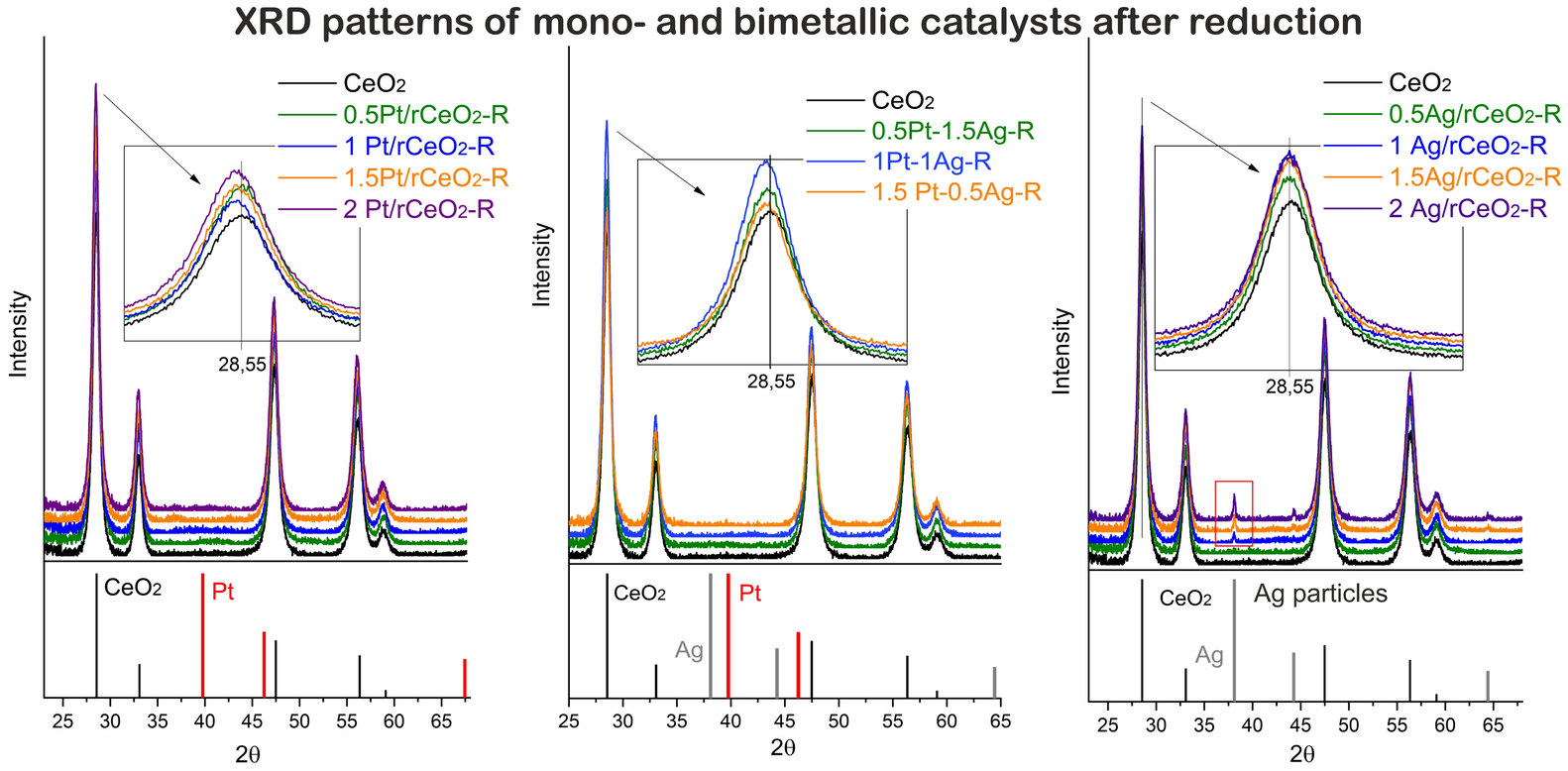
It is known that bimetallic nanoparticles feature unique properties different from those of the corresponding single-metal materials. These properties are assumed to result from the interaction of the metals and also depends on the preparation conditions and support used. The Pt-based catalysts are used in a wide range of oxidative and reductive reactions . The addition of the second metal to the supported Pt catalysts results in an increase of the selectivity towards the target products in the reduction reactions and a decrease of the loading of expensive platinum. High catalytic activity of these catalysts can be achieved due to the synergistic effect of the metals. One of the approaches towards the formation of the bimetallic particles is the preparation of catalyst based on the prereduced CeO_2. The use of the support reductive pretreatment leads to the formation of a large number of surface Ce(III) sites in the CeO_2 structure that react with the precursor of the active components during the impregnation step with high metal–support interaction and the formation of the metal/CeO_2 interface.

The present work is focused on the metal-support interaction and interaction of Pt and Ag in the ceria-supported Pt-Ag bimetallic catalysts and their catalytic activity in p-nitrophenol reduction with $NaBH_4$.

SAMPLE PREPARATION

Bimetallic catalysts were prepared by sequential impregnation. First, the prereduced CeO_2 was impregnated with the H_2PtCl_6 solution. Prior to the addition of the second component, the catalyst was dried at 120 °C and reduced again. Then the catalysts were impregnated with the $AgNO_3$ solution. The total content of the metals in the (n-x)PtxAg/CeO_2, (n) was 2 wt%, and x was 0.5, 1.0 or 1.5 wt%. Then all samples were dried in air at 120 °C and reduced in 10%H_2/Ar flow at 300 °C.

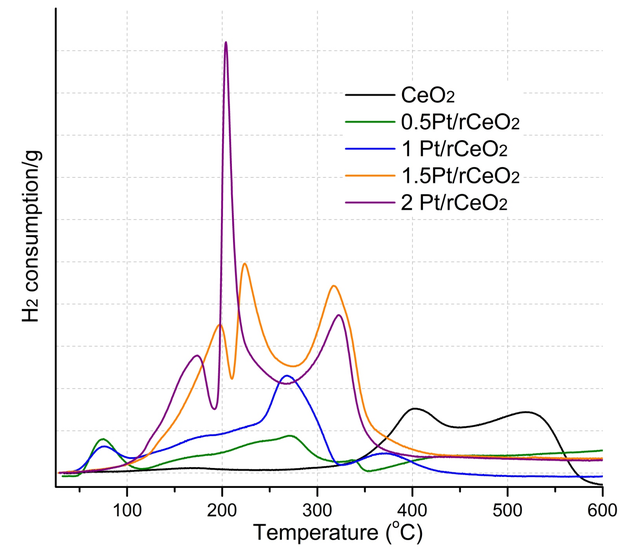
XRD patterns of mono- and bimetallic catalysts after reduction



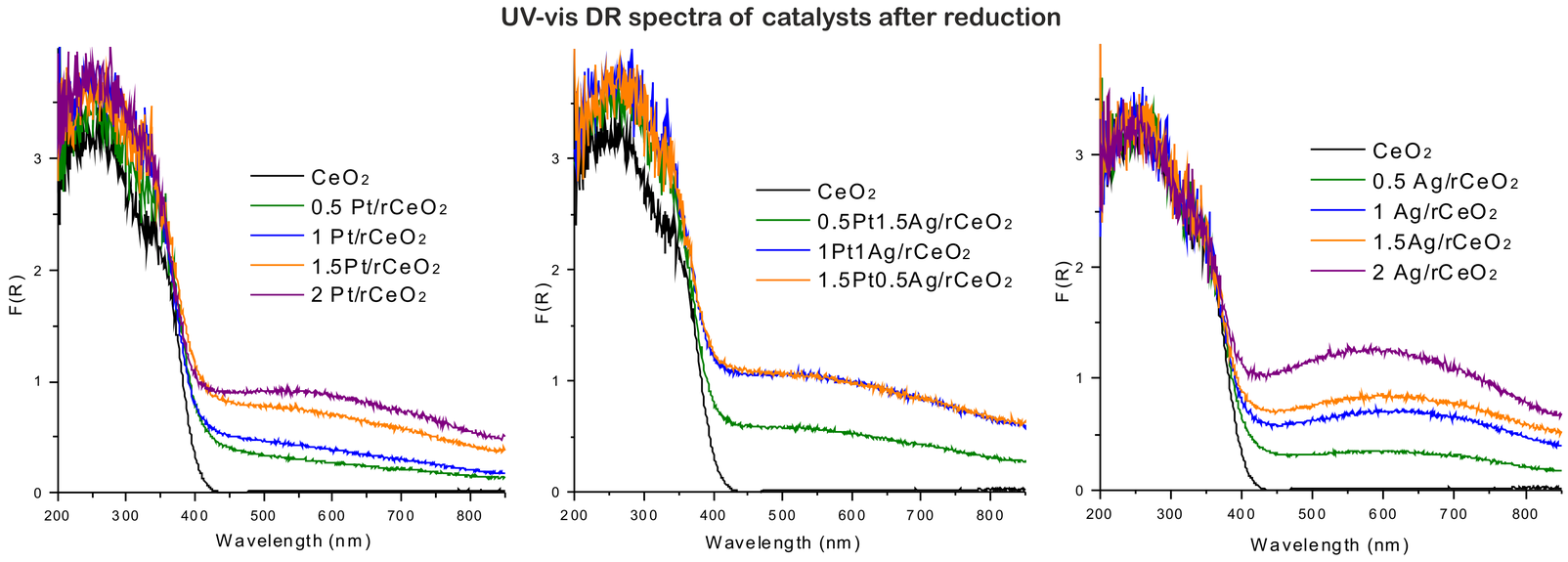
Hydrogen consumption of samples obtained

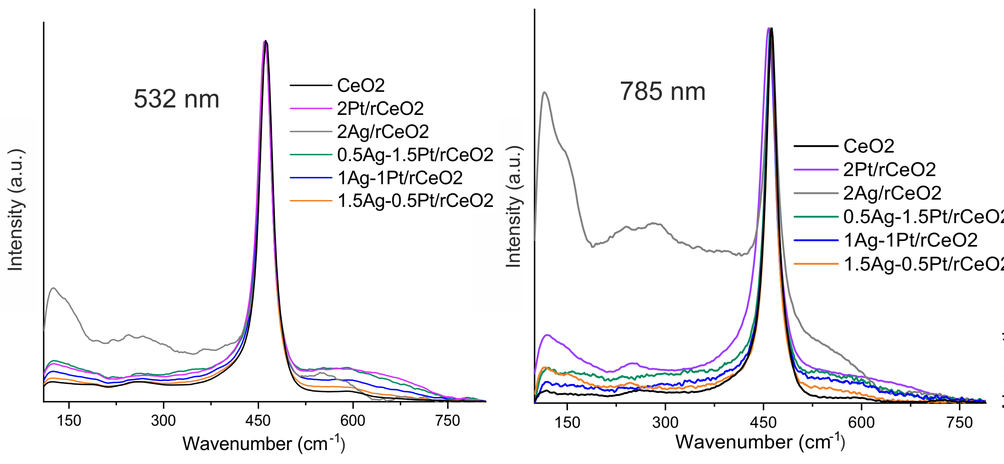
Sample	n(H_2), mmol/g		
	experimental	$Pt^{4+} \rightarrow Pt^0$	$Ag^+ \rightarrow Ag^0$
CeO_2	0.397	-	-
0.5 Pt/rCeO_2	0.214	0.051	-
1 Pt/rCeO_2	0.324	0.103	-
1.5 Pt/rCeO_2	0.822	0.154	-
2 Pt/rCeO_2	0.806	0.205	-
0.5 Ag/rCeO_2	0.392	-	0.023
1 Ag/rCeO_2	0.456	-	0.046
1.5 Ag/rCeO_2	0.502	-	0.069
2 Ag/rCeO_2	0.560	-	0.093
0.5Pt1.5Ag/rCeO_2	0.205	0.051	0.023
1Pt1Ag/rCeO_2	0.109	0.103	0.046
1.5Pt0.5Ag/rCeO_2	0.083	0.154	0.069

H_2-TPR profiles of catalysts dried at 120 °C



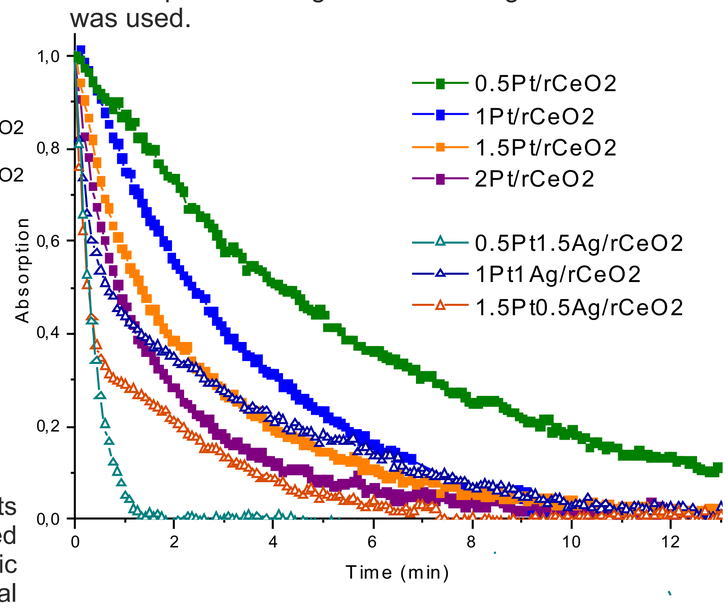
UV-vis DR spectra of catalysts after reduction





Raman spectra (532 and 785 nm) of reduced catalyst

The catalytic activity was tested in the 4-nitrophenol hydrogenation with $NaBH_4$ at 19 °C. To control the consumption of reagent a wavelength of 400 nm was used.



Summary

In the present work the series of ceria-supported monometallic (Pt or Ag) catalysts were prepared by wetness impregnation. The consecutive impregnation of the reduced support firstly with H_2PtCl_6 and then with $AgNO_3$ was used to synthesize the bimetallic Pt-Ag catalysts. The catalysts were characterized by a complex of physical-chemical methods, including lowtemperature N_2 adsorption-desorption, XRD, Raman and UV-vis DR spectrometries as well as temperature-programmed reduction in hydrogen. The catalytic activity was tested in 4-nitrophenol hydrogenation with $NaBH_4$.

The conditions of support treatment of bimetallic catalysts significantly affected the catalyst performance. In particular, the bimetallic 2-xPtxAg/CeO_2 samples showed higher catalytic activity as compared to monometallic catalysts. The reduction of the support allowed forming the PtAg species that improved the redox properties and catalytic characteristics. The Ag introduction facilitated the reduction of Pt catalysts and enhanced their reactivity in the 4-nitrophenol hydrogenation with $NaBH_4$. Moreover, Pt in bimetallic catalysts, in turn, promotes an increase of the dispersion of silver.

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