



Tuning the Activity and Selectivity of Pt/TiO₂ Ammonia Slip Catalysts by Surface Modification

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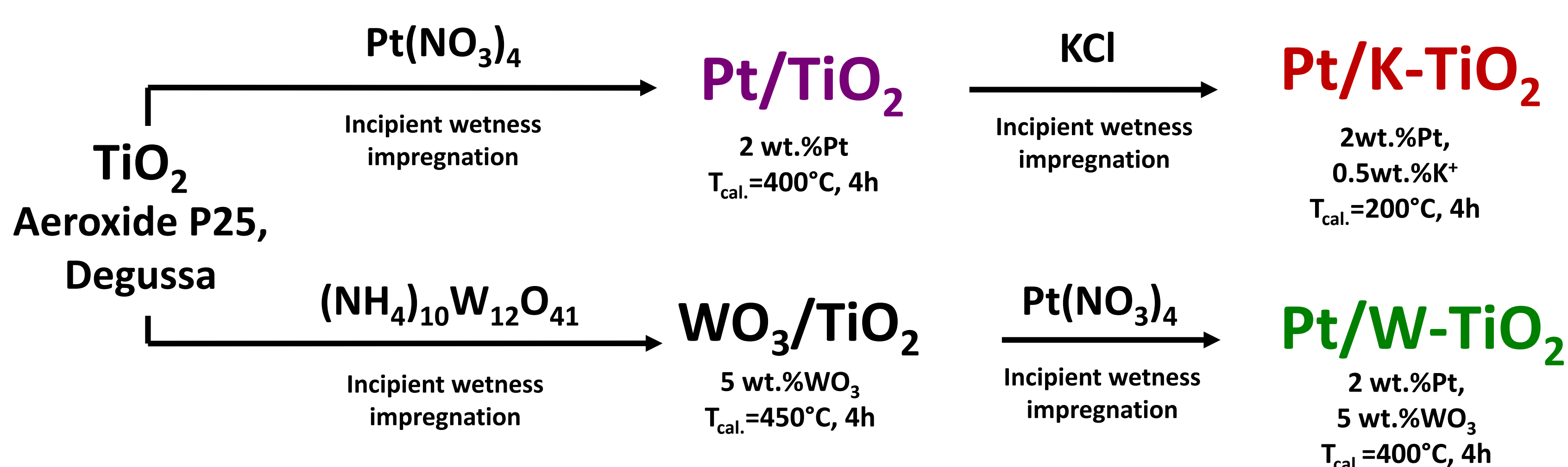
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Scope

Ammonia is an important substance for nitric acid and fertilizer production, petroleum refining, etc. It is also used for selective catalytic reduction (SCR) of NO_x from automotive exhaust. During operation of the SCR system, the excess of ammonia is dosed, resulting in its inevitable emission into the environment. Thus, the so-called ammonia slip catalysts (ASCs) oxidizing ammonia to harmless N₂ is required to control NH₃ emission. Although the ACSs have been used for a long time, there is still a challenge to increase their activity and N₂ selectivity at T < 300°C. In the present work, we focused on the tuning the low-temperature activity and selectivity of the Pt/TiO₂ catalysts by the modification of the acid-base properties of the samples surface.

Preparation of the samples



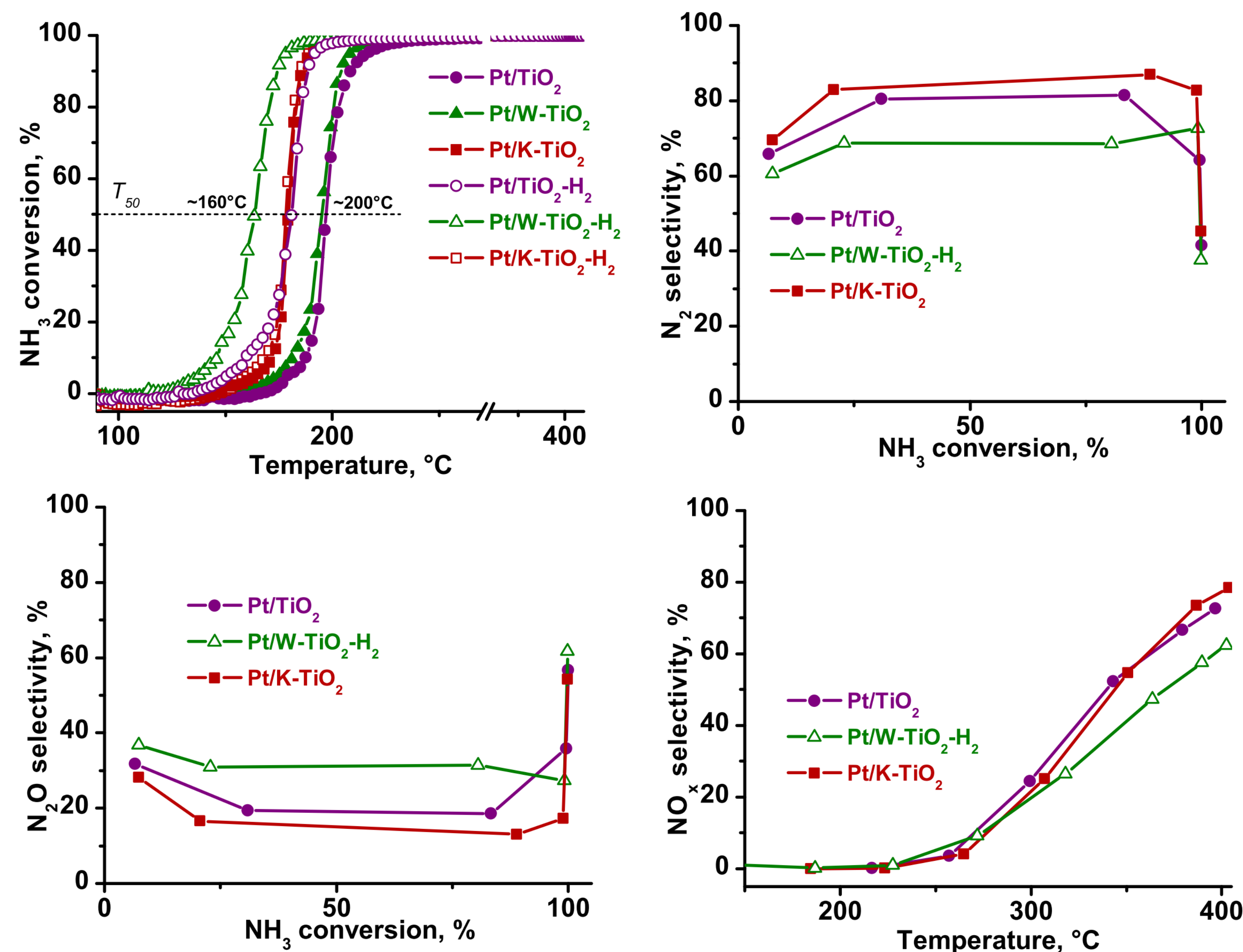
Three set of the samples were prepared: Pt/TiO₂, Pt/K-TiO₂, Pt/W-TiO₂. Influence of the reductive pretreatment was studied by heating of the samples in H₂ flow at 250°C for 2h. Pre-reduced samples are denoted as Pt/TiO₂-H₂, Pt/K-TiO₂-H₂, Pt/W-TiO₂-H₂.

Structural and acidic properties of the samples

Sample	XRD				S _{BET} m ² /g	TPD-NH ₃ μmol/m ²
	TiO ₂ -anatase		TiO ₂ -rutile			
	D, nm	wt. %	D, nm	wt. %		
Pt/TiO ₂	33(2)	83(1)	67(20)	17(1)	49.2	3.4
Pt/K-TiO ₂	34(2)	85(1)	65(18)	15(1)	48.6	2.6
Pt/W-TiO ₂	33(2)	86(1)	63(21)	14(1)	51.6	4.3

XRD data show presence of the anatase and rutile phases of TiO₂. Modification of the samples with W does not result in the additional phases. No platinum-containing phases can be detected as well, pointing to the formation of the highly dispersed and/or amorphous Pt species. However, XRD patterns of the samples after reductive pretreatment contain reflections of Pt⁰ phase (d(Pt⁰)~2-4 nm).

Temperature-programmed NH₃ oxidation reaction

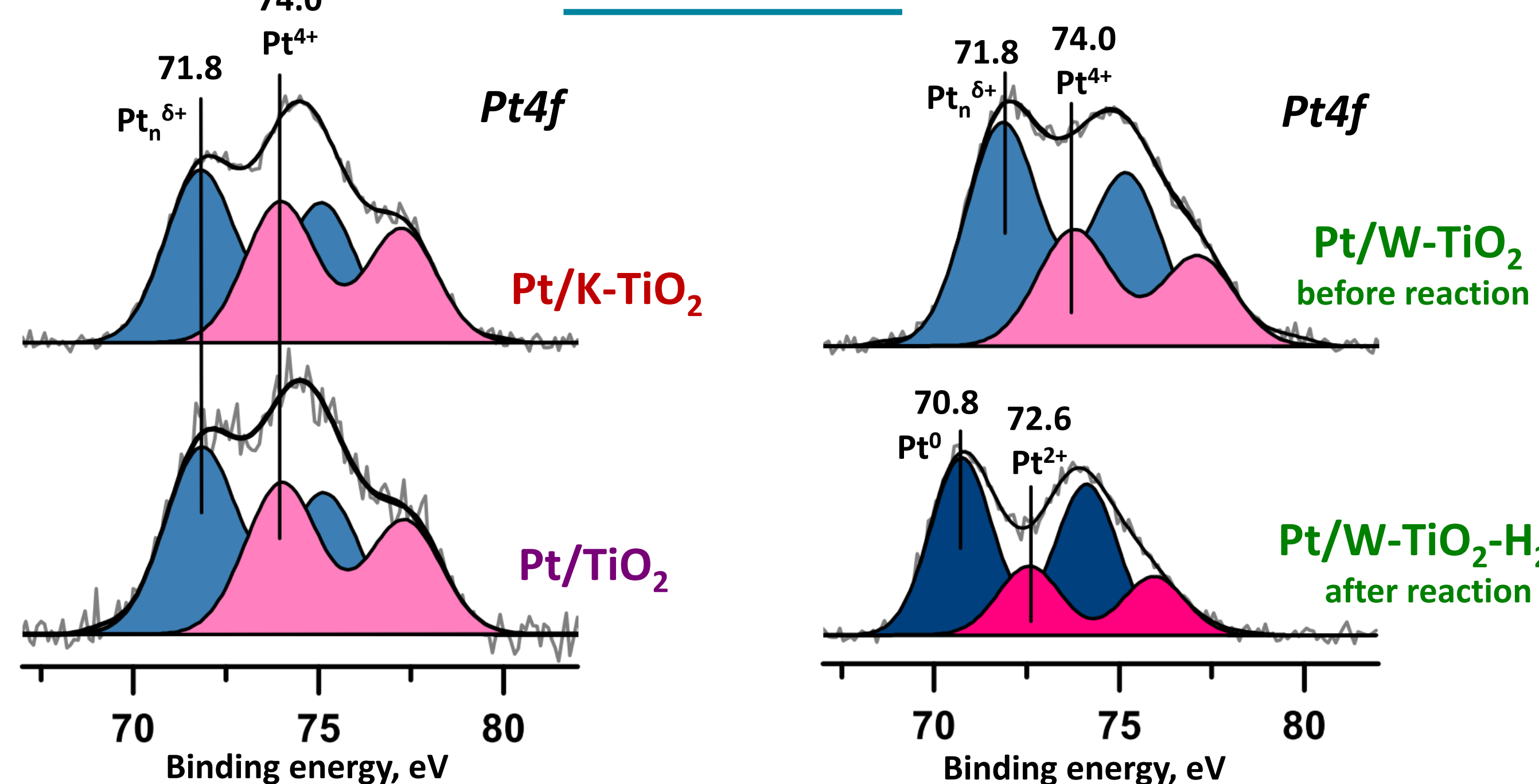


Reaction mixture: 0.1 vol.% NH₃, 4 vol.% O₂, (Ar-balance). Rate: 500 cm³/min.

The Pt/TiO₂ and Pt/W-TiO₂ samples show similar dependence of NH₃ conversion on temperature. The temperature of 50% conversion of NH₃ (T₅₀) is ~200°C. The reductive pretreatment substantially improves the low-temperature activity of the Pt/W-TiO₂ sample (T₅₀~160°C) and less effective for the Pt/TiO₂ sample. The Pt/K-TiO₂ sample demonstrates intermediate characteristics with T₅₀~180°C, and its activity is not influenced by H₂ pretreatment.

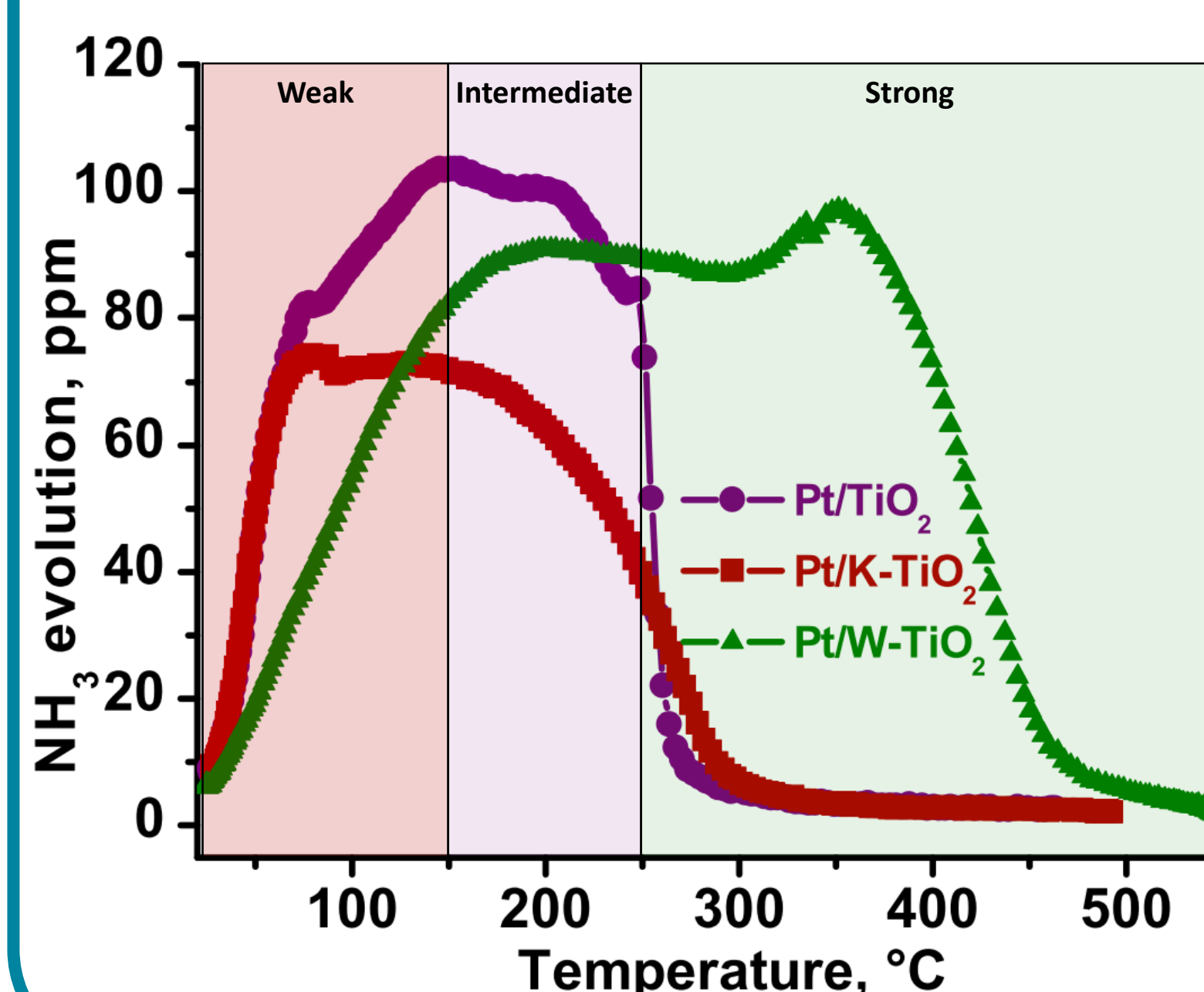
For all samples, molecular nitrogen and N₂O oxide are the main products of NH₃ oxidation at T < 250°C. The Pt/K-TiO₂ sample shows the highest selectivity towards N₂ (S_{N₂}~90%). The lowest selectivity is observed for the Pt/W-TiO₂-H₂ sample (S_{N₂}~70%).

XPS data



Platinum is present as the highly dispersed Pt^{nδ+} clusters and Pt⁴⁺ ions. Treatment of the samples in H₂ results in the reduction of the platinum species with the formation of the Pt⁰ species strongly interacting with the support.

Temperature-programmed NH₃ desorption



The TPD-NH₃ data show the acid centers characterized by desorption at T < 150°C (weak) and 150°C < T < 250°C (intermediate) for all samples. The Pt/W-TiO₂ sample contains also the strong centers (the NH₃ desorption is at T > 250°C).

The Pt/K-TiO₂ sample shows the lowest number of the acid centers, the Pt/W-TiO₂ – the highest.

Thus, the modification of the Pt/TiO₂ samples with tungsten in combination with reductive pretreatment provides the decrease of the onset temperature of NH₃ oxidation. However, the selectivity of thus modified samples towards molecular nitrogen is not very high. The modification with potassium proved to be the optimal way for the increase in the selectivity of the samples towards N₂ formation in low-temperature range.

The performed experiments provided an opportunity to establish the correlation between the acidic properties of the surface and the activity of the catalysts in ammonia oxidation reaction together with the selectivity towards molecular nitrogen at low temperature.