Electronic Supplementary Information (ESI)

In situ probing of Pt/TiO₂ activity in low-temperature ammonia oxidation

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Fig.S1. Experimental and calculated X-ray diffraction patterns for Pt/TiO₂-IMP and Pt/TiO₂-LAL samples. The differential curves are shown at the bottom. The calculated patterns were obtained by the Rietveld structure refinement.

Based on the XRD data we can estimate the degree of crystallinity of the support in the Pt/TiO_2 -LAL sample. For Pt/TiO_2 -LAL sample an additional peak was added to the refinement that corresponds to the amorphous phase. A ratio between peak's area corresponded to the crystallized and amorphous TiO_2 phases gave the degree of crystallinity (a fraction of the crystallized phases). The resulting value for Pt/TiO_2 -LAL sample was about 30%.



Fig.S2. Ti2p and O1s XP spectra for Pt/TiO₂-LAL and Pt/TiO₂-IMP samples. Spectra were collected in UHV.

Ti2p spectra are fitted with one doublet with $E_b(Ti2p_{3/2})=458.6$ eV related to the Ti⁴⁺ species.^{1,2} O1s spectra present the main peak at 529.9 eV related to the lattice oxygen of TiO₂.^{1,2} The peak observed at the $E_b(O1s)$ range 530.0-533.0 eV is usually attributed to the $-CO_x$, -OH, and H_2O species adsorbed on the sample surface^{1,2} or other oxygen species adsorbed on the defects of TiO₂ surface (peroxo-, superoxo*etc*. oxygen).³



Fig.S3. in situ Ti2p and O1s XP spectra for Pt/TiO₂-IMP and Pt/TiO₂-IMP-H samples. Spectra were collected in Ar (p(Ar)~1 mbar, RT).



Fig.S4. MS data collected at the NAP-XPS spectrometer during heating of the samples in the NH_3+O_2 mixture ($NH_3:O_2$ ratio of 1:40, total pressure $p_2 \sim 1.4$ mbar). (a) heating of the Pt/TiO_2-IMP-H sample from 50°C to 400°C, (b) blank experiment: heating of the NAP-XPS cell with an empty sample holder from 50°C to 450°C. (The lines are labelled by the corresponding m/z).

An additional blank experiment was performed in the NAP-XPS setup. The NAP-XPS cell with an empty sample holder was heated in the NH_3+O_2 mixture up to 450°C. No activity was observed at T<225°C, while for the Pt/TiO₂ catalysts the NH_3 conversion at this temperature already reached 100%.

Analysis of the in situ Pt4f spectra

The full widths at half maximum (FWHM) of the Pt peaks in *in situ* Pt4f spectra are not identical for different temperature points. The reason for this inconsistency is different charging observed for TiO_2 surface under the reaction conditions during the XPS measurements. The charging effect during NAP-XPS experiments is a known problem for the supported powder catalysts. The conductivity of the particle surface might change during the reaction due to the removal or accumulation of O-containing surface groups, resulting in variation of the dynamic charge over the sample surface. This effect is especially pronounced for supports like TiO_2 which is a semiconductor material.

Generally, charging effect causes a dynamic shift and broadening of all spectral photoelectron lines during XPS measurements. The value of such shift additionally depends on the reaction conditions and time of data acquisition. It is especially critical for the spectral regions, which require prolonged time of signal collection due to low intensity (Pt4f region in our case). Spectra collected in such way are usually broadened. Keeping in mind the described charging problems, we performed collection of the Pt4f spectra simultaneously with the reference $Ti2p_{3/2}$ spectra. In this way we eliminated the influence of the charging effect on the E_b values of the Pt4f peaks. However, the FWHM of the obtained spectra were slightly different for various temperature points due to the different line shifts during NAP-XPS measurement. Thus, we performed fitting of the Pt4f spectra taking into account the FWHM values of the reference $Ti2p_{3/2}$ lines. The resulting FWHM values for Pt4f and $Ti2p_{3/2}$ lines and their ratios are given in Table S1. It can be seen that the variations of FWHM values for Pt4f and $Ti2p_{3/2}$ regions follow the same law so that their relative difference is almost constant. It confirms that the observed broadening of Pt4f lines is caused by the charging effect and not related to the appearance of the new Pt species.

Sample	T, °C	FWHM		FWHM(Pt4f)/
		Pt4f	Ti2p _{3/2}	FWHM(Ti2p _{3/2})
Pt/TiO₂-IMP-H	50	1.15	1.0	1.15
	175	1.25	1.05	1.2
	225	1.55	1.3	1.2
	400	1.5	1.25	1.2
Pt/TiO ₂ -IMP	50	1.8	1.45	1.25
	175	1.45	1.1	1.3
	225	1.6	1.3	1.2
	400	1.3	1.05	1.2

Table S1. The FWHM values for in situ Pt4f and $Ti2p_{3/2}$ spectra for Pt/TiO₂-IMP-H and Pt/TiO₂-IMP samples acquired during heating of the sample in the NH₃+O₂ mixture.



Fig.S5. in situ O1s and C1s spectra acquired during heating of the Pt/TiO₂-IMP-H sample in the NH₃+O₂ mixture. (NH₃:O₂ ratio of 1:40, total pressure p_{Σ} ~1.4 mbar).

O1s spectra can be fitted with one main peak at 529.9 eV related to the lattice TiO₂ oxygen, while oxygen-containing surface species give contributions at higher binding energy.^{1,2} Peaks at 530-533 eV are related to the oxygen species adsorbed on the surface. Peaks at 530.6 and 531.4 eV can be related to –C-OH and/or –CO_x species absorbed on the surface of the sample, while peak at ~ 532.2 eV can be caused by the adsorbed –OH/H₂O species.^{1,2} Note that the C1s spectra of the sample also reveal presence of oxygen-containing carbon impurities on the surface of the samples (E_b(C1s)~286 eV). Also other oxygen species adsorbed on the defects of TiO₂ surface (peroxo-, superoxo- *etc.*) can contribute to the E_b(O1s) range of 530-532 eV.³

Due to the high intensity of the peak from the lattice titania oxygen and presence of the variety of surface oxygen-containing groups, the analysis of the oxygen species (O_{ad} and $-OH_{ad}$) which might form during the NH_3+O_2 reaction is rather complicated. Günther *et al.* using model system showed that the O_{ad} species formed during ammonia oxidation over platinum surface are characterized by the $E_b(O1s)^{\sim}529.7-529.9 \text{ eV}.^4$ Thus, for Pt/TiO₂ samples the formation of the O_{ad} species adsorbed on the platinum surface during the reaction cannot be reliably detected due to overlapping with intense signal from the titania oxygen. The analysis of the OH_{ads} species is also complicated as the other oxygen-containing groups can give contributions in O1s spectra at the similar $E_b(O1s)$ range of 530-532 eV.

A slight decrease of the peaks with $E_b(O1s)= 530.6 \text{ eV}$, 531.4 eV can be seen in the O1s spectrum after treatment of Pt/TiO₂-IMP-H sample in the NH₃+O₂ mixture at 400°C. (Fraction of these surface oxygen species to the overall O1s spectrum decreases from 15 to 11%). Analysis of the C1s spectra also shows the decrease of the peak related to the -C-OH/-CO_x species ($E_b(C1s)=286.1 \text{ eV}$) after heating of the sample at 400°C. We can assume that the observed changes in the O1s spectrum are mainly caused by the decrease of the amount of carbon impurities after treatment at high temperature.

Thus, analysis of O1s spectra cannot provide reliable data on the oxygen species (O_{ad} and $-OH_{ad}$) which might form during the NH₃+O₂ reaction.



Fig.S6. Curve-fitted in situ N1s XP spectra of Pt/TiO₂-IMP-H sample during heating in the NH₃+Ar mixture (NH₃:Ar ratio of 1:40, total pressure p_{Σ}^{\sim} 1.4 mbar).



Fig.S7. (a) Evolution of in situ Pt4f XP spectra for Pt/TiO₂-IMP sample during heating in 1 mbar of O₂. (b) Variation of the fraction of Pt^0 species ($E_b(Pt4f_{7/2})=71.0-71.4 \text{ eV}$) to the overall Pt4f signal intensity during heating of Pt/TiO₂-IMP sample in O₂ or O₂+NH₃ mixture.



Fig.S8. TEM study of Pt/TiO₂-IMP sample after NH₃+O₂ reaction: (a) TEM image, (b) HAADF-STEM image, (c) Pt particle size distribution.



Fig.S9. k^2 -weighted EXAFS functions for Pt/TiO₂-LAL sample under treatment in the NH₃+O₂ mixture at different temperatures.



Fig.S10. EXAFS fits for Pt/TiO₂-LAL sample under treatment in the NH₃+O₂ mixture at different temperatures.



Fig.S11. (a) operando XANES data collected during heating of Pt/TiO_2 -LAL in the NH_3+O_2 mixture, (b) Selection of every 5th operando XANES spectra (provided for better representation). Grey field marks the "white line" peak. The reaction mixture: 880 ppm NH_3 , 10 vol.% O_2 , and 10 vol.% N_2 in He.

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