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Investigation of concentration hysteresis in methane oxidation on bimetallic Pt–Pd/Al_2O_3 catalyst by *in situ* XPS and mass spectrometry

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Catalyst preparation

Bimetallic Pd-Pt/Al_2O_3 catalyst was prepared by wet impregnation of the pre-dried support (γ-Al_2O_3, Sasol, S_{BET} = 215 $m^2 \times g^{-1}$) with a mixture of the corresponding nitrate solutions with the fixed Pt/Pd molar ratio. Sample was dried at 120 °C for 3 hours followed by calcination at 400°C for 4 hours. Details of the sample preparation procedure have been reported earlier[S1,S2].

It should be noted that bimetallic sample prepared using this method has the “egg (alumina) – shell (supported metal)” granule structure that improves XPS signals from active components (Pd and Pt). The studied bimetallic sample was denoted as $Pd_{0.63}Pt_{0.18}$, where the numbers are the palladium and platinum content in wt%.

Experimental technique

In situ XPS experiments were carried out on a photoelectron spectrometer VG ESCALAB "High Pressure" (Vacuum Generators, UK). This spectrometer equipped with a special gas cell which makes it possible to measure *in situ* XPS spectra at pressures up to 0.1 mbar[S3–S5]. The energy scale of the spectrometer was preliminarily calibrated by the position of peaks of the $Au4f_{7/2}$ (84.0 eV) and $Cu2p_{3/2}$ (932.67 eV) core levels from the gold and copper foils. Photoelectron spectra were recorded using Al K_α radiation ($h\nu$=1486.6 eV), with a 0.1 eV step of the binding energy at a pass energy of 20 eV and with dwell time of 1 second for each data point. To take into account the effect of surface charging, we used the Al2s line (BE = 119.3 eV) from the support (γ-Al_2O_3) as an internal standard. Additionally it is a well-known fact that reaction mixture and heating (the experimental conditions) partially offset the differential charging effect. Also, to avoid its possible impact, each spectral region was extracted for individual scans and each of it was checked for shape and position changing.. The integral intensities for all spectra were corrected with corresponding atomic sensitive factors (ASF) taken from[S6]. Spectral analysis of the photoelectron spectra (Pt4f + Al2p, Al2s, C1s, Pd3d + $Pt4d_{3/2}$

and O1s) and data processing were performed with a XPS Peak 4.1 program[S7]. The peak fitting parameters for all Pt and Pd species are presented in Table 1.

Table 1. The peak fitting parameters for different Pd and Pt states.

Pd states	$Pd3d_{5/2}$ BE (eV)	FWHM (eV)	G/L
Pd^0	335.1±0.1	1.8	20
Pd^{2+}	336.4±0.1	2.3	40
Pd^{4+}	338.3±0.1	2.5	40

Pt states	$Pt4f_{7/2}$ BE (eV)	FWHM (eV)	G/L
Pt^0	71.2±0.1	1.9	20
Pt^{2+}	72.3±0.1	2.2	40
Pt^{4+}	74.2±0.1	2.4	40

It is well known that analysis of Pt4f region for such systems (supported on Al_2O_3) is rather difficult due to the overlapping of Al2p peak from the support with the Pt4f doublet. To evaluate the contribution of the Al2p line we determined its parameters relating to the parameters of another characteristic line, Al2s, in the spectrum of pure support (γ-Al_2O_3). A similar situation is with the overlapping lines Pd3d and $Pt4d_{3/2}$. The shape and intensity of $Pt4d_{3/2}$ peak used for fitting were calculated from a more intensive $Pt4d_{5/2}$ one, which does not overlap with the Pd3d line.

A special sample holder for catalyst granules (mesh stainless steel) was designed for the *in situ* XPS and MS experiments. The sample holder was heated resistively and the temperature was monitored with an alumel–chromel thermocouple spot-welded directly to the holder of the sample. The accuracy hold of temperature was about 0.5°C. The XPS and MS experiments were conducted at the constant methane concentration ($P(CH_4) = 0.008$ mbar) at the temperature of 430°C with varying the O_2:CH_4 ratio in the range from 5:1 to 0.2:1. To control the purity of the injected gases and the composition of the reaction products in the cell the quadrupole QMG-220 mass spectrometer (Pfeiffer Vacuum, Germany) equipped with a differential pumping system was used. The methane and oxygen flows were regulated separately with the SEC-Z512MGX mass flow controllers (Horiba, Japan). The total pressure in the gas cell was measured with a MKS type 121A Baratron (MKS Instrument, USA). The reaction rate of methane oxidation was monitored by a change in the intensity of the mass spectrometric signal with m/z = 18 (H_2O) and

44 (CO_2). Simultaneously, we recorded other signals (m/z): H_2 (2), CH_4 (15, 16), CO (28), and O_2 (32).

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