



Alumina-supported platinum catalysts: Local atomic structure and catalytic activity for complete methane oxidation



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ABSTRACT

The structure of platinum species in a model set of monodisperse Pt/ γ -Al₂O₃ catalysts was studied using radial distribution function (RDF) of electron density. Catalyst preparation conditions were revealed to considerably affect the dispersion and structure of supported platinum. Cation vacancies on the γ -Al₂O₃ surface were essential to anchor electron deficient platinum atoms and clusters. Platinum segregation with forming finely dispersed metal particles was evident in some catalysts. The methane total oxidation over the Pt/ γ -Al₂O₃ catalysts was established to depend strongly on the platinum oxidation state. The catalysts containing oxidized platinum species and highly dispersed oxidizable Pt⁰ particles were more active. The metal–support interaction improved the performance of the catalysts indirectly, by stabilizing the platinum dispersion.

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1. Introduction

Alumina-supported platinum (Pt/ γ -Al₂O₃) catalysts appear to be one of the most attractive catalysts in a variety of practically important processes such as oxidation of hydrocarbons [1,2], gasoline reforming processes [3], CO oxidation [4,5], etc. Dispersion, structure, oxidation state of the active component as well as metal–support interaction are well known to impact significantly on catalytic performance. Thus, the total oxidation of methane over the Pt/ γ -Al₂O₃ catalysts was shown to be highly structure sensitive [6]. Hence, comprehensive studies on the atomic-scale structure and properties of catalytically active sites of the Pt/ γ -Al₂O₃ catalysts appear to be a challenge.

Numerous studies were aimed at the state and structure of platinum in the Pt/ γ -Al₂O₃ systems. Both metallic Pt⁰ and oxide PtO_x species were detected by high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) [7,8]. X-ray absorption fine structure (XAFS) analysis revealed that three types of the Pt/ γ -Al₂O₃ catalysts with metal, oxide and metal-oxide platinum species were formed depending on a preparation procedure [6,9]. Belyi et al. used chemical adsorption for

quantitative determination of the metallic and ionic platinum species in the Pt/ γ -Al₂O₃ catalysts [10,11]. It was found that Pt ions, unlike Pt⁰ atoms, formed strong σ -donor bonds with water [10]. Strong interaction with the support was suggested to cause a high thermostability of the ionic platinum species [11].

The data on characterization of the Pt⁰ particles are unambiguous, but this is not the case with the PtO_x species. As a rule, the PtO_x species are highly dispersed and disordered that makes it impossible to use traditional X-ray and electron diffraction methods for structural studies. Extended X-Ray Absorption Fine Structure (EXAFS) analysis was used to elucidate the structure of the PtO_x species [6,9,12,13]. The EXAFS analysis detected 6-fold oxygen coordination of Pt⁴⁺ ions; that implied an octahedral geometry typical of α -PtO₂ phase [6,9,12]. Considerable reduction and absence of longer Pt–Pt contributions indicated a lack of long-range atomic order in the PtO_x species [9,12,13]. Detection of one Pt–O coordination shell did not allow the PtO_x species to be unambiguously assigned to the α -PtO₂ phase. The formation of highly dispersed disordered PtO_x clusters on the support surface or coordination of the Pt ions with support oxygen ions seems more reliable.

The interface features, metal–support interaction are not clearly understood. Several ideas were suggested, among which were binding the Pt⁰ atoms to the support oxygen ions [14,15] and incorporating the Pt ions into the alumina surface [16–22]. The commonly accepted opinion is that defects of the support surface are pinning sites for highly dispersed platinum species.

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EXAFS data reported by Koningsberger et al. [14,15] revealed the interaction between the alumina surface and Pt⁰ clusters as an important factor for the cluster anchoring. In spite of a catalyst pre-reduction, Pt–O interatomic distance was identified and assigned to coordination of the interfacial Pt⁰ atoms by the support oxygen ions.

In terms of another model, the metal–support interaction consists of insertion of the Pt ions into cation vacancies of the γ -Al₂O₃ structure. A stabilization of the Pt ions in the vacant octahedral sites of the spinel-like alumina structure was suggested recently using RDF of electron density [16,17]. Different characterization techniques also indicated a platinum dissolution in the surface Al₂O₃ layers. Some studies [18–20] showed a formation of platinum-alumina complexes, which, in contrast to the crystalline PtO₂ particles, were soluble in acids and acetylacetone. The metal–support interaction was detected by temperature-programmed reduction (TPR). The platinum oxide species interacting with the support required high reduction temperature (~220 °C) and were identified as PtAl₂O₄ species, whereas the crystalline platinum oxide particles were reduced at a lower temperature (≤ 100 °C), which is close to the one for the bulk α -PtO₂ phase [18,22].

The studies of model Pt/ γ -Al₂O₃ systems also showed a possibility of the Pt diffusion into the alumina. The Pt nanoparticles were deposited on γ -Al₂O₃ films [23,24]. Scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and Ion Scattering Spectroscopy (ISS) data indicated the Pt dissolution in the alumina after calcination at 300–530 °C [23].

In summary, data on the structure of the platinum oxide species in the Pt/ γ -Al₂O₃ catalysts are still deficient; a nature of the metal–support interaction is not well understood.

We report here a rigorous structural study of the Pt/ γ -Al₂O₃ catalysts with different performance to the CH₄ oxidation. The local atomic structure of the supported platinum species was determined by RDF of electron density method. This method can reveal atomic arrangement in material in the range of 0.1–2 nm.

2. Experimental

2.1. Catalyst preparation

A series of monodisperse 0.75 wt% Pt/ γ -Al₂O₃ catalysts were prepared using the technique described earlier [6]. Commercial γ -Al₂O₃ (Puralox, Sasol Germany GmbH; 98% purity, $S_{\text{BET}} = 215 \text{ m}^2 \text{ g}^{-1}$, grain size 0.25–0.5 mm) was impregnated with aqueous platinum nitrate solutions with different Pt:HNO₃ ratios. The freshly impregnated samples were dried at 120 °C for 4 h and then calcined at 400 °C for 4 h or at 600 °C for 2 h. Details of the preparation procedure for all catalysts are shown in Table 1.

Table 1
Characteristics of the Pt/ γ -Al₂O₃ catalysts under study.

Catalyst	Precursor (Pt:HNO ₃ ratio)	Calcination temperature (°C)	d_1 (nm)	d_{vs} (nm)	D_{M} (%)
I ^a	1:0	400	0.6 ± 0.3	1.0	100
II ^a	1:5 ^d	400	1.1 ± 0.3	1.3	84.8
III ^a	1:5 ^c	400	2.2 ± 0.4	2.7	42.2
IV ^b	1:1	400	1.3 ± 0.4	1.6	70.6
V ^a	1:5 ^c	600	8.5 ± 1.8	9.2	12.2

^a Non-pretreated support.

^b Acetic acid pretreated support.

^c The precursor solution was alkalized with tetramethylammonium hydroxide up to pH 8.5.

^d Citric acid was added to the precursor solution.

2.2. Catalyst characterization

High-resolution transmission electron microscopy was used to determine the average size of supported Pt particles. HRTEM studies were carried out using a JEOL JEM-2010 electron microscope with 1.4 Å lattice resolution at a 200 kV accelerating potential. The samples were ground, suspended in ethanol and mounted on a copper grid coated with a porous carbon film. Average linear (d_1) and volume-surface (d_{vs}) particle diameters were calculated using equations $d_1 = \sum n_i d_i / \sum n_i$ and $d_{\text{vs}} = \sum n_i d_i^3 / \sum n_i d_i^2$, where n_i is the number of particles with diameter d_i . A set of 200–700 particles was analyzed for each sample.

The samples after 6 h-aging (430 °C; 1 vol % CH₄, 20.8 vol % O₂, rest N₂) were studied by X-ray diffraction methods. Earlier, XAFS and HRTEM studies showed an absence of significant changes in the Pt oxidation state and Pt particle sizes after the aging [6,9]. Diffraction experiments were performed using a high-resolution diffractometer at the Siberian Synchrotron and Terahertz Radiation Centre (SSTRC, Budker Institute of Nuclear Physics, Novosibirsk, Russia). The measurements were carried out with step of 0.1° in the 2θ range of 3–145° at a wavelength of 0.703 Å or in terms of magnitude of a scattering vector, $h = 4\pi \sin(\theta)/\lambda$, in the range of 0.5–17 Å⁻¹.

The structural features of the supported platinum species were determined by analyzing radial distribution functions of electron density $4\pi r^2 \rho(r)$, where $\rho(r)$ is the electron density at distance r . These functions were obtained by the Fourier transformation of normalized scattering intensity in the X-ray diffraction [25–28]. The procedure used for calculating RDF (see elsewhere for details [16,26,29]) allows interatomic distances (r) and coordination numbers (CN) to be determined from position and area of peaks in the RDF curve. Accuracy of the r and CN values determination is 0.5% and 5%, respectively. Analysis of RDF provides information about the local atomic structure and makes it possible to identify phases with a crystallite size smaller than 3 nm. A comparison between the experimental RDF and RDF calculated from structural models is usually performed [16,29]. Data required for the model RDFs, such as interatomic distances and coordination numbers of compounds investigated here, were calculated from structural data of the ICSD database [30].

2.3. Catalyst testing

Catalysts for the complete methane oxidation were tested using a flow-circulation reactor BI-CATr (Borekov Institute of Catalysis, Novosibirsk) at atmospheric pressure and a constant temperature of 430 °C. The construction features of the BI-CATr setup were described elsewhere [31,32]. In brief, this set-up provides the gradientless mode and allows measuring the catalytic activity with a high accuracy due to an absence of temperature and concentration gradients in a catalyst bed [33]. The catalyst samples (weight (w_{cat}) was equal to 1 g) were placed in a steel reactor (i.d. = 25 mm). A multiplicity of reaction mixture circulation through the catalyst bed was varied from 17 to 280. It is sufficient to establish the gradientless mode.

The composition of the outlet gas mixture (OGM) was identified in a stationary state, which stability was examined within an hour. The concentration of CH₄ ($C_{\text{CH}_4}^{\text{OGM}}$) was analyzed using an express chromatograph with a thermocatalytic detector, the concentrations of CO₂, H₂O and O₂ were analyzed by a gas chromatograph “Chromos GH1000” (“Chromosib”, Russia) equipped with a thermal conductivity detector and two columns (Porapak N, Zeolite Molecular Sieve 5A).

The flow rate (U) of the initial gas mixture (IGM) was varied from 50 to 1100 ml/min with a constant composition (1 vol%

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