

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Influence of preparation conditions on catalytic activity and stability of platinum on alumina catalysts in methane oxidation



Anna V. Nartova^{a,b,*}, Larisa M. Kovtunova^{a,b}, Alexander K. Khudorozhkov^a, Kristina I. Shefer^{a,b}, Genrikh V. Shterk^{a,b}, Ren I. Kvon^a, Valerii I. Bukhtiyarov^{a,b}

^a Boreskov Institute of Catalysis SB RAS, Lavrentieva Ave., 5, Novosibirsk, 630090, Russia
^b Novosibirsk State University, Pirogova St., 2, Novosibirsk, 630090, Russia

| ARTICLE INFO | A B S T R A C T |
|---|--|
| Keywords: Pt/alumina catalysts Methane oxidation XPS TEM XRD | The TEM, XPS, and XRD methods were used to study the influence of conditions of catalyst preparation on the activity and stability of platinum on alumina catalysts in methane oxidation reaction. The catalyst samples were prepared by wet impregnating the γ -Al ₂ O ₃ support with the solutions of precursors prepared on the commercial platinum nitrate. In the course of the study the composition of the precursor solution and pretreatment of the support were varied. It was shown that the highest catalytic activity and stability to sintering of the active component nanoparticles in methane oxidation is reached in the case of strong interaction of the active component with the support surface providing for the stabilization of the ionic forms of platinum. The use of modifying additives (tetramethylammonium hydroxide, glacial acetic acid) facilitates reduction of the active component both in thermal treatment and in catalytic reaction, which causes a decrease in catalytic activity and |

stability of the system under used conditions.

1. Introduction

Alumina-supported Pt particles are frequently used as catalysts for a number of processes, due to activity of platinum in the reactions of oxidation, hydrogenation, isomerization, etc. For example, the total oxidation of hydrocarbons over Pt/Al₂O₃, particularly, of methane, is of interest for many branches of industry. Numerous study of the system have shown that the activity and selectivity of the supported catalysts are influenced by the phase composition and particle size of the active component, as well as the support nature [1-4]. The most suitable phase for the reactions of deep oxidation of hydrocarbons is the metal oxide phase, whereas the reduced phase (metal platinum) suits better for the hydrogenation reactions. However, it is not a rare case when the simultaneous presence of both metal and oxide phases in the active center is the most efficient for catalysis [5,6]. Among numerous modifications of alumina, γ -Al₂O₃ with a large amount of Broensted and Lewis centers is the most suitable one for catalysis. These centers are able not only to coordinate the compounds of precursors of the active component and, later, the active component itself, but also to participate in catalytic reaction in some cases [7,8].

It is also known that the properties of the obtained catalysts depend strongly on the conditions of their preparation. The treatment of the surface with acids or bases, doping with metals [8–11], application of various precursors [1,12–14], addition of certain compounds into the impregnating solution can promote stabilization or, on the contrary, agglomeration of the synthesized particles of active component. Therefore, the detailed investigation of the influence of preparation condition on catalyst behavior is of great importance, since optimization of the system parameters in the course of preparation is necessary to get best catalyst performance.

It should be however noted that the optimum for the ratio of the oxidized and reduced forms of the active component varies for different compositions of the reaction mixture, i.e., the $CH_4:O_2$ ratio in the case of total methane oxidation. Therefore, application of the same conditions is necessary for the comparison of the different catalysts (for example, monometallic platinum and palladium and bimetallic Pt-Pd catalysts) followed by the elucidation of the general regularities for the development of the most effective systems. Since co-existence of different states of Pt is very important for the catalytic oxidation of methane [5,6,15,16], it is necessary to investigate the influence of preparation conditions on active component state stability, which has to be taken into account during comparison of catalysts searching for the most optimal one.

The present work is the essential part of two long-term studies

* Corresponding author at: Boreskov Institute of Catalysis SB RAS, Lavrentieva Ave., 5, Novosibirsk, 630090, Russia. *E-mail address*: nartova@catalysis.ru (A.V. Nartova).

https://doi.org/10.1016/j.apcata.2018.08.029 Received 29 June 2018; Received in revised form 27 August 2018; Accepted 31 August 2018 Available online 03 September 2018 0926-860X/ © 2018 Elsevier B.V. All rights reserved. performed in our laboratory and devoted to catalytic oxidation of methane over alumina-supported platinum/palladium and platinum-palladium catalysts [3,15–17]. We report here the results of the combined transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) studies of the Pt/ γ -Al₂O₃ catalysts prepared with the various composition of the impregnating solution and pretreatment of the support, immediately after preparation and after testing in the methane oxidation in a continuous stirred-tank reactor in order to determine the factors influencing the catalytic activity.

2. Experimental

2.1. Materials

For preparation of the catalysts the commercial solution of platinum nitrate (Delphi, 24.77 wt. % of platinum), γ -Al₂O₃ (Sasol, S_{BET} = 198 m²/g, granule fraction 0.1-0.2 mm), tetramethylammonium hydroxide (TMA) (Acros, 25%, cas. 75-59-2), glacial acetic acid (Reachem, cas. 64-19-7) and nitric acid (Reachem, 78%, cas. 7697-37-2) were used.

2.2. Methods

The study by transmission electron microscopy was performed on a JEM-2010, Jeol Co., Japan, with the lattice resolution of 0.14 nm with accelerating voltage of 200 kV. The samples for study were fixed on the standard copper meshes placed into the holder and put in the chamber of electron microscope. To determine the particle size the "Analysis,iTEM v.5" software was used (Soft Imaging System GmbH, 2004). For analysis the selections of no less than 250 measured particles for each sample were used.

The measurements by X-ray photoelectron spectroscopy were performed at a VG ESCALAB HP photoelectron spectrometer. The nonmonochromatic Mg K_{α} line was used as the primary excitation. To calibrate the XP-spectrometer the Au4 $f_{7/2}$ (binding energy $E_b = 84.0 \text{ eV}$) and $Cu2p_{3/2}$ (E_b = 932.7 eV) lines from metallic gold and copper foils were used [18]. The C1s ($E_b = 284.5 \text{ eV}$) line of carbon present in the surface impurities was used as the internal standard for spectra calibrating [18,19]. Spectral analysis and data processing were carried out with Peak 4.1 XPS. The E_b values and the areas of XPS peaks were determined after subtraction of Shirley background and analysis of line shapes. Curves were fitted with Gaussian-Lorentzian functions for each XPS region. To calculate the atomic ratios XPS peak areas were corrected with their respective atomic sensitivity factors for spectra collected using the VG ESCALAB spectrometer [19]. The samples were fixed on the holder with the 3 M double sided adhesive copper conducting tape. The X-ray radiation heats the sample and has a reducing influence on it; to minimize that while studying the ionic forms of platinum with XPS we decreased the source power (down to 150 W) and used the mode of rapid spectra recording enabling us to obtain the spectrum of the Pt4f + Al2p region in 180s from the moment the source was turned on.

The diffraction images were obtained with the use of a Thermo ARL X'tra device, with the CuK α -radiation ($\lambda = 1.5418$ Å), focusing geometry θ - θ in the scanning mode within the range of angles of $2\theta = 10 \div 75$ °C with the step of 0.1°. The experimental data were juxtaposed with the diffraction pattern of γ -Al₂O₃ ICDD PDF# 01-079-1558. For identifying aluminium diacetate AlOH(CH₃COO)₂ the theoretical diffractogram ICDD PDF# 13-0833 was used. The values of the sizes of the coherently scattering domains were calculated with the Scherrer formula [20].

Platinum loading (Pt wt %) values were obtained during elemental analysis after final air calcination at 400 °C of samples with X-ray fluorescent method on an ARL PERFORM'X analyzer with the Rh-anode of X-ray tube. The calibration plots were used to increase accuracy of metal loading determination. The adsorption studies were conducted by the isotherms of N_2 adsorption at 77 K, measured on an ASAP-2400 Micromeritics (USA) setup after training the samples in vacuum at 150 °C. The isotherms were used to calculate the total available surface by BET [21,22].

2.3. Catalyst testing

For conducting the catalytic tests of the prepared catalysts in steadystate conditions the laboratory catalytic set-up with a continuous stirred-tank reactor was used. Analysis of the final reaction mixture (FRM) was performed on a gas chromatograph "Tsvet 500 M" upgraded with a control unit IRM-10 made by "Khromosib" company, with the help of a system of three detectors: two parallel detectors of thermal conductivity (katharometers) for analyzing the oxygen content (K-1) and for analyzing the water vapor content (K-2), and flame ionization detector (FID) for determining the methane content, attached in a cascade after K-1. A methanator is installed into the plant between K-1 and FID for more accurate determination of carbon dioxide and carbon monoxide concentrations in FRM. To divide the components of FRM a chromatography column was used with a length of 2.0 m and diameter of 2.0 mm filled with absorbent carbon. To determine the amount of water vapor in FRM a chromatography column was used with a length of 1.5 m and diameter of 2.0 mm filled with Porapak-T adsorbent. The data of the chromatographic analysis were processed with "Khromos" program. The catalytic testing of the prepared samples on the laboratory set-up was conducted in isothermal mode.

The reaction rate (W) with the fixed value of flow u for the first order reaction of methane was calculated with the formula:

$$\mathbf{w}\left(\frac{ml}{mol_{Pt}} \cdot s\right) = \frac{C_0(CH_4) - C(CH_4)}{m(g_{Pt})} \times u\binom{ml}{s} \times 195. \ 1\binom{g}{mol},$$

where *m* is the mass of Pt in the sample; $C_0(CH_4)$ and $C(CH_4)$ are the initial and current bulk concentrations of methane measured at the same temperature (vol.%), respectively.

The prepared samples were tested for endurance with determining the changes in the sample activity in time at a given temperature (380 °C), constant flow rate (20 l/h) and fixed composition of the initial reaction mixture (IRM) (1% CH₄, 5% O₂, balanced with He). The registration of the change in the degree of conversion in time allows calculation of specific rate of the catalytic reaction of complete methane oxidation at intervals of 3–5 min. The reaction rate after 240 min of reaction (W₂₄₀) averaged by the three last points was taken as the measure of activity of the studied catalysts. When conducting the endurance tests the batches of the catalysts were selected so that the initial conversion of methane was 50 \pm 10%.

To account for the influence of the Pt particle dispersion on the activity of the samples we used the value of turnover frequency (TOF, $\rm s^{-1})$ at a temperature T calculated with the formula:

$$TOF_T(s^{-1}) = \frac{W_{240}\left(\frac{ml}{molp_l} \cdot s\right)}{22414\frac{ml}{mol} \times D_m} \times 100\%,$$

where W_{240} is the reaction rate after 4 h since the start of experiment at a temperature T; D_m is the dispersion of the Pt particles, %.

3. Results and discussion

3.1. Catalyst preparation

At first alumina was dried in air at 120 °C for 8 h. The Pt/Al_2O_3 catalysts (1 wt.% Pt) were prepared by wet impregnation [23,24]. The excess of the solvent was removed at 40 °C on a rotary evaporator. All prepared samples of the catalysts were dried at 120 °C, and then calcined in air at 400 °C for 4 h. To study the influence of the preparation method on the stability of the catalysts in reaction the conditions of the

Download English Version:

https://daneshyari.com/en/article/10130694

Download Persian Version:

https://daneshyari.com/article/10130694

Daneshyari.com