Short communication

Effect of Pd deposition procedure on activity of Pd/Ce$_{0.5}$Sn$_{0.5}$O$_2$ catalysts for low-temperature CO oxidation

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ABSTRACT

Two methods for the preparation of Pd/Ce$_{0.5}$Sn$_{0.5}$O$_2$ catalysts have been used: solution combustion (SC) of Pd, Ce and Sn precursor mixtures, and incipient wetness impregnation by [Pd(NO$_3$)$_2$(H$_2$O)$_2$] solution of Ce$_{0.5}$Sn$_{0.5}$O$_{2-\delta}$ support, obtained by the SC technique (SC + IWI). The formation of metallic palladium was observed in addition to ionic palladium in a Pd$_x$(Ce$_{0.5}$Sn$_{0.5}$)$_{1-x}$O$_{2-x-\delta}$ solid solution due to high-temperature Pd precursor decomposition during the SC process. IWI of Ce$_{0.5}$Sn$_{0.5}$O$_{2-\delta}$ support has been demonstrated to lead to a uniform solid solution of Pd^{2+} ions in the Ce$_{0.5}$Sn$_{0.5}$O$_{2-\delta}$ matrix at 1% Pd content that resulted in high catalyst activity towards CO oxidation. The increase of Pd content to 5% showed no influence on catalytic activity. This observation is explained by the formation of low active PdO species when Pd content is more than 1%. The proposed SC + IWI method allows obtaining highly active Pd/Ce$_{0.5}$Sn$_{0.5}$O$_2$ catalysts with low palladium content.

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1. Introduction

Cerium-based oxides are high-usage supports for heterogeneous catalysts. The easy transition between oxidation states Ce^{3+}–Ce^{4+} and unique oxygen storage capacity (OSC) of CeO$_2$ is essential to promote catalysis of oxidation reactions [1]. Partial substitution of Ce(IV) ions with isovalent ions (Sn(IV), Ti(IV), Zr(IV), Hf(IV)) gives the opportunity to enhance OSC and lattice oxygen mobility [2–10]. The loading of palladium in such a mixed oxide supports yields catalysts with palladium centers localized in a controlled environment. Ionic palladium interacting with a ceria-based oxide lattice is proposed to be an active component of low-temperature CO oxidation catalysts (LTO CO, T < 150 °C) [2,11–16] due to the absence of a well-known CO inhibition effect that takes place on metallic Pd or PdO nanoparticles supported on Al$_2$O$_3$, SiO$_2$ [17–20].

The preparation of the mixed oxide systems is traditionally based on coprecipitation, hydrothermal or sol–gel methods, but these methods allow one to produce single phase mixed solutions only in the composition range of solubility of corresponding oxides into each other. For instance, less than 20 mol% Sn could be introduced into ceria lattice with single fluorite phase formation [5], on the other hand, about 7%

Ce could be introduced into SnO$_2$ with single rutile phase formation [6,21]. The so-called solution combustion (SC) technique allows one to successfully prepare the metastable Ce$_{1-x}$Sn$_x$O$_2$ solid solutions with a fluorite structure with x in a range up to 0.5 [2,22].

As reported in [12], the SC method also allows one to introduce the noble metals (NM) in the fluorite structure with the formation of an ionic state of NM in mixed oxides NM$_x$Ce$_{1-x-y}$X$_y$O$_{2-\delta}$ (NM = Pd, Pt, X = Ce, Sn, Ti, Hf). However, part of NM was occasionally found to form a metallic state [23,24], most probably due to decomposition of NM precursors at high temperature combustion processes. On the other hand, it is known that incipient wetness impregnation (IWI) of ceria by an NM precursor and further calcination leads to the incorporation of NM ions into the fluorite structure with the formation of an ionic NM state in NM$_x$Ce$_{1-x}$O$_{2-\delta}$ mixed solution [16,25]. From this point of view it seems reasonable to apply the traditional IWI preparation technique to the supports obtained by SC for more efficient NM deposition.

The aim of the present paper was to study how the method of palladium introduction into the Ce$_{1-x}$Sn$_x$O$_2$ mixed solution influences the electronic and structural state of palladium in Pd/Ce$_{1-x}$Sn$_x$O$_2$ catalysts and its catalytic properties in low-temperature CO oxidation.

In this work we prepared two series of Pd/Ce$_{0.5}$Sn$_{0.5}$O$_2$ catalysts. The first one was prepared through the SC of all Pd, Ce, Sn precursors, the second one was prepared by IWI of Ce$_{0.5}$Sn$_{0.5}$O$_{2-\delta}$ support obtained by SC with palladium precursor. We studied how the way of palladium

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introduction influences its interaction with fluorite lattice, and how it results in catalytic properties in a low-temperature CO oxidation reaction.

2. Experimental

2.1. Catalysts preparation

2.1.1. Preparation by an overall solution combustion method (SC series of catalysts)

Starting reagents cerium ammonium nitrate (CAN) $(NH_4)_2[Ce(NO_3)_6]$ and SnC_2O_4 were prepared according to the methods reported in ref. [2,26] from $CeCl_3 \cdot 6H_2O$ and $SnCl_2$ (Sigma Aldrich, 99.9%). Palladium nitrate $([Pd(NO_3)_2(H_2O)_2])$ was prepared from Pd powder by the method reported in [27]. Glycine (Gly) of analytical grade quality was used as the fuel.

A mixture of SnC_2O_4, $(NH_4)_2[Ce(NO_3)_6]$, $[Pd(NO_3)_2(H_2O)_2]$ and glycine (typical reagents loadings are described in Table 1) were grinded and then dissolved in minimal volume of 12 M nitric acid. The resulting clear solution was placed into a ceramic boat and evaporated at room temperature in air stream to give a wet crystals mixture. Then boat was placed in a tube furnace preheated up to 350 °C where the combustion reaction started after melting of the mixture. The process of combustion was completed within 0.1–0.5 s and resulted in the formation of a pale-yellow powder product. After the SC step, the temperature was increased to 450 °C and the sample was kept at this temperature in static air atmosphere for 1 h then cooled down to room temperature and collected.

2.1.2. Preparation by impregnation of the support (SC + IWI series of catalysts)

Pure CeO_2–SnO_2 support was prepared as mentioned in the Section 2.1.1 combustion procedure from a solution of SnC_2O_4, $(NH_4)_2[Ce(NO_3)_6]$ and glycine in 12 M HNO_3. Acetone-absorbing capacity of freshly calcined CeO_2-SnO_2 support was determined (about 5 ml/g). Palladium nitrate was dissolved in an appropriate amount of acetone and the resulting solution was deposited on the support by incipient wetness impregnation. The product was dried in air at 40 °C for 2 h and finally calcined in the furnace at 450 °C for 1 h.

2.2. Characterization

2.2.1. X-ray diffraction study (XRD)

X-ray diffraction study (XRD) of polycrystalline samples was carried out on a DRON-SEIFERT-RM4 diffractometer (CuK$_\alpha$ radiation, graphite monochromator on the diffracted beam, scintillation detector with amplitude discrimination). The patterns were recorded in the step mode in the angular range $2\theta = 20°$–60. Indexing of the diffraction patterns was carried out using the data reported in the JCPDS Data Base [28]. The lattice parameters were refined by the full-profile technique within the whole diffraction range with Powder Cell 2.4 software [29]. The volume-average crystallite sizes (D) were estimated using the integral broadening of the (200) and (220) peaks using WINFIT 1.2.1 software [30] and the Scherrer formula.

2.2.2. The X-ray photoelectron spectroscopy (XPS)

An XPS study was performed using KRATOS ES300. Non-monochromatic MgK$_\alpha$ radiation was used. Spectra were recorded using a low power X-ray source and cooling of the samples in order to prevent a photoinduced reduction of a sample surfaces. The spectra were calibrated against 916.7 eV of the Ce3d line U‴ component. Details of the samples preparation, parameters of spectra registration and mathematical treatments can be found in [31].

2.2.3. Transmission electron microscopy investigation

Transmission electron microscopy investigation was performed by using a JEM-2200FS (JEOL Ltd., Japan) electron microscope operated at 200 kV. The STEM HAADF mode was employed together with the EDX spectroscopy. The samples for the TEM study were dispersed ultrasonically and deposited on a holey carbon film mounted on a copper grid.

2.3. Catalytic activity measurement

The catalysis in CO oxidation was studied with an automated installation in a continuous flow reactor using a temperature-programmed reaction [32]. The gas composition was monitored with mass-spectrometry. A sample of powder was compacted and crumbled into grains with sizes 0.25–0.5 mm (volume 0.25 cm^3), and was then placed in a stainless steel reactor. The reaction mixture containing 0.2 vol.% CO, 1.0 vol.% O_2, 0.5 vol% Ne (balance helium) with the rate 1000 cm^3/min ($GHSV = 240{,}000$ h^{-1}) was fed to reactor which was preliminary cooled to -10 °C. The catalyst was heated from -10 °C to 450 °C at the rate of 10 °C/min followed by cooling and another heating in the reaction mixture. The concentration of CO, O_2 and CO_2 was monitored in the course of the reaction at a 0.34 Hz frequency.

3. Results and discussion

The catalysts phase composition is represented mainly by a fluorite phase with a reduced lattice parameter (Table 1) compared with pure ceria (a = 5.411 Å) and agree well with that reported earlier [2] for $Ce_{0.5}Sn_{0.5}O_2$ solid solution (a ≈ 5.29 Å).

Minor reflections of SnO_2 phase (less than 2%) were observed in addition to fluorite $Ce_{1-x}Sn_xO_2$ phase on XRD patterns of catalysts with 5 at.% Pd, which could be seen on XRD patterns presented in logarithmic scale (Fig. 1). No reflections of Pd^0 or PdO phase are detected in the diffraction patterns of the catalysts with 1 at.% Pd content prepared through both the SC and SC + IWI routes.

Diffuse peaks at 37°, 39° and 44.5° are present on the XRD pattern for 5% Pd-SC catalyst (indicated as "1", "2", and "3" on Fig. 1); also additional weak Pd(111) reflection at 40° is observed. These peaks could be referred to palladium alloys with tin or cerium. These alloys were probably formed during palladium precursor decomposition to metallic Pd at high temperatures of the SC process and occlusion of foreign atoms (Sn, Ce) in the metal structure. The formation of metallic palladium was also observed earlier for 5% Pd/CeO$_2$, catalysts prepared by SC. Moreover, no reflections corresponding to palladium phases were observed on the XRD pattern for 5% Pd-SC + IWI catalyst.

Table 1
Characterization of synthesized samples.

Sample	Reagents, g				XRD		S$_{BET}$, m^2/g	
	CAN	SnC$_2$O$_4$	Gly	[Pd(NO$_3$)$_2$(H$_2$O)$_2$]	a, Å	D, nm	BR[1]	AR[2]
1% Pd-SC				0.028	5.290	10	14	30
5% Pd-SC	3.36	1.27	2.26	0.140	5.299	11	13	26
1% Pd-SC + IWI				0.028	5.317	9	33	31
5% Pd-SC + IWI				0.150	5.320	9	36	37

[1] BR — before reaction (measurements performed before treatment by reaction mixture).
[2] AR after reaction (measurements performed after treatment by reaction mixture).