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A study on structural features of bimetallic Pd-M/C (M: Zn, Ga, Ag) catalysts for liquid-phase selective hydrogenation of acetylene

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ABSTRACT

The present work is devoted to the study of doping effects of zinc, gallium and silver on the structure of active sites and catalytic properties of carbon-supported 0.5 wt% Pd catalysts in the liquid-phase selective hydrogenation of acetylene to ethylene. Carbonaceous graphite-like material Sibunit was used as a support. The reaction was performed in a medium of *N*-methyl-2-pyrrolidone at 55 °C. It was shown that the bimetallic Pd-Zn/C, Pd-Ga/C and Pd-Ag/C catalysts exhibit better activity and selectivity towards target product if compare with the monometallic Pd/C catalyst. The ethylene yield increases in a row as follows: Pd/C (19%) < Pd-Ag/C (34%) < Pd-Ga/C (42%) < Pd-Zn/C (53%). Using X-ray absorption spectroscopy and transmission electron microscopy it was found that an improvement of the selectivity is stipulated by the formation of bimetallic PdZn, Pd_xGa_y and PdAg nanophases. In the case of Pd-Zn/C and Pd-Ag/C systems, an increased distance between neighboring Pd atoms (2.82–2.89 Å) in relation with monometallic Pd/C, where this distance is 2.72 Å, was observed. The higher activity of modified bimetallic systems is connected with increased number of active sites due to enhanced dispersity of supported palladium doped with second metal.

1. Introduction

Nowadays, palladium supported on different carriers is one of the most intensively studied catalytic systems. Pd-based catalysts exhibit excellent activity in such important from practical point of view processes as hydrogenation of organic acids and oils [1,2] and halogen-substituted organic compounds [3,4], selective hydrogenation of polyunsaturated compounds [5] and acetylene [6–12], reduction of aromatic nitrocompounds [13], oxidation of methane [14–16] and carbon monoxide [17–20], etc. At the same time, a tendency towards using the bimetallic [21–29] or even trimetallic [30] systems instead of Pd-only catalysts has to be stated. Doping the Pd-based catalysts with second metal creates a new type of active sites consisting of palladium and modifying metal atoms. As a rule, such sites facilitate an improvement of the process selectivity thus increasing the yield of the target product. In the case of bimetallic catalysts for the selective hydrogenation of acetylene to ethylene, a key role is considered to be played by a dilution of Pd atoms with atoms of modifying metal within the structure of the nanophases being formed. This leads to an increase of the distance between neighboring atoms of palladium from 2.75 Å for metallic Pd to approximately 2.82–2.99 Å depending on the applied modifier [27,31–33]. Such structure of the active sites practically rules out the possibility for strong multisite adsorption of acetylene and, thereby, prevents the realization of secondary reactions such as the hydrogenation of ethylene to ethane and formation of C_{4+} oligomers [21,32]. At the same time, a contribution of electron interaction of Pd with modifier is of significant importance. Atoms of second metal act as donors of electron density for vacant *d*-orbitals of palladium that suppresses an affinity of Pd towards adsorption of unsaturated compounds, facilitates desorption of ethylene and impedes its complete hydrogenation to ethane [21,34].

Among the promising catalysts for the selective hydrogenation of acetylene, Pd-containing catalytic systems doped with silver, gold, zinc, gallium, indium, copper and manganese should be mentioned

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[21,22,34]. These catalysts were reported to be efficient as for industrial gas-phase purification of ethylene from acetylene traces, as for hydrogenation of relatively large amounts of C_2H_2 (above 4 vol.%). For example, the latter process is used in an experimental technology patented by Synfuels International Inc., where acetylene obtained via pyrolysis of natural and associated oil gases is subjected to hydrogenation procedure in order to produce marketable ethylene and/or high-octane components of engine fuels [35,36]. Because the process is strongly exothermic ($\Delta H = 174.5$ kJ/mol), this requires to be performed in a solvent medium for the safety reasons. This approach allows one not only removing the reaction heat but facilitates an improvement in selectivity towards ethylene. On the other hand, a description in the literature of the bimetallic catalysts applied for the considered process is limited by the mentioned patents [35,36]. Thereby, a detailed research in this field attracts both the fundamental and practical interests.

Recently we have already reported about carbon-supported Pd-Ga catalysts for the liquid-phase hydrogenation of acetylene [6,37–39]. Porous carbonaceous material Sibunit was used as a support, which choice was stipulated, first of all, by absence of strong surface acid sites responsible for oligomerization of acetylene [40,41]. Moreover, carbon materials are more preferable than oxide supports (for instance, Al_2O_3) because in the case of the latter a part of modifier's atoms can be lost due to their incorporation into the support bulk with formation of solid solutions [42]. Carbon materials, in their turn, were reported to show a weak or even negligible metal-support interaction [43]. It is obvious that elimination of the negative metal-support interaction should intensify the efficiency of Pd-M interaction (where M is second metal) resulting in the formation of more active and selective bimetallic phases [38]. As it was shown for Pd-Ga/C catalysts, an increase of selectivity (on about 20 rel.%) in relation to the monometallic Pd/C catalyst is connected with the presence of alloyed Pd-Ga particles being formed during the catalyst preparation at the stage of its reductive treatment in a hydrogen flow [6,44]. Possibility in principle for the formation of Pd-Zn and Pd-Ag bimetallic systems characterized with enhanced selectivity in the hydrogenation of acetylene to ethylene was described elsewhere [44]. In the present research, the structural features of carbon-supported bimetallic Pd-Ag, Pd-Zn and Pd-Ga catalysts prepared by an incipient wetness impregnation of Sibunit with solutions of corresponding nitrates are studied in detail. A special attention was paid to intercommunication between the data of transmission electron microscopy (TEM), and X-ray absorption spectroscopy and the catalytic performance of the samples in the liquid-phase hydrogenation of acetylene to ethylene.

2. Experimental

2.1. Preparation of the catalysts

In the present study, porous carbonaceous material Sibunit (fraction of 0.07–0.09 mm) with a specific surface area of 335 m^2/g was used as a support [45]. It should be noted that Sibunit is able to reduce palladium in the solution of its salts with formation of a particulate palladium black. In order to prevent this undesired process, the support was preliminary treated with a 5% solution of nitric acid with subsequent evaporation of the latter on a water bath. Then, the support was dried on air. Such treatment leads to formation of the oxygen-containing functional groups (carboxyl, lactonic and phenolic) on the surface [46], which presence increases the affinity of the carbon support to interaction with the precursors of the active component.

The supported bimetallic catalysts were prepared via an incipient wetness impregnation of the pretreated support with joint aqueous solution of nitrates of corresponding metals ($Pd(NO_3)_2$ and $Ga(NO_3)_3$, $Zn(NO_3)_2$ or $AgNO_3$). The solution was added dropwise to the support's sample at intensive stirring. It should be noted that this preparation technique differs from that previously used for obtaining the similar catalysts [44], when the sample of the support was added to a constant volume of the joint solution and thoroughly stirred until the formation of slurry.

The obtained samples were dried on air at 120 °C for 2 h. The only exception was Pd-Ag/C sample, which was dried in complete darkness at room temperature for 24 h. Then, the samples were reduced in a hydrogen flow (with a flow rate of 60 ml/min) at 500 °C for 5 h. Finally, the palladium loading was 0.5 wt%, and molar ratio Pd:M was 1:1. The reference monometallic Pd/C sample containing 0.5 wt% of palladium was prepared in the similar way.

2.2. Testing the catalytic performance

Catalytic properties of the samples were studied in a non-gradient temperature-controlled shaker-type flow reactor at 55 °C and atmospheric pressure as described elsewhere [40]. The sample of the catalyst (20 mg) was loaded into the reactor along with 8.0 ml of N-methyl-2-pyrrolidone, which was used as a solvent characterized with a high capacity towards acetylene and worse solubility towards ethylene and other reaction products [47]. Then, the reactor was fed with a reaction gas mixture containing 4 vol.% C_2H_2 and 96 vol.% H_2 with a flow rate of 100 ml/min. The reaction was performed under intensive shaking of the catalytic reactor with a frequency of 7–8 s^{-1}. The duration of the catalytic test was 220 min that allows determining the activity under steady state conditions.

The reaction mixture on the inlet and outlet of the reactor was analyzed using a Chromos GC-1000 gas chromatograph equipped with a capillary column (stationary phase SiO_2) and a flame ionization detector. Nitrogen was used as a carrier gas. The catalytic parameters (conversion of acetylene, X_{C2H2}, %; selectivity towards ethylene, S_{C2H4}, %, and ethane, S_{C2H6}, %) were calculated by the normalization method. The selectivity towards oligomers was obtained as follows: $S_{C4+} = 100\% - (S_{C2H4} + S_{C2H6})$. The yield of ethylene (Y_{C2H4}, %) was calculated as a product of acetylene conversion and ethylene selectivity ($Y_{C2H4} = X_{C2H2} \times S_{C2H4}$). The blank catalytic tests carried out for bare Sibunit and Sibunit-supported zinc, gallium and silver (0.3-0.5 wt%) samples have revealed an inertness of these materials in the reaction under study.

2.3. Characterization of the samples

Transmission electron microscopic studies of the samples were performed using a JEOL JEM 2100 microscope with an accelerating voltage of 200 kV and resolution of 0.14 nm. During the pretreatment procedure, the samples were grinded in an agate mortar for 30 s, the obtained powder was mixed with ethanol and dispersed using an ultrasonic equipment (UZDN-2T, Russia). The resulted suspension was deposited on a carbon support fixed on a copper grid. Gold monocrystals with corresponding Miller indexes (111) and interatomic distance of 0.235 nm were used as a reference. The TEM data were used to estimate the average particle size of the supported metals and their particle size distributions. Chemical analysis was carried out using an INCA-250 X-ray energy dispersive spectrometer (Oxford Instruments) with a Si(Li)-detector provided resolution of 130 eV.

The chemical state and structure of local environment of Pd, Zn, Ga and Ag atoms were studied by X-ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopies. The XAS measurements were carried out at the "Structural Materials Science" beamline at the Kurchatov synchrotron radiation source (SRC "Kurchatov Institute", Moscow). The energy of electron beam in the storage ring was 2.5 GeV. Monochromation of the synchrotron radiation was performed using a silicon channel-cut single crystal Si(311) for Pd and Ag K-edge spectra at an energy resolution of $\Delta E/E = 1 \times 10^{-4}$, and Si(111) for Zn and Ga K-edge spectraat $\Delta E/E = 2 \times 10^{-4}$ in the form of monoblock with a cutaway "Butterfly" installed on a goniometer head. All the spectra were measured in a