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Versatile PdTe/C catalyst for liquid-phase oxidations of 1,3-butadiene

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ABSTRACT

A commercial Pd catalyst based on Sibunit carbon support was treated with H_6TeO_6 in a reducing media to obtain a Te coating on the surface of Pd particles. The PdTe/C catalyst prepared in this way showed the ability to control the radical chain oxidation of 1,3-butadiene by promoting the selective formation of 2-butene-1,4-diol, 4-hydroxybut-2-enal and furan in DMA (total selectivity of 61% and yield of 7%). At the same time, the catalyst induced oxidation of 1,3-butadiene by a non-radical heterolytic mechanism involving the formation of two groups of primary products: (1) crotonaldehyde and methyl vinyl ketone and (2) the products of oxygenation at the 1,4-positions. The compounds of the second group including 1,4-dimethoxy-2-butene and maleic acid dimethyl ester were formed on PdTe centers in MeOH. Increasing the Te concentration in the PdTe/C catalyst forced the conversion of 1,3-butadiene toward 1,4-oxygenation and simultaneously decreased the intensity of secondary oxidation, resulting in the selective formation of derivatives of the 1,4-oxygenation—1,4-dimethoxy-2-butene and allenic alcohol methyl ether (total selectivity of 84% and yield of 48%).

1. Introduction

1,3-Butadiene (BD) is readily oxidized and can be a feedstock in numerous catalytic reactions, such as epoxidation [1], obtaining furan, maleic anhydride, and crotonaldehyde [2–4]. Under liquid-phase oxidation conditions, there may be different routes for BD conversion. Interacting with oxygen at a temperature above 50 °C, individual BD and BD in a nonpolar solvent form peroxides with a polymeric structure consisting of 1,2- and 1,4-units [5], whose thermal decomposition [6] yields 1,4- and 1,2-butenediols and products of further conversion, such as furan and acrolein [7,8]. In aqueous solutions of $PdCl_2$ and $CuCl_2$, BD is oxygenated at one of the double bonds to form crotonaldehyde [9]. In a solution of a Pd catalyst and P–Mo–V heteropolyacid as an oxidizer, BD was converted to furan [10]. Furan formation has also been observed in the presence of iodides and a Pd/C catalyst [11], in the presence of NaJ and a mixture of $CuCl_2$–NaCl–HCl chlorides [12], and other transition metal complexes [13]. On PdTe/C catalysts in acetic acid, BD undergoes diacetoxylation with predominant formation (98% selectivity) of 1,4-diacetoxybutene [14,15]. This process has been implemented on a commercial scale by Mitsubishi Chemical Corporation. Other compositions of platinum-group metals with oxides of transition metal different from Te have been tested in this reaction [16,17], where the presence of acetic acid is necessary to stabilize the product in the form of diether [18,19]. BD oxidation on a Pd–Te catalyst was carried out in alcohol to obtain alcoholates of 1,2- and 1,4-diols [20]; a PdTe/C catalyst was also used in this study.

Palladium on carbon catalysts are often used in oxidation reactions due to the ability of metallic Pd to activate oxygen and due to the high absorption capacity of carbon supports for Pd° and Pd^{2+} ions. The active component is not removed from the catalysts, and in the case of oxidation, they can be regenerated in a reducing atmosphere. Promoting effect of Te has been noted in several Pd catalyzed oxidations. In addition to the synthesis of 1,4-diacetoxybutene, several other applications of Pd–Te catalysts to aerobic oxidation of multiple bonds are known. For example, PdTe/C catalysts have been patented for oxidation of 1-butene in vapor to methylethylketone [21], and isobutylene in a water-*t*-butanol solvent to methacrolein and methacrylic acid [22]. Promotion of Pd catalysts with tellurium raises the activity and particularly selectivity of the synthesis of acetic acid from ethylene [23,24], the oxidation of alcohols to carbonyl compounds ([25] and references therein), glucose to gluconic acid [26], sodium lactate to pyruvate [27,28], para-alkoxytoluenes to alkoxybenzaldehyde and alkoxybenzyl acetate [29], and lactic acid to pyruvic acid [30]. The nature of the promoting effect of Te, and Se, Bi, Sb, Tl, etc.,

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in supported bimetallic catalysts has been discussed in the literature [16,30–32]. It is suggested that in the case of tellurium, the effect is due to the fairly strong interaction between Pd and Te, which leads to a charge redistribution between the atoms [18]. Attempts have been made to explain the promoting effect by the formation of palladium tellurides, which acts as a coupled redox system. In several studies, telluride phases of the compositions Pd_3Te/C [30], PdTe/C and $PdTe_2/C$ [32], $PdTe_n/SiO_2(Al_2O_3)$, $n = 1$ and 2 [26], and $PdTe/SiO_2$ [16] were detected by XRD. However, it has not been possible to relate the activity of the catalysts to the presence of a particular phase; in other cases, Pd–Te phases have not been detected, perhaps because of the high dispersion of the active components on the surface of the carbon support [18].

In the present study, we investigated the catalytic properties of PdTe/C catalysts prepared from a commercial palladium catalyst by precipitation of tellurium on a palladium surface in a reducing media. The catalyst performance was studied in the oxidation of 1,3-butadiene involving several competing mechanisms. Parameters of the catalytic system that can force the oxidation to follow each route, in particular, oxygenation at the 1,4-positions of BD were determined.

2. Experimental

The commercial catalyst IKT-3-23 4.8%Pd/C (Pd/C) was prepared by hydrolytic deposition of palladium from H_2PdCl_4 solution on carbon support (Sibunit, S_0 400 $m^2 g^{-1}$, powder with a particle size of 100 μm) in the presence of sodium formate reducing agent. To obtain the Pd–Te samples, the Pd/C sample was suspended in H_6TeO_6 solution sufficient to obtain 0.5, 2.5 and 5% Te in the samples. Sixfold molar excess of formalin was added, and the mixture was kept 1 h at 60 °C. The sample was filtered from solution and dried at 60 °C under reduced pressure. The Te/C sample was prepared by addition of telluric acid H_6TeO_6 to carbon suspended in water. Reducing and other procedures were made as previously described. The Pd and Te contents in the catalysts were determined by XRF (X-Ray Fluorescence) analysis. The catalysts obtained had the following composition: 4.7% Pd + 0.5% Te/C (Pd0.5Te/C), 4.7% Pd + 1.8%Te/C (Pd1.8Te/C), 4.7% Pd + 2.7% Te/C (Pd2.7Te/C) and 5%Te/C (TeO_2/C). The catalysts were in contact with air during storage.

CO adsorption measurements were made on AutoChemII 2920 (Micromeritics) instrument. Pd dispersion in the Pd/C catalyst was determined based on CO/Pd = 1 stoichiometry, and Pd particle size (nm) was calculated as 1.13/dispersion [33].

XRD (X-Ray Diffraction) patterns of the catalysts were recorded on ARL X'TRA diffractometer using CuK radiation (1.54184 Å). The definition of phase composition was performed by comparing the positions and intensities of the diffraction peaks with data cards PC-PDF ICSD. The mean sizes of Pd crystallites were determined from the full widths on a half of maximum of the (2 2 0) peak, using the Scherrer equation.

HAADF-STEM (High Angle Annular Dark Field Scanning Transmission Electron Microscopy), EDX (Energy Dispersive X-ray spectroscopy) and elemental mapping were made on JEM 2200FS (JEOL, Ltd.) microscope. Suspension of the catalyst in ethanol was deposited on carbon-film-coated copper grids. EDX mapping and line analysis were obtained on C K ($E = 0.266$ keV), Pd L ($E = 2.836$ keV) and Te L ($E = 4.424$ keV) edges. Locality of line analysis was about 1 nm.

Catalytic experiments were carried out in a 300 ml steel reactor (Parr Instrument). The reactor with a catalyst and solvent was sealed, air was removed by pump, the reactor was loaded with a fixed volume of BD under stirring and heated to reaction temperature. The reactor was pressurized with a gas of composition O_2: N_2 = 10: 90 to $P = 40$ atm, and stirring was started. After some time, the reactor was cooled to 15 °C and depressurized. The liquid was centrifuged to remove the catalyst and analyzed by gas chromatography (GC), instrument Kristall 2000, SPB-1000, 30 m × 0.53 mm capillary column. Identification of the products was based on retention times and data of GC–MS, HP-5 column.

Pd and Te in solution after catalysis were determined by ICP (Inductively Coupled Plasma Atomic Emission Spectroscopy) technique, and peroxide content was determined by iodometric titration.

3. Results and discussion

3.1. The state of Pd and Te in the catalysts

The chemisorption measurements of the Pd/C sample showed adsorption of 0.25 mol CO per 1 g-atom of Pd. Based on the

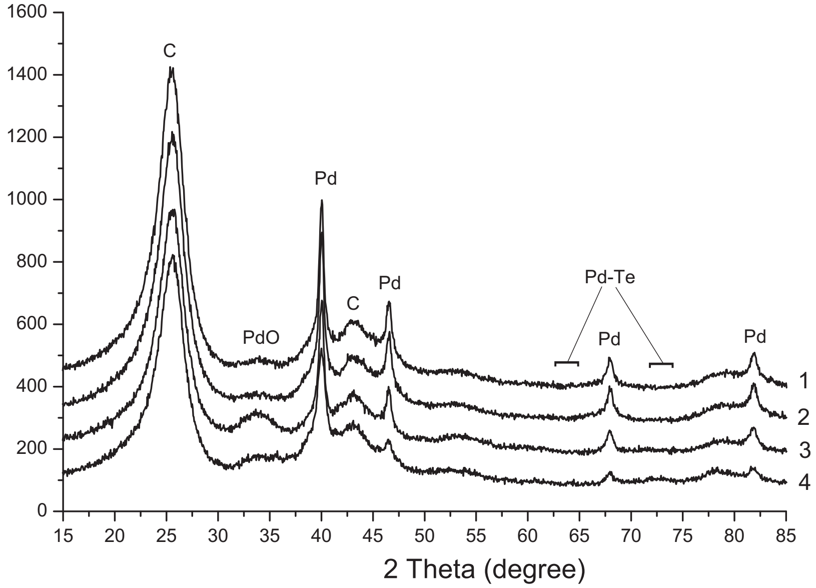

Fig. 1. Diffraction patterns of catalysts Pd/C (1), Pd0.5Te/C (2), Pd1.8Te/C (3), Pd2.7Te/C (4). Reflections of observed phases and positions of suggested Pd–Te phases are indicated.