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Highly selective/enantioselective Pt-ReO$_x$/C catalyst for hydrogenation of L-malic acid at mild conditions

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ABSTRACT

The catalyst preparation strategy was based on a strict introduction sequence of rhenium and platinum precursors and their strong interaction with carbon support resulted in the formation of 0.5 nm Pt-ReO$_x$ species of atomic dispersion, where platinum is metallic, while monolayer rhenium is partially oxidized (Re^{2+}). The reaction kinetics was studied taking into account the process of L-malic acid association leading to the formation of inactive cyclic oligomeric species. High TOFs (ca. 50 h^{-1}), selectivities (ca. 99%) and stability of Pt-ReO$_x$/C catalysts in aqueous-phase hydrogenation of L-malic acid, which are close to those of the homogeneous pincer type complexes, were revealed at mild conditions ($T = 90$–130 °C). Taking into account that (i) hydrogenation reaction occurred 2–3 orders of magnitude faster than its racemization and (ii) association of L-malic acid dominates at low temperatures and in a concentrated solution, special reaction conditions that allow obtaining chemically and optically (ee > 99%) pure *(S)*-3-hydroxy-γ-butyrolactone and *(S)*-1,2,4-butanetriol were found. Basing on HAADF-STEM, EDX, XPS, and kinetic studies, the structure of active species and basic reaction pathways are proposed.

1. Introduction

Carboxylic acids form a large class of biomass-derived molecules, which are produced via biocatalytic transformations. However, if only biomass conversion is used, it is difficult to synthesize chemically and optically pure substances that can be obtained from petroleum feedstock. So, at a certain stage of biosynthesis it is necessary to employ the possibilities of heterogeneous catalysis. In the case of hydrogenation of carboxylic acids, selectivity/enantioselectivity to alcohols depends to a great extent on conditions of the heterogeneous catalytic reaction, primarily on the number and type of functional groups in the platform molecule. Impressive selectivities to alcohols were reached in recent years upon hydrogenation of fatty acids [1–8], bifunctional acids having an additional carbonyl (for example, levulinic acid [9,10]) or hydroxyl group (lactic acid as a typical example [11,12]), and dibasic carboxylic acids (mostly succinic acid [9,13–15]). Products of the indicated reactions – mono- and diatomic alcohols – are the key intermediates for the production of lubricants, surfactants, plasticizers, and other specialty chemicals and polymers.

The most active catalysts in selective hydrogenation of carboxylic acids are the TiO_2, C or SiO_2 supported platinum group metals (mostly Pt, Pd and Ru) that are modified with transition metals of groups 6 and 7 (mostly Re) [9,12–15]. The effect of rhenium was attributed to the chemical interaction between noble metal and rhenium, which results in the formation of active bifunctional sites where the state of a noble metal is close to zero-valent, while rhenium is in the oxidized state. As follows from scanning transmission electron microscopy (STEM), X-ray absorption spectroscopy (XAS) and XPS data, the active sites in bimetallic catalysts are nano- and subnanometer particles of a noble metal (Pt, Pd, Ru or Rh) covered with low-valent ReO$_x$ species of atomic dispersion [6,8,12,15–21]. It is assumed that heterolytic dissociation of molecular hydrogen with the formation of metal hydrides (H^-) proceeds on adjacent metal and oxide sites, and protons are stabilized on the basic oxygen atom in rhenium oxide clusters [6,8]. Thus, the higher activity and selectivity of bimetallic catalyst in comparison with monometallic one are attributed to the formation of reactive metal hydrides, which can efficiently hydrogenate carbonyl group to the alcohol one under quite mild conditions of the reaction. In distinction to heterogeneous systems, homogeneous Ru(II) complexes with N-heterocyclic carbene ligands can quantitatively hydrogenate esters to alcohols even under milder conditions ($T = 50$ °C, $P_{H2} = 25$ atm) [22]. In addition, homogeneous metal-organic complexes of Ru, Pd, Ir with bulky pincer-type ligands containing donor heteroatoms (mostly N) also showed an extremely high performance in hydrogenation/hydrogenolysis of carboxylic acids and esters [23–25]. It seems that the homogeneous systems with bifunctional acid-base properties are able to perform more efficiently a heterolytic cleavage of the H–H bond in a

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hydrogen molecule. As a result, hydrogenation/hydrogenolysis of carboxylic acids to alcohols proceeds at high rates, virtually quantitatively, and under very mild reaction conditions.

Much less attention was paid to hydrogenation of trifunctional acids, in particular malic acid, which has chiral properties. At the same time, it is known that hydrogenation products of malic acid, (S)−3-hydroxy-γ-butyrolactone (3-HBL) and (S)−1,2,4-butanetriol (BT), are valuable chiral building blocks for the production of such cholesterol-lowering drugs as Crestor [26,27]. However, we found only two examples of selective L-malic acid hydrogenation to (S)−3-HBL and (S)−1,2,4-butanetriol using mono- and bimetallic catalysts [28,29]. In addition, optically pure (S)−3-HBL can be produced by chemoenzymatic method, i.e., via selective hydrogenation of malic acid over zinc borohydride catalyst followed by hydrolysis with enzymes [30] or via direct biosynthesis from glucose [31].

The present work is devoted to selective hydrogenation of an aqueous solution of L-malic acid to lactones and alcohols over Pt-ReO_x/C catalysts. The activated carbon was selected as an acid-resistant support since malic acid is quite strong. The catalysts were prepared according to method developed in our previous work for synthesis of Pt-ReO_x/TiO_2 [6]. The catalyst preparation strategy was based on a (i) strict sequence of metal introduction: rhenium prior to platinum; (ii) strong interaction of the forming low-valence ReO_x species with support and further Pt(II) complexes with highly dispersed ReO_x species to form atomically dispersed Pt^0–ReO_x ($x \leq 1$, Re/Pt = 2) active sites. The prepared catalysts were tested in selective hydrogenation of hexanoic acid to compare their performance with those obtained for Pt-ReO_x/TiO_2 [6].

However, the main emphasis was made on studying the selective hydrogenation of an aqueous solution of L-malic acid to lactones and alcohols with due regard to racemization of the acid and reaction products. Data on hydrogenation kinetics of the acids were used to propose the basic reaction pathways of malic acid towards lactones and alcohols. Oligomerization of L-malic acid was studied by in situ FTIR. Probably, for the first time the reaction rates were calculated taking into account a real concentration of the L-malic acid monomers directly involved in the hydrogenation process. Since L-malic acid as well as 3-HBL and BT have chiral properties, racemization kinetics was studied, in addition to kinetics of the hydrogenation reaction, in order to obtain optically pure products of the reaction.

2. Experimental

2.1. Catalysts synthesis

The activated carbon (Norit SX Ultra, fraction 50–100 µm) was used as a support for preparation of Pt-ReO_x catalysts. This carbon support has a specific surface area of 1000 m^2/g, S_{BET} of micropores of 630 m^2/g and pore volume of 0.87 cm^3/g, which includes volumes of micro- and mesopores of 0.29 and 0.58 cm^3/g, respectively. The Pt-ReO_x/C catalysts were synthesized by the adsorption method; rhenium was introduced prior to platinum, because the reverse order of their introduction gave a much lower activity. The amount of deposited rhenium was 10% and 20%, the last one approximately corresponding to a monolayer coverage of the mesopore surface. Platinum content in the sample was varied from 5% to 15%. As the catalyst is highly pyrophoric, all stages of the synthesis were performed without contact with air in a special heat-resistant vessel that allows for heating in a sand bath, evacuation and purging of the vessel with dry helium or hydrogen for thermal treatments in a reducing medium. Prior to the impregnation, the support was evacuated with a water-jet pump at 300 °C for 2 h. After cooling to room temperature, activated carbon was supplemented with an excess of deionized water (7 mL/g), and the resulting suspension was stirred for 30 min. This was followed by the addition of ammonium perrhenate (JSC KRASTSVETMET, Russia, CAS 13,598-65-7, 69.4% Re) solution (2 mL/g) with a concentration of 0.14 g_{Re}/mL on metallic rhenium base. The suspension was heated to 40 °C and stirred in vacuum for 5 h until complete evaporation of water. Upon drying, the sample was heated to 250 °C in flowing helium and held at this temperature for 30 min to provide full decomposition of ammonium perrhenate. This was accompanied by intensive release of molecular nitrogen, which indicates the intramolecular reduction of Re^{7+} cations by ammonium. The sample was cooled and evacuated, then platinum was introduced by the same method: first an excess of water (7 mL/g) was poured and then a $[Pt(NH_3)_4](NO_3)_2]$ (JSC AURAT, Russia, 48.1% Pt) solution (2 ml/g) with different platinum concentrations, and the resulting suspension was stirred at 40 °C for 5 h in vacuum to provide a complete removal of water.

After that, the sample in a dry box was transferred to a tubular reactor, where it was reduced for 2 h in flowing hydrogen at 450 °C, and then the sample in a dry box was transferred to a Parr reactor for catalytic testing.

2.2. Kinetics studies

Comparative testing of the best 10%Pt-15%ReO_x/TiO_2 and 10%Pt-20%ReO_x/C catalysts in the hydrogenation of hexanoic acid was performed in a high-pressure unit with a 450 mL Parr reactor at a temperature of 130 °C and hydrogen pressure 50 bar. A reduced catalyst sample (2 g) in a dry box was introduced to 150 mL of a 5% solution of the acid in dodecane. After that, the reactor was purged with nitrogen and heated to 130 °C, and hydrogen pressure was set at 50 bar. The reaction was carried out under stirring of the catalyst suspension at 700 rpm, at a hydrogen flow rate of 1 L/h, with periodic sampling of the liquid and gas to analyze the acid and the reaction products by GC and GC–MS methods (see Supporting Information).

The kinetics of malic acid hydrogenation and racemization of chiral substances was studied in the same unit using the Parr reactor having a Teflon insert. A reduced catalyst sample (2.6–5.2 g) in a dry box was added to 100 mL of an aqueous solution of the acid. Concentration of malic acid was varied from 0.5 to 15 wt%, which corresponded to changes in the initial pH value of the solution from 2.2 to 1.1. After purging the reactor with nitrogen, hydrogen was admitted to a pressure of 90 bar, and reactor was heated to a specified temperature (90, 100, 110, 130 and 150 °C). The reaction was performed under stirring at 700 rpm, at a hydrogen flow rate of 1 L/h, with periodic sampling of the liquid and gas to analyze the acid and the reaction products by GC, HPLC and GC-MS methods (see Supporting Information). Optical purity of the acid and its hydrogenation products was measured by polarimetry and HPLC with a chiral column (see Supporting Information).

Special experiments revealed that in the studied temperature and pressure range the reaction proceeds in the kinetic region and is not limited by diffusion (Figs. S1 and S2 in the Supporting Information). To determine the reaction order on hydrogen, pressure in the reactor was varied from 1 to 75 bar.

2.3. Characterization of catalysts

The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained with a JEM-2200FS electron microscope (JEOL, Japan) equipped with a Cs-corrector and an omega-type energy filter. Local energy-dispersive X-ray analysis (EDX) was carried out on an EDAX spectrometer (EDAX Co) fitted with a Si(Li) detector with a resolution of 130 eV. To avoid contact with air, a freshly reduced sample was placed in

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