



Role of the electronic state of rhodium in sodium borohydride hydrolysis

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ABSTRACT

The activity of Rh/TiO₂ catalysts subjected to a thermal treatment at different temperatures prior to their reduction has been studied in a NaBH₄ hydrolysis medium. It was found that the sodium borohydride hydrolysis rate increases with increasing the treatment temperature of unreduced catalysts. The state of rhodium in reduced Rh/TiO₂ has been studied by a set of physical methods. In the catalyst calcined at 300 °C, nanoscale electron-deficient particles of rhodium were observed on the surface of titanium dioxide. The study confirmed that the decrease in the electronic density on the metal particles was due to interfacial charge redistribution between metal and semiconducting oxide. The presence of electron-deficient Rh particles on the catalyst surface leads to an enhanced decomposition of negatively charged BH₄⁻ ions and reduction of water to hydrogen proceeding by an electrochemical mechanism.

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1. Introduction

The current investigations of the catalytic hydrolysis of NaBH₄ are mainly focused on searching for active and stable catalysts, optimizing the process conditions and improving the generator design. However, the results obtained by different research groups on the influence of the nature of metals on catalytic activity in NaBH₄ hydrolysis are rather controversial [1]. Thus, according to Brown et al. [2], rhodium and ruthenium are the most active metals in NaBH₄ hydrolysis, while Kojima et al. [3] and Garron et al. [4] reported that it is platinum that shows the highest activity. Unfortunately, the electrochemical mechanism of borohydride anion interaction with water on the catalytically active surface proposed by Holbrook and Twist [5] was not taken into consideration to explain these results. This mechanism has been confirmed experimentally by a Lithuanian research team headed by Prokopchik when studying NaBH₄ hydrolysis in the presence of massive rhodium and copper catalysts [6,7].

The state of the active component of sodium borohydrolysis catalysts has been given little attention. But this issue cannot be ignored in the case of oxide supports where there may be strong

interaction between the support and the active component precursor during preparation and reduction processes. The main signs pointing to the presence of a strong metal–support interaction are the formation of inter-metallic compounds, a change in dispersion of the active component and its decoration by the support as well as a change in the charge state of the metal [8–10] as a result of which the activity of catalytic systems may vary in different processes [11]. The strong interaction of platinum group metals (Pt, Pd, Rh, Ru, Ir) with titanium dioxide is well explainable within the general Cabrera–Mott theory which was used by Fu and Wagner to describe this phenomenon [12]. The contact between the metal and its oxygen-containing surface layer will make an additional influence on the charge state of both the metal and the surface oxide film, especially in the case of nanoscale particles of the active component [13,14]. Depending on Fermi energy levels in the metal and the surface oxide film the electronic density of the metal particles will be either increased or decreased [15–17] which will influence the rate of catalytic processes involving charged ions.

In the present work, rhodium catalysts based on a TiO₂ nanopowder reduced in sodium borohydride medium were used as objects of the study. The effect of calcination temperature of unreduced Rh/TiO₂ catalysts on the rate of sodium borohydride hydrolysis has been studied. Using HR TEM, XPS, EXAFS–XANES-spectroscopy the state of rhodium in Rh/TiO₂ catalysts which had

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different extents of support–precursor interaction (due to different thermal pretreatment temperatures) has been investigated.

2. Experimental

2.1. Catalyst preparation

The Rh/TiO₂ catalysts were prepared using TiO₂ nanopowder (Aldrich, CAS 1317-70-0) which was calcined at 500 °C for 4 h. The specific surface area of the sample was 107 m²/g. X-ray diffraction analysis revealed that TiO₂ sample was fully crystallized and appeared to be highly phase-pure anatase. The coherent scattering on the anatase (101) plane was 110 Å. The small particle size of TiO₂ was used to avoid mass transfer limitations. Chemical analysis revealed no impurities in the catalysts, thus enabling their study by magnetic susceptibility measurements.

The Rh/TiO₂ catalysts were prepared by incipient wetness impregnation of titanium dioxide with an aqueous solution of RhCl₃ (Joint Stock Company Aurat). After the impregnation, the catalyst sample was dried under an IR lamp at 50–60 °C and then in air at 110–130 °C for 2 h, after which a portion of the sample was calcined at 300 °C in air for 4 h. The content of rhodium was 5.95 ± 1 wt%. The catalysts are denoted as Rh/TiO₂-X, where X indicates the calcination temperatures of the unreduced catalyst.

2.2. Catalyst characterization

The state of rhodium in Rh/TiO₂ catalysts depending on the thermal treatment temperature of the unreduced catalyst was studied by high-resolution transmission electron microscopy (HR TEM), X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure spectroscopy (EXAFS), X-ray absorption near edge structure spectroscopy (XANES) and magnetic susceptibility. Unlike our earlier studies [18–20], in this work the catalysts were stored and handled under argon (except for calcination) to prevent any changes in the state of the active component that may be caused by oxygen and water vapors present in the air.

The contents of Rh and Cl were determined by X-ray fluorescence method on a VRA-30 instrument with a Cr anode of the X-ray tube.

The phase analysis of titanium dioxide was performed on a URD-63 (Seifert-FPM, Germany) diffractometer with a CuK α radiation. The coherent scattering region was calculated by the Debye–Scherrer formula. The contents of individual crystalline phases in the sample were determined using the PCW program.

The HR TEM studies of the catalysts were carried out on a JEM-2010 (JEOL, Japan) instrument with a lattice resolution of 1.4 Å and an accelerating voltage of 200 kV. The samples were fixed on “holey” carbon films supported on copper grids and examined with an electron microscope. To construct the particle size distribution diagrams, the diameters of at least 300 particles were determined. The mean Pd particle sizes are quoted [21] as both a number average diameter (\bar{d}_n),

$$\bar{d}_n = \frac{\sum_i n_i d_i}{\sum_i n_i}, \quad (1)$$

and surface area-weighted diameter (\bar{d}_s),

$$\bar{d}_s = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}, \quad (2)$$

where n_i is the number of particles of diameter d_i .

X-ray photoelectron spectra were recorded on a SPECS (Germany) photoelectron spectrometer using a hemispherical PHOIBOS-150-MCD-9 analyzer and FOCUS-500 (Al K α radiation, $h\nu = 1486.74$ eV, 200 W) monochromator. The binding energy (BE)

scale was pre-calibrated using the positions of the peaks of Au4f_{7/2} (BE = 84.0 eV) and Cu2p_{3/2} (BE = 932.67 eV) core levels. The samples in the form of small granules or powder were placed onto a conducting double-sided copper scotch. The Ti2p_{3/2} peak at 458.7 eV of the titanium oxide support was used as internal standard. In addition to the survey photoelectron spectra, more narrow spectral regions B1s + Cl2p, C1s, Cl2p, Rh3d, Ti2p, O1s and the valence band were recorded. The survey spectra were taken at analyzer pass energy of 50 eV and the detailed spectra were registered at 20 eV. Analysis of the individual spectral regions allowed determination of peaks, identification of the chemical state of elements and calculation of atomic concentration ratios of elements on the sample surface. The concentration ratios of elements on the catalyst surface were calculated from the integral photoelectron peak intensities which were corrected with theoretical sensitivity factors based on Scofield's photoionization cross sections [22]: B1s—0.486, Cl2p—2.29, C1s—1, Rh3d—14.2, Ti2p—7.81, O1s—2.93.

EXAFS and XANES spectra of the K absorption edge of rhodium were measured at the EXAFS station of the Siberian Synchrotron Radiation Center. The spectra were recorded in the VEPP-3 storage ring at an energy of electrons of 2 V and an average current of 80 mA in the transmission mode of operation. The spectrometer has a cut-off two-crystal Si(111) monochromator and proportional chambers as detectors. The EXAFS and XANES spectra were measured in steps of 2 and 0.4 eV, respectively. Data processing was performed by the standard procedure using the VIPER software package [23] to isolate the oscillating part of the absorption coefficient, and FEFF-7 software [24] to calculate the modeling parameters. The XANES spectra were normalized to the absorption jump maximum by means of XANDA [23]. The first derivatives were used to determine the inflection point of the XANES spectrum.

Magnetic susceptibility in the temperature interval 1.5–300 K was measured with a SQUID magnetometer MPMS-5XL (Quantum Design) at field strength of 1 kOe.

2.3. Reaction

Sodium borohydride hydrolysis was carried out at 40 °C in a temperature-controlled glass reactor equipped with a magnetic stirrer operating at 800 rpm. At stirring rates of higher than 200 rpm the influence of the external diffusion processes was shown to be negligible. A weighed amount of NaBH₄ (0.0465 g; 1.2 mmol; Acros Organics, 98 wt%) was loaded into the reactor and dissolved in 10 ml of distilled water. A weighed amount of the catalyst (0.0062 g) was then added and the volume of the generated hydrogen gas was measured with a gas burette. The catalysts were reduced directly in the reaction medium of sodium borohydride. After the reaction was complete, the catalysts were separated from the reaction medium, washed with distilled water, dried at 40 °C for 4 h under argon and then studied by the above physical methods.

3. Results

3.1. Sodium borohydride hydrolysis over Rh/TiO₂ catalysts

Rhodium-titanium catalysts reduced in a sodium borohydride hydrolysis medium at ambient temperature were the objects of study. Prior to the reduction, the catalysts (RhCl₃ supported on TiO₂) were subjected to a thermal treatment in air: Rh/TiO₂-110 was dried in a drying box at 110–130 °C and Rh/TiO₂-300 was calcined in a muffle furnace at 300 °C. The activity of the catalysts was studied in the reaction of sodium borohydride hydrolysis. The results are shown in Fig. 1.

According to the data of Fig. 1, in the initial stage of the reaction, when the reduction of the catalysts takes place, the rate of

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