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Noble metal catalysts supported on gadolinium doped ceria used for natural gas reforming in fuel cell applications

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Abstract

An attractive possibility to simplify a fuel cell system would be the use of a sulfur-tolerant reforming catalyst. In an effort to find such a catalyst, platinum, rhodium and ruthenium catalysts supported on ceria doped with 20% gadolinium and on pure ceria were synthesized and characterized. A temperature-programmed reduction study of the reduction behavior of the catalysts showed that the doping of ceria with gadolinium enhances the low temperature reduction, while the high temperature reduction is suppressed. The activity as well as the stability of the catalysts can be correlated with the reducibility of the materials. The most stable catalyst, rhodium supported on gadolinium doped ceria, shows promising sulfur-tolerance.

Keywords: Ceria; Gadolinium; Rhodium; Fuel cells; Reforming; Sulfur; Poisoning; Metal-decoration

1. Introduction

Polymer-electrolyte-membrane (PEM) fuel cells convert oxygen and hydrogen into heat and electrical energy. While oxygen is directly available from air, hydrogen must be produced from suitable feedstocks. For decentralized power generation with small fuel cell systems, natural gas can be used as feed, as it is often readily available through existing pipeline systems in cities. Considering the planned mass production of devices for decentralized combined heat and power generation, their design must accommodate all possible feed qualities with only minor modification.

The composition of natural gas varies in time as well as in location, both in the hydrocarbons contained and in regards to impurities, such as sulfur compounds. Sulfur compounds typically encountered in raw natural gas include low molecular weight compounds such as hydrogen sulfide (H_2S), carbon oxysulfide (COS), carbon disulfide (CS_2), and organic compounds such as sulfides (R–S–R′), disulfides (R–S–S–R′), and mercaptans (R–SH). Before transportation, these compounds are largely removed, since they are mostly toxic and corrosive in combination with water. The purified natural gas, however, still contains trace amounts of H_2S, COS, CS_2, as well as short chain mercaptans and sulfides.

For safety reasons, natural gas distributed to households is odorized with a strong scent, the odorant. In the USA, the UK and Japan, mainly mercaptan mixtures (based on isopropylmercaptan, IPM or tert-butyl mercaptan, TBM) are used for this purpose, while in Germany and most of Europe tetrahydrothiophene (THT) is preferred. Typical odorant loadings are about 15–20 mg m^{-3} for THT and 5–7 mg m^{-3} for mercaptan mixtures. Assuming a sulfur-poor gas with about 0.5 mg m^{-3} sulfur and a sulfur-rich gas with about 8 mg m^{-3} sulfur, one can estimate the total sulfur loading of distributed gas to somewhere between 2.3 and 15.3 mg m^{-3}. Thus, for fuel cell applications, a total sulfur content in the natural gas of about 10–15 mg m^{-3} is a good assumption, however, short duration peaks in sulfur content up to 150 mg m^{-3} are nevertheless allowed (German regulation [1]).

Sulfurous compounds have to be removed from the feed stream prior to the hydrogen production because of their poisonous effects on the catalysts used [2]. An attractive possibility to simplify a fuel cell system would be the use of a sulfur-tolerant reforming catalyst. In this scheme, the reformer would also act as hydrotreating reactor, converting all sulfurous compounds to H_2S, which can be easily removed downstream

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from the reformer. The main advantage of such a system would be a much simpler operation and faster dynamic response because of the elimination of one process step and of the hydrogen recycle. In addition, the required investment is reduced because fewer vessels, piping and control equipment are needed.

Such a sulfur-tolerant catalyst, though, is not available at this time. Mainly, the use of ceria-based materials similar to the ones commonly used in three way catalysts for exhaust gas treatment have been proposed to improve the reforming catalysts regarding their sensitivity to deactivation by carbon deposition [3–5]. Ahlborn et al. [6], however, also claim that the addition of ceria to noble metal catalysts increases their sulfur-tolerance in autothermal reforming. In addition, Krumpelt et al. [7,8] report that a platinum catalyst supported on gadolinium doped ceria showed good sulfur-tolerance. In their work on autothermal reforming of diesel for transportation applications, up to 1300 ppm of benzothiophene (weight basis) could be added to the feed without noticeable change in product gas composition.

Gadolinium doped ceria (CGO) has received much attention as anode material in solid-oxide-fuel-cell (SOFC) technology [9,10]. The use of CGO as support material for catalysts, however, is not yet researched. We, therefore, prepared noble metal catalysts supported on gadolinium doped ceria and evaluated these catalysts concerning their activity, stability and sulfur-tolerance. For comparison with other published results, similar catalysts supported on pure ceria were also prepared.

2. Experimental

2.1. Sample preparation

The ceria sample was prepared by glycine–nitrate combustion according to a procedure similar to the one presented by Purohit et al. [11]. Cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) and the stoichiometric amount of glycine (as described in Ref. [11]) were dissolved in a small amount of water. The liquid was placed in a pressure-vessel and heated. After evaporation of the water, the vessel was closed and further heated until ignition. After the vessel had cooled down, the resulting powder was transferred to an oven and calcined at 550 °C for 2 h in air.

For the doped ceria sample, a Ce:Gd molar ratio of 0.8:0.2 was chosen, since this material is well studied due to its electrochemical properties [9] and because it was preferred by Krumpelt et al. [7,8]. The material $Ce_{0.8}Gd_{0.2}O_{1.9-\delta}$ is further referred to as CGO for simplicity. Preparation was accomplished by adding gadolinium nitrate ($Gd(NO_3)_3{\cdot}6H_2O$) to the synthesis solution as described above and adjusting the amount of glycine accordingly. Similarly, the metal-containing materials were prepared by further adding the desired amount of the metal precursor to the mixture. $Ru(NO)(NO_3)_3$, $Rh(NO_3)_3$, and $Pt(NH_3)_3(NO_3)_3$, respectively, were used as metal precursors, the noble metal loading Y_{NM} was 2.5 wt.% for the reduced catalyst. For these samples, calcination was also carried out at 550 °C for 2 h in air. All chemicals were supplied by Alfa Aesar, Karlsruhe, Germany.

2.2. Characterization

The specific surface area (according to the BET method, S_{BET} [12]) was determined by a Micromeretics ASAP 2010 unit using argon at 77.35 K.

For scanning electron microscopy (SEM), the fresh catalysts were mounted on carbon foil, coated with a thin Pt film using a sputtering device and examined using a Leo 1530 Gemini microscope operating at 3 kV. For high-resolution transmission electron microscopy (HR-TEM) the samples were dispersed in acetone using ultrasound and the suspension was flash-evaporated on a copper grid. The samples were examined with a Phillips CX200 microscope operating at 200 kV offering a spatial resolution of about 0.2 nm. The microscope was equipped with an energy dispersive X-ray microanalysis system (EDX, Noran Voyager). From the noble-metal particle size, the dispersion can be derived using a correlation given in [13].

Powder X-ray diffraction (XRD) spectra were collected with a Siemens D500 diffractometer in the range of $2\Theta = 20–80^\circ$ using Cu Kα radiation, a step size of 0.01° and an acquisition speed of $0.5^\circ\ min^{-1}$. Peak positions and lattice parameters were refined using the least-squares refinement program ERACEL [14].

For elemental analysis, the samples were dissolved in sulfuric acid and the solution was analyzed with an inductively coupled plasma optical emission spectrometer (ICP-OES, Vista-Pro, Varian).

Temperature-programmed reduction (TPR) was carried out by heating a 100 mg sample under flowing 5 vol.% H_2 in Ar from room temperature to 800 °C with a heating rate of $15\ K\ min^{-1}$. At 800 °C, the experiment was continued isothermally to determine the maximum amount of oxygen that can be extracted from the sample until this temperature. The effluent gases were monitored using a mass-spectrometer (MKS Minilab).

2.3. Catalytic performance

The catalytic tests were conducted in a fixed-bed ceramic reactor with 7 mm inner diameter. One hundred milligrams of the fresh catalyst was diluted with about 300 mg quartz, and the mixture placed in the reactor supported on a quartz wool plug. The reactor was equipped with a thermocouple to monitor the temperature at the outlet of the catalyst bed. The reactor was heated with an electrical oven, the gases were dosed using mass flow controllers. Liquid water was dosed with a mass flow controller and was evaporated using the reactant gas flow to spray the mixture in a falling film vaporizer.

The gas composition was monitored using a Varian CP-2003 Micro-GC equipped with a molsieve 5A, a PoraPlotQ column and thermal conductivity detectors; helium was used as carrier gas.

Prior to the catalytic tests, the catalysts were reduced in a flow of 20 vol.% H_2 in N_2 at 500 °C for 3 h. For the catalytic tests, the pressure on the reactor outlet was held constant at 0.3 bar above ambient pressure. Since the flow rate is changed by the reaction, nitrogen is added as internal standard.