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Zirconium phosphate-based porous heterostructures: A new class of materials for ammonia sensing

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ABSTRACT

Metal(IV) phosphates such as zirconium phosphate (ZrP) are well known proton conductors based on the mobility of protons localized at Brønsted-acid sites. By introduction of mesoporous silica into the inter-layer region, these compact materials are transformed into Porous Phosphate Heterostructures (PPH). Here we studied the electrical properties of PPH and show that the proton conductivity is supported by ammonia, which does not occur neither in ZrP nor in the mesoporous silica. This demonstrates that transforming the layer structure of ZrP into a mesoporous hybrid material leads to a new ammonia gas sensing material. This concept might be promising for the development of new gas sensor materials in general.

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1. Introduction

Over the last years ordered meso- and microporous porous materials have been widely explored for gas sensing applications [1–4]. Compared to conventional solid gas sensor materials, meso- and microporous materials, such as zeolites or mesoporous silica, provide large surface-to-volume ratios, which is advantageous for the adsorption and rapid diffusion of gas molecules. The interaction between the adsorbed gas molecules and the porous sensor material gives rise to a change of the physical properties of the respective material, which can be read out by, e.g. electrical or optical means. For example, zeolites with high Brønsted acidity have been applied as sensor material for the detection of ammonia or water by monitoring the proton transport by means of impedance spectroscopy [5–7]. These sensors have shown to be useful for the detection of ammonia in exhaust gases or to detect traces of humidity under harsh conditions.

Recently, the sensing properties of zeolite MFI were successfully applied for the *in situ* monitoring of the selective reduction of NO_x by ammonia (DeNO_x-SCR), where the proton-conducting zeolites served as catalyst and sensor at the same time [8–10].

This unique feature is of great interest for the monitoring of the catalytic DeNO_x reaction in exhaust gas aftertreatment in stationary and mobile applications. These applications require Brønsted acidity and proton conductivity on the one side, as well as high porosity on the other side. However, this combination of properties is still restricted to zeolites and a few related micro- or mesoporous structures.

Layered metal(IV) phosphates, such as zirconium(IV) phosphate (ZrP), which are technically relevant catalysts, have a large number of Brønsted sites. It is known that the proton conductivity in such materials is increased by solvate molecules, like water or ammonia [11–13], which makes these materials potentially suited for gas sensing applications as well. However, the vast majority of the Brønsted sites point to the interlayer region, and thus is hardly accessible for catalytic or sensing processes. This means that only the P–OH groups at the surface of the compact metal(IV) phosphates are available as Brønsted sites for gas interaction and thus can contribute to proton conduction [14,15]. Therefore, it is straight forward to increase the accessibility of the Brønsted sites in the interlayered region to enhance the gas sensing properties of such layered materials [16–18].

Several methods have been developed to increase the accessibility of the acidic sites in layered phosphates, like exfoliating of the layers [19], intercalating with organic surfactants [20] or expanding the layers by inorganic pillars [21]. Among those, the combination of Brønsted-acidic metal(IV) phosphate layers and mesoporous silica was introduced recently by means of the synthesis of Porous

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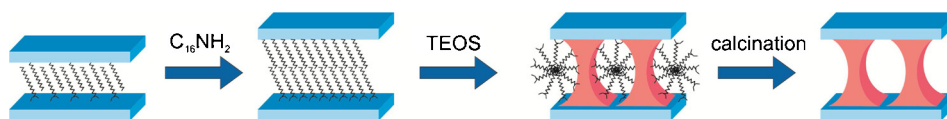


Fig. 1. Synthesis of the Porous Phosphate Heterostructures (PPH). Adapted from [22].

Phosphate Heterostructures (PPH) [22]. In this synthesis, lamellar micelles are formed in surfactant expanded ZrP layers. After addition of tetraethyl orthosilicate (TEOS), silica galleries in the interlayer space are formed (see Fig. 1). The resulting material was found to be mesoporous and with an adjustable number of Brønsted sites comparable to zeolites [23]. Due to their fascinating properties, this class of materials was comprehensively studied in gas separation [24], as matrix for quantum dots [25,26], as adsorbent for heavy metal ions [27], as catalysts [28,29] or as active material in DeNO_x-SCR [30].

In this work we explored for the first time the electrical response of PPH on the application of ammonia at elevated temperature by means of impedance spectroscopy. We compared the impedance of compact ZrP and mesoporous MCM-41, respectively, with the impedance of mesoporous PPH and found that the introduction of the mesoporous silica phase leads to a significantly increased ammonia response, which we attribute to an increased accessibility of the Brønsted-acid sites.

2. Experimental

2.1. Materials

PPH was synthesized as described in detail elsewhere [22]. In brief, to an aqueous suspension of a cetyltrimethylammonium expanded ZrP precursor hexadecylamine in *n*-propanol was added as co-surfactant. Afterwards TEOS in *n*-propanol was added as silica source and after stirring three days, washing and drying in air at 60 °C, the obtained solid was calcined at 550 °C. For this work, a Si/P molar ratio of 3 and a C₁₆NH₂/P molar ratio of 0.2 were applied in the synthesis, leading to the PPH 3-SiPPH(0.2) as is referred on the previous work [22]. This specific composition was chosen, since it has proven the highest porosity and acidity in the previous studies.

The metal(IV) phosphate used was a commercial zirconium(IV) hydrogenphosphate (Aldrich) and was converted to anhydrous zirconium pyrophosphate (ZrP₂O₇) by heating at 400 °C in nitrogen flow.

The porous silica MCM-41 was synthesized following the previously published synthesis route [31], and was used without further modification.

2.2. Experimental setup

For gas sensing experiments, interdigital electrodes (IDEs; electrode spacing 125 μm) on an alumina substrate with integrated active backside heater were used (see Fig. 2, details of electrode design are given elsewhere [7,32]). The tested materials were deposited as a film of 50 μm on the IDE structure.

These sensor chips were placed in a steel measuring chamber (see Fig. 2) equipped with a 4-channel gas control and mixing system (MKS 647 C with Mass Flow Controllers MKS1179A; both MKS-Instruments GmbH). The temperature regulation of the integrated heater was performed by a SourceMeter™ 2400 (Keithley Instruments Inc.) after calibration by a Spectral Pyrometer (KT 19.82, Heitronics GmbH). The electrical impedance at different temperatures and gas conditions was measured with an Impedance Analyzer combined with a Dielectric Interface (SI 1260 and SI 1296, both Solartron Group Ltd.), enabling measurements in the

impedance range up to 10¹⁴ Ω (±1%). In all measurements a constant gas flow of 100 sccm (i.e. 100 cm³ min⁻¹) was applied. All samples were held at 400 °C in nitrogen flow for at least 1 h before measurements to avoid effects of solvent molecules.

3. Results and discussion

3.1. Proton conductivity

A first set of temperature dependent measurements was performed to observe the proton conductivity of the materials. All samples were heated up in nitrogen atmosphere in different temperature steps. In the low temperature range (100–300 °C) in steps of 5 °C, in 10 °C steps in the mid temperature range (300–400 °C) and in 20 °C steps in the high temperature range (400–500 °C). After each temperature step the electrical impedance was measured with 100 mV measuring voltage (rms) in the frequency range from 10⁻¹ to 10⁶ Hz with 10 measuring points per frequency decade in equidistant logarithmic steps after an equilibration time of 15 min.

To determine the resonance frequency of the charge carrier and the corresponding admittance $Y(v_{res})$ these spectra were plotted as Modulus-Plots, i.e. the imaginary part of the modulus M'' against frequency ν . The imaginary modulus M'' is derived from the real part of the impedance Z' and the admittance Y , respectively, following $Y' = 1/Z' = (2\pi\nu C_0)/M''$, with C_0 = capacitance of the empty cell. In Fig. 3 the Modulus-Plots for PPH is shown for four temperatures. The distinct maximum of each plot corresponds to the resonance frequency of the charge carriers. At low temperatures and in the range of 50 Hz the spectra are very noisy. In order to visualize the respective maximum, in a first approximation a data fit with a simple circuit equivalent consisting of a resistor in parallel to a constant phase element, as it has been established in previous studies of zeolite materials [33], was applied (see Fig. 3).

The determined Y' could be plotted as $\ln(Y'(v_{res})T)$ against the inverse temperature in an Arrhenius diagram [34].

$$\ln(Y'(v_{res})T) \sim \ln(\sigma) = \ln\left(\frac{\sigma_0}{T}\right) - \frac{E_A}{RT} \quad (1)$$

The resulting Arrhenius diagram for the three materials is shown in Fig. 4 and the activation energies are calculated according to Eq. (1). PPH and ZrP exhibit almost the same activation energy of 97 kJ mol⁻¹, while MCM-41 shows an activation energy of 86 kJ mol⁻¹. For ZrP and PPH we attribute this activation energy

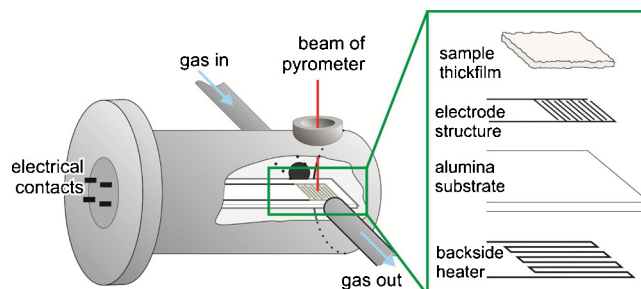


Fig. 2. Experimental setup: schematic drawing of measurement chamber. Exploded drawing of the interdigital electrode structure. Adapted from [9].

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