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SCR-Catalyst Materials for Exhaust Gas Detection

Daniela Schönauer-Kamin, Ralf Moos
University of Bayreuth, Functional Materials, 95440 Bayreuth, Germany
Daniela.Schoenauer-Kamin@Uni-Bayreuth.de

Abstract:
The application of SCR-catalyst materials like vanadia-doped tungsten-titania (VWT) and iron-exchanged zeolites (Fe-ZSM-5) for analyte detection in exhaust gases is investigated. Three detection modes are covered by this overview: the detection of certain gas concentrations with sensing devices comprising SCR-materials, the measurement of the electrical properties of the catalyst materials itself, and the direct determination of the catalyst status during operation by microwave method (an in-operando method). In this work, an overview on the suitability of SCR materials for gas detection at high temperatures (500 – 600 °C) is given. Various sensing principles, like mixed-potential, impedimetric, or resistive sensing, are discussed with respect to NH_3 and SO_2 response. A promising NH_3 sensor behavior was found in case of a mixed-potential sensor with a VWT catalyst layer. Additionally, an impedimetric sensor with a VWT functional layer provides a selective NH_3 response with marginal NO cross interference. Initial results of an impedimetric Fe-ZSM5 sensor indicate a strong NH_3 dependency but a high NO_x interfering effect is observed. For SO_2 detection in coal combustion processes, two promising sensor setups utilizing VWT are investigated. Furthermore, the applicability of contactless radio-frequency method for direct determination of the amount of stored ammonia in a zeolite-based catalyst is shown.

Key words: SCR-catalyst material, exhaust gas sensor, ammonia storage, NH_3 sensor, SO_2 detection

Introduction

Increasing demands for exhaust gas aftertreatment systems in addition to the need to control the systems and to monitor the functionality (On-board Diagnosis of the catalyst) require new sensing technologies. For most applications, knowledge of the catalyst status (e.g. loading degree, ageing or defects) is of the highest importance.

A novel trend, is to use well-known catalyst materials with a proven long-term stability in exhaust gas as functional layers for gas sensing devices [1, 2]. Another approach is to use the catalyst material itself as a sensor for direct detection of the catalyst status [3, 4], e.g. by monitoring changes of the electrical properties. A contactless method for direct determination of the catalyst status during operation, based on radio-frequency technology is discussed in [2]. In all cases, commercial catalysts are applied as functional materials.

This overview focuses on the application of commercial SCR-catalyst materials for gas sensing purposes. As SCR-materials vanadia-doped tungsten-titania and iron-exchanged zeolites are investigated for ammonia and SO_2 detection.

Mixed potential ammonia gas sensor

In [1], a novel mixed-potential type NH_3 sensor for automotive exhaust gas is suggested. It provides a semi-logarithmic characteristic curve with a high NH_3-sensitivity of 88 mV / decade and a marginal NO_x cross-interference at 550 °C. The sensor setup is shown in Fig. 1.

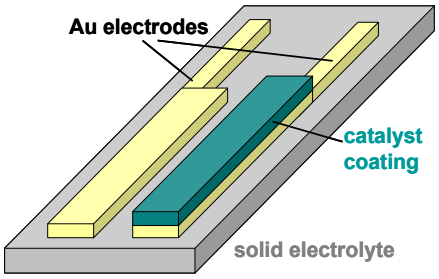

Fig. 1. Schematic sensor setup of potentiometric NH_3 sensor with a solid electrolyte (substrate or thick film), two Au electrodes and an SCR-catalyst coating.

On top of the oxygen ion conducting solid electrolyte YSZ (substrate or screen-printed thick film), two porous gold electrodes are located, whereby one electrode is covered by a catalyst film. As catalyst, commercially available SCR-materials like V_2O_5-WO_3-TiO_2 (VWT) and iron-exchanged zeolites (Fe-ZSM-5) are applied. Additionally, other zeolites like Fe-Beta, Fe-SAPO-5 and Fe-SAPO-34 are tested.

The potential difference, *U*, between both electrodes is the sensor signal. It was measured in dependence of the NH_3-concentration in a base gas composition near λ = 2 (10 % O_2, 6.5 % CO_2, 2.5 % H_2O, N_2 balance) at an operating temperature of 550 °C (the sensor temperature is adjusted by an external furnace).

The characteristic curves of the sensors with different catalyst coatings behave all semi-logarithmic (see Fig. 2). The sensitivity depends on the type of the catalysts. The highest sensitivity is obtained with VWT. Sensors with Fe-zeolites as catalysts are only slightly sensitive to NH_3. The differences among various zeolites are marginal. With VWT, a promising sensor behavior can be observed, which was further investigated in [1] and seems to be appropriate for NH_3 detection compared to zeolites. Additionally, for application of the sensor downstream of SCR-catalysts, the NO_x interfering effect is marginal [1].

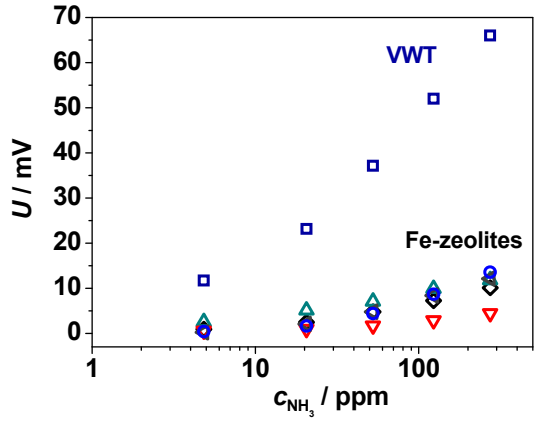

Fig. 2. Semi-logarithmic characteristic ammonia sensor curves for various SCR-catalyst materials. The VWT-based sensor provides the highest sensitivity compared to the tested zeolites.

The sensing mechanism is based on mixed potentials. Competing electrochemical reactions like NH_3 oxidation and O_2 reduction at the three-phase boundary Au-YSZ-gas form mixed electrode potentials which depend on the gas composition. A more detailed investigation of electrode effects is given in [5].

Reasons for the signal difference among the catalysts could be varying catalytic properties and distinct adsorption capabilities. It is assumed that the stability of adsorbed NH_3 species is different for VWT and Fe-ZSM-5 and influences the electrochemical NH_3 oxidation.

Impedimetric ammonia gas sensor

Another possibility for NH_3 detection with SCR catalysts bases on an impedimetric sensor setup (Fig. 3) [6, 7]. Interdigital photolithographically patterned gold electrodes (Au-IDE, 20 µm/20 µm) covered by a functional film are applied on alumina substrates (99.6 % Al_2O_3). As functional layers, commercial SCR catalyst formulations based on VWT are investigated as well as exhaust gas proven Fe-ZSM-5. The sensor device is equipped with a platinum heater structure and a protection layer on the reverse of the substrate to keep the sensor at operating temperature between 300 °C and 500 °C.

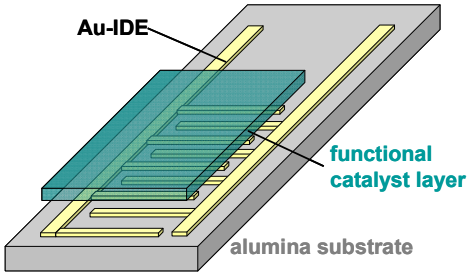

Fig. 3. Impedimetric sensor setup with a functional layer and an Au-IDE on top of an alumina substrate.

The test conditions are similar to the procedure described before. The electrical properties of the functional layers are measured in dependence on the gas composition by an impedance analyzer between 1 Hz to 10 MHz (U_{eff} = 1 V).

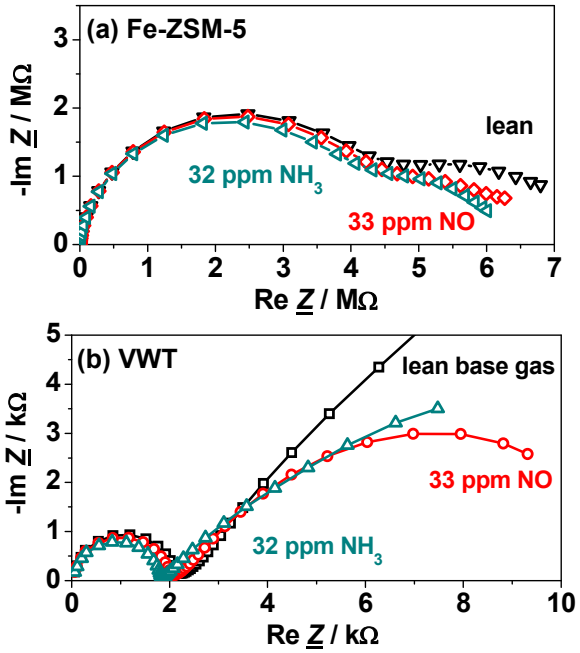

Fig. 4. Nyquist-Plots obtained in lean base gas and under exposure to 33 ppm NO or 32 ppm NH_3 at 500 °C for a Fe-ZSM-5 (a) and a VWT (b) coated sensor. Please note the different scales of the axes.

Initial Nyquist-Plots at 500 °C show a semi-circular shape in the high frequency range and an additional low frequency contribution (Fig. 4). For Fe-ZSM-5, shown in Fig. 4(a), a small “tail” can be found, which could be

interpreted as small semi-circle. Our interpretation is that the material behavior can be described by the semicircle, whereas the tail can be attributed to effects at the electrode interface. The semicircle is almost independent on NO addition, but the diameter, representing the resistance, decreases due to NH_3 exposure.

The VWT sensor (Fig. 4(b)) behaves almost similar, but a huge semicircle at low frequencies is observed. The results of a VWT sensor with 100/100 µm Au-IDE in [6] show the same overall behavior, but the semicircle-like shape in the low frequency range was not observed. This indicates that low frequency effects stemming from electrode effects are more pronounced for the 20/20 µm IDE structure. In accordance to [6], the high-frequency semicircle - depending on the gas composition - is attributed to material properties (contribution of bulk and inter-grain effects).

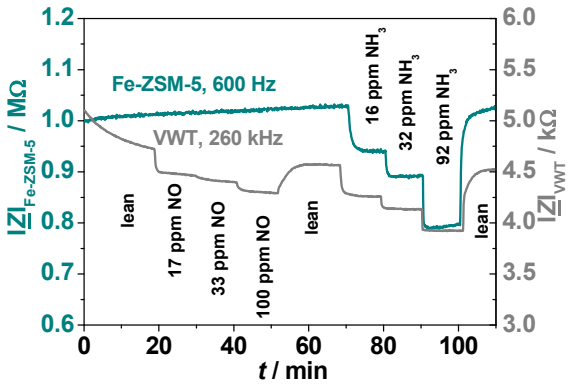

Fig. 5. Sensor impedance for the Fe-ZSM-5 sensor at 600 Hz and the VWT sensor at 260 kHz, both at 500 °C, when exposed to varying NO and NH_3 concentrations.

For time dependent impedance records, measurement frequencies in the high-frequency semicircle were chosen (600 Hz for Fe-ZSM-5 and 260 kHz for VWT) to ensure that the material properties and not the electrode effects are investigated. In Fig. 5, the resulting $|\underline{Z}|$ is plotted in lean gas and during exposure to varying NO (17, 33, 100 ppm) and NH_3 (16, 32, 92 ppm) concentrations. For Fe-ZSM-5 no response to NO was found, whereas a strong NH_3 effect is observed. The value of the sensor impedance strongly decreases with increasing NH_3. In contrast, the sensor impedance of VWT depends on NO and NH_3, whereby the sensor response to NH_3 is more pronounced than the NO response.

A more detailed investigation on VWT and Fe-ZSM-5, regarding NO_x cross interferences, can be found in [6, 7, 8]. For VWT, it was shown that the NO-interfering effect on the NH_3 sensor response is marginal, but the NO_2 interference needs to be considered. In this context it has to be noticed that the VWT-sensor is NO sensitive even without NH_3 in the gas. However Fe-ZSM-5 which seems to be insensitive to NO (cf. Fig. 5) provides a strong NO dependency of the NH_3 sensor signal [8].

For both SCR-materials a conductivity increase with increasing NH_3 concentration occurs due to changes of the bulk properties. It is assumed that NH_3 is adsorbed on the catalyst surface and reacts, in the case of VWT, with adsorbed oxygen species. The behavior is typical for an n-type semiconducting material. Fe-ZSM-5 has a high NH_3 adsorption capability due to Brønsted acidic sites. NH_3 adsorption results in increased proton conductivity [9].

Radio frequency measurement of zeolite-based SCR catalyst

An interesting method to determine the ammonia loading of a zeolite-based SCR catalyst is proposed in [10]: The microwave-cavity perturbation method. Electromagnetic waves are coupled by probe feeds (antennas) into the cylindrical waveguide (metallic catalyst housing) of the SCR catalyst (cf. Fig. 6). The reflected signals e.g. the resonance frequencies are measured by a vector network analyzer.

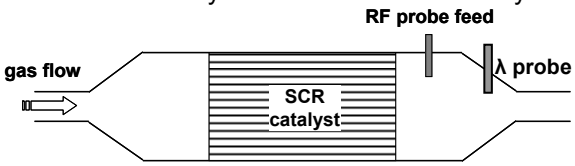

Fig. 6. Schematic setup for radio frequency measurements of the NH_3 storage of a zeolite-based SCR-catalyst.

Loading the zeolite SCR catalyst at 300 °C (synthetic exhaust gas test bench, base gas: N_2 and 5 % H_2O) with 500 ppm NH_3 changes the resonance curve shapes and reduces the resonance frequencies. The resonance frequencies at which the reflection coefficient shows a minimum depend almost linearly on the NH_3 loading of the SCR catalyst. This can be correlated to changes of the electrical properties of the zeolites when NH_3 is stored. The ammonia storage of the catalyst itself can be determined directly and during operation with the microwave method.

Potentiometric SO_2 gas sensor

A planar potentiometric SO_2 gas sensor for high temperatures is discussed in [11]. The setup is similar to Fig. 1, but NASICON, a Na^+- ion conducting material, is used as an electrolyte instead of YSZ. The sensors were tested at 300 °C to 600 °C in a synthetic gas flow consisting of compressed air and 20 to 200 ppm SO_2.

With Au electrodes, a stable voltage signal which increases with increasing SO_2 concentration was observed at high temperatures (500 - 600 °C). A semi-logarithmic relationship between voltage and the logarithm of SO_2 concentration was found, whereby the slope increases with temperature. The SO_2 sensitivity is 75 - 85 mV/decade SO_2 at 600 °C. The marked cross sensitivity to NH_3 and H_2 seems to be negligible for monitoring of coal combustion exhausts.

The sensing mechanism is attributed in [11] to a mixed potential behavior, but the occurring electrode reactions are under discussion.

Resistive type SO_2 sensor

A study on the application of VWT as functional material for SO_2 detection is conducted in [12]. The sensor device is schematically shown in Fig. 3. As electrodes 100/100 µm Pt or Au interdigital electrodes are used. Here, the sensor resistance was measured by a digital multimeter. The sensors, heated to 400 °C, were exposed to a compressed air flow with SO_2 admixtures.

The resistance decreases with increasing SO_2 concentration and is almost constant within 5 min. The sensor response, defined as $(R_0-R) / R_0$ (with R_0 base gas resistance), depends on $\log c_{SO2}$ and increases with the SO_2 concentration. Sensors with Au-electrodes provide a larger response compared to Pt-electrodes and show the best response values. Main cross interferences are NH_3 and NO and for the practical application the NO cross sensitivity needs to be compensated.

The suggested sensing mechanism to explain the conductivity increase due to SO_2 is based on the oxidation of SO_2 to SO_3 and a valence change of V^{5+} to V^{3+}. The V^{3+} could react with oxygen molecules or adsorbed oxygen species from TiO_2 or WO_3 and as result, an additional conduction electron is formed. For more details refer to [12].

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