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Detection mechanisms of smoke compounds on homogenous semiconductor sensor films

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Abstract

The conductivity changes of tin oxide sensor films kept at 270 °C to various organic compounds originating during the combustion of wood were investigated by HRGC/SOMMSA (high resolution gas chromatography/selective odorant measurement by multisensor array). The films show high sensitivity and selectivity to organic compounds with hydroxyl groups. Phenolic structures lead to strong conductivity increases. Exposure to toluene, furfural and acetone does not change the film conductivity. The reaction of the films to beech wood smoke is primarily due to 2-methoxyphenol and 2,6-dimethoxyphenol derivatives with para-substituted alkyl and alkenyl groups, which originate in hardwood lignia. Both types of compounds occur in relatively high concentrations during smouldering and both are sensitively detected. In spruce wood smoke only reactions to 2-methoxyphenol derivatives occur. Reaction mechanisms are discussed in some details.

Keywords: Tin oxide; Gas sensor; Gas chromatography; Wood smoke

1. Introduction

Within the past years the detection of complex mixtures by gas sensors gained growing interest and made substantial progress. Important application fields are food control and fire detection. For sensor evaluation the HRGC/SOMMSA (high resolution gas chromatography/selective odorant measurement by multisensor array) approach has been established [1,2]. An essential part of this method is the use of a gas chromatographic column ending in a split with the sensors working in parallel to a reference detector [1]. In an earlier study we presented results of sensor evaluation for the detection of specific organic smoke compounds by using the HRGC/SOMMSA approach [3,4]. The smouldering fires of wood were made in ambient atmosphere. In beech wood smoke the ratio of CO to CO_2 concentration was 7:15. Smoke was sampled by different kinds of sample preparation. Settings were identical to settings in this study. It was shown that the reaction of an SnO_2 sensor to beech wood smoke is primarily due to 2-methoxyphenol and 2,6-dimethoxyphenol derivatives with para-substituted alkyl and alkenyl groups, which originate by decomposition of hardwood lignia. Lignia is a polymer. Some of its precursors are shown in Fig. 1; they are arranged in a 2D structure. Fig. 2 gives an example. 2-Methoxyphenoles and 2,6-dimethoxyphenoles occur in relatively high concentrations during smouldering and both are sensitively detected by SnO_2 sensors. In spruce wood smoke nearly only reactions to 2-methoxyphenol derivatives occur. Differences between beech wood and spruce wood smoke are due to structural differences in the composition of hardwood and softwood lignia. Softwood lignia is dominated by phenolic structures with one methoxy group (guaiacol units), while hardwood lignia consists of phenolic structures with two methoxy groups (syringol units), too [5]. For beech wood 2-methoxyphenol (guaiacol) and 2,6-dimethoxyphenol (syringol) derivatives can be regarded as monomers of the corresponding lignia. Both are important for smoke flavour [6] and curing processes of meat [6,7]. 2-Methoxyphenol (guaiacol) is a tracer compound for the detection of forest

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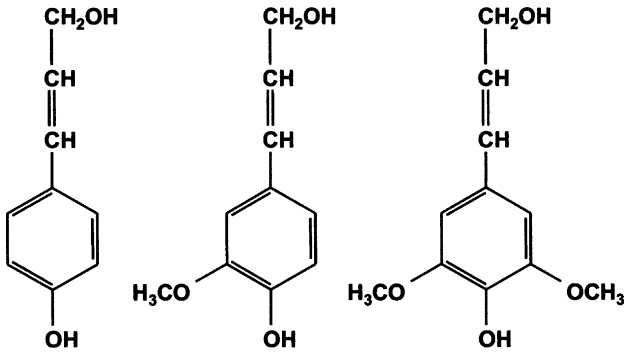

Fig. 1. Precursors of lignia formation: left side: *p*-coumaryl alcohol (phenolic structure without a methoxy group); middle: coniferyl alcohol (phenolic structure with one methoxy group); right side: phenolic structure with two methoxy groups.

fires by potato beetles [8] and a pheromone of gut bacteria in locusts [9].

From the other organic components in wood smoke (more than 100) only benzenediols and some individual components like hydroxyacetone and furfuryl alcohol cause significant sensor signals. A hydroxyl group was found to be part of any compound evoking a signal of the sensor. In all of these compounds the hydroxyl group acts as functional group and is not part of a carboxy group. About 20 of these compounds were found in the emissions of smouldering beech wood. Signals of organic compounds with hydroxyl groups dominate in the investigated sensor temperature range between 165 °C and 330 °C. The highest sensitivities occur at 270 °C to 330 °C.

2. Experimental

Thick film sensors were prepared by applying a suspension (Merck, SnO_2 99%) on an alumina substrate with interdigital platinum electrodes. Details are described in Ref. [1]. Sensors were sintered for 7 h, during which the surface temperature was increased steadily up to 550 °C, in synthetic air (50% R.H.). The sensor elements were pretreated sequentially in 100 ppm NO_2, 40 ppm diethylamine and 100 ppm CO for 5 s at a temperature of 270 °C. Standard solutions used for calibration are listed in Table 1. 1 μl (equivalent to 10 ng) of each standard solution was

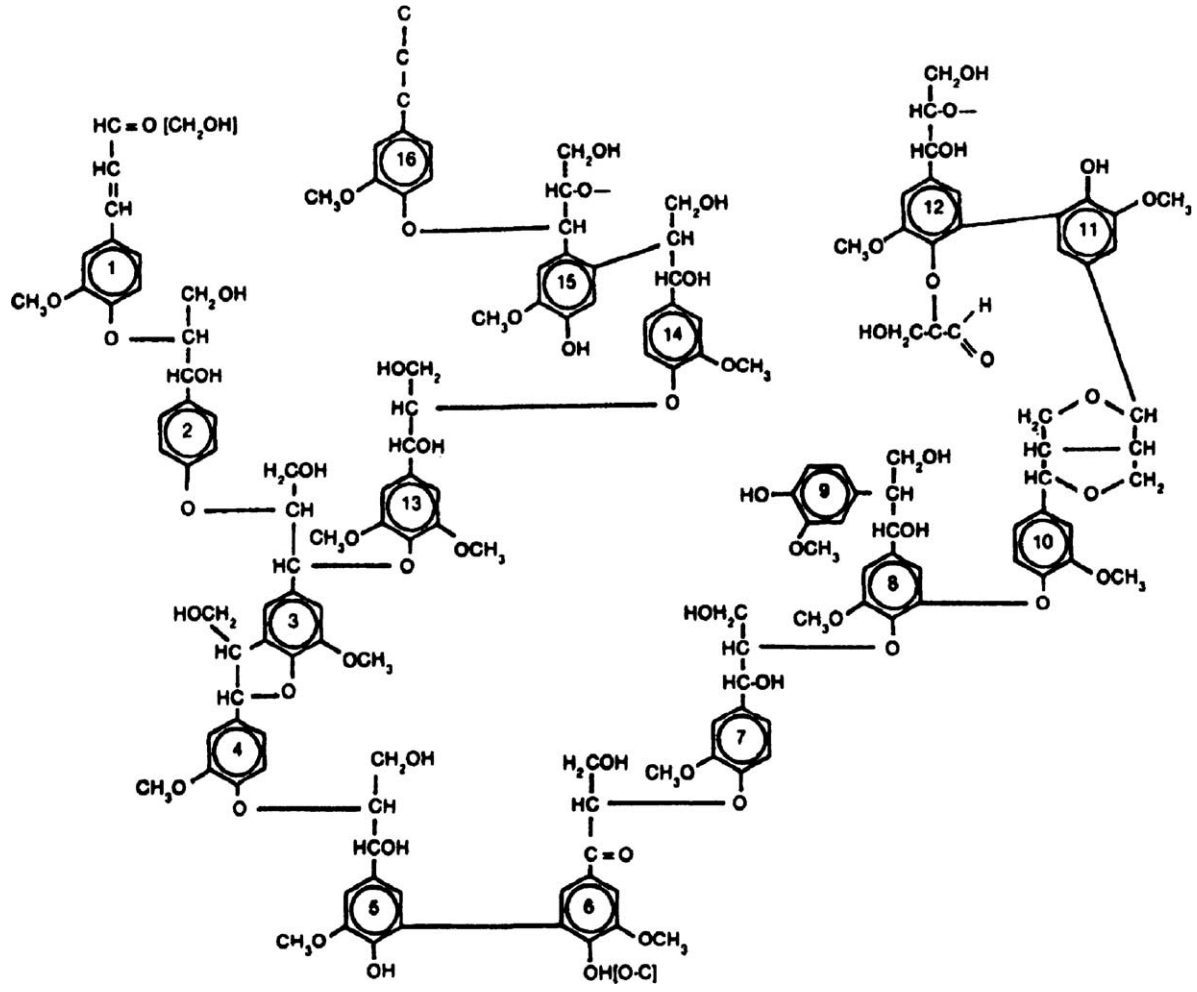

Fig. 2. X2D lignia structure of spruce wood containing nearly no phenolic structures with two methoxy groups.