H_2S gas sensors based on catalysed WO_3 nanocrystalline powders

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Hydrogen sulphide detection is nowadays a very important target for different processes, such as coal or natural gas manufacturing. This gas is not only bad smelling, but it can also be very dangerous for human bodies if present in concentrations over 250 ppm. Unfortunately, the precise details of interaction between H_2S and WO_3, as well as the role played by catalytic additives, are not well understood yet.

In this context, the aim of this work is to contribute to the study of the interaction between H_2S molecules and WO_3-based nanopowders modified with catalytic additives.

Firstly, H_2S sensing properties of gas sensors based on copper, chromium and vanadium catalysed WO_3 were analysed. These additives were introduced in 0.2 and 2% nominal atomic concentration. Fig. 1 shows the sensor response (R_{AIR}/R_{H2S}) of these materials to 20 ppm of H_2S in synthetic air. Sensors based on chromium modified WO_3 were able to improve the sensor response exhibited by pure WO_3. Therefore, chromium catalysed WO_3 was considered to be worthy of further studies.

Chromium centres were characterised by XPS and Raman spectroscopy. The former technique revealed that surface chromium species were Cr(III) oxidised centres (577 eV). Besides, a rather wide Raman vibration was found around 990 cm^{-1} (Fig. 2). This mode has been reported to correspond to the Cr=O terminal vibration. These results suggest that most chromium centres may have only one Cr=O terminal bond (monoxo species) and thus chromium would be mainly present on the surface of WO_3 as monochromate species. The presence of these terminal Cr=O bonds may be the responsible for the sensor response improvement, as H_2S is reported to interact with M=O centres of different metal oxides.

Finally, interaction between H_2S molecules and chromium catalysed, as well as pure, WO_3 was also studied by Temperature Programmed Desorption (TPD). H_2S was adsorbed at different temperatures and amounts of desorption products (H_2S, SO_2 and H_2O) were recorded as functions of desorption temperature. This technique revealed two different H_2S species are adsorbed on the surface of pure WO_3 at room temperature (Fig. 3). According to literature, they belong to dissociative and nondissociative adsorptions. Only the dissociative adsorbed species were desorbed when adsorption temperature was higher. As to chromium catalysed samples, a new H_2S dissociative adsorbed species was clearly identified when this gas was adsorbed at room temperature. Besides, the amount of desorbed SO_2 increased when chromium was added, showing the ability of this additive to promote the catalytic conversion of H_2S and so increase sensor response.

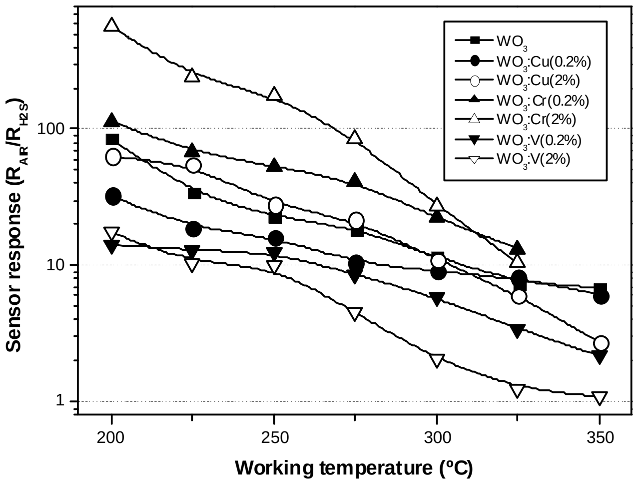

Fig. 1: Sensor response of pure and catalysed WO_3 to 20 ppm of H_2S in air.

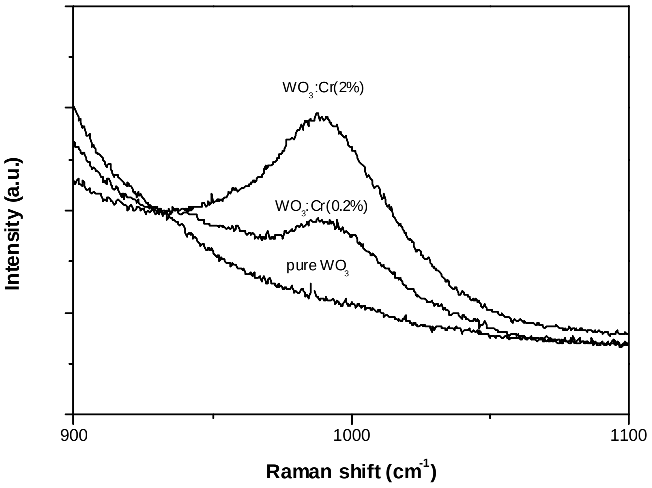

Fig. 2: Raman spectra of pure and chromium catalysed WO_3. The latter presents a Cr=O terminal vibration.

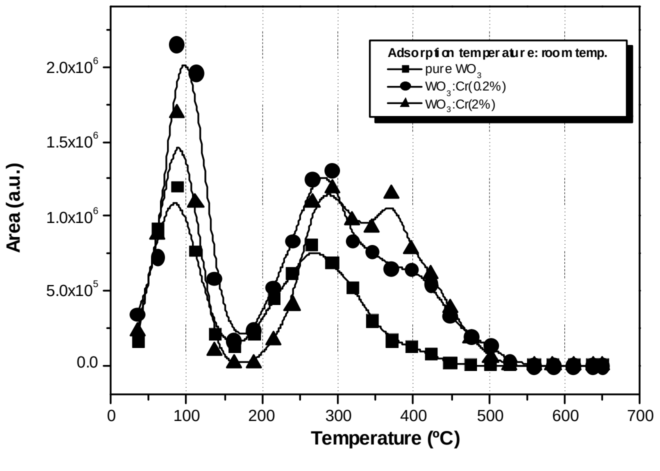

Fig. 3: Desorption spectra of H_2S from H_2S-preadsorbed pure and chromium catalysed WO_3

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