V_2O_5-based Hydrocarbon Sensors

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V_2O_5 supported on ZrO_2 is found to be an excellent sensor for n-propane–butane mixtures at 625 K; *in-situ* X-ray diffraction studies show that V_2O_5 is reduced to VO_2 with a metastable monoclinic structure on contact with the hydrocarbons and is oxidised back to the parent oxide on exposure to air.

Hydrocarbon gases, widely used as fuels for industrial and domestic purposes, have often proved to be hazardous because of explosions caused by leaks. It is therefore important to develop good sensors for hydrocarbon gases. There have been attempts to use different materials as hydrocarbon sensors, but good sensitivity has been obtained only with platinum supported on ZnO or SnO_2.[1–4] Supported Pt is, however, not as selective as one would desire, for it also acts as a sensor for H_2 and alcohol. Palladium dispersed on Fe_2O_3 detects hydrocarbons, but with considerably lower sensitivity.[5] We have been carrying out investigations to develop a suitable alternative to supported platinum for sensing saturated hydrocarbons such as n-propane and n-butane. In this communication we present the results which have made use of the known catalytic activity of supported V_2O_5 for the oxidation of hydrocarbons.[6–9]

V_2O_5 was supported on TiO_2 (anatase), ZnO, γ-Al_2O_3, 20% γ-Al_2O_3 + 80% $LaCoO_3$, SiO_2 and ZrO_2 by the wet impregnation method using NH_4VO_3 followed by calcination at 673 K for 6 h. The metal oxide supports were generally prepared by the hydrolysis of the nitrates; in the case of SiO_2, fumed silica was used. Pellets (10 mm diameter, 2 mm thick) prepared under pressure and heated at 770 K for 12 h as well as screen-printed thick films of supported V_2O_5 were used to measure the gas-sensing characteristics. The sensitivity, S, of the sensor is expressed as $(\sigma_g - \sigma_a)/\sigma_a$ where σ_g is the conductivity of the sensor in the presence of the gas and σ_a the conductivity of the sensor in air. Commercial LPG (liquefied petroleum gas) which is essentially a mixture of n-propane and n-butane was used to study the gas-sensing properties. For comparison, sensitivity to H_2, CO and ethanol were also studied.

A comparative study of the gas sensing characteristics with different loadings of V_2O_5 showed 20 mol% loading to be optimal. Of the various gases studied, the sensitivity was highest for LPG as shown in Fig. 1. Thus, 20% V_2O_5/ZrO_2

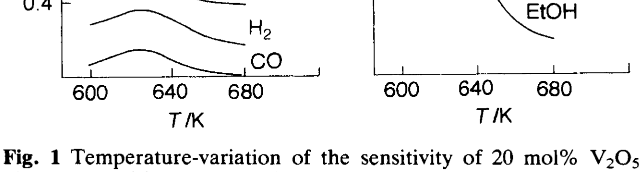

Fig. 1 Temperature-variation of the sensitivity of 20 mol% V_2O_5 dispersed on (*a*) ZrO_2 and (*b*) TiO_2 for different gases

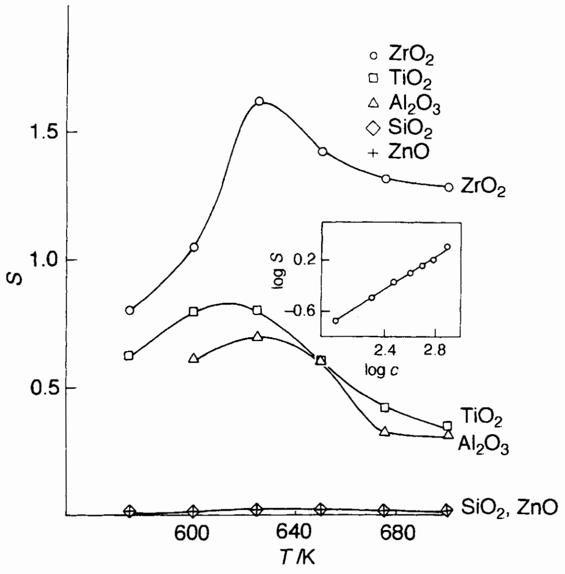

Fig. 2 Temperature-variation of the sensitivity of 20 mol% V_2O_5 dispersed on ZrO_2, TiO_2, Al_2O_3, SiO_2 and ZnO for 400 ppm LPG. The inset shows the log sensitivity–log concentration plot for 20 mol% V_2O_5/ZrO_2.

shows a sensitivity of 1.65, 0.70, 0.35 and 0.15 for LPG, ethanol, H_2 and CO respectively at 625 K. Pellets of 20% V_2O_5 supported on γ-Al_2O_3, TiO_2 and ZrO_2 all showed good sensitivity to LPG with satisfactory reproducibility and reversibility, but the sensitivity of 20% V_2O_5/ZrO_2 was far greater than on any other oxide support studied (Fig. 2). The response time was generally less than 2 s at 625 K. In the inset of Fig. 2 we show the variation of log S with log c for the 20% V_2O_5/ZrO_2 at 625 K. The plot is linear up to 1000 ppm or more and the minimum detection limit is *ca.* 10 ppm. Since the lower flammability limit is 2000 ppm, the sensitivity of 20% V_2O_5/ZrO_2 is more than adequate for sensing purposes. At 1000 ppm concentration, the sensitivity of 20% V_2O_5/ZrO_2 is 2.7 compared to 0.9 for Pd/γ-Fe_2O_3, 0.7 for γ-Fe_2O_3 and 3.0 for Pt/ZnO.[4,5] Since 20% V_2O_5/ZrO_2 also shows good selectivity and shows little fatigue after repeated cycling, we believe that this oxide system may also have good technological possibilities. It is also noteworthy that the sensitivity with thick films is only slightly lower than that of pellets.

The hydrocarbon-sensing property of supported V_2O_5 involves oxidation of the hydrocarbon. In order to understand the actual changes occurring in V_2O_5 in the sensing process, we have carried out *in-situ* X-ray diffraction and ESR measurements. *In-situ* X-ray diffraction studies show that V_2O_5 is reduced to VO_2 on contact with LPG at 625 K and to V_2O_3 at higher temperatures. Since the sensitivity is highest at 625 K, reduction beyond the VO_2 stage is not relevant for sensing purposes. The resulting VO_2 has a unique B' monoclinic structure[10] (a = 12.03, b = 3.693, c = 6.42 Å, β = 107°, space group $C2/m$) which is different from the stable room-temperature monoclinic structure (a = 5.752, b = 4.538, c = 5.383 Å, β = 122.6, space group $P2_1c$) or the well-known 340 K rutile structure (a = 4.551, c = 2.851 Å, space group $P4/mmm$). The B' monoclinic phase is related to V_6O_{13} and is transformed to the stable structures on cooling. The VO_2 produced in the sensing reaction at 625 is oxidized back to V_2O_5 within a minute on exposure to air. ESR experiments support the results from X-ray diffraction studies showing the evolution of the V^{4+} signal when exposed to LPG at 625 K and its disappearance on exposure to air.

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