Sensitivity of Nanocrystalline Metal Oxides to CO and Ammonia Determined by Active Sites

Artem V. Marikutsa[1], Lili Yang[1], Marina N. Rumyantseva[1], Dirk Lamoen[2], Joke Hadermann[2], Maria Batuk[2], Alexander M. Gaskov[1]
[1] _Chemistry Department, Moscow State University, Vorobyevy gory 1-3, Moscow 119991, Russia_
[2] _EMAT, University of Antwerp, Groenenborgerlaan 171, Antwerpen B-2020, Belgium_
artem.marikutsa@gmail.com

Abstract:

Effect of active sites of nanocrystalline tin(IV), tungsten(VI), and zinc-indium oxides on sensing behavior to CO and ammonia is analyzed. The oxides were synthesized by aqueous deposition routes, and subsequently modified by catalytic (Pd, Ru) and/or adsorptive (In, SO_4) additives. Surface sites and gas-solid interaction were investigated by HRTEM, EDX-mapping, FTIR, probe molecule methods, sensing test and DRIFT spectroscopy. CO sensitivity of ZnO(In) increased with the dopant amount, in agreement with DFT-predicted catalytic activity of In(III) in CO oxidation. The largest catalytic effect favoring CO detection down to 1 ppm at room temperature was shown for Pd-modified sensors. Gas-solid interaction route in such systems was controlled by CO chemisorption on Pd-clusters irrespective of the supporting matrix. The sensitivity of SnO_2/SO_4 and WO_3 to ammonia was improved by increasing surface acidity. The largest NH_3 sensitivity was observed for the materials with modified by Ru clusters, which provide catalytic oxidation of target molecules. Surface acidity in the latter case should not be too strong for not to deactivate the adsorbed ammonia species.

Key words: Tungsten oxide, tin oxide, zinc oxide, gas sensor, carbon oxide, ammonia, active sites.

Motivation

Designing materials for chemical sensors of toxic, flammable gases and biomarkers requires understanding the factors influencing sensing behavior. Aside from the well-known ones (crystal structure, particle size, porosity, electric properties), surface reactivity is necessary to be addressed. It determines gas reception and could be controlled via chemical modification of sensing material. In this work we analyze the effect of materials composition on active sites (chemisorbed oxygen, acid sites, catalytic noble metal clusters) of pristine and modified SnO_2, WO_3, $ZnO-In_2O_3$ and sensing behavior to CO and NH_3 gases.

Results

The underlying principle of materials synthesis was chemical modification, so as to obtain nanoparticles of semiconductor oxides with controlled amount of additives. The additives were to specifically improve adsorption and/or catalytic oxidation of CO and NH_3 on the surface (Fig. 1a). Nanocrystalline ZnO/In (0 – 8 at.% In) obtained by coprecipitation consisted of agglomerated ZnO particles with amorphous In_2O_3 segregations (Fig. 1b). DFT modelling CO

adsorption showed that In atoms at ZnO(In) surface increase adsorption energy, elongate C-O bond and favors charge transfer to the surface (Fig. 2a). It agrees with experimental observation of improved CO sensitivity with the amount of In in ZnO/In (Fig. 2b). The more prominent catalytic effect was provided by deposited Pd clusters on semiconductor oxides (Fig. 1c). The Pd-modified semiconductor oxides showed CO sensitivity at room temperature that was dependent on particle size rather than on the origin of sensing matrix (Fig. 3a). DRIFT results suggested that the key interaction step was CO chemisorption on Pd sites irrespective of the supporting oxide. The sensitivity to NH_3 gas was greatly improved for Ru-modified semiconductor oxides (Fig. 3b). Catalytic oxidation of adsorbed ammonia was confirmed by DRIFT over Ru clusters (Fig. 1d). The adsorption efficiency and sensitivity was increased by modification of surface acidity via tin oxide sulfation (1 – 3 wt.% SO_4) or changing the oxide matrix by a more acidic tungsten oxide (Fig. 3c). On highly acidic surfaces NH_3 was too strongly adsorbed and its conversion was inhibited.
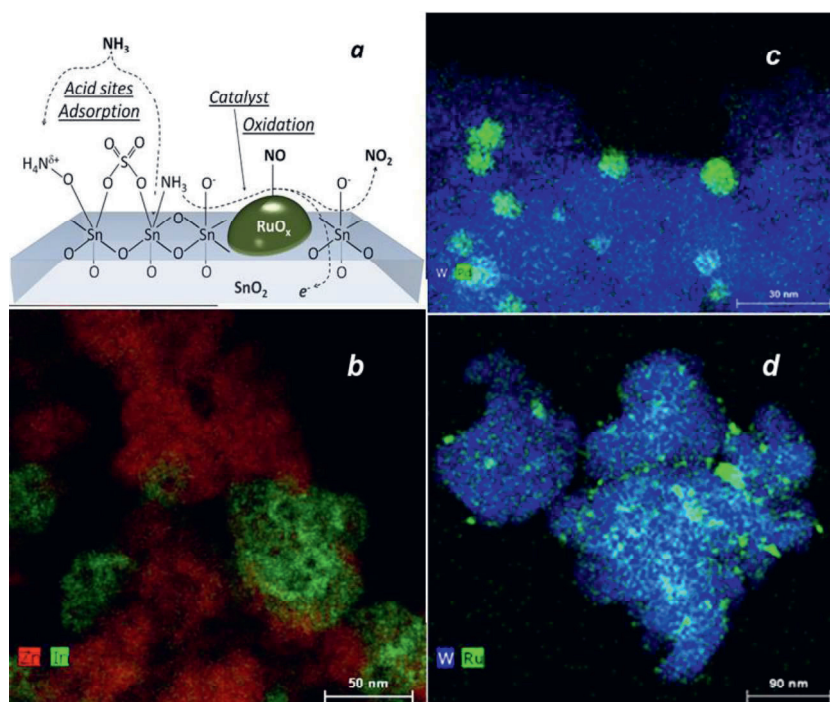
Fig. 1.   Scheme of active site on chemically modified tin oxide surface (a). HAADF-STEM-EDX maps of ZnO/In(5%): In green, Zn red. (b), WO₃/Pd(1%): Pd green, W blue (c), WO₃/Ru(1%): Ru green, W blue (d).

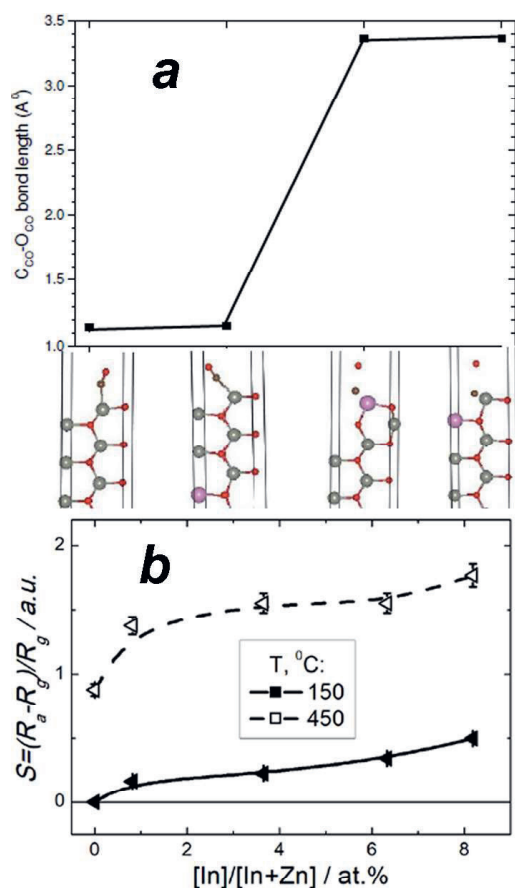

Fig. 2.   Interatomic bond length in CO adsorbed on doped ZnO/In surface depending on In position (a). Sensor signal of ZnO/In to 5 ppm CO depending on In content (b).
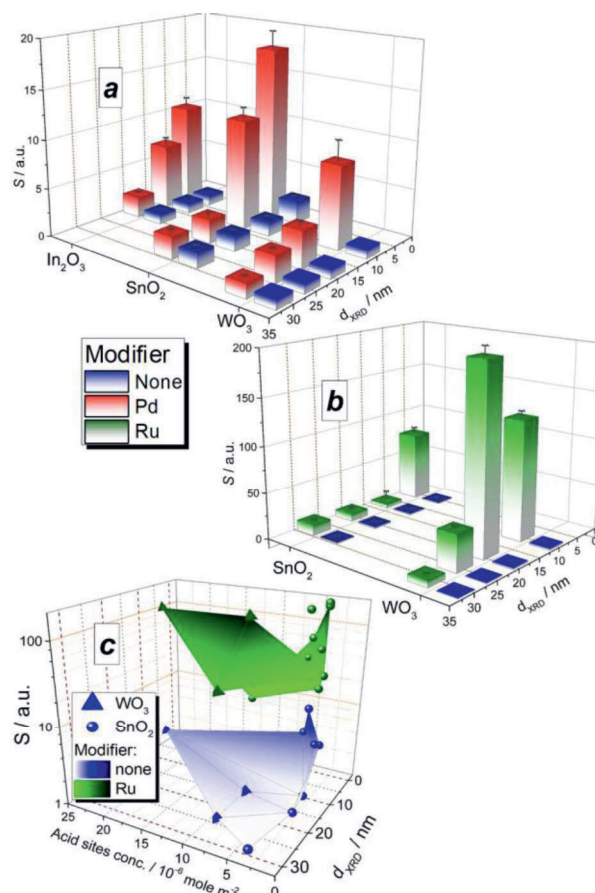
Fig. 3.   Sensor signal to 20 ppm CO (a) and 20 ppm NH₃ (b, c) of blank and modified SnO₂, WO₃, In₂O₃ in relation to particle size (a, b) and concentration of Lewis acid surface sites (c).