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Synergistic Effect of Surface Acidity and PtO\(_x\) Catalyst on the Sensitivity of Nanosized Metal–Oxide Semiconductors to Benzene

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Abstract: Benzene is a potentially carcinogenic volatile organic compound (VOC) and its vapor must be strictly monitored in air. Metal–oxide semiconductors (MOS) functionalized by catalytic noble metals are promising materials for sensing VOC, but basic understanding of the relationships of materials composition and sensors behavior should be improved. In this work, the sensitivity to benzene was comparatively studied for nanocrystalline \(n\)-type MOS (ZnO, In\(_2\)O\(_3\), SnO\(_2\), TiO\(_2\), and WO\(_3\)) in pristine form and modified by catalytic PtO\(_x\) nanoparticles. Active sites of materials were analyzed by X-ray photoelectron spectroscopy (XPS) and temperature-programmed techniques using probe molecules. The sensing mechanism was studied by in situ diffuse-reflectance infrared (DRIFT) spectroscopy. Distinct trends were observed in the sensitivity to benzene for pristine MOS and nanocomposites MOS/PtO\(_x\). The higher sensitivity of pristine SnO\(_2\), TiO\(_2\), and WO\(_3\) was observed. This was attributed to higher total concentrations of oxidation sites and acid sites favoring target molecules’ adsorption and redox conversion at the surface of MOS. The sensitivity of PtO\(_x\)−modified sensors increased with the surface acidity of MOS and were superior for WO\(_3\)/PtO\(_x\). It was deduced that this was due to stabilization of reduced Pt sites which catalyze deep oxidation of benzene molecules to carbonyl species.

Keywords: semiconductor metal oxides; gas sensor; benzene; active sites; platinum; supported noble metal catalyst

1. Introduction

The search for sensitive and low-cost detectors of volatile organic compounds (VOC) is motivated by the needs of environmental safety, healthcare, non-invasive medical diagnostics, etc. Metal–oxide semiconductor (MOS) sensors are efficient for detecting VOC at the ppb–ppm concentration level in air \([1,2]\). Extensive research has been carried out to improve the sensitivity and selectivity of conventional sensors based on zinc oxide, indium oxide, tin oxide, tungsten oxide, and titania \([3–5]\). The search for sensors with improved behavior is mainly focused on the design of new morphologies of nanomaterials, elaboration of new mixed-metal oxides, and composites with catalytic additives (noble metals and transition-metal oxides), heterojunctions \((p-n, n-n, \text{ and } p-p)\), and graphene-based materials \([3,5–9]\). However, there is a lack of basic understanding of the relationships between the fundamental properties of sensor materials and sensing behavior in the detection of VOC. Benzene \((\text{C}_6\text{H}_6)\) is a potentially carcinogenic pollutant emitted into the air from oil and coal industries, plastics, solvents, and smoke. The threshold limit value \((8–h \text{ TWA})\) for benzene recommended by OSHA is 1 ppm \([10]\). Benzene is a primary aromatic compound. Establishing the trends in sensitivity of noble-metal-loaded MOS may open a way towards rational design of sensors with improved sensitivity to aromatic VOC. Extensive research of materials for sensing benzene and other aromatics (toluene and xylene) have been performed. It was mainly focused on \(n\)-type and \(p\)-type MOS with various morphologies.
(nanowires, nanoparticles, and hollow spheres) as heterojunctions and nanocomposites with noble metal nanoparticles [11–16]. However, in the literature there is a lack of systematic comparative studies of materials that have different chemical composition but similar morphologies, which would be helpful in establishing the fundamental regularities in sensing benzene.

Key processes of gas sensing consist of target molecules’ adsorption and redox conversion by chemisorbed or lattice oxygen at the oxide surface. It is similar to the functioning of heterogeneous catalysts. There are a number of fundamental approaches for the design of VOC oxidation catalysts based on metal oxides and supported noble metals (Pt, Pd, and Au) that rely on energetic and structure–activity relations [17–20]. Conventionally, metal–oxygen bond energy ($E_{M-O}$) has been considered as a descriptor of surface oxygen activity in the catalyzed reactions [21–23]. It is challenging to distribute such an approach in the field of gas sensors. In our previous work, we showed that the trends in sensitivity of Au-modified MOS to acetone and methanol could be rationalized in terms of surface oxygen reactivity which was tailored by optimal metal–oxygen bond energy in metal oxides [24].

This work is focused on a comparative study of active surface sites and sensitivity to benzene of nanocrystalline metal oxide semiconductors—ZnO, In$_2$O$_3$, SnO$_2$, TiO$_2$, and WO$_3$—in pristine form and modified by catalytic PtO$_x$ nanoparticles. The aim of the present work was to analyze the correlations between the sensitivity to benzene and fundamental parameters of sensing materials. It is challenging to determine the possible reasons for the differences in materials’ sensitivity to benzene considering the impacts of active sites at the materials surfaces—acid sites and oxidation sites—which were probed by temperature-programmed techniques. Distinct trends were observed in the sensitivity of pristine and PtO$_x$−modified MOS using metal–oxygen bond energy as a descriptive parameter. These correlations were rationalized by the impacts of active sites at the materials’ surfaces and PtO$_x$ nanoparticles in the sensing mechanism, which was studied by in situ infrared (DRIFT) spectroscopy.

2. Materials and Methods

The materials investigated were nanocrystalline $n$-type MOS—ZnO, In$_2$O$_3$, SnO$_2$, TiO$_2$, and WO$_3$—which have been conventionally used in gas sensors. The oxides possess wide bandgap energies in the range 2.5–3.6 eV and distinct fundamental parameters: cationic charge and radius, metal–oxygen bond energy, and formation enthalpy (Table 1).

Table 1. Parameters of metal–oxide semiconductors used in the work: $r(M^{n+})$—effective cationic radii coordinated by oxide anions [25], metal–oxygen bond energy $E_{M-O}$, formation enthalpy $\Delta H^\circ (M,O_y)$ per metal atom, and band gap energy ($E_g$) [26–28].

| MOS   | $r(M^{n+})$, Å | $E_{M-O}$, eV | $-1/x \Delta H^\circ (M,O_y)$, eV | $E_g$, eV |
|-------|----------------|---------------|---------------------------------|---------|
| ZnO   | 0.60           | 10.4          | 3.6                             | 3.4     |
| In$_2$O$_3$ | 0.79       | 12.4          | 4.8                             | 2.8     |
| SnO$_2$ | 0.69           | 15.5          | 6.0                             | 3.6     |
| TiO$_2$ | 0.61           | 20.7          | 9.8                             | 3.0–3.2 |
| WO$_3$ | 0.58           | 36.6          | 8.7                             | 2.5–2.8 |

*a Bond energy in metal oxides calculated from thermodynamic parameters [26]: $E_{M-O} = (-\Delta H^\circ (M,O_y) + x\Delta_{sub}H^\circ (M) + y/2\Delta_{sub}H^\circ (O_2) + y\Delta_{sub}H^\circ (O) + \sum \Delta_{ion}H^\circ (M)/(y-CN_O))$, where $\Delta_{sub}H^\circ (M)$—sublimation enthalpy of metal, $\Delta_{sub}H^\circ (O_2)$—dissociation enthalpy of oxygen molecule, $\Delta_{sub}H^\circ (O)$—electron affinity of oxygen atom, $\sum \Delta_{ion}H^\circ (M)$—sum of ionization potentials of metal cation, CN_O—coordination number of oxygen in the oxide.

2.1. Material Preparation

The materials were obtained by chemical aqueous deposition techniques previously described in detail [24,29]. ZnO, In$_2$O$_3$, SnO$_2$, and TiO$_2$ were synthesized by deposition of metal hydroxides from aqueous solutions with subsequent heat treatment. Analytical
pure grade Zn (CH₃COO)₂·2H₂O, InCl₃·4H₂O, SnCl₄·5H₂O, and TiCl₄ (Sigma-Aldrich, St. Louis, MO, USA) were used as precursors. An excess of 1 M aqueous ammonia was added dropwise to the stirred solutions of precursors. The final pH = 6 was reached for the deposition of SnO₂·nH₂O and TiO₂·nH₂O, and Zn (OH)₂ and In (OH)₃ were deposited at pH = 9. Tungstic acid was deposited at 80 °C by the addition of 7.8 M nitric acid to 16 mM ammonium paratungstate (APT) solution in the volumetric ratio 2.6:1. The APT solution was prepared from (NH₄)₁₀W₁₂O₄₁·5H₂O (Sigma-Aldrich, >99%). The deposits were washed by deionized water, centrifuged, and dried at 80 °C. Nanocrystalline ZnO, In₂O₃, SnO₂, and WO₃ were obtained after the calcination of metal hydroxides at 300 °C for 24 h. TiO₂ was annealed at 700 °C for 24 h. Nanocomposites MOS/PtOₓ (1 wt.% Pt) were synthesized by impregnation of metal–oxides powders with ethanol solution of Pt(acac)₂ (Sigma-Aldrich, 98%). The obtained suspensions of MOS/Pt(acac)₂ were dried and annealed at 220 °C for 24 h to decompose platinum (II) acetylacetonate.

2.2. Material Characterization

X-ray powder diffraction was measured using a DRON-3M diffractometer, Cu Kα radiation (λ = 1.5406 Å). Crystallite size was calculated by the Sherrer equation using full width of half maximum of most intense peaks. Specific surface area (S_BET) was measured by nitrogen adsorption by the Brunauer-Emmett-Teller (BET) method in the single-point mode (p/p₀ = 0.3) using the Chemisorb 2750 (Micromeritics, Norcross, GA, USA) instrument equipped with thermal conductivity detector. X-ray photoelectron spectroscopy (XPS) was performed on the XPS system (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a hemispherical analyzer using monochromatic Al Kα radiation (1486.7 eV); binding energy (BE) was calibrated by C 1s peak at 285.0 eV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM), selected area electron diffraction (SAED), and scanning transmission electron microscopy in high-angle annular dark-field mode (STEM-HAADF) were performed using a Libra 200 microscope (Carl Zeiss) with an accelerating voltage 200 kV. The energy-dispersive X-ray spectroscopy (EDX) signal was recorded on a silicon drift X-MAX 80 T detector.

Temperature-programmed reduction (TPR) by hydrogen was registered using the Chemisorb 2750 (Micromeritics) instrument. The samples (20 mg) were pretreated in dry air at 200 °C to desorb humidity and cooled down to room temperature. TPR was registered during the samples’ heating to 900 °C at the rate of 10 °C/min under the flow of H₂ (8 vol.% in Ar with the flowrate 50 mL/min). Diffuse-reflectance infrared Fourier-transformed (DRIFT) spectra were registered by Frontier (Perkin Elmer, Waltham, MA, USA) spectrometer at ambient conditions with automatic H₂O/CO₂ compensation. DiffusIR annex and heated flow chamber HC900 (Pike Technologies, Fitchburg, WI, USA) sealed by KBr window were used for in situ spectra registration in the wavenumber range 4000–700 cm⁻¹ with the resolution 4 cm⁻¹, averaging 30 scans. Powders (50 mg) were placed in alumina crucibles (6 mm diameter) and pretreated in dry air at 150 °C. DRIFT spectra were registered at room temperature under the gas flow (200 ppm) and at temperature 25–220 °C under the flow of benzene (10 ppm) in air with the reference to pure air.

Temperature-programmed desorption of ammonia (TPD) was measured by the Chemisorb 2750 (Micromeritics) instrument. Quadrupole mass spectrometer was used to analyze the desorbed gas. Samples (100 mg) were granulated and the fraction with 0.25–0.50 mm-sized grains was tested. After pretreatment in He at 200 °C for 1 h and in dry air for 1 h, the samples were cooled to room temperature and held under the flow of NH₃ (8 vol.%): He gas mixture. Then, the samples were evacuated in He at 50 °C for 20 min to desorb the physically adsorbed ammonia. TPD patterns were registered in the flow of He (30 mL/min) while heating the test tube with samples to 800 °C at the rate of 10 °C/min. Mass spectra of desorbed gas were acquired for mass numbers 16, 17, 18, 28, 30, 32, and 44.
2.3. Evaluation of Sensitivity of Sensor

Sensors were prepared as thick films (~10 µm) deposited on alumina substrates embedded in TO-8 packages. The sensor substrates were provided vapor-deposited Pt contacts (size 0.3 × 0.2 mm, gap 0.2 mm) and Pt meander. Sample powders were dispersed in terpineol and drop-deposited by a micropipette. The images of substrates before and after thick film deposition are in Supplementary data (Figure S1). The sensors were tested by a PC-controlled electrometer with a gas flow chamber. Sensors were heated at 220 °C for 12 h to remove organic binder and form the sensing layer. DC-resistance was measured with the applied voltage 1.3 V at temperature 100–220 °C. The reference gas was pure air from a generator of pure air model “2.0–3.5” (Himelectronica, Moscow, Russia); contamination level was in the limit of 10 ppm H₂O, 2 ppm CO₂, 0.1 ppm hydrocarbons. Certified gas mixture C₆H₆:N₂ (52 ± 4 ppm, Monitoring) was used as the source of target gas. Gas flows were controlled by mass-flow controllers EL-FLOW (Bronkhorst, Ruurlo, The Netherlands). Pure air and C₆H₆:N₂ flows were mixed using pipelines and fittings (Camozzi, Brescia, Italy) to prepare the test gas with different benzene concentrations. Gas flowrate was 100.0 mL/min in the sensing tests. Sensor signal $S$ was defined as relative resistance change according to Equation (1):

$$S = \frac{R_a - R_g}{R_g}, \quad (1)$$

where $R_a$ is resistance in air, and $R_g$ is resistance in test gas.

3. Results

3.1. Material Characterization

The compositions and parameters of microstructure of materials—crystallite size (specific surface area evaluated by XRD) and BET measurements—are summarized in Table 2. The phase compositions of pristine metal oxides were similar to those of $n$-type MOS in the previous work [24]. Single-phase wurtzite-like ZnO, cubic In₂O₃, rutile-like SnO₂, and monoclinic γ-WO₃ were obtained according to XRD (patterns are in Supplementary data, Figure S2). Mixed-phase composition of TiO₂ was the result of incomplete transition of anatase to the more thermodynamically stable rutile during the calcination at 700 °C.

Table 2. Composition of samples, annealing temperature of MOS (T$_{\text{anneal}}$), crystallite size ($d_{\text{XRD}}$), and BET area ($S_{\text{BET}}$).

| MOS    | T$_{\text{anneal}}$ (°C) | Additive | Phase Composition | $d_{\text{XRD}}$ (nm) | $S_{\text{BET}}$ (m²/g) |
|--------|--------------------------|----------|-------------------|-------------------------|-------------------------|
| ZnO    | none (none)              | PtOₓ      | ZnO wurtzite      | 18–20                   | 18–21                   |
| In₂O₃  | 300          | none      | In₂O₃ cubic       | 8–10                    | 103–110                 |
| SnO₂   | none          | PtOₓ      | SnO₂ tetragonal   | 4–6                     | 95–100                  |
| WO₃    | none          | PtOₓ      | γ-WO₃ monoclinic  | 9–12                    | 32–35                   |
| TiO₂   | 700          | none      | TiO₂ anatase (33 mol.%), TiO₂ rutile (67 mol.%) | 27–30 (anatase) 38–46 (rutile) | 7–8                     |

In the PtOₓ−modified samples, no crystalline phases related to platinum were detected by diffraction tools. Investigation of samples’ microstructure by electron microscopy revealed a mostly irregular spherical shape of metal–oxide nanoparticles (Figure 1). The majority of MOS nanoparticles had the size that agreed with the crystallite size estimated by XRD within approximately $d_{\text{XRD}} \pm 5$ nm intervals (Table 2). The nanoparticles were agglomerated into aggregates with the size of 30–250 nm. Electron diffraction patterns
were relevant to MOS phases detected by XRD; no contribution from platinum was observed. However, Pt-enriched nanoparticles segregated at the surface of agglomerated MOS nanoparticles were revealed by HAADF-STEM and EDX mapping (Figure 1e,f). The particle size distribution of PtO\textsubscript{x} was in the range 3–15 nm with the majority of nanoparticles having an average size 5–10 nm, independent of the supporting MOS.

Figure 1. HRTEM images of nanocomposites ZnO/PtO\textsubscript{x} (a), SnO\textsubscript{2}/PtO\textsubscript{x} (b), and In\textsubscript{2}O\textsubscript{3}/PtO\textsubscript{x} (c); TEM image of TiO\textsubscript{2}/PtO\textsubscript{x} (d); HAADF-STEM micrograph of WO\textsubscript{3}/PtO\textsubscript{x} (e), and overlaid EDX map of W L-signal (blue) and Pt L-signal (orange) (f).

XPS analysis confirmed the purity of obtained materials and the elements’ oxidation states were determined. In the spectra of pristine MOS, only the peaks of oxygen and corresponding metals in the relevant oxidation states were observed: Zn\textsuperscript{+2} in ZnO, In\textsuperscript{+3} in In\textsubscript{2}O\textsubscript{3}, Sn\textsuperscript{+4} in SnO\textsubscript{2}, and Ti\textsuperscript{+4} in TiO\textsubscript{2} (Figure 2a). The Tungsten W 4f signal was asymmetric and could be deconvoluted into two doublets. The major signal was due to W\textsuperscript{+6} oxidation state. The minor doublet was due to W\textsuperscript{+5} cations. The percentage of W\textsuperscript{5+} in pristine WO\textsubscript{3} was approximately 10 at. % of the overall W amount. The presence of reduced W\textsuperscript{5+} cations indicated a significant oxygen deficiency in WO\textsubscript{3-δ} (δ \approx 0.05) under UHV conditions of the XPS measurements. Oxygen O 1s signals were dominated by the peak at 530.0 \pm 0.5 eV
due to $O^{2−}$ anions in the oxides bulk (Figure 2b). The minor O 1s peak due to surface species (surface anions, OH-groups, and adsorbed oxygen) was distinguished at higher BE = 531.0–532.5 eV. The higher ratios of surface-to-bulk O 1s peaks areas for In$_2$O$_3$ and SnO$_2$ correlated with the larger specific surface areas of these oxides (Table 1).

The introduction of PtO$_x$ did not affect the oxidation states of metal cations and oxygen anions, but the positions of Ti$^{4+}$, W$^{6+}$, and O$^{2−}$ peaks shifted to higher binding energies. This may be due to a catalyst-supported electronic interaction, namely, electron donation from TiO$_2$ and WO$_3$ to the supported PtO$_x$ nanoparticles. Platinum was observed mainly in the Pt$^{2+}$ oxidation state with the Pt 4f$_{7/2}$ peak position at 72.5–74.0 eV (Figure 2c). Two Pt$^{2+}$ states were observed in the ZnO—supported sample; the one with the Pt 4f$_{7/2}$ signal centered at 72.8 ± 0.2 eV . From the peaks area ratio, the fraction of Pt$_0$ was estimated to be 27–28 at.% of the total Pt content in TiO$_2$/PtO$_x$ nanocomposites.

3.2. Active Sites at the Surface of Materials

TPR patterns are shown in Figure 3. Hydrogen consumption bands of In$_2$O$_3$, SnO$_2$, and WO$_3$ at temperatures above 350–600 °C were due to reduction of metal–oxide bulks to metals. Reduction of WO$_3$ was completed at a higher temperature (600–950 °C) relative to SnO$_2$ and In$_2$O$_3$ (350–650 °C). This agrees with the larger stability of tungsten oxide: higher metal–oxygen bond energy and lower enthalpy of formation, in comparison with other MOS (Table 1). The weak $H_2$ consumption bands below 300–350 °C were attributed to the reduction of surface species (oxidative sites), such as metal cations (i.e., oxygen vacancy formation), chemisorbed oxygen, and hydroxyl groups. Zinc oxide and titania could not be reduced completely in the TPR experiments and demonstrated continuous $H_2$ consumption at temperatures above 80–200 °C. To uniformly compare the concentrations...
of oxidative sites at the surface of different samples, the equivalent H₂ amounts consumed below the conditional threshold temperature 300 °C were quantified. The results are shown in Figure 4a.

![Figure 3. TPR patterns of pristine and PtO₃ modified metal–oxide semiconductors.](image)

In the PtO₃ modified materials, reduction of surface species and bulk oxides (SnO₂, In₂O₃, and WO₃) started at a temperature that was lower by 50–100 °C with respect to pristine MOS (Figure 3). This indicates the catalytic effect of Pt on the reactions involving hydrogen. In the calculation of oxidative sites concentration at the surface of nanocomposites (Figure 4a), the uptake of hydrogen was taken into account for the reduction of certain amounts of Pt²⁺ determined by XPS.

Figure 4b demonstrates the concentrations of acid sites at the surface of MOS evaluated by temperature-programmed desorption (TPD) of ammonia. The obtained results were almost the same as those described previously [24]. The data for ZnO and In₂O₃ were revised in this work, because the oxides were prepared differently than in the cited work.
Broensted-type (acidic OH−-groups) and Lewis-type acid sites (coordinately unsaturated surface cations) were determined by quantifying ammonia desorption at temperatures 50–200 °C and 200–600 °C, respectively [30]. TPD patterns and mass spectra of evolved gases are in Supplementary data (Figure S3). The acidity of nanocomposites MOS/PtOx could not be determined by TPD because of PtOx-catalyzed ammonia oxidation to N2O, NO, and H2O prior to NH3 desorption, as was detected by mass spectrometry. The acid sites of nanocomposites MOS/PtOx was qualitatively characterized by DRIFT spectroscopy of ammonia adsorption. Figure 5 shows DRIFT spectra of materials exposed to NH3 (200 ppm) at room temperature. The positive peak evolved at 3100–3200 cm−1 due to stretching N–H vibrations, at 1260 cm−1 and 1610 cm−1 due to symmetric and asymmetric bending NH3 vibrations, respectively, and at 1460 cm−1 due to symmetric bending NH4+ vibrations of adsorbed ammonia [31]. The negative band above 3600 cm−1 in the stretching O–H vibration range could be due to the depletion of OH−-groups (Broensted acid sites) as a result of ammonia adsorption. The positions and intensities of peaks of adsorbed NH3 and NH4+ species were close for pristine MOS and nanocomposites MOS/PtOx.

![Figure 5. DRIFT spectra of pristine and PtOx-modified MOS exposed to 200 ppm NH3 at room temperature for 1 h. Positions of stretching (ν N-H) and symmetric (δs) and asymmetric (δas) vibrations of adsorbed NH3 and NH4+ species are shown.](image)

3.3. A Comparison of Sensitivity to Benzene Vapor

Figure 6a shows the dynamic response to increasing concentration of benzene vapor on the example of pristine and PtOx-modified WO3 sensors. The responses of other sensors are in Supplementary data (Figure S4a). For all the samples, the resistance of MOS/PtOx-based sensors was higher by an order of magnitude than the resistance of MOS sensors. It can be explained by electronic donation from n-type MOS to the supported catalytic nanoparticles, probably due to higher work function of PtOx. It agrees with the XPS data for TiO2- and WO3-based materials. The sensors signals are plotted in relation to target gas concentration in Figure 6b for the WO3-based sensors, and the data for the other MOS and MOS/PtOx sensors are in Supplementary data (Figure S4b). The plots of sensor signals vs. benzene concentration were linear in logarithmic axes fitting the relation S ~ Cα. The power α varied in the range α = 0.6–0.9 depending on MOS: α = 0.6 for In2O3 and TiO2, α = 0.7 for ZnO, α = 0.8 for SnO2, and the higher value
$\alpha = 0.9$ was characteristic of the WO$_3$-based sensors. No effect of the additive PtO$_x$ on the value of the power $\alpha$ was observed. Temperature plots of the sensors signals to 2 ppm of benzene are compared in Figure 6c. The sensitivity increased with temperature, and the highest sensitivity was observed at 200–220 °C which is the maximum limit of operation temperature for PtO$_x$-modified sensors. MOS/PtO$_x$ sensors demonstrated higher sensitivity to benzene, in comparison to pristine MOS. In Table 3, the sensing performance in the detection of benzene is compared with data in the literature. The presently investigated materials WO$_3$/PtO$_x$ and SnO$_2$/PtO$_x$ demonstrated a promising sensing behavior: the relatively high sensor signals of $S \approx 5.7$–7.8 were registered at a low benzene concentration of 2 ppm. An advantage of the present WO$_3$/PtO$_x$ and SnO$_2$/PtO$_x$ sensors is the low operation temperature (200–220 °C), in comparison with the higher operation temperatures above 300 °C that have often been applied for metal–oxide-based benzene sensors.

![Figure 6](image_url)

**Figure 6.** Dynamic response of WO$_3$ and WO$_3$/PtO$_x$ sensors to increasing concentration of benzene at 220 °C (a); dependence of sensor signals of WO$_3$ and WO$_3$/PtO$_x$ sensors on C$_6$H$_6$ concentration at 220 °C (b); sensor signals of pristine and PtO$_x$-modified MOS to 2 ppm C$_6$H$_6$ in relation to temperature (c).

| Material       | Morphology          | Benzene Concentration, ppm | Sensor Signal, $S = (R_a - R_g)/R_a$ | Operation Temperature, °C | Ref.   |
|----------------|---------------------|----------------------------|--------------------------------------|---------------------------|--------|
| SnO$_2$/Cu$_2$O | nanowires           | 10                        | 11.5                                 | 300                       | [11]   |
| ZnO/Pt         | nanowires           | 10                        | 0.05                                 | 100                       | [12]   |
| WO$_3$/Al$_2$O$_3$/Pt | nanoparticles    | 1                         | 0.97                                 | 250                       | [13]   |
| SnO$_2$/TiO$_2$/Rh | hollow spheres   | 5                         | 80                                   | 325                       | [14]   |
| SnO$_2$/Pd     | nanowires           | 1                         | 24.5                                 | 300                       | [15]   |
| SnO$_2$/Pt     | nanowires           | 1                         | 7.3                                  | 300                       | [15]   |
| WO$_3$         | nanoneedles         | 1                         | 1                                    | 200                       | [16]   |
| SnO$_2$/PtO$_x$ | nanoparticles      | 2                         | 7.8                                  | 200                       | this work |
| WO$_3$/PtO$_x$ | nanoparticles      | 2                         | 5.7                                  | 220                       | this work |

**Table 3.** Composition of sensing behavior to benzene of the presently investigated resistive sensors and literature data.
For the sake of comparison, the sensor signals were normalized per the materials’ BET area and the effective sensor signal was determined according to Equation (2):

$$S_{\text{eff}} = S/S_{\text{BET}} \times 50 \text{ m}^2/\text{g}$$

A conditional unit of 50 m$^2$/g was used for normalization as an average specific surface area of the investigated samples. Figure 7 shows the highest effective sensor signals, $S_{\text{eff}}$, to 2 ppm benzene registered at 200–200 °C for different sensing materials in relation to metal–oxygen bond energy of the oxides, which was used as a descriptive parameter. For pristine MOS, the sensitivity increased with $E_{\text{M-O}}$ in metal oxides from ZnO to SnO$_2$ and was almost the same for SnO$_2$, TiO$_2$, and WO$_3$. Another trend was found in the sensitivity of MOS/PtO$_x$ in relation to $E_{\text{M-O}}$ of the supporting metal oxide. The sensitivity of PtO$_x$–modified samples steadily increased with metal-oxygen bond energy in the entire range of investigated MOS, i.e., from ZnO- to WO$_3$-based nanocomposites.

![Figure 7. Maximum effective sensor signals of pristine and PtO$_x$–modified MOS to 2 ppm C$_6$H$_6$ in relation to metal–oxygen bond energy in MOS.](image)

To highlight the difference in benzene-sensing routes by pristine and PtO$_x$–modified MOS, the sensitivity was plotted against active sites concentrations (Figure 8). The underlying hypothesis is that sensor signal is directly proportional to the concentration of active sites responsible for target gas conversion. It follows from mass action law applied to a generalized reaction in a stationary state Equation (3):

$$G + <\text{AS}>^m \rightarrow P + m e^-,$$

$$S = (R_a - R_g)/R_g = (\sigma_a - \sigma_g)/\sigma_a - \Delta n \sim C^\alpha N_{\text{AS}}^\beta,$$  

where G is a target gas; $<\text{AS}>$ is an active site of target gas conversion with a localized negative charge; P is the product of target gas conversion; m $e^-$ is a number of released electrons; $N_{\text{AS}}$ is concentration of active sites; $\sigma_a$ and $\sigma_g$ are electric conductance in presence of target gas and in air, respectively; $\Delta n$ is change of free electrons concentration as a result of target gas conversion; C is target gas concentration; and $\alpha$ and $\beta$ are rate orders by target gas and active site, respectively. Through compilation of the data of effective sensor signals (Figure 7) and active sites concentrations at the surface of different samples (Figure 4), two relations of sensitivity vs. active sites concentrations were distinguished. The one shown in Figure 8a is the dependence of sensitivity of pristine MOS on the summary concentrations of oxidative sites ($N_{\text{H}_2\text{TPR}}$ measured by TPR) and acid sites ($N_{\text{acid sites}}$ estimated by TPD) at the surface of MOS. The sum of concentrations of both types of active sites in the $x$–axes was chosen to satisfy the initial assumption that sensitivity is proportional to the number
of acid sites Equation (3). Figure 8b shows the plot of MOS/PtOx sensitivity vs. acid sites concentration at the material surfaces. In this case, when the concentration of oxidative sites at the surface of MOS/PtOx was summed with that of acid sites, no correlation with the sensitivity was found.

3.4. DRIFT Study of Material Interaction with Benzene Vapor

DRIFT spectra were registered during the materials exposure to benzene vapor at room temperature to characterize the adsorption and at raised temperature (220 °C) to investigate the redox conversion of target molecules. The pattern of adsorbed C₆H₆ onto the surface of MOS was observed by FTIR spectroscopy of metal oxides impregnated with liquid benzene and dried at room temperature (Figure 9a). It demonstrates the peaks of aromatic ring vibrations at 1480 cm⁻¹, stretching C=C vibrations at 1580–1540 cm⁻¹, stretching C-H vibrations at 3040–3100 cm⁻¹, and overtones at 1800 cm⁻¹ and 1960 cm⁻¹. DRIFT spectra of pristine MOS and PtOx—modified MOS exposed to benzene vapor at room temperature are shown in Figure 9b. The peak of aromatic ring vibrations at 1480 cm⁻¹ and the band of stretching C=C vibrations at 1580–1540 cm⁻¹ in adsorbed C₆H₆ were observed on the DRIFT spectra of TiO₂— and WO₃—based materials. The more intense peak of polar C=O group stretching vibrations evolved at 1670 cm⁻¹ on the spectrum of pristine WO₃ exposed to benzene (Figure 9b). This peak, in combination with the stretching C=C vibrational band at 1580–1540 cm⁻¹, is typical of 0-benzoquinone [32], and its appearance indicates a partial oxidation of adsorbed benzene at the surface of tungsten oxide. Figure 9c shows DRIFT spectra of nanocomposites MOS/PtOx exposed to benzene at room temperature. The evolved peaks were similar to those on the spectra of pristine MOS (Figure 9b). Additionally, on the spectrum of WO₃/PtOx, two minor positive peaks appeared at 2100 cm⁻¹ and 1860 cm⁻¹; this can be due to trace amounts of adsorbed CO resultant from a catalytic oxidation of benzene, as discussed below. The minor negative IR absorption bands at 1540–1560 cm⁻¹ and 1260–1300 cm⁻¹ on the spectra of ZnO—I and In₂O₃—based samples can be attributed to bidentate carbonate species [33] which exist at the surface of basic oxides due to CO₂ adsorption and can be partially removed in the process of interaction with the target gas molecules.
DRIFT study of benzene conversion on pristine MOS at temperature 220 °C showed the prominent spectral on the spectrum of WO3 (Figure 10a). The peaks at 1670 cm$^{-1}$ and 1560 cm$^{-1}$ evolved, suggesting benzoquinone formation from the oxidation of benzene. Simultaneously, the W–OH band at 1410 cm$^{-1}$ and the O–H stretching vibrational band at 3200–3600 cm$^{-1}$ decreased. Thus, oxidation of benzene at the surface of WO3 involved reactive surface oxygen species and OH-groups Equation (4):

\[
C_6H_6(g) + 3/n \text{O}_n^{m−}(\text{surf}) \rightarrow C_6H_4O_2(\text{ads}) + \text{H}_2\text{O}(g) + 3m/n \text{e}^− \tag{4}
\]

DRIFT spectra of PtO$_x$–modified MOS exposed to benzene at 220 °C displayed the peak of in-ring C=C vibrations (1540 cm$^{-1}$), like in adsorbed benzene or benzoquinone; the peak of C=O stretching vibrations (1670 cm$^{-1}$) characteristic of benzoquinone was weak (Figure 10b). The main distinctive feature on the spectra of PtO$_x$–functionalized MOS was the evolution of C≡O vibrational peak at 2100–2140 cm$^{-1}$, like in adsorbed CO [33]. In comparison with the benzoquinone-like C=O peak at 1670 cm$^{-1}$, the peak of Pt-bound CO (2140 cm$^{-1}$) was more intense (Figure 10b). The minor peak which evolved at 1860 cm$^{-1}$ could be attributed to Pt–bound CO in a bridging conformation, and the stronger peak at 2140 cm$^{-1}$ is typical of terminal Pt–CO groups [33]. Thus, in the presence of a PtO$_x$ catalyst, the oxidation of adsorbed benzene results in the formation of CO according to reaction 5:

\[
C_6H_6(g) + 9/n \text{O}_n^{m−}(\text{surf}) \rightarrow 6 \text{CO}(\text{ads}) + 3 \text{H}_2\text{O}(g) + 9m/n \text{e}^− \tag{5}
\]

The evolution of Pt–CO species was observed by DRIFT spectroscopy for nanocomposites based on acidic MOS: SnO$_2$, TiO$_2$, and WO$_3$ (Figure 10b). The intensity of carbonyl
peaks increased in the same order, corresponding to the increment of metal–oxygen bond energy and surface acidity of MOS.

![DRIFT spectra](image)

**Figure 10.** DRIFT spectra of pristine MOS (a) and PtO$_x$–modified MOS (b) exposed to 10 ppm C$_6$H$_6$ for 1 h at 220 °C.

### 4. Discussion

This work is a comparative and systematic study of active sites and sensitivity to benzene of $n$–type wide bandgap MOS that are often used as VOC sensors: ZnO, In$_2$O$_3$, SnO$_2$, TiO$_2$, and WO$_3$ [1,3–6]. These oxides differ widely in the fundamental parameters such as cationic charge/radius ratio, metal–oxygen bond energy, and formation heat (Table 1). It is of interest to uniformly compare surface reactivity and sensing behavior to benzene of pristine MOS and of the oxides modified by catalytic PtO$_x$ nanoparticles. In order to obtain the comparable microstructures of sensing materials, the samples of nanocrystalline MOS were obtained under similar synthetic conditions by the aqueous chemical deposition route followed by thermal treatment of deposited metal hydroxides. Although the materials had similar morphologies of irregularly shaped agglomerated nanoparticles (Figure 1), the microstructural parameters of the obtained MOS differed in definite ranges: crystallite size 5–50 nm and BET surface area 5–100 m$^2$/g (Table 2). This results from distinct energetics and kinetics of crystallization of metal oxides and complicates the comparison of sensing behavior because the sensitivity depends on the microstructure of a sensing material [34,35]. In addition, the elevated annealing temperature of titania (700 °C), relative to that of other MOS (300 °C), was used to lower the intrinsically high electric resistance of TiO$_2$-based sensors which could not have been measured otherwise.

PtO$_x$ nanoparticles with the size 5–10 nm (Figure 1e,f) were immobilized onto the surface of MOS via the impregnation technique. The absence of diffraction peaks from PtO$_x$ phases in XRD (Figure S2) and ED (insets in Figure 1a–d) patterns could be due to the low percentage of the additive and/or its poor crystallinity. By XPS, it was shown that Pt$^{2+}$ was the predominant oxidation state of the catalytic additive. The oxidized state of platinum could be due to adsorbed oxygen on surface platinum atoms, provided that the small PtO$_x$ nanoparticles have high surface-to-volume ratio. A minor fraction of reduced Pt$^0$ species was found in the nanocomposites TiO$_2$/PtO$_x$ and WO$_3$/PtO$_x$. The presence of reduced platinum atoms in these nanocomposites may be attributed to the electronic interaction...
of PtO$_x$ nanoparticles with the supporting oxides, as follows from the shifts of XPS peaks of Ti$^{4+}$, W$^{6+}$, and O$^{2-}$ relative to pristine MOS (Figure 2a,b). That the electronic donation was observed only from TiO$_2$ and WO$_3$ can be explained by the higher concentration of oxygen vacancies in these oxides, compared with ZnO, In$_2$O$_3$, and SnO$_2$. The single changed spin centers $V_O$ were determined by EPR in similar MOS samples in our previous works, as summarized in the recent review [36]. The higher oxygen deficiency of tungsten was observed only from TiO$_2$, as the spillover effect of PtO$_2$.

The DRIFT spectra (Figure 5) were registered under the conditions of NH$_3$ adsorption. Because in TPD method the use of elevated temperature is inherent, the surface acidity can be affected by the catalytic PtO$_2$ -modified oxides, as compared with pristine MOS, but the general trend in relation to metal–oxygen bond energy was the same (Figure 4a). This may be due to the catalytic (spillover) effect of PtO$_3$ nanoparticles, which facilitates oxygen exchange between gas phase and supporting oxide surface [43].

Acid sites of the Broensted-type (acidic OH-groups) and Lewis-type (coordinately unsaturated surface cations) were determined by TPD of ammonia. Lewis acid sites play a crucial role in the adsorption of gas molecules having lone-electron-pair donor atoms which contain, for example, nitrogen or oxygen. Therefore, quantification of acid sites is helpful to understanding the sensing behavior to target gases with Lewis base properties. As follows from Figure 4b, surface acidity of MOS increased in the order ZnO $\approx$ In$_2$O$_3$ $<$ SnO$_2$ $<$ TiO$_2$ $<$ WO$_3$, which agrees with the increment of metal–oxygen bond energy. The origin of this correlation should be the increase of cationic charge/radius ratio (Table 1): the larger the positive charge density at the cation, the stronger its lone-pair acceptor behavior (Lewis acidity) and the higher the ionic bond energy with oxide anions. Because in TPD method the use of elevated temperature is inherent, the surface acidity of catalytically PtO$_3$-modified materials could not be measured by this method due to catalytic oxidation of probe molecules prior to desorption. To overcome this difficulty, we used DRIFT spectroscopy to estimate the surface acidity of nanocomposites MOS/PtO$_x$.
respectively. Although the quantitative information could not be obtained from DRIFT spectra, the peak intensities of adsorbed NH$_4^+$ and NH$_3$ species were close for pristine MOS and nanocomposites MOS/PtO$_x$. This provides evidence that the relative concentrations of acid sites at the oxides surfaces were unaffected by the supported PtO$_x$ nanoparticles, likely due to low percentage (1 wt.%) of the additive.

The materials were sensitive to 0.5–5 ppm of benzene vapor in air. In comparison with pristine MOS, the PtO$_x$−modified sensors had an improved sensitivity to benzene in the entire tested ranges of target gas concentration (Figure 6b) and operation temperature (Figure 6c). This is explained by the catalytic effect of metal–oxide-supported platinum in the oxidation of organic molecules [18,44]. In order to reveal the effect of materials composition and active sites concentrations on the sensitivity, we introduced the effective sensor signal defined by Equation (2). This is an attempt to uniformly compare the sensitivity of materials with different chemical compositions without regard to the influence of distinct microstructure parameters (Table 2). It was commonly noticed that sensor signals to reducing gases were linear if plotted against the surface-to-volume ratio of a sensing material, i.e., inversely proportional to an average particle size or directly proportional to specific surface area [34,35]. This dependency was theoretically substantiated by that which was reported by Rothschild and Komem, (2004) [45]. Comparing the trends in active site concentrations (Figure 4) and in the sensitivity to benzene (Figure 7) in relation to metal–oxygen bond energy, one can suggest distinct impacts from the active sites to the sensing process in the absence and in the presence of PtO$_x$ catalyst. The trend in effective sensor signals to benzene of pristine MOS in relation to $E_{M-O}$ is similar to that previously observed for the sensitivity of $n$−type MOS to methanol and acetone [24]. This assumes that the sensitivity to these different classes of organic molecules is controlled by similar factors.

Different correlations between the sensitivity to benzene and the concentrations of active sites were deduced for pristine MOS and nanocomposites MOS/PtO$_x$. For pristine MOS, comparison of the plots of sensitivity (Figure 7) and active sites concentrations in relation to $E_{M-O}$ (Figure 4) led to an intuitive conclusion that oxidative sites and acid sites were equivalently responsible for the conversion of benzene. Plotted against the total concentration of oxidative and acid sites, the sensitivity to C$_6$H$_6$ continuously increased in the entire range (Figure 8a). A similar result was previously obtained for the sensitivity of $n$-type MOS to acetone and methanol [24,36]. The role of oxidative sites is evidently the oxidation of VOC target molecules, and acid sites can influence the adsorption of Lewis base molecules possessing donor oxygen atoms (e.g., alcohols or ketones). For the conversion of benzene, the role of oxidative sites is likely binding the conversion product (benzoquinone) rather than the target molecules (DRIFT results in Section 3.4). For PtO$_x$−modified sensors, the graph of sensitivity to benzene vs. $E_{M-O}$ (Figure 7) resembles that of acid site concentration at the surface of MOS (Figure 4b). Supported by the DRIFT study of ammonia adsorption at room temperature (Figure 5), it was assumed that the relative acidity of modified MOS was unaffected in the presence of a low percentage (1 wt.%) of the additive PtO$_x$. The steady growth of MOS/PtO$_x$ sensitivity with the concentration of acid sites suggests that surface acidity is of primary importance for the efficient conversion of benzene in the presence of PtO$_x$ catalyst.

Using DRIFT spectroscopy, the distinction in sensing mechanisms of pristine and PtO$_x$−modified MOS was revealed. DRIFT spectra demonstrated minor traces of adsorbed benzene. This could be due to low concentration of target gas (10 ppm), as well as low activity of infrared vibrations of non-polar C−C and weakly polar C−H bonds in C$_6$H$_6$ molecules. The adsorption of C$_6$H$_6$ could be observed on the acidic oxides TiO$_2$ and WO$_3$ (Figure 9b) along with the product of partial benzene oxidation: ω-benzoquinone C$_6$H$_4$O$_2$. The molecules of benzoquinone possess polar C=O groups which have a highly active infrared vibrational mode at 1670 cm$^{-1}$. The modification of MOS by catalytic PtO$_x$ nanoparticles did not affect the adsorption of benzene, as follows from the evolution of the same peaks on the room temperature DRIFT spectra of MOS (Figure 9b) and MOS/PtO$_x$ (Figure 9c). At raised temperature (220 °C), simulating the conditions of sensors operation,
benzene molecules were partially oxidized, yielding o-benzoquinone Equation (4). The stronger DRIFT signals observed for WO$_3$-based samples correlate with the higher sensitivity to benzene. The high sensitivity and surface reactivity to benzene can be rationalized by enhanced surface acidity of tungsten oxide. Lewis acid sites, i.e., coordinately unsaturated cations, act as adsorption sites for benzoquinone molecules via the lone-pair donor O-atoms. This favors the oxidation reaction Equation (4) through binding the product of benzene oxidation. At the surface of PtO$_x$—modified MOS at raised temperature (220 °C), oxidation of benzene results in the formation of CO (Equation (5)), i.e., proceeds deeper than on pristine MOS. It can be the reason for higher sensitivity of nanocomposites MOS/PtO$_x$ to benzene. However, this route of PtO$_x$—catalyzed benzene oxidation was strongly dependent on the surface acidity of supporting MOS. The intensity of the evolved peaks of Pt-bound CO on the DRIFT spectra of MOS/PtO$_x$ (Figure 1b) steadily increased with the increment of oxides surface acidity in the order ZnO ≈ In$_2$O$_3$ <SnO$_2$ < TiO$_2$ < WO$_3$. This agrees with the increasing sensitivity of MOS/PtO$_x$ sensors to benzene (Figure 8b).

A similar effect of the acidity of supporting oxides was observed for catalytic activity of supported platinum in the combustion of hydrocarbons [18,46]. It was argued that zero-valent Pt$^{0}$ atoms were the key catalytically active sites. The appearance of reduced Pt$^{0}$ species in the catalytic cycle was favored on acidic supports because basic oxides stabilized oxidized platinum in the form of platinates [46]. In the present work, the occurrence of reduced Pt$^{0}$ species in PtO$_x$—modified acidic oxides TiO$_2$ and WO$_3$ was confirmed by XPS (Figure 2c). Thus, surface acidity of MOS plays a dual role in improving the sensitivity of MOS/PtO$_x$ nanocomposites to benzene. On the one hand, it facilitates the occurrence of Pt$^{0}$ sites which catalyze deep benzene oxidation to CO. On the other hand, acid sites favor the adsorption of benzoquinone which is a by-product or an intermediate in the catalytic benzene oxidation. The catalytic impact of PtO$_x$ nanoparticles facilitated by surface acidity of supporting MOS is likely more important in determining the sensitivity of MOS/PtO$_x$ respective of the role of native oxidative sites (surface oxygen species, and hydroxyls) in the oxidation of benzene at the MOS surfaces. This may be the reason for the independence of nanocomposite sensitivity on the concentration of oxidative sites (Figure 8b).

5. Conclusions

Active surface site concentrations and sensitivity to benzene were compared for pristine and PtO$_x$-modified n-type metal oxide semiconductors. MOS and MOS/PtO$_x$ materials showed different trends in the sensitivity to benzene in relation to metal–oxygen bond energy and active site concentrations, related to distinct sensing mechanisms. The higher sensitivity of pristine SnO$_2$, TiO$_2$, and WO$_3$ was enabled by equivalently important roles of acid sites and oxidation sites in the processes of benzene conversion and adsorption of the resultant benzoquinone. Modification by PtO$_x$ improved the sensitivity to benzene due to catalytic deep oxidation of target molecules to carbonyl species. The sensitivity of PtO$_x$—modified MOS increased with the surface acidity of supporting oxide. The synergistic effect of surface acidity and PtO$_x$ catalytic activity on the sensitivity of nanocomposites MOS/PtO$_x$ to benzene was rationalized by the stabilization of zero-valent Pt species, which is critical for the deep oxidation of benzene to CO. These things considered, acid sites favor benzene oxidation through binding benzoquinone which is one of the target gas oxidation products.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/s22176520/s22176520/s1](https://www.mdpi.com/article/10.3390/s22176520/s22176520/s1), Figure S1: microscope images of sensor substrate before and after thick film deposition; Figure S2: XRD patterns of MOS and MOS/PtOx samples; Figure S3: patterns of ammonia TPD from the surface of MOS (thermal conductivity detector, TCD) and mass-spectrometric analysis (MS) of desorbed gas; Figure S4: dynamic response of pristine and PtOx-modified ZnO, In2O3, SnO2, and TiO2 to 0.5–5 ppm benzene at 220 °C (a), and sensor signals in relation to benzene concentration at 220 °C (b).
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