Van der Waals Interactions Between Non-polar Alkyl Chains and Polar Oxide Surfaces Prevent Catalyst Deactivation in Aldehyde Gas Sensing

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Catalysis-based electrical sensing of various volatile organic compounds (VOCs) on metal oxide surfaces is a powerful method for electrical molecular discrimination. However, it suffers from catalyst deactivation caused by the poisoning of catalytic sites by residual analytes and/or catalyzed products on the surface during sensing operations. This study highlights the underestimated role of van der Waals interactions between hydrophobic aliphatic alkyl chains and hydrophilic ZnO surfaces in catalytic molecular sensing. These interactions significantly mitigate catalyst deactivation during the electrical sensing of aliphatic aldehydes on ZnO sensor surfaces. To achieve this, hydrophobic aliphatic phosphonic acids (octadecylphosphonic acid-ODPA) were immobilized on ZnO nanowire sensor surfaces. Electrical sensing measurements indicated that ODPA surface modification significantly reduced the recovery time of sensor responses to nonanal molecules by an order of magnitude without compromising sensitivity. Spectroscopic measurements revealed that nonanal molecules directly coordinated with surface Zn ions as oxidized carboxylates by penetrating *trans*-zigzag ODPA self-assembled monolayers (SAMs). Temperature-programmed measurements demonstrated a significant reduction in the desorption temperature of carboxylates as reaction products on ODPA-modified ZnO surfaces to below 150 °C, whereas the carboxylates on bare ZnO nanowires remained above 300 °C, indicating a significant decrease in catalyst deactivation. IR *p*-polarized multiple-angle incidence resolution spectroscopy using deuterated SAMs revealed changes in the conformation and orientation of alkyl chains within the SAMs caused by aldehyde adsorption. Density functional theory calculations revealed that accumulated van der Waals interactions between hydrophobic long aliphatic alkyl-chains and hydrophilic ZnO surfaces significantly contributed to adsorption molecular kinetics. Consequently, a model is proposed based on alkyl-chain-driven dynamic surface-covering behavior to destabilize catalytically oxidized product carboxylic acids on sensor surfaces.