We investigated the origin, chemistry, and formation mechanisms of the free radicals on the surface of respirable dust-composing ultrafine coal-quartz, coal-pyrite and vitrinite of various ranks. Ab initio computations revealed that the interaction of H₂O molecule with quartz and pyrite is respectively more and less favorable than that of O₂. Unlike the quartz of various ranks showing an isoelectric point (IEP) around pH 2, IEP of pyrite samples varies between pH 2 and 3. Vitrinite of various ranks show an IEP around 3.5 for the anthracite and high-volatile bituminous, and between pH 5 and 6 for medium-volatile and low-volatile bituminous samples. IR spectra of the fresh and aged samples were compared. Neither the fresh nor the aged anthracite vitrinite exhibit an IR absorption peak for hydroxyl groups. The higher the volatile matter content in the coal dust the higher is its potential for toxicity. Identical to pyrite samples of various ranks, two peaks at 3621 cm⁻¹ and 3694 cm⁻¹ could be assigned to the hydroxyl groups. Because of the aging, two new absorption peaks appear at 3404 cm⁻¹ and 3545 cm⁻¹ for the pyrite samples that could be assigned to H-bond hydroxyls. For the coal-quartz, we assign the band at 3622 cm⁻¹ to hydroxyl species formed on the aged surface owing to the formation of isolated and bridged silanol groups on the quartz surface. In our ongoing efforts, we employ spectrofluorometer to study the non-hazardous chemical additives to inhibit or reduce the toxicity of the dust composing particulates.