DFT study for adsorptive decomposition of 1,3-dimethyltrisulfane (DMTS) over gold nano clusters: the elimination of aged odour in Japanese sake

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The flavor of Japanese sake changes during storage. There are two types of flavors generated in this process. One is favorable matured aroma and the other is unfavorable aged odor that is called hineka. From the research works of the flavor of Japanese sake, it is found that sotolon is responsible for the matured aroma, while 1,3-dimethyltrisulfane (DMTS) is the major component for the unfavorable aged odor. In order to eliminate the aged odor, activated carbon has been commonly used. However, activated carbon adsorbs a wide range of molecules into their micro pores. This resulted in a production of an unscented sake. Thus, there is a demand for selective removal of aged odor without decrease of favorable flavors. It is well known that supported metal nanoparticles have been applied for adsorptive desulfurization of fuels to ppm levels because noble metals have high affinity with Sulphur compounds. Part of our authors were carried out deep desulfurization of Japanese sake by gold nanoparticles and found that they eliminate DMTS selectively. In order to elucidate the mechanism of the adsorptive decomposition of DMTS, DFT calculations are performed for DMTS adsorbed on Auₙ (n=6,10, 24 and etc.) cluster model systems. In all calculations, DFT with PBE0 functional was used. The scalar relativistic effective core potential (ECP) with double-zeta basis sets (LANL2DZ) for all gold atoms and 6-31+G(d) basis sets were applied for the hydrogen, carbon and sulfur atoms. All the geometries of the model cluster systems were fully optimized. Vibrational analysis was performed for the optimized geometries of the transition states and local minima. To characterize the stationary points, a frequency analysis was done for all stationary points at this level. To establish the relevant species, the intrinsic reaction coordinate (IRC) pathway was also run for all the transition states presented. All the calculations were carried out using the Gaussian 09 software package. In the case of Au₂₄ model system, it was found that two S–S bonds in DMTS are completely dissociated on the surface of Au₂₄ clusters, while the first and second activation barriers of this reaction are 10.2 and 103.3 kJ mol⁻¹, respectively. Consequently, two CH₃S groups and S atom are generated on Au₂₄ cluster. The stapler like Au–S–Au–S–Au bonding structure is generated on Au₂₄ in the final structure (FIN) of the reaction pathway. This stapler structure is a bonding mode that is well known in the gold cluster complex.

Figure 1. Final structure of Au₂₄ with fully decomposed DMTS

References

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