DFT calculations for Au adsorption to reduced TiO_2 (110) surface with the coexistence of Cl

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Highly dispersed gold supported catalysts can exhibit surprisingly high catalytic activity for many reactions, such as CO oxidation, odor decomposition, propylene epoxidation, and glucose partial oxidation. It is said that residual chlorines are apt to promote the aggregation of gold nanoparticle during the preparation process of Au supported catalysts. Accordingly, chlorine free Au precursors or chlorines elimination by basis are applied, for the preparation of highly dispersed gold catalysts. However, the detailed mechanism of Au aggregation caused by chlorine is still unknown. In order to investigate this mechanism, DFT calculations were carried out.

GGA-PBE exchange-correlation functional and plane wave basis were adapted with ultra-soft pseudo potentials. Three dimensional periodic slab of rutile TiO_2 (110) 1×2_5layers with vacuum region was used. The energy cut off was 25Ry for wave function, and 225Ry for charge. Geometry optimization was carried out by (2×2×1) Monkhorst-Pack meshes of k point. The other physical quantities were calculated by (4×4×1) Monkhorst-Pack meshes of k point.

From the calculation results of Au and Cl atom adsorption to oxygen defect site on reduced TiO_2 (110) surface, it is turned out that Cl atom adsorb to reduced TiO_2 (110) surface stronger than Au atom. Au adsorption to Cl adsorbed $rTiO_2$ (reduced TiO_2) was also investigated. This calculation results shows that the interaction between Au and $rTiO_2$ becomes weaker by the Cl adsorption.

Table1. Adsorption energies to model surfaces E_{ads} ($E_{ads} < 0$ is stable).

model surface	adsorbate	site	E_{ads} /eV
$rTiO_2$[a]	Cl atom	oxygen defect	-4.07
	Au atom	oxygen defect	-2.49
$Cl+rTiO_2$[b]	Au atom	on Cl	-0.15
		on Ti[5][c]	-1.24
		on O^B[d]	-0.40

[a] reduced TiO_2 (110) surface, [b] reduced TiO_2 (110) surface adsorbed by Cl to oxygen defect on, [c] coordinative unsaturation Ti, [d] bridging oxygen