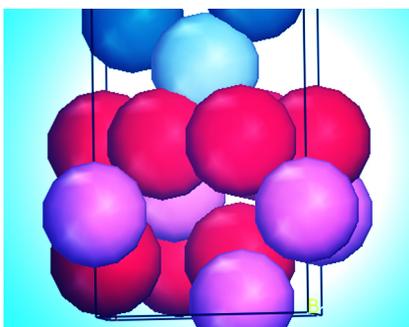


# STUDIES OF CATALYTIC OXIDE SUPPORTS - COMPARATIVE BEHAVIOR OF PD AND AG DEPOSITION ON CLEAN $\alpha$ - $\text{Al}_2\text{O}_3$ (001) SURFACES



The results explain the reason for a higher stability of the clusters generated over alumina support with silver and palladium and the reason for the difference of activity of the supported metal interactions.

## Module used

- CASTEP

## Industry sectors

- Catalysis
- Sensors
- Electronics

Reporting in the journal *Molecular Simulation*,<sup>1</sup> researchers have used the density functional theory modeling program CASTEP to investigate palladium and silver deposition on the surface of alumina.

These metal-oxide materials are used widely in catalysis, photolysis and photooxidation reactions, electrocatalysis, and gas sensors. Experimental studies in this area prove difficult owing to the complexity of bulk and surface oxide structures and difficulties in crystal preparation.

The nature of bonding at the interface between deposited silver/palladium and clean Al-terminated (001) surfaces of  $\alpha$ - $\text{Al}_2\text{O}_3$  has been investigated using the periodic *ab initio* method CASTEP. Substantial inter-planar relaxations within the alumina were found at both the interfaces and the bulk. The periodic calculation with both Ag and Pd deposition shows that 10% of loading on alumina results in maximum stability. Surface energy and work function calculations

were performed to propose the stability for the cluster on the studied surfaces. The deposited Ag forms a 3-D cluster on top of the alumina surface. The Pd cluster formed on the alumina surface is 2-D and is more distorted to accommodate the Ag cluster in its domain. The results are discussed in view of the existing experimental data.<sup>2,3</sup>

The metal-ceramic based materials play a significant role in catalysis, photolysis and photooxidation reactions, electrocatalysis, and gas sensors etc. Aluminum oxide is one of the most widely used supports for catalytic purposes because of both its mechanical and thermal resistance. The electronic structure calculations were performed on both hydroxylated and clean alumina surface to compare their

stability and activity.<sup>4</sup>Verdozzi *et al.*<sup>5</sup> have shown that, while isolated adatoms are oxidized and bind strongly as ions if coordinated to two or more other metal adatoms, the adsorbates are metallic, showing negligible charge transfer to the surface and relatively weak adsorption, mainly by polarization.

The results from the geometric parameters show that the Pd stays much relaxed on the clean alumina surface compared to that of the silver, for a similar 1 ML of geometric coverage (Fig.1). The results were further validated by choosing a mixture composition with 2/3 Pd and 1/3 Ag to trace the activity of the components (Fig. 2). The added activity of Ag causes it to act as the active ingredient for catalytic reaction, the presence of palladium give the structure an added stability. The silver forms a cluster over the Al layer of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> just on top of the hexagonal hole. The silver/ palladium bonding and activity are much more dependent on the structural relaxation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as observed from the surface energy and work function as shown in Table 1.

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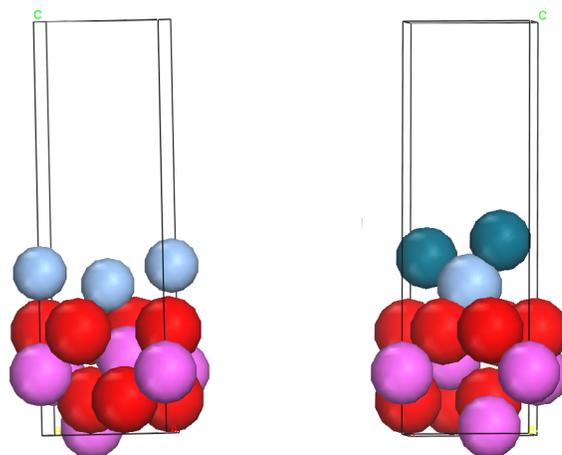


Fig. 1: Ag<sub>3</sub> cluster over Alumina surface.

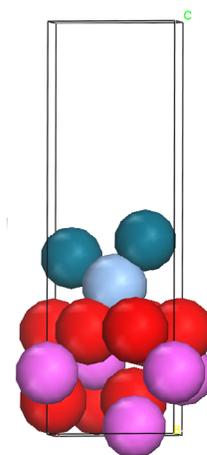


Fig.2: Pd<sub>2</sub>Ag<sub>1</sub> cluster over alumina surface.

Cell	s eV/atom				f (eV)			
	GGA	LDA	Expt.	Al-Al <sub>2</sub> O <sub>3</sub>	GGA	LDA	Expt.	Al-Al <sub>2</sub> O <sub>3</sub>
Ag (111)	0.357	0.530	0.55 <sup>a</sup>	0.489	4.65	4.98	4.465	5.73
Pd (111)	0.587	0.791	0.82	0.779	5.23	5.11	4.85	5.65
Ag (100)	0.432	0.633	0.88 <sup>a</sup>	0.591	4.33	4.82	4.225	5.41
Pd (111)	0.382	0.523	0.61	0.512	4.76	4.92	4.56	5.29
Ag (110)	0.649	0.952	1.18 <sup>a</sup>	0.862	4.30	4.66	4.145	5.17
Pd (110)	0.219	0.417	0.54	0.389	3.89	3.76	4.10	5.01

Table 1: Surface energy ( $\sigma$ ) and work function ( $\phi$ ) of Ag/Pd cluster calculated using GGA and LDA functional and compared with experiment.