

## Quantum-mechanical calculation of solid-state equilibrium: ruthenium and rhodium rutile vs corundum phases

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Commercial needs for improving durability and performance of supported ruthenium and rhodium catalysts drive attention in investigating structural changes occurring at high oxidizing environments. In rhodium catalysts, formation of reducible rhodium sesquioxide ( $\text{Rh}_2\text{O}_3$ <sup>1</sup>) has been associated to *deactivation* towards carbon monoxide (CO) oxidation, and of Rh-based three-way emission control catalysts<sup>2</sup>. In contrast,  $\text{Ru}_2\text{O}_3$  has not been detected yet, but instead, the dioxide phase ( $\text{RuO}_2$ ) has been suggested to be the *active* phase for CO oxidation<sup>3</sup>. Using density-functional theory within the generalized gradient approximation, the sesquioxide vs dioxide equilibrium with respect to ambient molecular oxygen and bulk metal chemical potentials, respectively, is investigated for both ruthenium and rhodium oxides. The ground-state energies of the corundum-type sesquioxides and rutile-type dioxides were calculated at different volumes, relaxing the corresponding structures. The Murnaghan equation of state, cohesive energies and elastic properties were derived. The oxygen pressure dependence of the enthalpy change of the corundum into rutile decomposition is consistent with the experimental observed preference of ruthenium oxide for the rutile- $\text{RuO}_2$  phase.

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<sup>1</sup> G.L. Kellogg, J. Catal. 92, 167 (1985); G. L. Kellogg, Surf. Sci. 171, 359 (1986).

<sup>2</sup> K.C. Taylor, Catal. Rev. Sci. Tech. 35, 457 (1993); M. Schelef and G.W. Graham, Catal. Rev. Sci. Eng. 36, 433 (1994).

<sup>3</sup> H. Over, Y.D. Kim, A.P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante and G. Ertl, Science 287, 1474 (2000).