Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2018

Electronic supplementary information

Morphological changes of catalyst materials in reacting conditions by combined *ab initio* thermodynamics and microkinetic modelling

Raffaele Cheula^a, Aloysius Soon^b and Matteo Maestri*^a

^a Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy.

^b Department of Materials Science and Engineering, Yonsei University, Seoul, Korea

E-mail: matteo.maestri@polimi.it

Section 1. Modelling of the annular reactor

The massive flow rates of gaseous species along the reactor coordinate are calculated by solving the set of differential equations:

$$\frac{dW_{i}}{dV} = k_{mat,i} \rho a_{V} \left(\omega_{i}^{wall} - \omega_{i}^{bulk} \right)$$
(S1)

where W_i is the mass flux of specie i, V is the reactor volume, $k_{mat,i}$ is the mass-transfer coefficient of specie i, ρ is the gas density and a_V is the specific catalyst surface per unit of volume, ω_i^{bulk} and ω_i^{wall} are the mass fraction of specie i in the gas bulk and on the catalyst surface.

The conservation of the mass on the catalyst surface boundary gives:

$$k_{mat,i} \rho a_{V} \left(\omega_{i}^{wall} - \omega_{i}^{bulk} \right) = \sum_{j=1}^{NR} v_{ij} r_{j} a_{Rh} MW_{i}$$
(S2)

where v_{ij} is the stoichiometric coefficient of specie i in reaction j, r_j are the reaction rates, a_{Rh} is the specific surface (per unit of volume) of the catalyst's active phase and MW_i are the molar masses.

The external mass transfer coefficient are calculated with the correlation proposed by Beretta et al.¹:

$$Sh_i = \frac{k_{mat,i} d_h}{D_i} = 5.21 + 6.874 \exp(-71.2 z_i^*) (1000 z_i^*)^{-0.35}$$
 (S3)

where D_i is the molecular diffusion coefficient, d_h is the hydraulic diameter of the reactor, and z_i^* is a dimensionless axial coordinate, calculated as:

$$z_i^* = \frac{z}{d_h \operatorname{Re} \operatorname{Sc}} = \frac{D_i z}{v d_h^2}$$
(S4)

where v is the gas velocity and z is the reactor axial coordinate.

The ratio between direct (\vec{r}_j) and reverse (\vec{r}_j) reaction rates of adsorption/desorption elementary steps are calculated in order to quantify the difference in chemical potential between adsorbates and their reservoirs in the gas phase:

$$\sum_{i} v_{ij} \mu_i = -RT \ln\left(\frac{\vec{r}_j}{\hat{r}_j}\right)$$
(S5)

where v_{ij} is the stoichiometric coefficient of species i for the elementary step j and μ_i is its chemical potential. When the elementary step is at equilibrium, the ratio between direct and reverse reaction is equal to one and the chemical potentials of reactant and products are equal.

Section 2. Details on the calculations of the morphology of Rh and Rh₂O₃ nanoparticles

The catalyst in oxidative conditions is described as Rh oxide nanoparticles in equilibrium with gaseous oxygen. Previous studies on highly correlated metal oxides revealed that the electron self-interaction error that characterize standard LDAs and GGAs can be relevant in the simulation of these systems. The most significant evidence is the underestimation of the band gaps. In fact, using pure PBE we calculate a Rh₂O₃ band gap of 0.60 eV, much lower than the experimental value of 1.20 eV². The approach selected to correct the self-interaction error in the study of Rh oxides systems is the DFT+U³, which was specifically developed for 3d-transition-metal oxides and includes an effective local two-electron repulsion term. The value of the U parameter is selected by testing different values and comparing the band gap of the relaxed bulk Rh (III) oxide with its experimental value. Applying a value of U = 3.5 eV to the Rh atoms we obtain a band gap of 1.20 eV, matching the experimental value.

The vibrational free energy of solid system, F^{vib}_{solid}, is calculated as:

$$F_{\text{solid}}^{\text{vib}} = \int d\omega \left(\frac{\hbar \omega}{2} + k_{\text{B}} T \ln \left(1 - \exp \left(\frac{\hbar \omega}{k_{\text{B}} T} \right) \right) \right) \sigma(\omega)$$
(S6)

where $\sigma(\omega)$ is the phonon density of states, calculated by density functional perturbation theory (DFPT).

In order to confirm our choice of the U parameter, we calculate and compared with experimental values the Gibbs free energy of formation of Rh oxides at 0 K and 0 atm, neglecting the differences in zero-point energies:

$$\Delta G_{Rh_xO_y}^f(0 \text{ K}, 0 \text{ atm}) = \left[E_{Rh_xO_y}^{\text{bulk}, \text{DFT}} - x E_{Rh}^{\text{bulk}, \text{DFT}} - \frac{1}{2} E_{O_2}^{\text{DFT}} \right]$$
(S7)

PBE without U corrections gives results (-3.297 eV for Rh₂O₃ and -2.264 eV for RhO₂) in poor agreement with experimental values (-3.552 eV⁴, -1.958 eV⁵). The most evident disagreement with the experimental observation is that pure PBE predicts that the Rh (III) oxide is only a metastable structure. Instead, by using PBE+U we obtained values of $\Delta G_{Rh_2O_3}^f = -3.432$ eV and $\Delta G_{RhO_2}^f = -1.954$ eV, in good agreement with the experimental data.

In the reduced zone of the reactor, the catalyst is modelled as a Rh nanoparticle partially covered by CO* and H*, the MARI estimated by the microkinetic analysis of the system. It is known that GGAs fail to predict the correct adsorption site of CO* molecules on Rh(111): standard DFT functionals predict CO adsorption in the hcp site, whereas experiments report that CO preferably adsorbs on the top site of Rh(111). Lazić et al.⁶ reported that the consideration of long-range interaction can solve the problem. Therefore, in order to correctly describe the catalyst surfaces in the presence of adsorbed CO*, we used the vdW-DF2 functional, obtaining a higher binding energies for the top site (1.47 eV) than for the hcp site (1.30 eV) at 0.25ML of CO* surface concentration.

The vibrational Helmholtz free energies of low coverage systems ($\vartheta_A < 0.25$ ML) are calculated in the ideal 2D lattice approximation, i.e. neglecting the interactions between adsorbates. The reference values of F_{vib} of the surface Rh atoms and of the adsorbates on different adsorption sites are calculated with 2×2 supercells as:

$$F_{Rh(hkl)}^{vib} = \frac{1}{4} F_{Rh(hkl)(2x2)}^{vib}$$
(10)

$$F_A^{vib} = F_{Rh(hkl)(2x2)+A}^{vib} - F_{Rh(hkl)(2x2)}^{vib}$$
(11)

The configurational entropy of disordered surface structures is calculated in the lattice 2D gas approximation, considering the adsorbates as indistinguishable ⁷:

$$S_{conf} = k_B \ln\left(\frac{M!}{N! (M-N)!}\right)$$
(16)

where N is the number of adsorbates on the surface and M is the number of surface sites. Using Stirling's approximation, the configurational entropy of a system with surface concentration equal to $\vartheta = N/M$ results in Equation (7).

The possibility of degeneracy of vibrational modes into translational modes on the catalyst surfaces (hindered translators) is neglected because the diffusion barriers of the adsorbates are much higher ($E_{act,CO}^{diff} = 0.14 - 0.17 \text{ eV}$, $E_{act,H}^{diff} = 0.10 - 0.19 \text{ eV}$) than the thermal energy of adsorbates in the range of considered temperatures (T < 1000 K).

Section 3. Details on the calculation of the interfacial energy between the catalyst and the support



Figure S1: sandwich-like slab characterized by inversion symmetry, used to calculate the interfacial energy between Rh(111) and Al₂O₃(0001). In light grey are represented Rh atoms, in dark grey Al atoms and in red O atoms.

The structures of the support and the catalyst surfaces usually have different periodicities. Therefore, they are cut along defined surface vectors which preserve their periodicities, rotated and then repeated in the x and y directions according to the ratio of the resulting supercells base lengths. In this way we produce supercells with similar base dimension. The catalyst structure is then then stretched to fit the dimensions of the support supercell base, to guarantee continuity in the periodic boundary conditions of the DFT calculations. Variable-cell calculations are employed to minimize the stress induced by the stretching of the structures.

The surface vectors utilized to cut the slabs are the following:

 $Rh(100) + Al_2O_3(0001)$: [[2, 0], [0, 3]] for Rh(100) and [[1, 0], [-1, 2]] for $Al_2O_3(0001)$

 $Rh(110) + Al_2O_3(0001)$: [[1, 0], [1, 2]] for Rh(110) and [[1, 1], [1, 5]] for $Al_2O_3(0001)$

 $Rh(100) + Al_2O_3(1-102)$: [[1, 1], [0, 1]] for Rh(100) and [[2, 0], [2, 2]] for $Al_2O_3(1-102)$

 $Rh(110) + Al_2O_3(1-102)$: [[1, 0], [2, 2]] for Rh(110) and [[4, -1], [1, 1]] for $Al_2O_3(1-102)$

 $Rh(111) + Al_2O_3(1-102)$: [[1, 0], [1, 1]] for Rh(111) and [[1, 1], [-1, 3]] for $Al_2O_3(1-102)$

 $Rh_2O_3(0001) + Al_2O_3(0001)$: [[1, 0], [0, 1]] for $Rh_2O_3(0001)$ and [[1, 0], [0, 1]] for $Al_2O_3(0001)$

 $Rh_2O_3(1-102) + Al_2O_3(0001)$: [[1, 0], [0, 3]] for $Rh_2O_3(1-102)$ and [[1, -1], [2, 2]] for $Al_2O_3(0001)$

 $Rh_2O_3(0001) + Al_2O_3(1-102)$: [[1, -1], [1, 1]] for $Rh_2O_3(0001)$ and [[2, 0], [0, 1]] for $Al_2O_3(1-102)$

 $Rh_2O_3(1-102) + Al_2O_3(1-102)$: [[1, 0], [0, 1]] for $Rh_2O_3(1-102)$ and [[1, 0], [0, 1]] for $Al_2O_3(1-102)$

Section 4. Surface structures of Rh₂O₃ and Rh



Figure S2: representations of different relaxed Rh₂O₃ surface terminations: (a) stoichiometric Rh₂O₃(0001), (b) over-stoichiometric Rh₂O₃(0001), (c) stoichiometric Rh₂O₃(11 $\overline{1}$ 02), (d) over-stoichiometric Rh₂O₃(11 $\overline{2}$ 3), (e) stoichiometric Rh₂O₃(11 $\overline{2}$ 0), (f) stoichiometric Rh₂O₃(10 $\overline{1}$ 0), (g) over-stoichiometric Rh₂O₃(11 $\overline{1}$ 01), (h) stoichiometric Rh₂O₃(10 $\overline{1}$ 1), (i) over-stoichiometric Rh₂O₃(10 $\overline{1}$ 1).

Rh(100)

CO* is stable in the top site until $\vartheta_{CO^*} < 0.75$ ML, then an ordered structure with CO* in top and in bridge ($\vartheta_{CO^*} = 0.75$ ML) is preferred (Gurney pattern, Fig. S3, panel a). Another ordered structure with CO* in top and bridge sites (Jong pattern, Fig. S3, panel b) becomes stable at higher CO* coverage ($\vartheta_{CO^*} = 5/6$ ML). H* is stable in the bridge site until $\vartheta_{H^*} = 1.00$ ML, then a structure with $\vartheta_{H^*} = 2.00$ ML in bridge is found. CO* and H* co-adsorption creates the following stable structures: CO* in top and H* in bridge until $\vartheta_{CO^*} = 0.25$ ML and $\vartheta_{H^*} = 0.25$ ML; $\vartheta_{CO^*} = 0.25$ ML in top and $\vartheta_{H^*} = 0.50$ ML in bridge; $\vartheta_{CO^*} = 2/3$ ML in bridge and $\vartheta_{H^*} = 1/3$ ML in bridge; $\vartheta_{CO^*} = 0.50$ ML in bridge; $\vartheta_{CO^*} = 2/3$ ML in bridge and $\vartheta_{H^*} = 1/3$ ML in bridge (Fig. S3, panel c).



Figure S3: ordered surface structures of CO* on Rh(100): (a) Gurney pattern, 0.75 ML $(4\sqrt{2}\times\sqrt{2})$ R45° structure with CO* on top and in bridge, (b) Jong pattern, 5/6 ML (6×2) structure with CO* on top and in bridge. $(3\sqrt{2}\times\sqrt{2})$ R45° slabs, with 2/3 ML CO* and 1/3 ML H* adsorbed in bridge sites (c).

Rh(110)

CO* is stable in top until $\vartheta_{CO^*} < 0.50$ ML, then an ordered structure with CO* in a shifted-hollow site ($\vartheta_{CO^*} = 1.00$ ML) is preferred (Fig. S4, panel a). H* is stable in short-bridge until $\vartheta_{H^*} = 1.00$ ML, then a structure with $\vartheta_{H^*} = 2.00$ ML in the shifted-hollow site becomes favoured (Fig. S4, panel b). CO* and H* co-adsorption creates the following stable structures: CO* in top and H* in short-bridge until $\vartheta_{CO^*} = 0.25$ ML and $\vartheta_{H^*} = 0.25$ ML; $\vartheta_{CO^*} = 0.25$ ML in top and $\vartheta_{H^*} = 0.50$ ML in short-bridge; $\vartheta_{CO^*} = 0.25$ ML in short-bridge and $\vartheta_{H^*} = 0.75$ ML in short-bridge; $\vartheta_{CO^*} = 0.50$ ML in short-bridge; $\vartheta_{CO^*} = 0$



Figure S4: (a) an ordered structure of CO* on Rh(110) (1×2) 1.00 ML p2mg. (b) (1×1) Rh(110) with two H* in the shifted-hollow site (2.00 ML). (c): (1×2) 0.50 ML CO* top and 1.00 ML H* shifted-hollow.

Rh(111)

CO* is stable in the top site until $\vartheta_{CO^*} < 0.75$ ML, then an ordered structure with CO* in top, fcc and hcp ($\vartheta_{CO^*} = 0.75$ ML) is preferred (Fig. S5, panel a). H* is stable in the fcc site until $\vartheta_{H^*} = 1.00$ ML, then a structure with $\vartheta_{H^*} = 2.00$ ML in fcc and hcp is found. CO* and H* co-adsorption creates the following stable structures: CO* in top and H* in fcc until $\vartheta_{CO^*} = 0.25$ ML and $\vartheta_{H^*} = 0.25$ ML; $\vartheta_{CO^*} = 0.25$ ML in top and $\vartheta_{H^*} = 0.50$ ML in fcc and hcp; $\vartheta_{CO^*} = 0.50$ ML in top and $\vartheta_{H^*} = 0.25$ ML in fcc.



Figure S4: (a) (2×2) Rh(111) with one CO* in top, one in fcc and one in hcp. (b): (2×2) Rh(111) with one CO* in top and two H*, one in fcc and one in hcp.

Rh(211)

CO* is stable in the top site until $\vartheta_{CO^*} = 1.00$ ML. H* is stable in the bridge site until $\vartheta_{H^*} = 1.00$ ML. CO* and H* coadsorption creates the following stable structures: CO* in top and H* in bridge until $\vartheta_{CO^*} = 1/6$ ML and $\vartheta_{H^*} = 1/6$ ML; $\vartheta_{CO^*} = 1/3$ ML in top and $\vartheta_{H^*} = 1/3$ ML in bridge; $\vartheta_{CO^*} = 2/3$ ML in top and $\vartheta_{H^*} = 1/3$ ML in bridge; $\vartheta_{CO^*} = 1/3$ ML in top and $\vartheta_{H^*} = 2/3$ ML in bridge.

Rh(311)

CO* is stable in the top site until $\vartheta_{CO^*} = 0.75$ ML. H* is stable in the bridge site until $\vartheta_{H^*} = 1.00$ ML. CO* and H* coadsorption creates the following stable structures: CO* in top and H* in bridge until $\vartheta_{CO^*} = 0.25$ ML and $\vartheta_{H^*} = 0.25$ ML; $\vartheta_{CO^*} = 0.50$ ML in top and $\vartheta_{H^*} = 0.25$ ML in bridge; $\vartheta_{CO^*} = 0.25$ ML in top and $\vartheta_{H^*} = 0.50$ ML in bridge; $\vartheta_{CO^*} = 0.50$ ML in top and $\vartheta_{H^*} = 0.50$ ML in bridge.

Rh(331)

CO* is stable in the top site until $\vartheta_{CO^*} = 1.00$ ML. H* is stable in the bridge site until $\vartheta_{H^*} = 1.00$ ML. CO* and H* coadsorption creates the following stable structures: CO* in top and H* in bridge until $\vartheta_{CO^*} = 1/6$ ML and $\vartheta_{H^*} = 1/6$ ML; $\vartheta_{CO^*} = 1/3$ ML in top and $\vartheta_{H^*} = 1/3$ ML in bridge; $\vartheta_{CO^*} = 0.50$ ML in top and $\vartheta_{H^*} = 0.50$ ML in bridge.

References

- 1 A. Beretta, P. Baiardi, D. Prina and P. Forzatti, *Chem. Eng. Sci.*, 1999, **54**, 765–773.
- 2 Y. D. Scherson, S. J. Aboud, J. Wilcox and B. J. Cantwell, J. Phys. Chem. C, 2011, 115, 11036–11044.
- 3 V. I. Anisimov, J. Zaanen and O. K. Andersen, *Phys. Rev. B*, 1991, 44, 943–954.
- 4 D. R. Lide, *Handb. Chem. Phys.*, 2003, **53**, 2616.
- 5 M. E. Grillo, *Phys. Rev. B Condens. Matter Mater. Phys.*, 2004, **70**, 1–6.
- 6 P. Lazić, M. Alaei, N. Atodiresei, V. Caciuc, R. Brako and S. Blügel, *Phys. Rev. B Condens. Matter Mater. Phys.*, 2010, **81**, 1–6.
- 7 L. H. Sprowl, C. T. Campbell and L. Árnadóttir, J. Phys. Chem. C, 2016, **120**, 9719–9731.