Interactions of Hydrogen and Methanol with MO_3 (M=W or Re) Surfaces: The Role of Interface on the Reactivity

Sanliang Ling[1], Donghai Mei[2] and Maciej Gutowski[1]
[1]*Chemistry-School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom*
[2]*Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, U. S. A.*
SL160@hw.ac.uk, donghai.mei@pnl.gov, m.gutowski@hw.ac.uk

Introduction

Conductive and narrow bandgap transition metal oxides have been known many years for various industrial applications. Tungsten trioxide (WO_3) and rhenium trioxide (ReO_3) are widely used as catalyst and support materials in heterogeneous catalysis and photocatalysis. For example, methanol was found to be molecularly adsorbed to the Lewis acid sites of oxidized WO_3(001) surface while dissociatively adsorbed to the Brønsted base sites of reduced WO_3(001) surface. [1] High catalytic activities and selectivities for the oxidation of methanol were also found on supported ReO_x surfaces. [2] With the advances in molecular beam epitaxy technology [3], new types of interface structures that are built by two structurally similar transition metal oxides provide promising enhanced catalytic performance due to the formation of new band structures near Fermi level. [4,5] In the present study, the reactivities of hydrogen and methanol on the interface structures of WO_3 and ReO_3 were explored by comparing with pure WO_3 and ReO_3 surfaces using density functional theory (DFT) calculations.

Materials and Methods

The periodic DFT calculations were performed with the Vienna Ab initio Simulation Package using a plane wave basis set with a cutoff energy of 400 eV. [6,7] The Perdew-Burke-Ernzerhof functionals with the projector augmented wave method was used to describe nuclei and core electrons. As shown in Figure 1, a non-polar surface model system with four unit MO_3 (M=W or Re) layers with missing two oxygen atoms in top and bottom layers was employed. A vacuum layer with thickness of about 15.0 Å in the z direction was used to separate the surface slabs to avoid the interactions between the surface slabs. Different Monkhorst-Pack schemes for sampling the Brillouin zone were tested and a 3x3x1 k-point sampling was used in the calculations. The interfacial structures of WO_3/ReO_3 and ReO_3/WO_3 were modeled by replacing the top unit layer with another oxide.

Results and Discussion

We studied adsorption and dissociation of hydrogen and methanol molecules on four model oxide surfaces shown in Figure 1. The reaction pathways of hydrogen adsorption on the clean ReO_3 and WO_3 surfaces are shown in Figure 2. On both ReO_3 and WO_3 surfaces, molecular adsorption of hydrogen at surface O_{1C} atom is energetically preferred (state 1 in Figure 2), Then one of hydrogen atoms from this H_2O-like adsorbate moves to the adjacent O_{2C} atom, forming two surface hydroxyl groups. The barriers for hydrogen dissociation on both surfaces are 58.4 and 70.9 kJ/mol, indicating ReO_3 is more reactive to hydrogen due to its conductive nature. Adsorption energies of a methanol molecule on four different surfaces are summarized in Table 1. Except for dissociative adsorption of methanol on WO_3, we found methanol could adsorb on all four surfaces in both molecular and dissociative modes. As only replacing the surface layer of pure WO_3 with ReO_3 for methanol molecule can dissociatively adsorb on this interfacial surface.

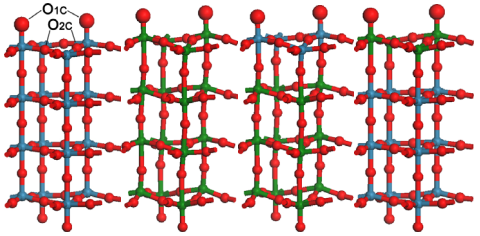

Figure 1. Sideviews of optimized clean (001) surface structures of (a) RRRR: pure ReO_3, (b) WWWW: pure WO_3, (c) WRRR: one layer of WO_3 on three layers of cubic ReO_3, and (d) RWWW, one layer of ReO_3 on three layers of monoclinic WO_3. Color scheme: Red – Oxygen; Blue – Re; Green – W. Large red spheres represent surface O_{1C} atoms.

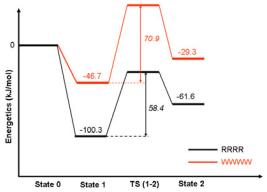

Figure 2. Hydrogen adsorption and dissociation on the clean ReO_3 and WO_3 surfaces. State 0 - clean surface; State 1 - molecular adsorption at O_{1C} site; State 2 - dissociative adsorption at O_{1C} and O_{2C} sites; TS(1-2) - transition state between states 1 and 2.

Table 1. Adsorption energies of methanol molecule on four different surfaces.

Adsorption Type	Adsorption energies (kJ/mol)[a]			
	RRRR	WWWW	WRRR	RWWW
molecular	-92.9	-65.6	-82.2	-83.7
dissociative	-85.3	36.9	-36.3	-44.3

[a] Negative values of adsorption energy indicate the adsorption is energetically favorable.

Significance

This theoretical study indicates the reactivities of the conductive and semiconductive transition metal oxides might be tuned by making overlayer-like interface structures. The possibilities for improved and optimal catalytic activities should be further explored by theoretical and experimental studies in the future.

References

1. Ma, S.; Amar, F. G.; Frederick B. G. *J. Phys. Chem. A* 107, 1413 (2003).
2. Yuan, Y.; Iwasawa, Y. *J. Phys. Chem. B* 106, 4441 (2002).
3. Chambers, S. A. *J. Phys.: Condens. Matter* 20, 264004 (2008).
4. Jaffe J. E.; Dupuis M.; Gutowski M. *Phys. Rev. B* 69, 205106 (2004).
5. Yakovkin I. N.; Gutowski M. *Surf. Sci.* 601, 1481 (2007).
6. Kresse, G.; Hafner, J. *Phys. Rev. B* 47, 558 (1993).
7. Kresse, G.; Furthmuller, J. *Comput. Mater. Sci.* 6, 15 (1996).

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