Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Surface Characterization and Methane activation on a $SnO_x/Cu_2O/Cu(111)$ Inverse Oxide/Metal Catalysts

Jindong Kang,[‡a] Ning Rui,[‡b] Erwei Huang,[‡a] Yi Tian,[a] Mausumi Mahapatra,[b] Rina Rosales,[a] Ivan Orozco,[a] Rui Shi,[a] Sanjaya D. Senanayake,[b] Ping Liu,[a,b] and José A. Rodriguez*[a,b]

a. Department of Chemistry, SUNY at Stony Brook, Stony Brook, NY, 11794 USA.

b. Chemistry Department, Brookhaven National Laboratory, Upton, NY, 11973 USA

‡ All these authors contributed in equal terms to this research.

* Corresponding author, E-mail: rodriguez@bnl.gov

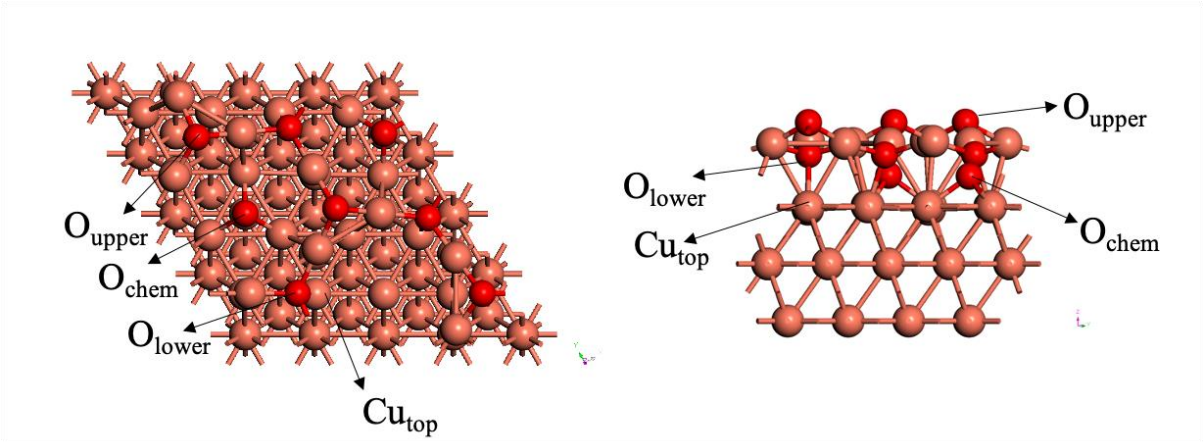

Fig. S1 Top (left) and side (right) view of Cu_mO/Cu(111) DFT model; Cu: brown; O: red.

Notes: The DFT-optimized atomic structure of Cu_mO/Cu(111) (m ≈ 1.13) is shown in Figure. S1. Specifically, the Cu(111)-supported $Cu_{1.13}O$ includes three types of oxygen species depending on their unique location, O_{chem}, O_{upper} and O_{lower} atoms, where both O_{chem} and O_{lower} bind with bottom Cu(111) surface directly. By including these directly bound Cu sites from Cu(111), the Cu_mO layer can reach to Cu_2O. Our previous studies have shown that such model system described well the 44 structure as observed (Ref. S1, Ref. S2). The 44 structure was observed on exposing Cu(111) to oxidizing atmosphere. I t is a Cu(111)-supported CuxO layer, which is different from Cu_2O(111) in term of atomic arrangement and chemical activity (Ref. S1).

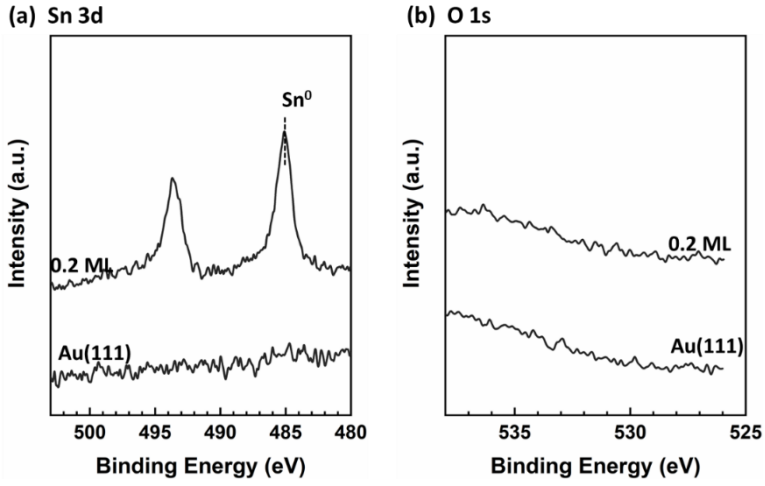

Fig. S2 (a) Sn 3d and (b) O 1s XPS spectra of pristine Au(111) and Sn/Au(111) surfaces. Coverage is estimated to be 0.2 ML. Sn was vapor deposited on the Au(111) surface under a background pressure of 5 x 10-7 torr of oxygen at 450 K.

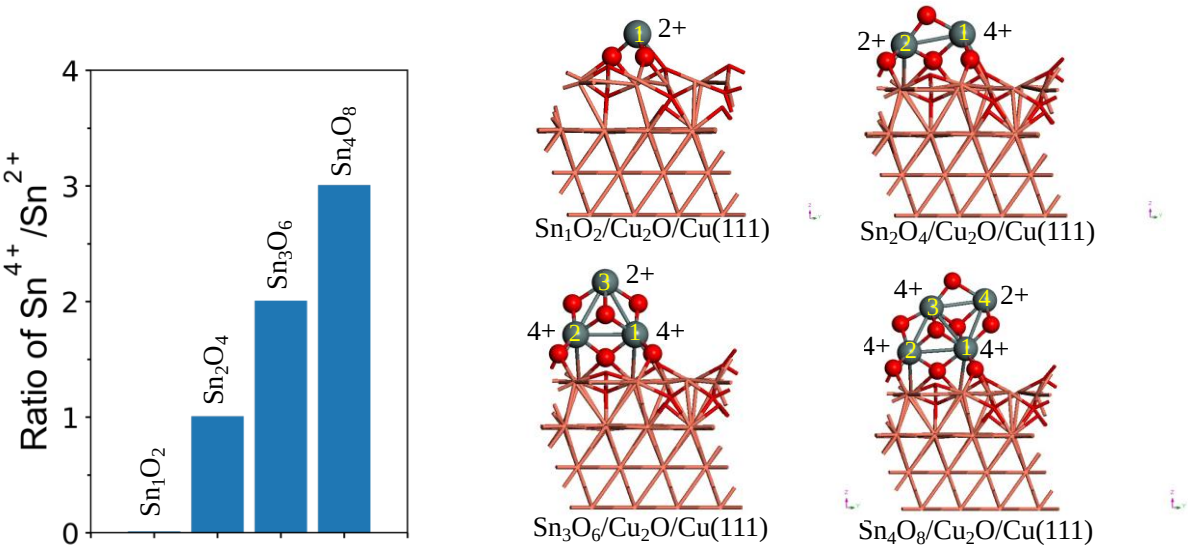

Fig. S3 (left) Distribution for Sn^{4+}/Sn^{2+} ratios of Sn_xO_y clusters supported by $Cu_2O/Cu(111)$ based on Bader charge analysis; (right) Detailed distribution of Sn^{4+} and Sn^{2+} for $Sn_xO_y/Cu_2O/Cu(111)$ models.

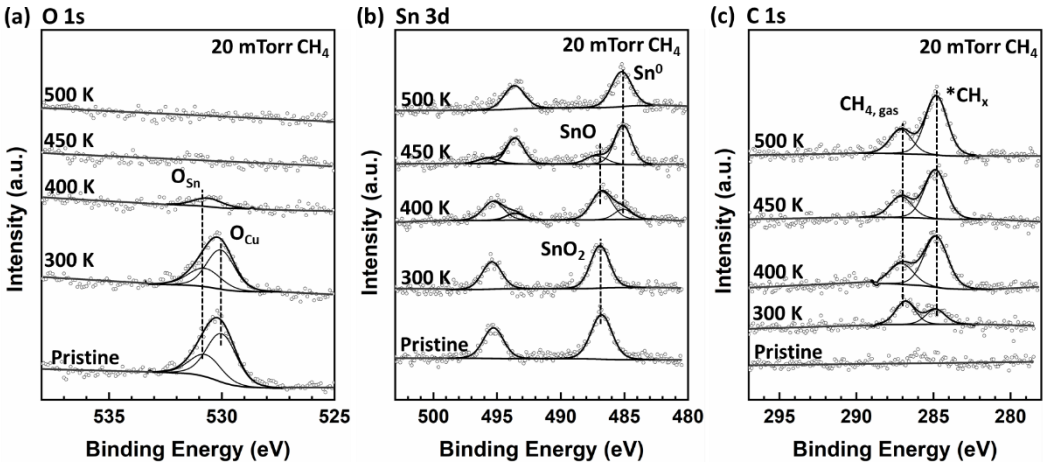

Fig. S4 (a) O 1s, (b) Sn 3d and (c) C 1s regions in AP-XPS spectra for the $SnO_2/Cu_2O/Cu(111)$ surface (θ_{SnO2} ~ 0.1 ML) when exposed to 50 mTorr of CH_4 at different temperatures.

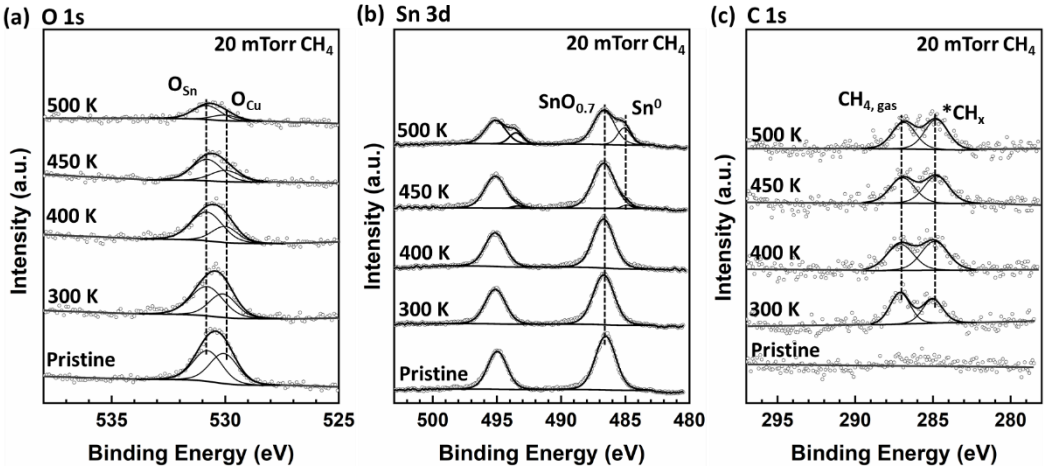

Fig. S5 (a) O 1s, (b) Sn 3d, and (c) C 1s regions in AP-XPS spectra for the $SnO_2/Cu_2O/Cu(111)$ surface (θ_{SnO2} ~ 0.6 ML) when exposed to 50 mTorr of CH_4 at different temperatures.

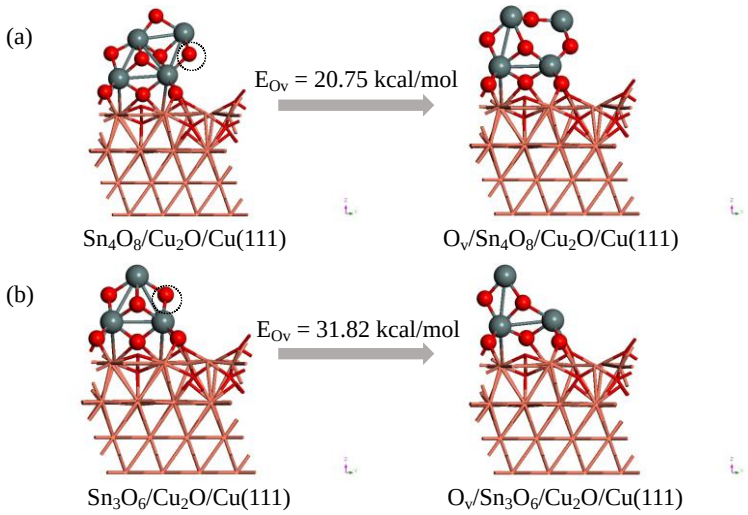

Fig. S6 Oxygen vacancy (O_v) formations on (a) $Sn_4O_8/Cu_2O/Cu(111)$ and (b) $Sn_3O_6/Cu_2O/Cu(111)$ models; The studied Sn^{4+}-O-Sn^{2+} bridge O was indicated by the dashed circle.

References:

S1 W. An, A. E. Baber, F. Xu, M. Soldemo, J. Weissenrieder, D. Stacchiola, P. Liu, *ChemCatChem* **2014**, *6*, 2364-2372.

S2 W. An, F. Xu, D. Stacchiola, P. Liu, *Chemcatchem* **2015**, *7*, 3865-3872.