Supporting Information

Rh-MnO Interface Sites Formed by Atomic Layer Deposition Promote Syngas Conversion to Higher Oxygenates

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1. Syngas conversion activity and selectivity of $Rh/MnO/SiO_2$ catalysts with different Rh loading.

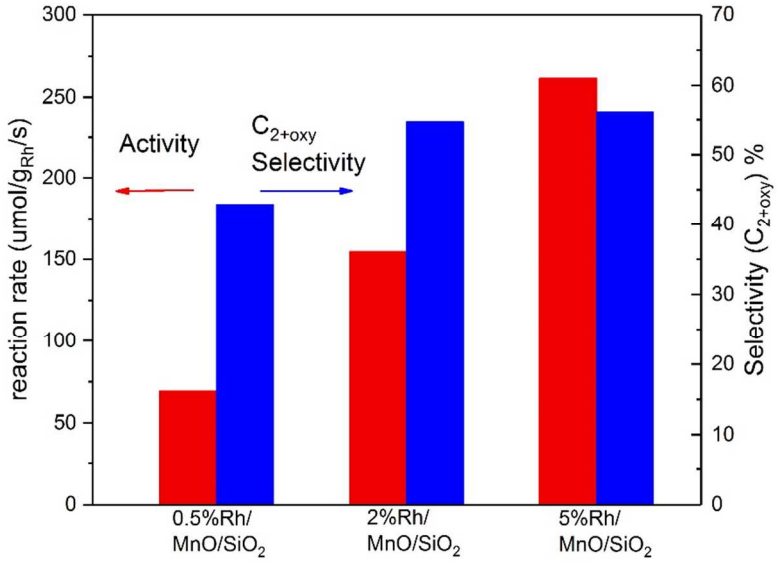

Figure S1. Activity (red) and C_{2+}oxy selectivity (blue) of 0.5wt%$Rh/MnO/SiO_2$, 2wt%$Rh/MnO/SiO_2$, and 5wt%$Rh/MnO/SiO_2$.

Table S1. CO chemisorption and dispersion of Rh/SiO_2 with 1% and 5% Rh loading

Sample	**CO chemisorption ($\mu mol/g_{cat}$)**	**Dispersion (%)**
1%Rh/SiO_2	44.3	45.6
5%Rh/SiO_2	178.6	36.8

The dispersion of 1%Rh/SiO_2 is higher than that of 5%Rh/SiO_2, as expected, indicating smaller Rh nanoparticle size on 1%Rh/SiO_2. However, the total amount of Rh surface atoms on 1%Rh/SiO_2 is only 25% of that on 5%Rh/SiO_2, based on the CO chemisorption values. Therefore, even with the lower dispersion, 5%Rh/SiO_2 still has a larger total Rh surface area, suggesting a higher contact area with the support. Since the size distribution of Rh nanoparticles remains similar on both the SiO_2 or MnO/SiO_2 supports, we conclude that the contact area between Rh and the MnO/SiO_2 support increases with higher Rh loading.

2. Additional data from DFT calculation

2.1 Structural illustration of MnO promoted Rh surface models used in DFT calculation

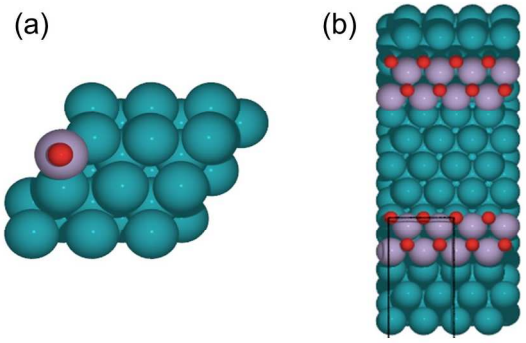

Figure S2. Surface model of MnO promoted Rh (111) (Rh: green, Mn: purple, O: red) (a) Rh/MnO (monomer) ; (b) Rh/MnO (stripe)

2.2 Free energy diagram of syngas conversion towards methane, acetaldehyde and ethanol on unpromoted and MnO promoted Rh (111) surface

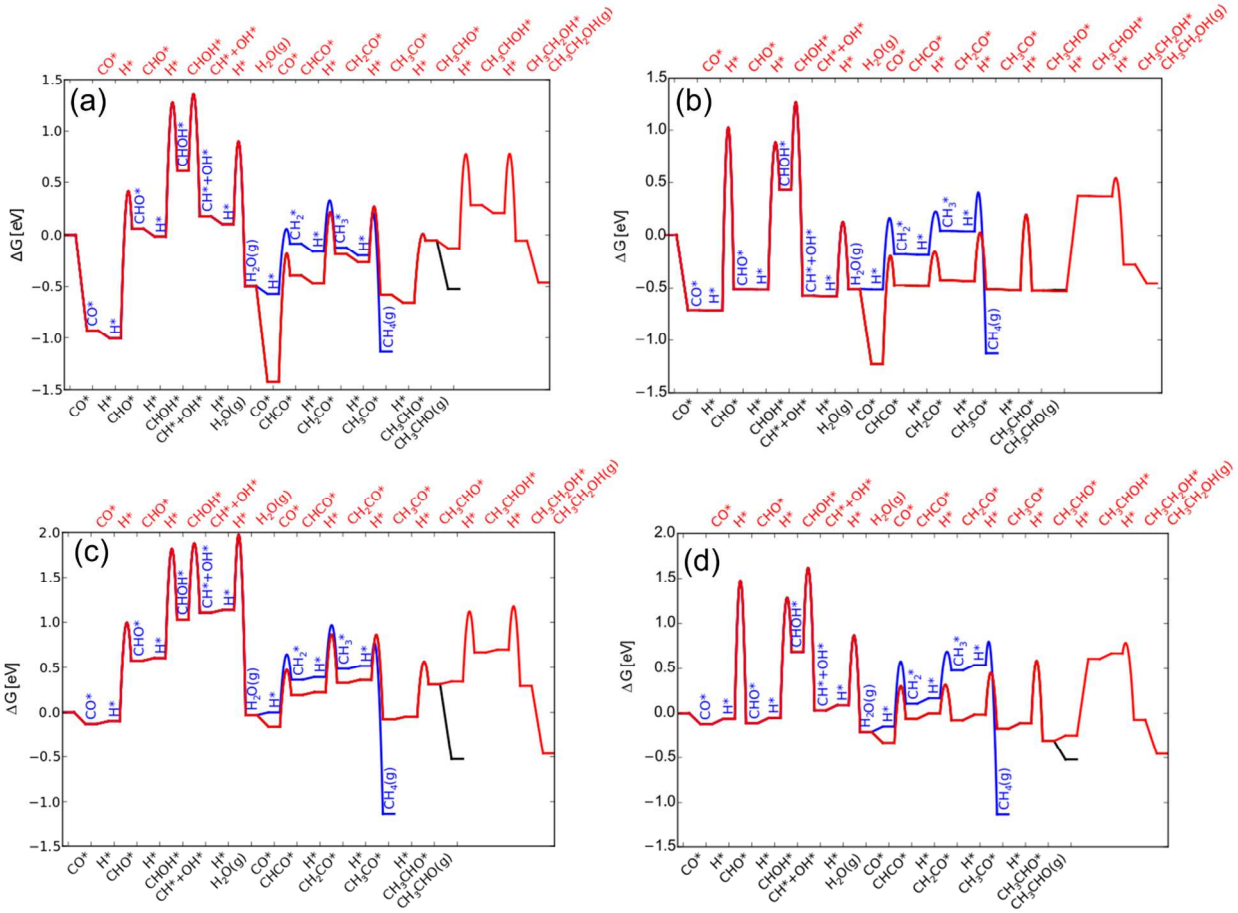

Figure S3. Free energy diagrams at 525 K on (a) Rh (111) and (b) Rh/MnO (monomer) without lateral adsorbate interaction and (c) Rh (111) and (d) Rh/MnO (monomer) with lateral adsorbate

interactions at steady state coverage. Red, blue and black color designate ethanol, methane and acetaldehyde formation pathways respectively. Reaction conditions are: P_{H2}= 13.33, P_{CO}= 6.66. All other free energies are calculated at standard states (1 bar pressure). (a) and (c) are adapted with permission from Yang, N.; Medford, A. J.; Liu, X.; Studt, F.; Bligaard, T.; Bent, S. F.; Nørskov, J. K. J. Am. Chem. Soc. 2016, 138 (11), 3705–3714. Copyright (2016) American Chemical Society.

3. Comparison between ALD and incipient wetness impregnation deposited MnO/Rh/SiO_2

Besides using ALD to deposit MnO film, we also synthesized MnO_2/Rh/SiO_2 by depositing MnO_2 on calcined Rh/SiO_2 using incipient wetness impregnation followed by calcination in air. This catalyst is designated as IMP-MnO_2/Rh/SiO_2. (MnO_2 should be reduced to MnO during the reduction step prior to syngas conversion.) The MnO_2 deposited by this impregnation method most likely exists as particles. The table below compares MnO/Rh/SiO_2 (i.e. Rh particles with MnO film) and IMP-MnO_2/Rh/SiO_2 (i.e. Rh particles with MnO particle). These two samples show similar activity, but ALD-MnO/ Rh/SiO_2 is more selective to C_{2+}oxy. It is difficult to quantify how much Mn is interacting with Rh in either case, but higher C_{2+}oxy selectivity from the sample could suggest that a more evenly distributed MnO film leads to better contact with Rh and therefore improves selectivity more than MnO particles.

Table S2. Syngas conversion activity and selectivity of ALD deposited MnO/Rh/SiO_2 and MnO_2/Rh/SiO_2 prepared by incipient wetness impregnation.

	CO conversion rate (µmol/gcat/s)	**S(CH_4) %**	**S(C_{2+}HC) %**	**S(AcH)%**	**S(EtOH)%**	**S(total C_{2+}oxy) %**
MnO/Rh/SiO_2	9.1	30	28.7	35	4.2	40.5
IMP-MnO_2/Rh/SiO_2*	7.9	41	33	17.8	6.2	24

*Mn/Rh atomic ratio = 1:5 in the impregnation sample.