# Supporting Information for

# Methanol Oxidative Dehydrogenation and Dehydration on Carbon Nanotubes: Active Sites and Basic Reaction Kinetics

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Table S1. Details of Raman signals deconvolution of pristine-CNT and oCNT.

| Raman deconvolution | | Peak area (a.u.) | | | | |
|---|---|---|---|---|---|---|
| | | D4 | D1 | D3 | G | D2 |
| Wavenumber ($cm^{-1}$) | | 1220 | 1340 | 1470 | 1574 | 1610 |
| Catalysts | CNT | 35.7 | 352.2 | 27.9 | 210.3 | 28.4 |
| | oCNT | 12.3 | 205.7 | 18.4 | 118.3 | 22.4 |

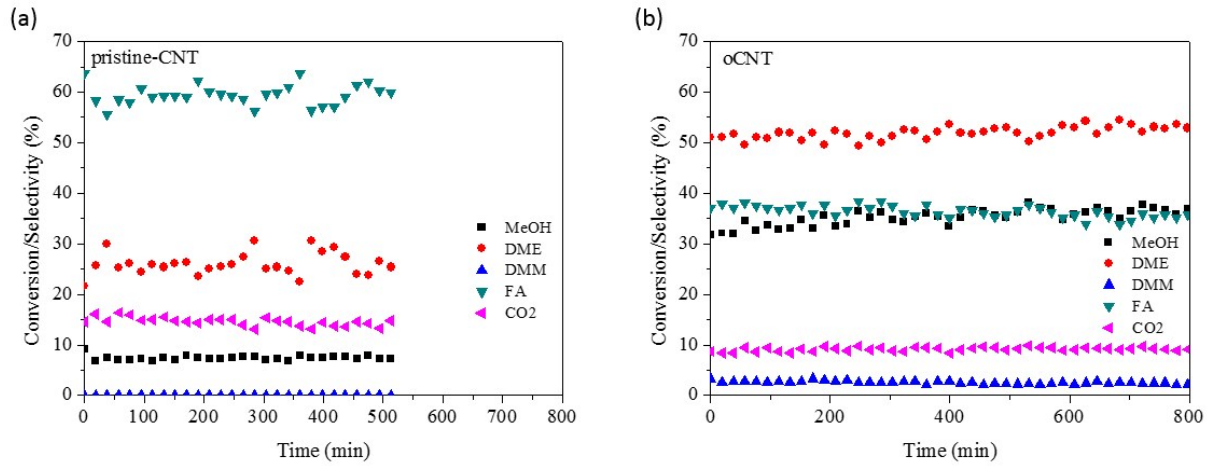


Figure S1. Catalytic reactivity comparison between pristine CNT (a) and oCNT (b). Conditions: 50 mg catalyst, 280 $^{o}$C, 8 % oxygen, 1 % methanol, 10 ml $min^{-1}$ total flow rate balanced by He.

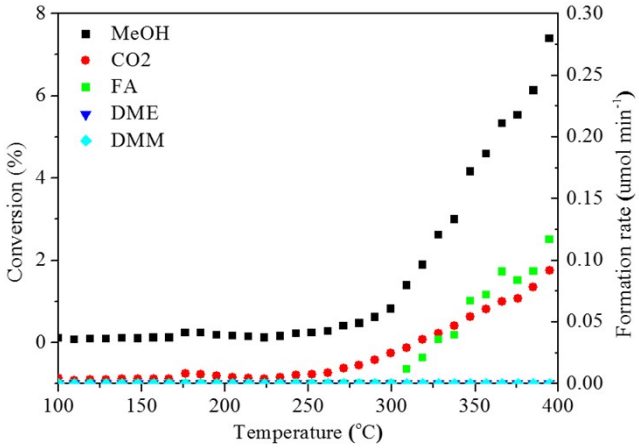


Figure S2. Blank experiment for methanol conversion reaction. Conditions: no catalysts but only silica wool, 8 % oxygen, 1 % methanol, 10 ml $min^{-1}$ total flow rate balanced by He.

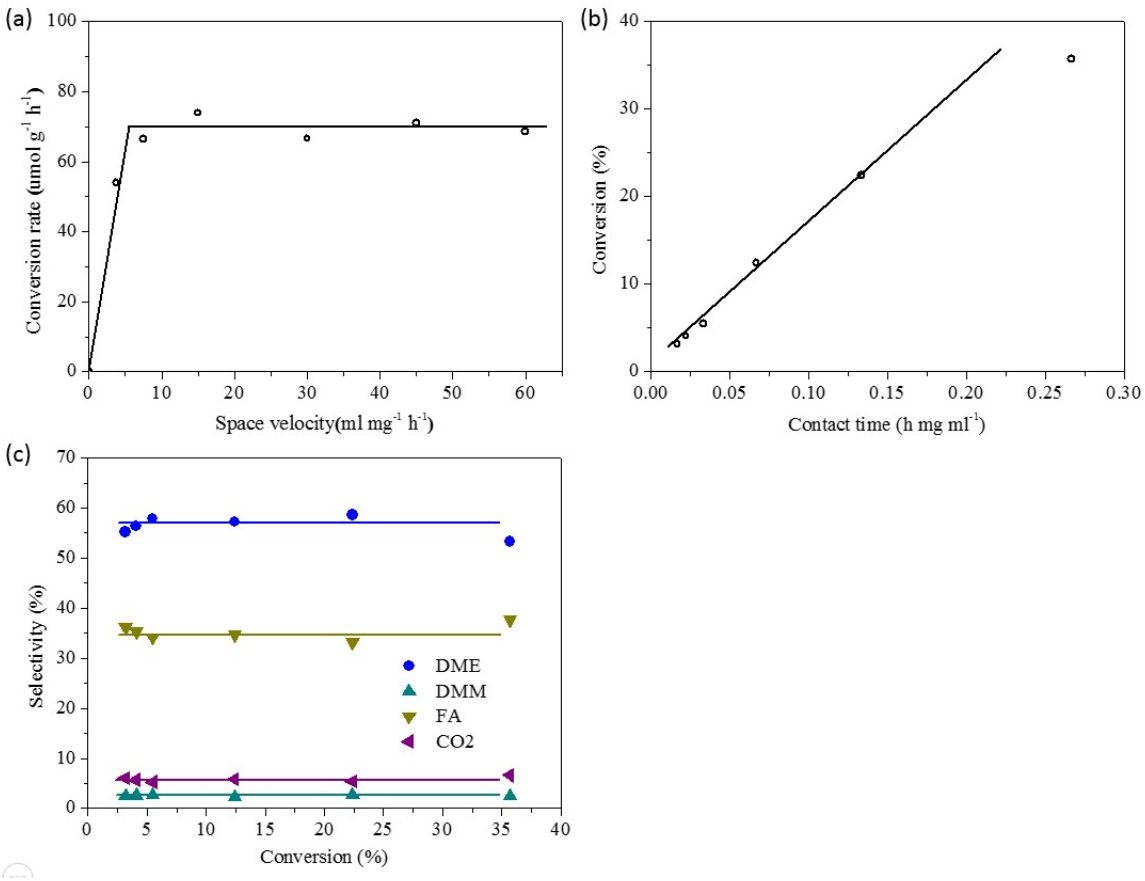


Figure S3. (a) Methanol conversion rate as a function of space velocity. (b) Methanol conversion as a function of contact time. (c) Products selectivity as a function of methanol conversion. Conditions: 10-100 mg oCNT, 280 $^{o}$C, 8 % oxygen, 1 % methanol, 5-20 ml min$^{-1}$ total flow rate balanced by He.

Table S2. Catalytic reactivity comparison between oCNT in this work and conventional metal based catalysts.

| Catalysts | Dosage (g) | T.(K) | Conversion (%) | Selectivity (%) | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | DME | FA | DMM | $CO_2$ | |
| oCNT | 0.05 | 593 | 60.0 | 60.0 | 35.0 | 1.0 | 4.0 | - |
| Ag | 11 | 773 | 85.4 | 0 | 82.5 | 0 | 14.7 | [1] |
| $Ag/SiO_2$ | 2.0 | 913 | 96.0 | 0 | 89.0 | 0 | 7.6 | [2] |
| Ag/ceramics | 3.0 | 893 | 95.9 | 0 | 93.1 | 0 | 7.1 | [3] |
| $Fe_2O_3$-$MoO_3$ | 0.5 | 648 | 85.0 | - | 50.0 | - | - | [4] |
| Modified FeMoO | 11.2 | 473 | 80.0 | - | 70.0 | - | - | [5] |

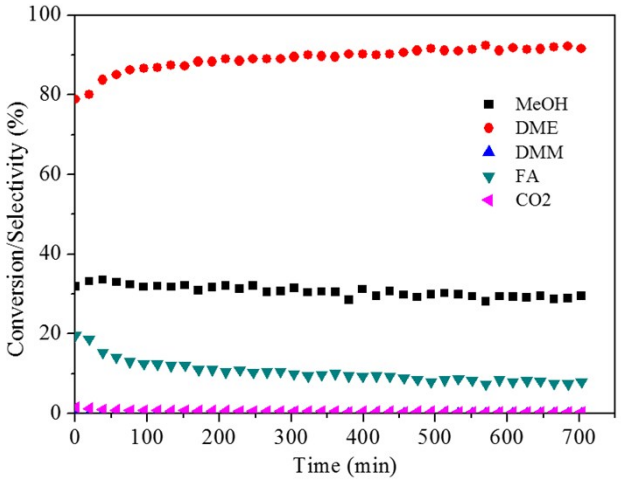


Figure S4. Catalytic performance of oCNT in methanol conversion reaction in the absence of oxygen. Conditions: 50 mg oCNT, 280 $^{o}$C, 1 % methanol, 10 ml $min^{-1}$ total flow rate balanced by He.

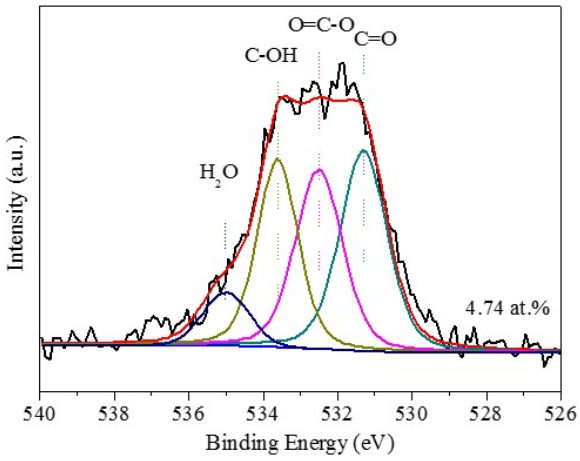


Figure S5. Deconvolution of O 1s XPS for oCNT after reaction.

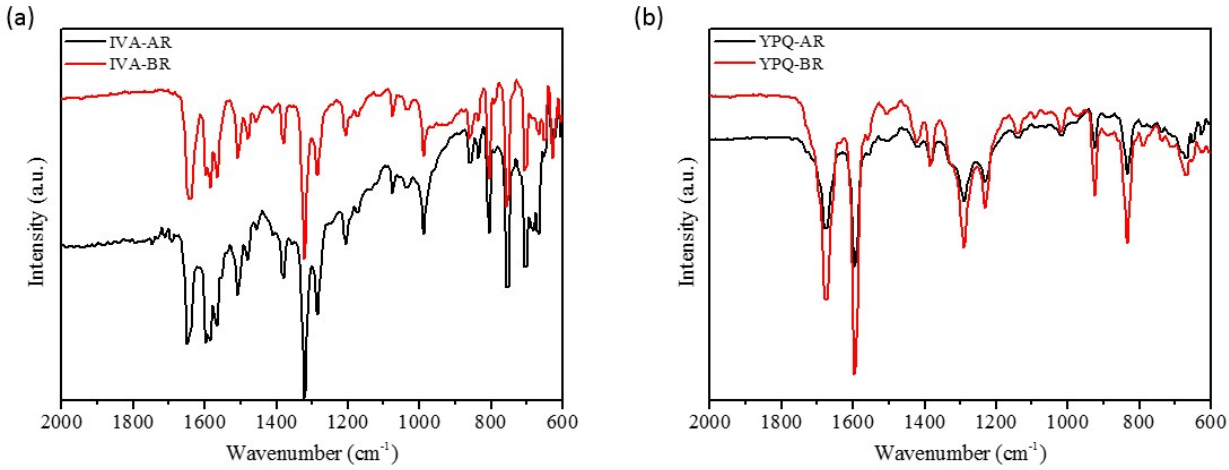


Figure S6. The FT-IR signals for two model catalysts IVA and YPQ. AR: after reaction. BR: before reaction.

## References

1. G. Waterhouse, *Appl. Catal. A*, 2004, 266, 257-273.
2. D. W. L. Cao Y, Deng J F., *Appl. Catal. A*, 1997, 158, 27-34.
3. D. W. L. Li J L, Dong Y, Deng J F, *Mater. Lett.*, 2000, 44, 233-236.
4. P. M. F. Soares A P V, Kiennemann A, *Catal. Commun.*, 2001, 2, 159-164.
5. T. H. Kim, B. Ramachandra, J. S. Choi, M. B. Saidutta, K. Y. Choo, S. D. Song and Y. W. Rhee, *Catal. Lett.*, 2004, 98, 161-165.