

## Supporting information

Co-Co<sub>2</sub>C catalyst supported on carbon-coated ordered mesoporous silica with promoted CO insertion and C-C coupling for higher alcohol synthesis from syngas

Zhuoshi Li <sup>a,b</sup>, Siqu Fan <sup>a</sup>, Zhuang Zeng <sup>a</sup>, Shaoxia Guo <sup>a</sup>, Xiaofeng Pei <sup>a</sup>, Shouying Huang <sup>a,c</sup>,

Yong Wang <sup>a</sup>, Yue Wang <sup>a,b,c\*</sup> and Xinbin Ma <sup>a,c</sup>

<sup>a</sup> Key Laboratory for Green Chemical Technology of Ministry of Education, Collaborative Innovation Center of Chemical Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

<sup>b</sup> Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou, 350207, China

<sup>c</sup> Haihe Laboratory of Sustainable Chemical Transformations, Tianjin, 300192, China

\* Corresponding author's E-mail address: yuewang@tju.edu.cn

**Table S1.** Physiochemical properties of Co/xC/OMS and Co/xC/SiO<sub>2</sub> catalysts.

| Catalyst                 | Loading <sup>a</sup><br>(wt.%) | Particle<br>size <sup>b</sup> (nm) | Dispersion <sup>c</sup><br>(%) | Surface ratio<br>of Co <sup>2+</sup> /Co <sup>0</sup> <sup>d</sup> | Surface area<br>of Co <sup>2+</sup> <sup>e</sup><br>(m <sup>2</sup> /g) |
|--------------------------|--------------------------------|------------------------------------|--------------------------------|--|---|
| Co/OMS                   | 11.5                           | 9.3                                | 10.7                           | 1.36   | 2.38  |
| Co/5C/OMS                | 10.9                           | 6.9                                | 13.9                           | 1.62   | 3.28  |
| Co/10C/OMS               | 10.6                           | 5.7                                | 16.9                           | 2.25   | 4.35  |
| Co/15C/OMS               | 10.7                           | 4.9                                | 19.0                           | 1.91   | 4.79  |
| Co/10C/ SiO <sub>2</sub> | 9.9                            | 6.2                                | 15.4                           | 1.59   | 3.41  |

<sup>a</sup> Determined by ICP-OES;

<sup>b</sup> Based on the TEM images of the carburized catalysts;

<sup>c</sup> Calculated on the basis of spherical model;

<sup>d</sup> Calculated from the Co 2p<sub>3/2</sub> spectra of carburized catalysts;

<sup>e</sup> Obtained from the XPS deconvolution results of carburized catalysts combined with the particle dispersion.

**Table S2.** Catalytic performance of higher alcohol synthesis over Co/xC/OMS and Co/10C/SiO<sub>2</sub> catalysts <sup>a</sup>.

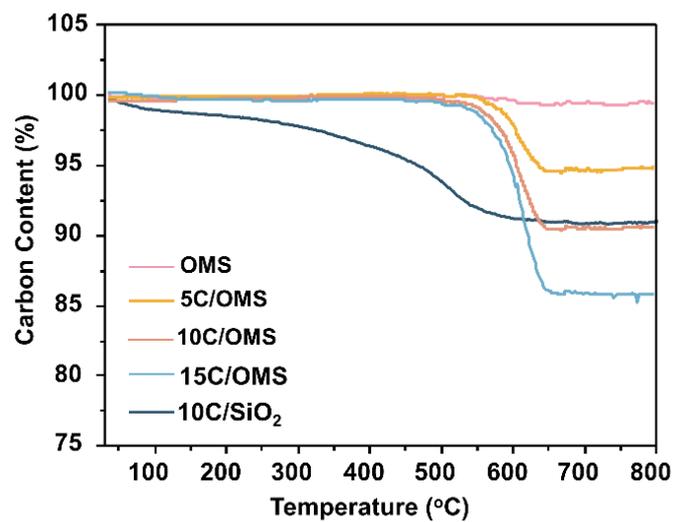
| Catalyst                             | CO conv. /% | STY of HA (mmol/g <sub>cat</sub> /h) | Selectivity/ C% |                 |                       |      |      | Alcohol distribution/ wt.% |                    |       |
|--------------------------------------|-------------|--------------------------------------|-----------------|-----------------|-----------------------|------|------|----------------------------|--------------------|-------|
|                                      |             |                                      | CO <sub>2</sub> | CH <sub>4</sub> | HC <sub>n</sub> (n>1) | ROH  | HA   | Me OH                      | C <sub>2</sub> +OH | Other |
| Co/OMS <sup>b</sup>                  | 20.1        | 3.6                                  | 1.0             | 26.4            | 49.2                  | 26.7 | 11.7 | 44.3                       | 54.2               | 1.9   |
| Co/5C/OMS <sup>b</sup>               | 29.2        | 8.2                                  | 0.8             | 27.0            | 38.5                  | 33.7 | 16.9 | 34.5                       | 63.3               | 2.2   |
| Co/10C/OMS <sup>b</sup>              | 63.2        | 23.7                                 | 0.4             | 20.6            | 37.7                  | 41.3 | 22.8 | 30.6                       | 67.6               | 1.8   |
| Co/15C/OMS <sup>b</sup>              | 59.8        | 22.2                                 | 0.5             | 22.0            | 39.8                  | 37.9 | 23.1 | 26.0                       | 72.4               | 1.6   |
| Co/10C/SiO <sub>2</sub> <sup>b</sup> | 10.6        | 3.0                                  | 2.4             | 29.1            | 37.4                  | 31.1 | 15.6 | 43.5                       | 55.3               | 1.2   |
| Co/10C/OMS <sup>c</sup>              | 12.2        | 7.3                                  | 0.5             | 25.9            | 39.3                  | 36.3 | 19.8 | 38.5                       | 60.6               | 0.9   |

<sup>a</sup> Before the catalyst evaluation, the calcined catalysts were first in situ reduced at 430

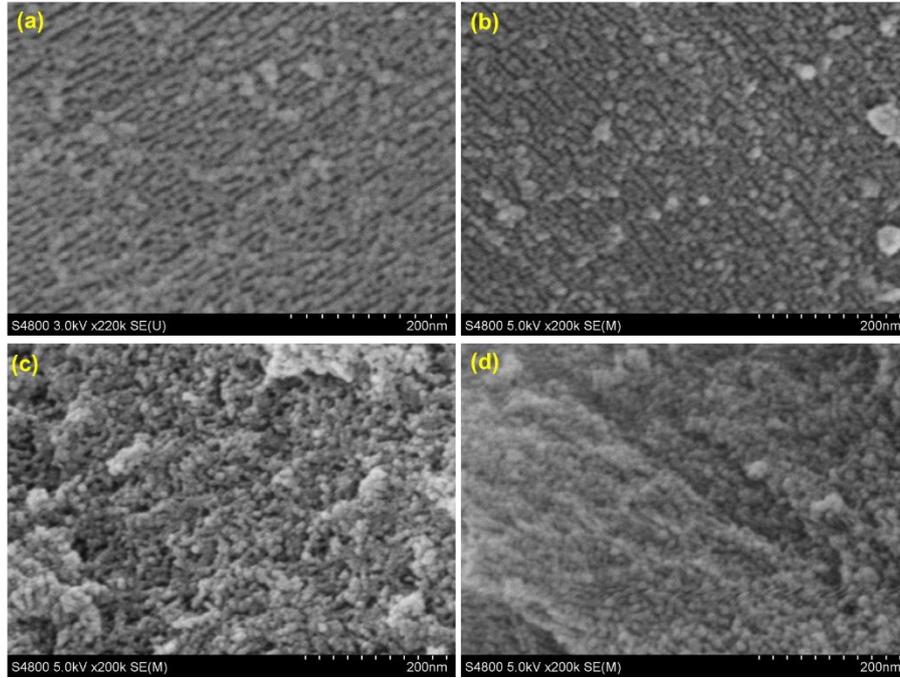
°C in hydrogen for 10 h, and then carburized at 225 °C for 24 h in CO flow;

<sup>b</sup> Reaction conditions: T = 225 °C, P = 3MPa, H<sub>2</sub>/CO = 2, GHSV = 10800 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>;

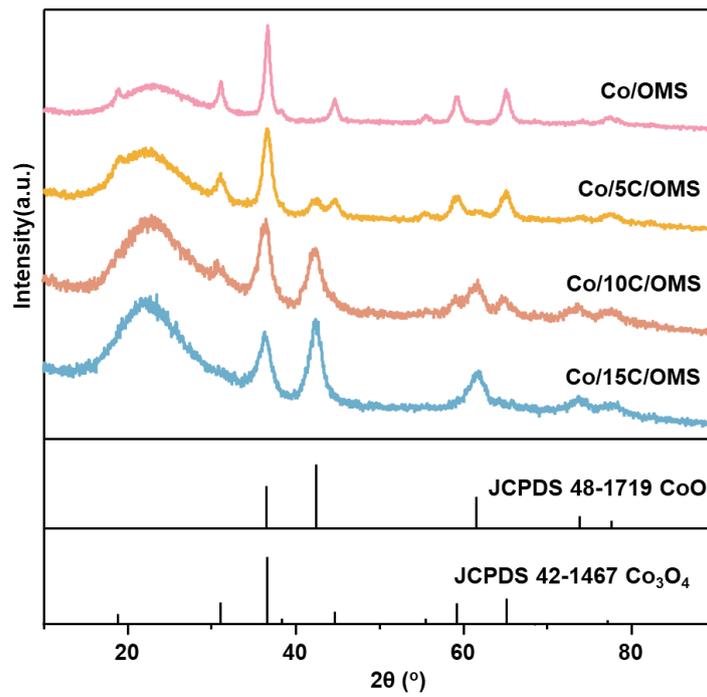
<sup>c</sup> Reaction conditions: T = 225 °C, P = 3MPa, H<sub>2</sub>/CO = 2, GHSV = 21600 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup>.



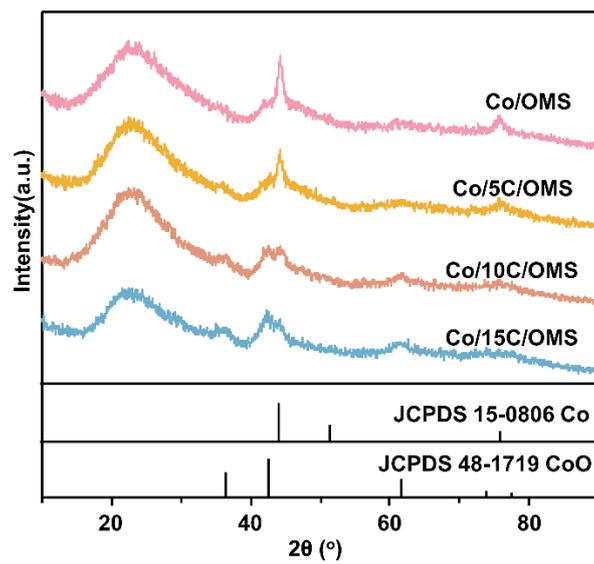
**Fig. S1.** TG analysis of the xC/OMS and 10C/SiO<sub>2</sub> supports.



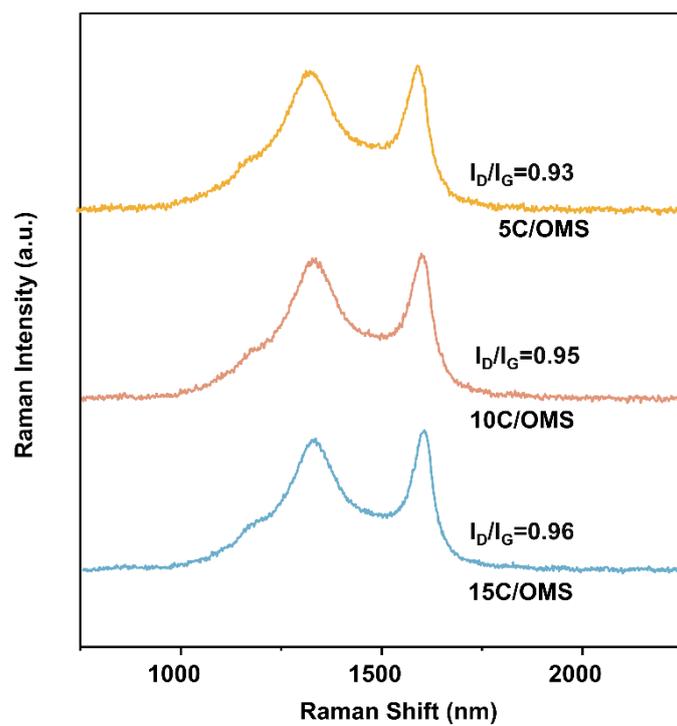
**Fig. S2.** SEM images of (a) OMS, (b) 5C/OMS, (c)10C/OMS and (d) 15C/OMS supports.



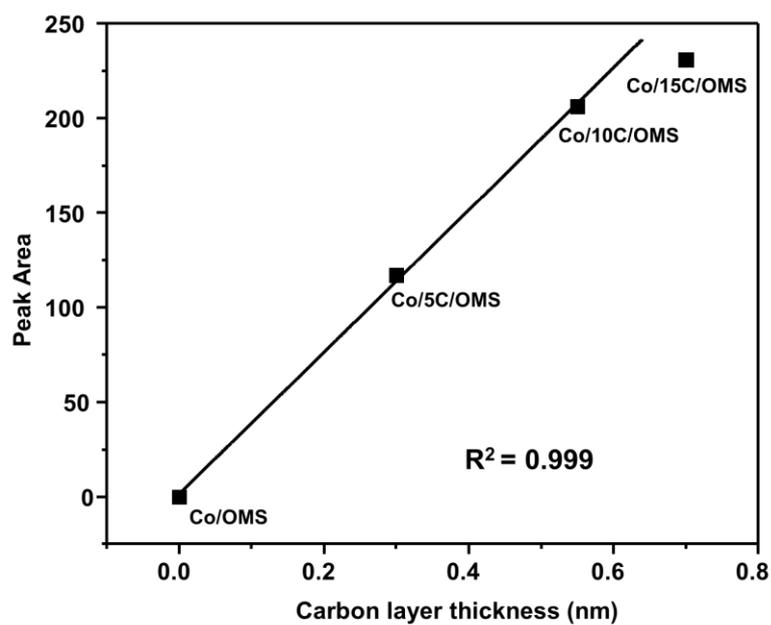
**Fig. S3.** XRD patterns of the calcined Co/xC/OMS catalysts.



**Fig. S4.** XRD patterns of the reduced Co/xC/OMS catalysts.



**Fig. S5.** Raman spectra of xC/OMS supports.



**Fig. S6.** Correlation between the carbon layer thickness with the peak area of H<sub>2</sub>-TPR-MS profiles.