**Supporting Information for:**

# The distinguished roles with various vanadium loadings of $CoCr_{2-x}V_xO_4$ ($x$ = 0-0.20) for methane combustion


Jinghuan Chen [+], Wenbo Shi [+], Shijian Yang [+], Hamidreza Arandiyan [+], Junhua Li [*,+,‡]

[+] *School of Environment, Tsinghua University, Beijing, 100084, China*

[‡] *State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Beijing, 100084, China*

[*] Corresponding author e-mail: lijunhua@tsinghua.edu.cn


**Number of Supporting Information pages (including this title page): 6**

**Results and discussion about figures in the Supporting Information (p. S2)**

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**Results and discussion about figures in the Supporting Information**

The $CoCr_{1.75}V_{0.25}O_4$ catalyst was prepared and investigated for methane combustion. Figure S1 shows the catalytic activity of the $CoCr_{1.75}V_{0.25}O_4$ catalyst as a function of the reaction temperature. For comparison purpose, the activity of the $CoCr_2O_4$ and $CoCr_{1.95}V_{0.05}O_4$ was also given. It can be observed that further vanadium doping significantly decreased the activity, the methane conversion at 700 $^{o}C$ over $CoCr_{1.75}V_{0.25}O_4$ was as low as 21%.

Transmission electron microscopy (TEM) was collected on a JEOL JEM 2010 microscope operating at 200 kV equipped with an energy dispersive X-ray (EDX) system. As shown in Figure S2, vanadium oxides cannot be observed even on well dispersed particles of the $CoCr_{1.80}V_{0.20}O_4$ sample.

For better comparison, pure oxides of cobalt, chromium and vanadium were prepared using the similar procedures with the $CoCr_{2-x}V_xO_4$ catalysts, and their catalytic performance, BET surface areas and XRD patterns were also investigated. As shown in Figure S3, the $VO_x$ was combined phases of $V_2O_5$ (JCPDS 41-1426), $VO_2$ (PDF 43-1051) and $V_6O_{13}$ (PDF 43-1050), while chromium and cobalt oxides were pure phase as expected according to $Cr_2O_3$ (JCPDS 6-0504) and $Co_3O_4$ (JCPDS 42-1467), respectively. The specific surface area was 9.5, 116.9 and 1.5 $m^2/g$ for $VO_x$, $CrO_x$ and $Co_3O_4$, respectively. Figure S4 shows the activity of the three oxides. Apparently, methane conversion over $CrO_x$ was better than $Co_3O_4$, however, if we take the surface area into account, the specific reaction rate of $Co_3O_4$ was much higher than that of the $CrO_x$ catalyst. In addition, $VO_x$ showed nearly no activity towards methane combustion.

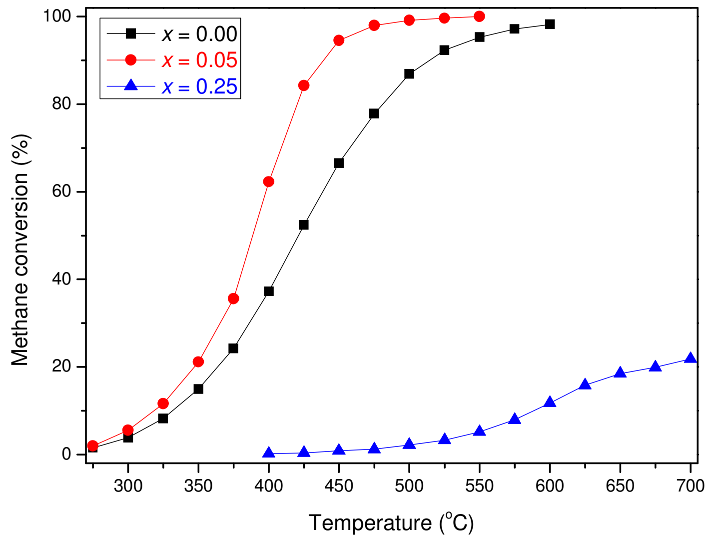



**Figure S1.** Methane conversion as a function of temperature over the $CoCr_{2-x}V_xO_4$ ($x$ = 0, 0.05 and **0.25**) catalysts. Reaction condition: 2000 ppm $CH_4$, 10 vol. % $O_2$, and $N_2$ as the balance gas, with a total flow rate of 150 mL/min, corresponding to a GHSV about 36,000 $mL{\cdot}h^{-1}{\cdot}g^{-1}$.

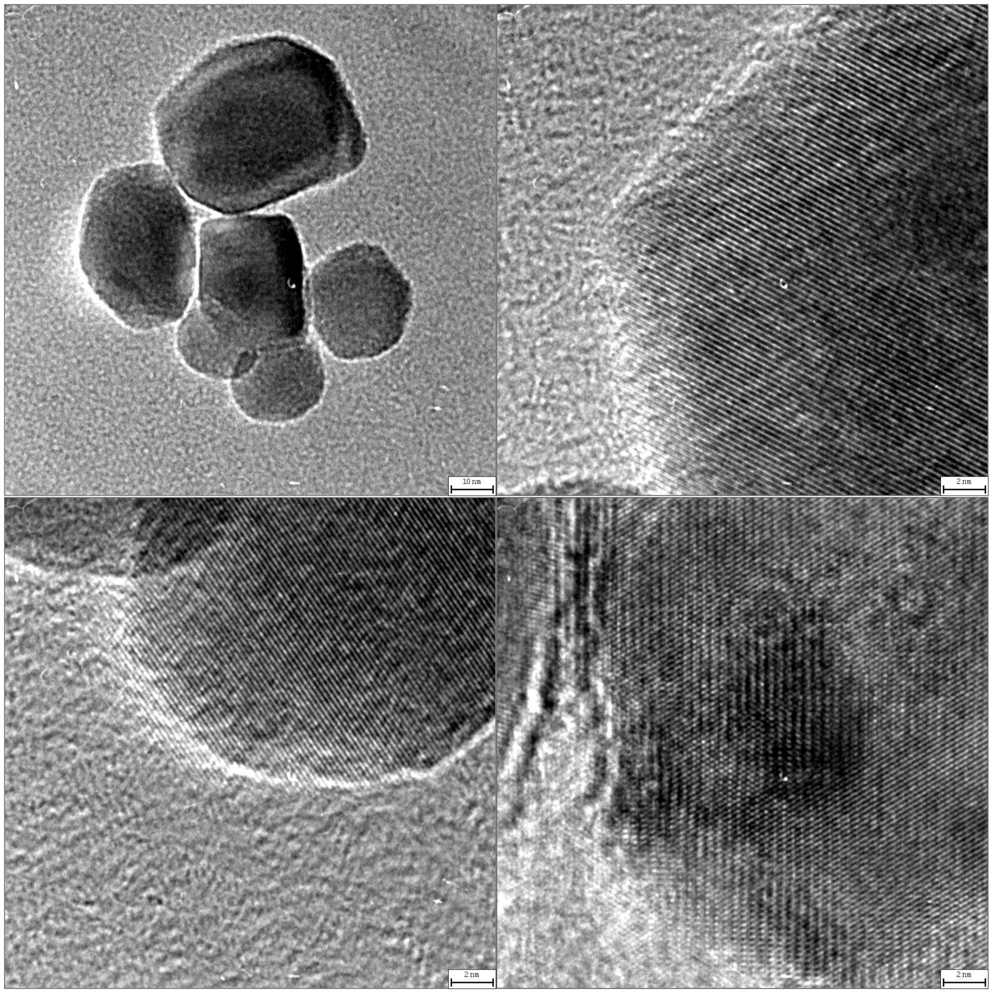



**Figure S2.** TEM images of the $CoCr_{1.80}V_{0.20}O_4$ catalyst.

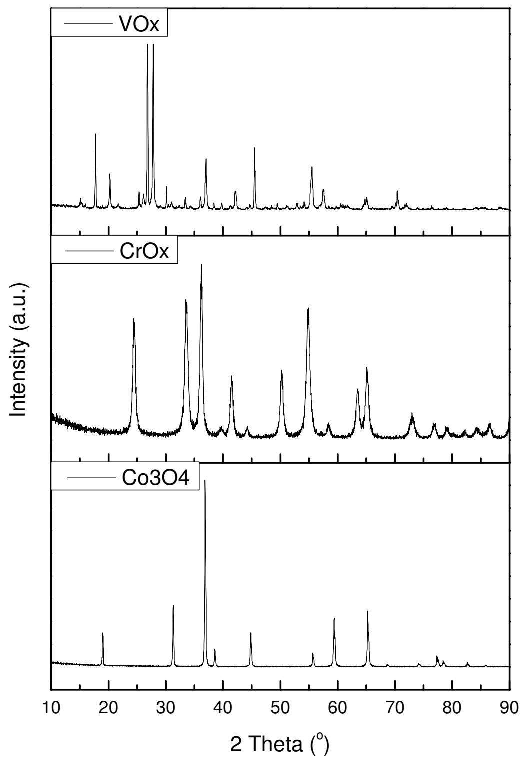
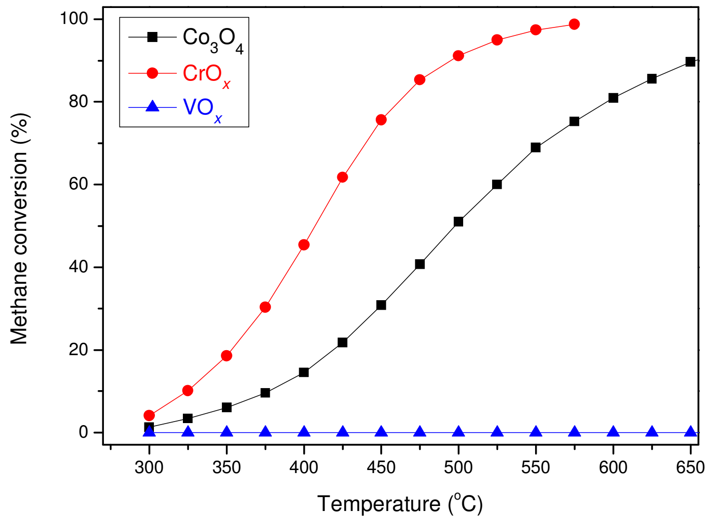
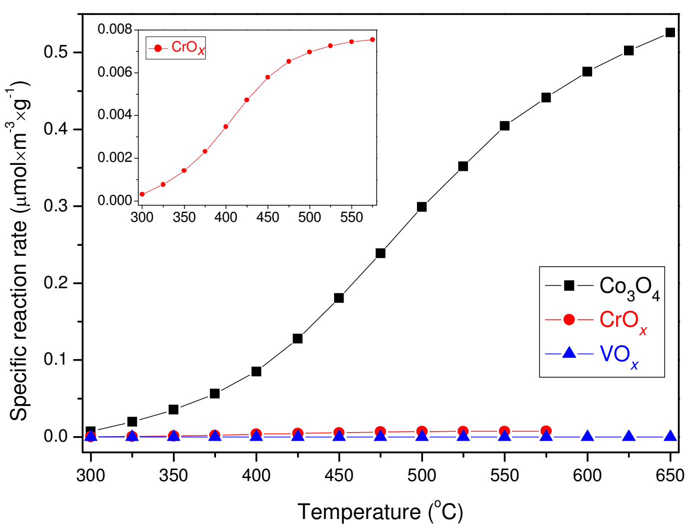



**Figure S3.** XRD patterns of the $Co_3O_4$, $CrO_x$ and $VO_x$ catalysts.




(A)




(B)

**Figure S4.** $CH_4$ conversion (A) and $CH_4$ specific reaction rate (B) as a function of temperature over the $Co_3O_4$, $CrO_x$ and $VO_x$ catalysts. Reaction condition: 2000 ppm $CH_4$, 10 vol. % $O_2$, and $N_2$ as the balance gas, with a total flow rate of 150 mL/min, corresponding to a GHSV about 36,000 $mL \cdot h^{-1} \cdot g^{-1}$.