Improved Durability of Co3O4 Particles Supported on SmMn2O5 for Methane Combustion

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S1. O$_2$-TPD results of Co/SMO samples from room temperature to 750 °C

Three desorption signals for Co$_3$O$_4$ deposition samples can be observed in Fig. S1. The oxygen species desorbed below 300 °C was $\alpha$-O, between 300 °C and 600 °C was $\beta$-O, while the oxygen desorbed above 650 °C resulted from the desorption of bulk lattice oxygen accompanied by the mullite structure and Co$_3$O$_4$ destruction was $\gamma$-O. It can be seen in Fig. S1a that the $\gamma$-O desorption temperature got decreased after loading Co$_3$O$_4$ and the desorption amount increased continuously with increasing Co$_3$O$_4$ content, implying additional bulk oxygen amount for SmMn$_2$O$_5$ caused by deposition of Co$_3$O$_4$. While the decreased desorption temperature indicated the more active bulk oxygen and led to weak thermal stability compared with SmMn$_2$O$_5$.

Fig. S1b exhibited the O$_2$-TPD results of Co/SMO-30%, 50% and 70% samples, the desorbed $\beta$ and $\gamma$-O amount for Co/SMO-50% was higher than that of Co/SMO-30% sample, which can be attributed to the increased Co$_3$O$_4$ loading amount. While the similar desorption curves for Co/SMO-50% and Co/SMO-70% samples indicated the similar Co$_3$O$_4$ loading amount, which can be ascribed to the saturated Co$_3$O$_4$ deposition amount on SmMn$_2$O$_5$.

Fig. S1 O$_2$-TPD results of Co/SMO-x samples a: x=0, 5%, 30% and 50%; b: x=30%, 50% and 70%

S2. Catalytic activity of Co/SMO-70% sample

Fig. S2 CH$_4$ conversion over Co/SMO-70% catalyst
S3. The effects of silica dilution on CH₄ combustion catalytic activity

Co₃O₄ and Co/SMO-50% samples were diluted with silica (80-100 mesh) and tested for CH₄ combustion. In detail, 100 mg catalysts were diluted with 100 mg silica in each test.

Fig. S3 CH₄ conversion over silica diluted Co₃O₄ and Co/SMO-50% samples

S4. The CH₄ combustion hysteresis behavior for Co₃O₄ and Co/SMO-50% samples

In order to investigate the hysteresis behavior, Co₃O₄ and Co/SMO-50% samples were tested by heating the reactor from room temperature to 600 °C and natural cooling the reactor from 600 °C to room temperature. The results showed that both catalysts exhibited a hysteresis behavior.

Fig. S4 CH₄ conversion over Co₃O₄ and Co/SMO-50% samples heating (solid line), cooling (-□-)

S5. Recycle tests of Co₃O₄ and Co/γ-Al₂O₃-50% samples for methane combustion

The recycle tests of Co₃O₄ and Co/γ-Al₂O₃-50% catalysts were conducted, the results were showed in Fig. S5a and b. It can be seen that the CH₄ conversion-temperature curve almost stayed unchanged after third cycle for Co₃O₄, suggesting the catalytic activity stayed stable after three times tests. As for the Co/γ-Al₂O₃-50% catalyst, the catalytic activity was comparable with Co₃O₄ for fresh sample, but decreased quickly for the third cycle, exhibiting similar catalytic activity with SmMn₂O₅.
S6. Catalytic activity of Co$_3$O$_4$/SmMn$_2$O$_5$ mixture

In order to confirm the promotional effect of Co/SMO composite catalysts, a mixture of Co$_3$O$_4$ and SmMn$_2$O$_5$ was prepared and tested for CH$_4$ combustion and compared with that of Co/SMO-50% sample. Assuming all the nominal Co formed Co$_3$O$_4$ on the SmMn$_2$O$_5$ surface in Co/SMO-50% catalyst, then the theoretical weight ratio of Co$_3$O$_4$/SmMn$_2$O$_5$ is 68%, therefore, a mixture with Co$_3$O$_4$ to SmMn$_2$O$_5$ weight ratio being 70% was prepared by mixing for 2-3 min using a spatula, insuring the Co/SmMn$_2$O$_5$ weight ratio was not lower than 50%. The catalytic activity was tested and shown in Fig. S6. It can be seen that the mixture exhibited better performance than SmMn$_2$O$_5$ due to the active Co$_3$O$_4$, while lower catalytic activity than Co/SMO-50% sample, which can be ascribed to the lack of intimate contact between Co$_3$O$_4$ and SmMn$_2$O$_5$. Overall, the higher catalytic activity for Co/SMO-50% than the mixture demonstrated the promotional interaction in deposition-precipitation prepared Co/SMO composite catalysts.

S7. The effect of WHSV on catalytic activity of Co$_3$O$_4$ and Co/SMO-50% samples
Fig. S7 The effect of WHSV on catalytic activity of Co$_3$O$_4$ and Co/SMO-50% samples. 60000 ml g$^{-1}$ h$^{-1}$ (solid line), 20000 ml g$^{-1}$ h$^{-1}$ (-○-)

**S8. Hydrothermal aged Co$_3$O$_4$ and Co/SMO-50% samples for CH$_4$ combustion**

The Co$_3$O$_4$ and Co/SMO-50% samples were hydrothermally aged to evaluate their susceptibility to H$_2$O. The hydrothermal aging conditions were set at 800$^\circ$C for 5h in 10% H$_2$O with air as balance and the total flow rate was set to 1000 ml min$^{-1}$. The results were given in Fig. S8.

After hydrothermal aged at 800 $^\circ$C for 5h, the catalytic activity of Co/SMO-50% almost stayed unchanged compared with thermal aged Co/SMO-50% sample, which can be attributed to the high hydrothermal resistance of SmMn$_2$O$_5$. The catalytic activity of hydrothermal aged Co$_3$O$_4$ further decreased than thermal aged sample, indicating poor hydrothermal resistance of Co$_3$O$_4$.

Fig. S8 CH$_4$ conversion over thermal aged (TA) and hydrothermal aged (HTA) Co$_3$O$_4$ and Co/SMO-50% catalysts