Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

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_3O_4 deposition samples can be observed in Fig. S1. The oxygen species desorbed below 300 °C was α-O, between 300 °C and 600 °C was β-O, while the oxygen desorbed above 650 °C resulted from the desorption of bulk lattice oxygen accompanied by the mullite structure and Co_3O_4 destruction was γ-O. It can be seen in Fig. S1a that the γ-O desorption temperature got decreased after loading Co_3O_4 and the desorption amount increased continuously with increasing Co_3O_4 content, implying additional bulk oxygen amount for $SmMn_2O_5$ caused by deposition of Co_3O_4. While the decreased desorption temperature indicated the more active bulk oxygen and led to weak thermal stability compared with $SmMn_2O_5$.

Fig. S1b exhibited the O_2-TPD results of Co/SMO-30%, 50% and 70% samples, the desorbed β and γ–O amount for Co/SMO-50% was higher than that of Co/SMO-30% sample, which can be attributed to the increased Co_3O_4 loading amount. While the similar desorption curves for Co/SMO-50% and Co/SMO-70% samples indicated the similar Co_3O_4 loading amount, which can be ascribed to the saturated Co_3O_4 deposition amount on $SmMn_2O_5$.

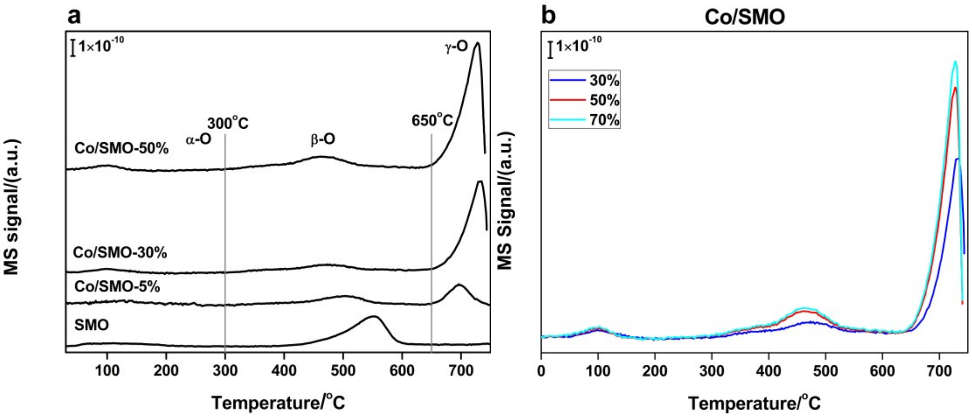

Fig. S1 O_2-TPD results of Co/SMO-x samples a: x=0, 5%, 30% and 50%; b: x=30%, 50% and 70%

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

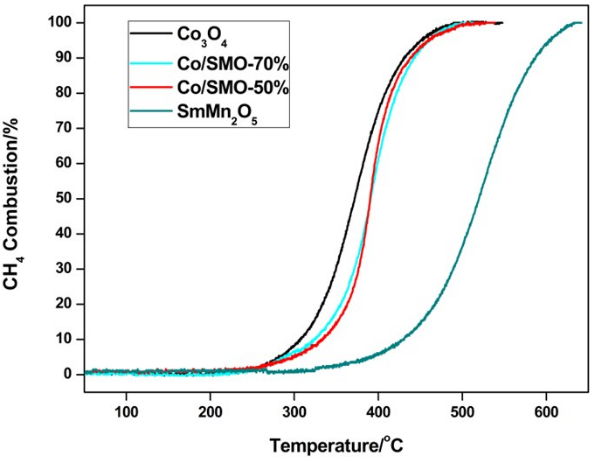

Fig. S2 CH_4 conversion over Co/SMO-70% catalyst

S3. The effects of silica dilution on CH_4 combustion catalytic activity

Co_3O_4 and Co/SMO-50% samples were diluted with silica (80-100 mesh) and tested for CH_4 combustion. In detail, 100 mg catalysts were diluted with 100 mg silica in each test.

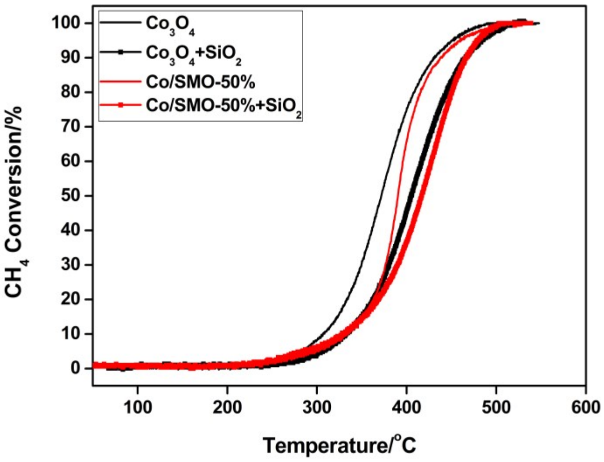

Fig. S3 CH_4 conversion over silica diluted Co_3O_4 and Co/SMO-50% samples

S4. The CH_4 combustion hysteresis behavior for Co_3O_4 and Co/SMO-50% samples

In order to investigate the hysteresis behavior, Co_3O_4 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.

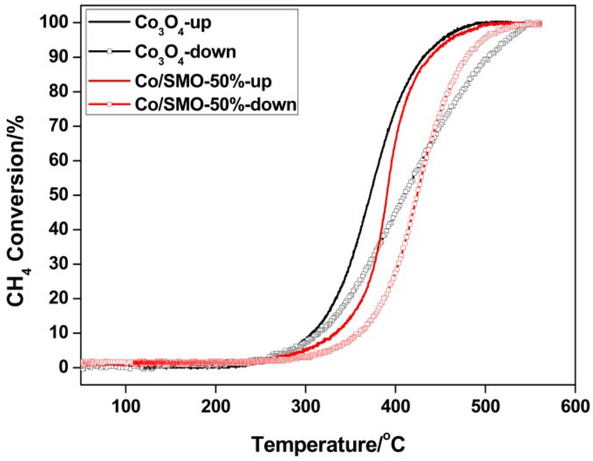

Fig. S4 CH_4 conversion over Co_3O_4 and Co/SMO-50% samples heating (solid line), cooling (-□-)

S5. Recycle tests of Co_3O_4 and Co/γ-Al_2O_3-50% samples for methane combustion

The recycle tests of Co_3O_4 and Co/γ-Al_2O_3-50% catalysts were conducted, the results were showed in Fig. S5a and b. It can be seen that the CH_4 conversion-temperature curve almost stayed unchanged after third cycle for Co_3O_4, suggesting the catalytic activity stayed stable after three times tests. As for the Co/γ-Al_2O_3-50% catalyst, the catalytic activity was comparable with Co_3O_4 for fresh sample, but decreased quickly for the third cycle, exhibiting similar catalytic activity with $SmMn_2O_5$.

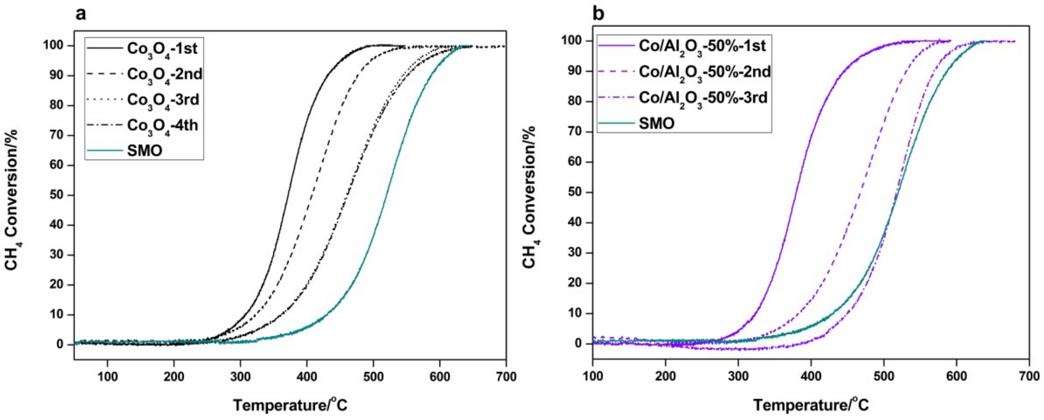

Fig. S5 recycle experiments on the a: Co_3O_4; b: Co/γ-Al_2O_3-50%

S6. Catalytic activity of Co_3O_4/$SmMn_2O_5$ mixture

In order to confirm the promotional effect of Co/SMO composite catalysts, a mixture of Co_3O_4 and $SmMn_2O_5$ was prepared and tested for CH_4 combustion and compared with that of Co/SMO-50% sample. Assuming all the nominal Co formed Co_3O_4 on the $SmMn_2O_5$ surface in Co/SMO-50% catalyst, then the theoretical weight ratio of Co_3O_4/$SmMn_2O_5$ is 68%, therefore, a mixture with Co_3O_4 to $SmMn_2O_5$ weight ratio being 70% was prepared by mixing for 2-3 min using a spatula, insuring the Co/$SmMn_2O_5$ 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 $SmMn_2O_5$ due to the active Co_3O_4, while lower catalytic activity than Co/SMO-50% sample, which can be ascribed to the lack of intimate contact between Co_3O_4 and $SmMn_2O_5$. Overall, the higher catalytic activity for Co/SMO-50% than the mixture demonstrated the promotional interaction in deposition-precipitation prepared Co/SMO composite catalysts.

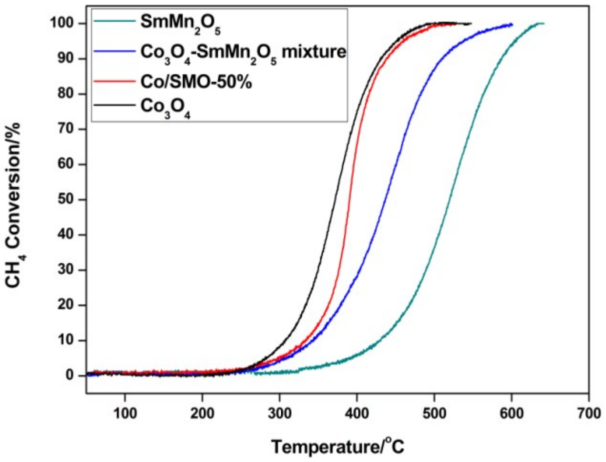

Fig. S6 CH_4 conversion over Co_3O_4 and $SmMn_2O_5$ mixture, $SmMn_2O_5$, Co_3O_4 and Co/SMO-50% catalysts

S7. The effect of WHSV on catalytic activity of Co_3O_4 and Co/SMO-50% samples

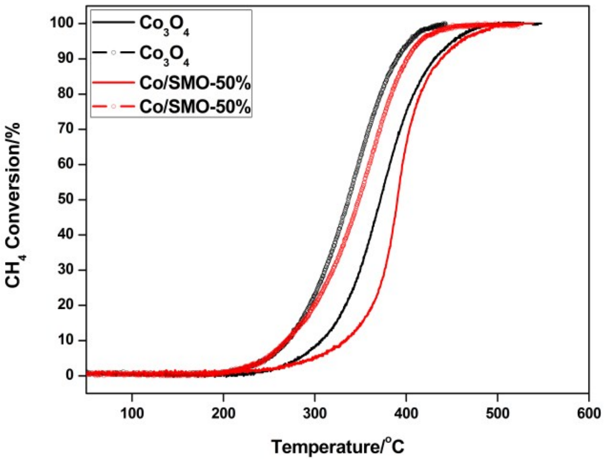

Fig. S7 The effect of WHSV on catalytic activity of Co_3O_4 and Co/SMO-50% samples. 60000 ml g^{-1} h^{-1} (solid line), 20000 ml g^{-1} h^{-1} (-○-)

S8. Hydrothemal aged Co_3O_4 and Co/SMO-50% samples for CH_4 combustion

The Co_3O_4 and Co/SMO-50% samples were hydrothermally aged to evaluate their susceptibility to H_2O. The hydrothermal aging conditions were set at 800°C for 5h in 10% H_2O 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 °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 $SmMn_2O_5$. The catalytic activity of hydrothermal aged Co_3O_4 further decreased than thermal aged sample, indicating poor hydrothermal resistance of Co_3O_4.

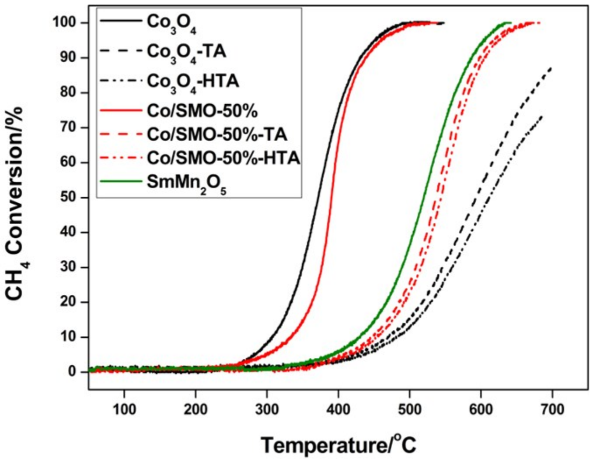

Fig. S8 CH_4 conversion over thermal aged (TA) and hydrothermal aged (HTA) Co_3O_4 and Co/SMO-50% catalysts