

Macroporous SmMn₂O₅ Mullite for NO_x-assisted Soot Combustion

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S1. Preparation, soot combustion and NO oxidation of Pt/ γ -Al₂O₃

The reference Pt/ γ -Al₂O₃ with 1wt.% content was synthesised by the incipient wetness method^{1,2} using Pt(NO₃)₂ (18.02 wt.% of Pt in water, Aladdin) as a precursor deposited on γ -Al₂O₃ (Aladdin), calcined at 700 °C in air for 5 hours.

The NO oxidation and soot combustion catalytic activities of Pt (1wt.%)/ γ -Al₂O₃ under NO_x+O₂ are evaluated and compared with SmMn₂O₅ catalysts using the same experimental conditions. The results are given in Fig. S1. We can see from Fig. S1a that all SmMn₂O₅ catalysts exhibited better activity than Pt/ γ -Al₂O₃ with lower T₁₀, T₅₀ and T₉₀ except HT sample, which showed higher T₉₀. The results indicated the potential of SmMn₂O₅ catalysts for soot combustion. As for the NO oxidation, the Pt/ γ -Al₂O₃ catalyst exhibited a maximum conversion of about 49% at 330 °C, lower than SmMn₂O₅ mullite catalysts. Note that less Pt content of 1 wt.% is used for soot combustion than that for NO oxidation of 2 wt.%, as a result, the NO conversion is lower than previous reports.^{3,4}

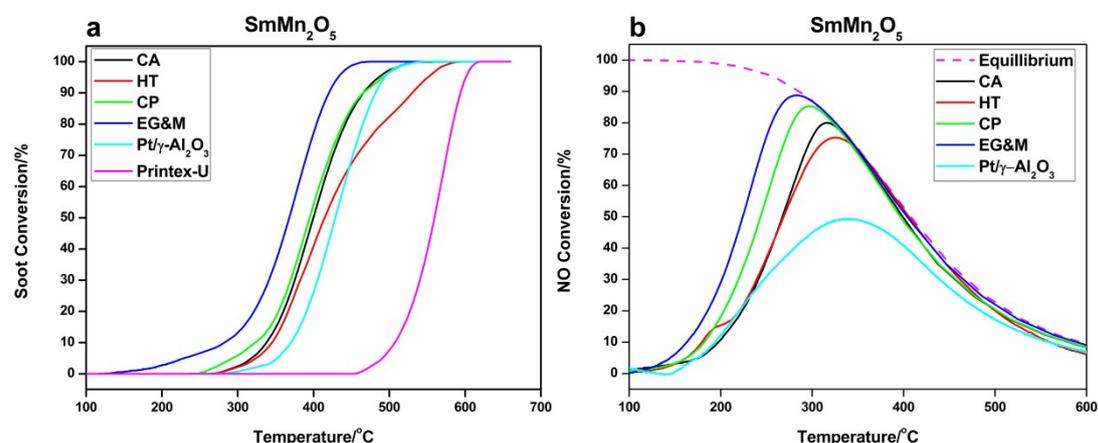


Fig. S1 a: Soot conversion over the SmMn₂O₅ catalysts, Pt/ γ -Al₂O₃ and Printex-U (no catalyst) using “loose” contact conditions; b: NO conversion over the SmMn₂O₅ catalysts and Pt/ γ -Al₂O₃. 400 ppm NO, 10% O₂ and N₂ as balance

S2. Reproducibility and stability of SmMn₂O₅ catalysts

We take the SmMn₂O₅-EG&M as representative to testify the catalytic activity reproducibility, as shown in Fig. S2a. Each sample was tested for three times, and we can see that the soot conversion curve is reproducible for fresh EG&M sample. Moreover, the stability of SmMn₂O₅-EG&M sample was also evaluated in Fig. S2b. After each test, the catalyst was taken to remix with soot and used to test again for another cycle. The results showed that though the activity slightly decreased after first cycle, especially at high temperature range, it still maintained high catalytic performance for soot combustion under NO+O₂ atmosphere.

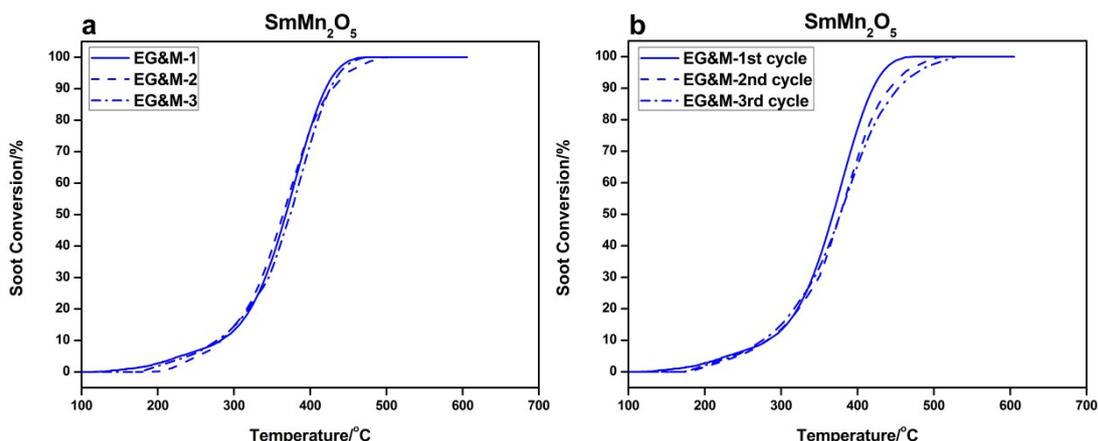


Fig. S2 a: Reproducibility of SmMn_2O_5 -EG&M sample; b: Stability of EG&M sample. 400 ppm NO, 10% O_2 and N_2 as balance

The reproducibility of HT sample was verified by testing fresh HT sample for three times, the results are given in Fig. S3, and the catalytic activities with different heating rates are also included. We can see from Fig. S3a that the soot conversion curve is reproducible for fresh HT sample, the results are similar. Moreover, the trends of conversion curves obtained under different heating rate are similar as well.

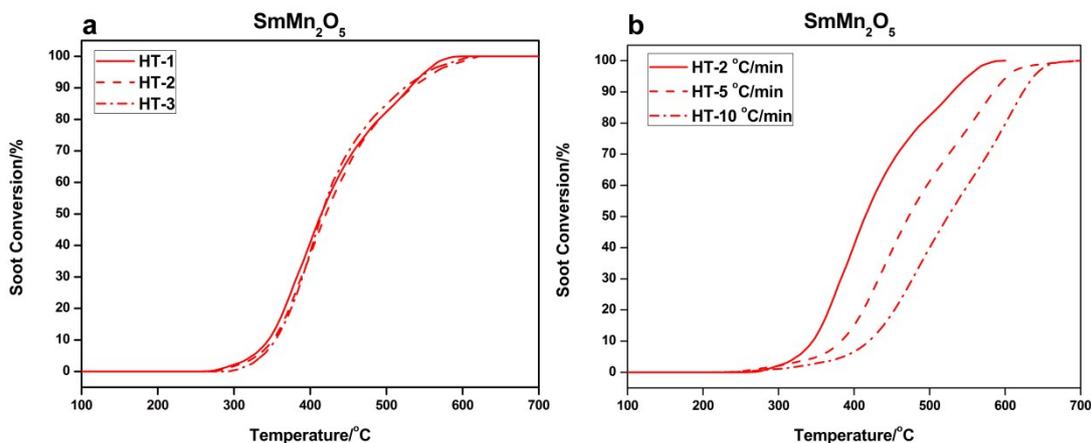


Fig. S3 a: Reproducibility of SmMn_2O_5 -HT sample; b: Soot conversion over HT sample with different heating rate. 400 ppm NO, 10% O_2 and N_2 as balance

S3. $\text{NO}+\text{O}_2$ -TPRD results of SmMn_2O_5 catalysts

The temperature programmed reaction and desorption (TPRD) of $\text{NO}+\text{O}_2$ experiments were carried out on a FINESORB-3010E instrument (Zhejiang Finetec Co.). 50 mg of sample was used in each $\text{NO}+\text{O}_2$ -TPRD measurement. The adsorption/reaction of ($\text{NO}+\text{O}_2$) on the catalyst sample was carried out at 150 °C with a flow of 400 ppm NO, 10% O_2 in N_2 balance (150 ml/min) for 1 hour followed by purging with a N_2 flow (200 ml/min) at the same temperature for 1 hour. The catalyst was then heated up to 800 °C at a rate of 5 °C/min. The composition of the desorbed gas

was continuously recorded with a chemiluminescence NO_x analyzer (EcoPhysics, CLD822Mh), which can detect NO and NO₂ simultaneously with a detection limit of 0.25 ppm.

The NO+O₂-TPRD experiment was conducted for the analysis of the concentration and easiness of desorbed NO_x species. NO and NO₂ were the main desorption species as shown in Fig. S4. Note that the pretreatment was carried out at 150 °C, at which the conversion of NO was low, it is reasonable that more NO desorbed than NO₂. NO₂ mainly desorbed below 300 °C, while for NO, the desorption process lasted to 400 °C for CA, CP and EG&M samples, 500 °C for HT sample.

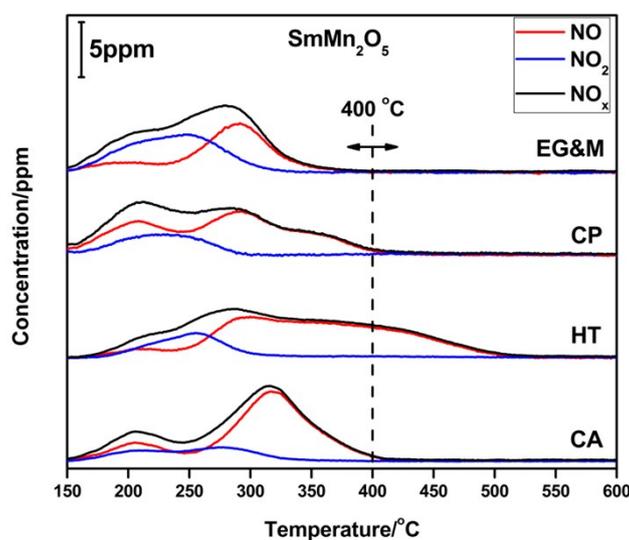


Fig. S4 NO+O₂-TPRD results of SmMn₂O₅ samples

S4. Estimation of NO-NO₂ recycle reaction

To estimate the NO-NO₂ recycle reaction, SmMn₂O₅-EG&M sample was taken as representative and additional dual-bed soot combustion test for Pt/γ-Al₂O₃ and SmMn₂O₅-EG&M catalysts is conducted under NO+O₂ atmosphere. Specifically, a catalyst bed (40 mg catalyst + 40 mg silica (80-100 mesh)) is located upstream the soot bed (10 mg soot + 40 mg silica (80-100 mesh)), being separated by quartz-wool.² The soot conversion and NO₂ concentration are monitored and compared with single-bed tests and shown in Fig. S5. The NO-NO₂ recycle reaction can be confirmed for Pt/γ-Al₂O₃ catalyst as NO₂ concentration is lower for dual-bed test above 300 °C. Besides, the soot combustion activity and CO₂ selectivity decrease for dual bed test without contact between soot and catalyst. This can be due to the lack of NO-NO₂ recycle reaction in dual-bed reaction as the formed NO₂ is reduced by NO₂-soot reaction back to NO, leading to lower NO conversion. In the single-bed test, the reduced NO can be reoxidized to NO₂ through NO-NO₂ reaction, resulting in higher NO conversion. While at temperatures below 300 °C, more NO₂ was detected for dual bed test, this can be ascribed to the active sites blockage by soot in single bed test as the soot combustion mainly started above 300 °C. SmMn₂O₅-EG&M sample showed similar trend with worse soot combustion catalytic activity and lower NO₂ concentration above 300 °C for dual-bed test, which can be attributed to the NO-NO₂ recycle reaction as well. Differently, NO₂ concentration is similar at low temperatures for SmMn₂O₅-EG&M sample with respect to different tests, which can be attributed to its macroporous structure avoiding the

blockage of active sites by soot particles.

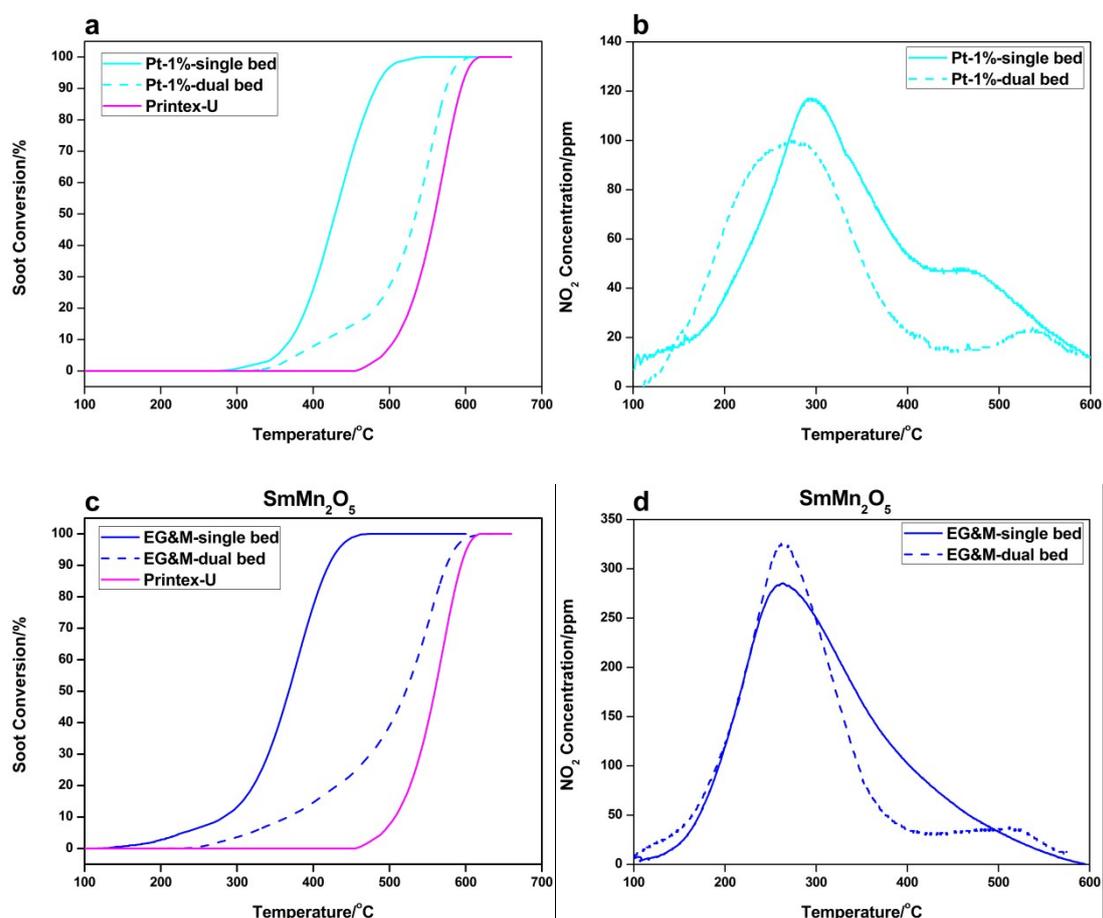


Fig. S5 a, c: Soot combustion activity; b, d: NO₂ concentration during soot combustion of Pt and SmMn₂O₅-EG&M catalysts, respectively. 400 ppm NO, 10% O₂ and N₂ as balance

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