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A new dynamic N_2O reduction system based on Rh/ceria-zirconia:

from mechanistic insight towards a practical application

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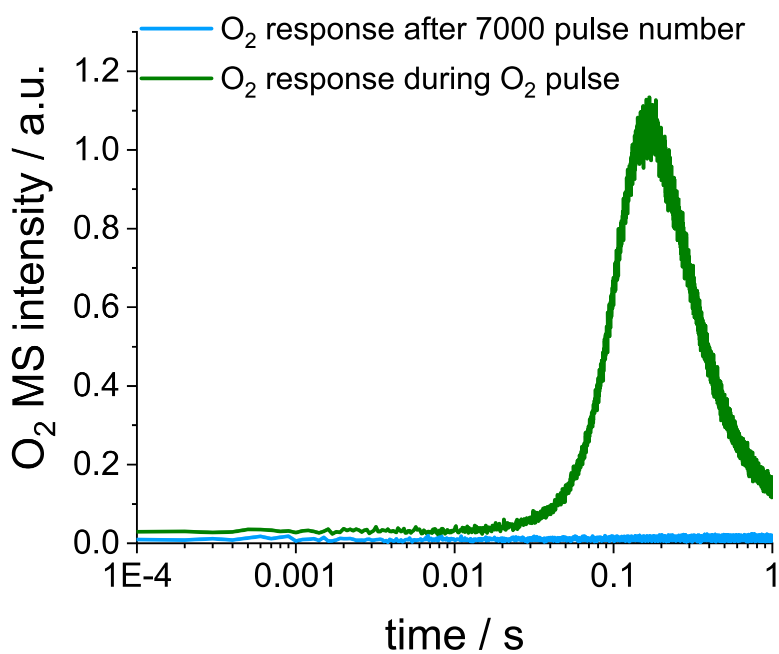

Figure S1. Comparison of O_2 response shape between the O_2 response during $^{15}N_2O$ pulses over oxidized state of Rh/CLZ as indicated in Figure 1in the main text and the O_2 response during O_2 pulses over an oxidized Rh/CLZ at 450 ˚C in TAP

H_2 was applied as reductant to pretreat the CLZ catalyst sample at 450 ˚C. The total amount of oxygen vacancies formed during the H_2 pre-treatment was calculated to be $6 \cdot 10^{16}$ oxygen atoms/mg_{cat}, corresponding to a 0.2-0.3 ceria layer reduction. This low degree of surface reduction by H_2 at 450 °C was also supported by the H_2-TPR, which showed that the reduction of surface CLZ support was centered at 430 ˚C [1]. The co-existence of H_2 and H_2O during the whole H_2 pulse experiment suggested the presence of an quasi-equilibrium between H_2, H_2O, Ce^{3+}, and Ce^{4+}, which may limit a deeper reduction of ceria by H_2 [2].

The product and reactant gas evolution during $^{15}N_2O$ pulses over H_2 pre-reduced CLZ at 450 ˚C is presented in Figure S2A and B. As shown in Figure S2A during the first 100 $^{15}N_2O$ pulses, the $^{15}N_2O$ conversion was 100 %, accompanying with the $^{15}N_2$ formation. The $^{15}N_2O$ conversion subsequently declined rapidly to around 12% and O_2 was gradually detected after 300 $^{15}N_2O$ pulses. From Figure S2B, the accumulative oxygen at the point, where $^{15}N_2O$ started to breakthrough, was around $3.5 \cdot 10^{16}$ oxygen atoms/mg$_{cat}$, equally to around 60 % of oxygen vacancies being refilled. The N balance showed that there was only a small amount of nitrogen species (less than 8 %) accumulation on the ceria surface during the first 100 $^{15}N_2O$ pulses. O_2 started to breakthrough at the point when the catalyst was almost oxidized.

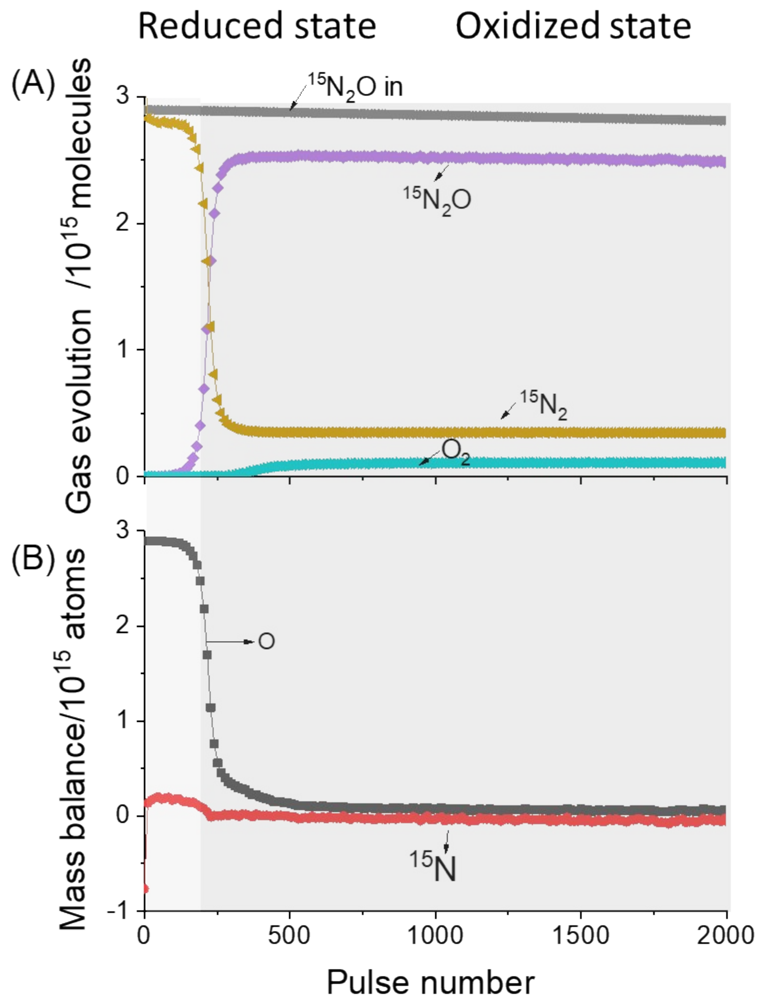

Figure S2. (A) Products and reactant evolution, and (B) O and ^{15}N balance *versus* pulse number during $^{15}N_2O$ multi-pulse experiment over a H_2 reduced CLZ at 450 ˚C in TAP

Figure S3 shows the normalized flux of $^{15}N_2$ during $^{15}N_2O$ pulse over a C_3H_6 reduced and H_2 reduced Rh/CLZ at 450 ˚C. The normalized $^{15}N_2$ response showed the same characteristic time regardless to the pretreatment condition by either H_2 or C_3H_6. The comparison of $^{15}N_2$ responses over C_3H_6 reduced and H_2 reduced sample showed an insignificant difference.

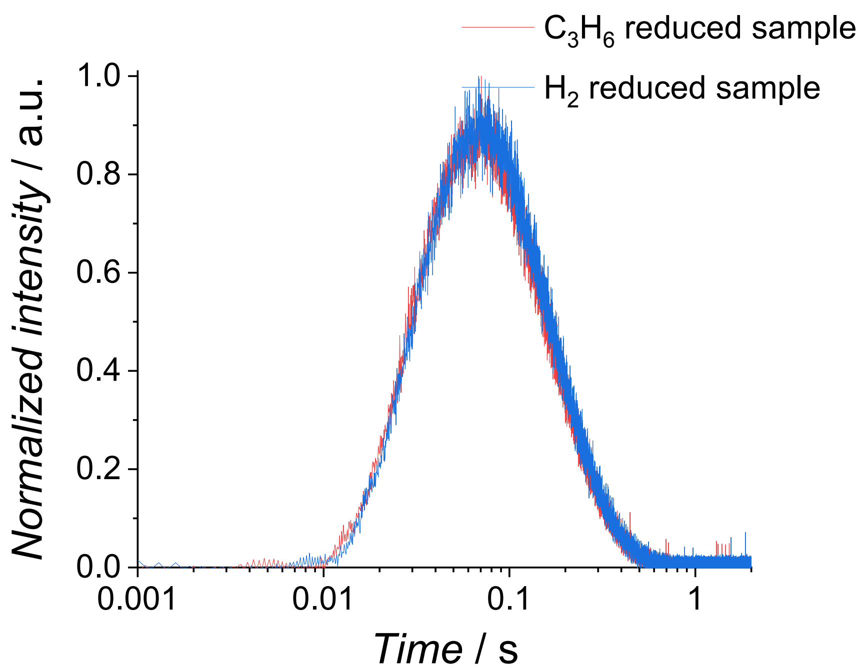

Figure S3. Flux of $^{15}N_2$ during $^{15}N_2O$ pulse over a C_3H_6 reduced and H_2 Rh/CLZ at 450 ˚C in TAP

Figure S4 shows the result of H_2 pulses over the pre-oxidized Rh/CLZ at 450 ˚C. For a very short period (pulse number 0–800, Figure S4A), 100 % H_2 conversion into H_2O was observed. The H_2 conversion and H_2O production decreased progressively during the remainder of the experiment (pulse number 800-end). The number of extracted oxygen atoms during the H_2 pulses experiment was shown in Figure S4B.

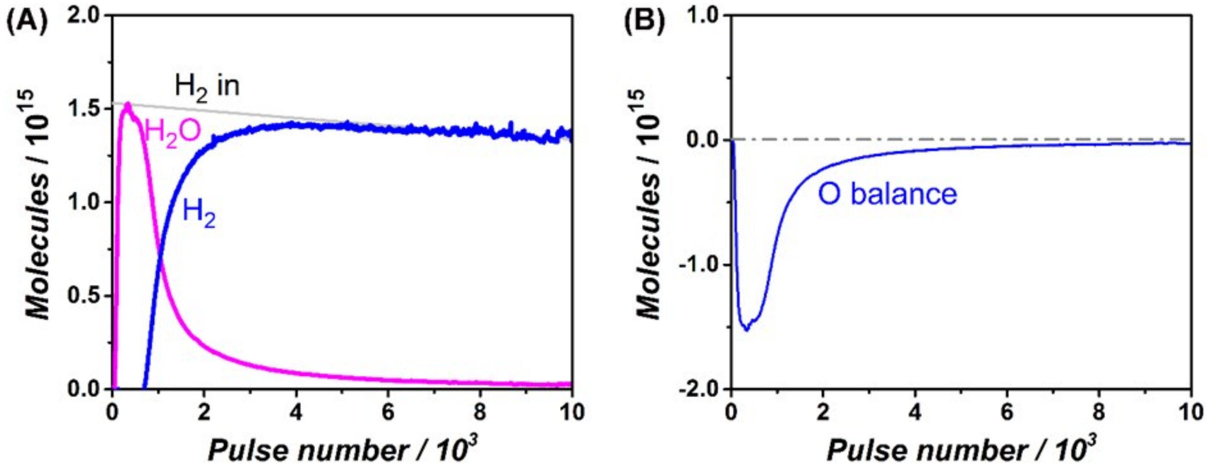

Figure S4. H_2 multi-pulse experiment over the pre-oxidized Rh/CLZ at 450 ˚C in TAP: (A) reactant and products and (B) oxygen balance *versus* pulse number

Figure S5 shows the result of C_3H_6 pulses over the pre-oxidized Rh/CLZ at 450 °C. Two types of C_3H_6 reactions were observed: C_3H_6 oxidation to CO_2 and H_2O and C_3H_6 oxidative cracking / dehydrogenation. The oxygen and carbon balances at each C_3H_6 pulse are displayed in Figure S5B. The formation of CO_2, H_2O, and CO caused partial reduction of ceria from Ce^{4+} to Ce^{3+}. Carbon deposition was calculated during both the complete oxidation and cracking reactions, as shown in Figure S5B.

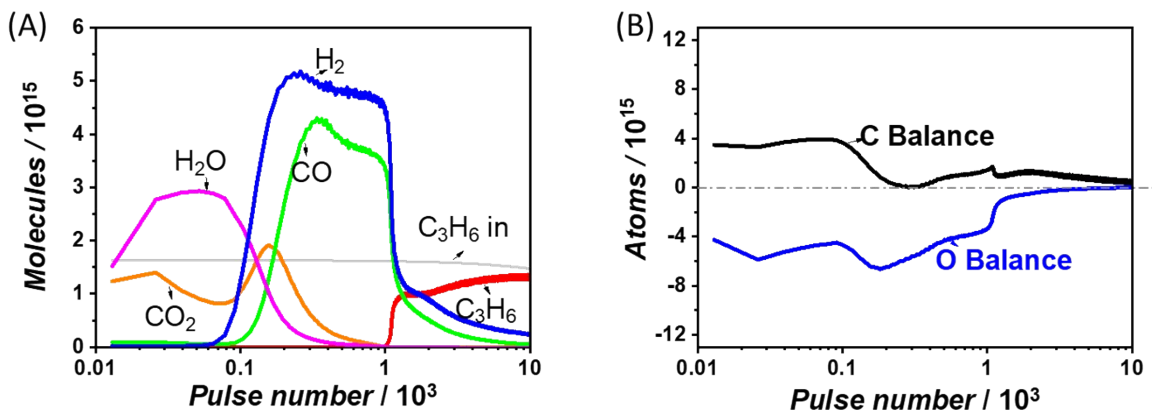

Figure S5. C_3H_6 multi-pulse experiment over the pre-oxidized Rh/CLZ at 450 ˚C in TAP: (A) reactant and products and (B) oxygen and carbon balance *versus* pulse number

References

1. Y. Wang, F. Kapteijn and M. Makkee, *Applied Catalysis B: Environmental*, 2018, **231**, 200-212.
2. Y. Wang and M. Makkee, *Applied Catalysis B: Environmental*, 2018, **223**, 125-133.