Supporting information

Oxide of lanthanoids can catalyze non-oxidative propane dehydrogenation: mechanistic concept and application potential of Eu_2O_3- or Gd_2O_3-based catalysts

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1 Experimental section

1.1 *Catalyst preparation*

Eu_2O_3 and Gd_2O_3 were synthesized according to Tyagi et. al.[1] Briefly, Europium(III) nitrate hydrate ($Eu(NO_3)_3 \cdot 6H_2O$) or Gadolinium(III) nitrate hydrate ($Gd(NO_3)_3 \cdot 6H_2O$) were used as oxidants and glycine (NH_2CH_2COOH) was used as fuel. Stoichiometric ratio of the oxidant to the fuel 1:1.0 was applied. In detail, to synthesize 1 g of product, $Eu(NO_3)_3 \cdot 6H_2O$ (2.54 g, 5.7 mmol) and glycine (0.43 g, 5.7 mmol) or $Gd(NO_3)_3 \cdot 6H_2O$ (3.09 g, 5.5 mmol) and glycine (0.41 g, 5.5 mmol), respectively, were dissolved in approximately 15 mL water in a 1 L beaker. The method is scalable up to 8 g, when using 3L beaker instead of 1L. The obtained solution was heated to 120 – 150 °C under stirring until yellow solid was formed. Auto-ignition occurs spontaneously after about 2 h tempering this solid above 250 °C. The chemical reaction for this preparation method using the stoichiometric ratio 1:1.0 of the oxidant to the fuel is given as follows.

$M(NO_3)_3 \cdot 6H_2O + NH_2CH_2COOH \rightarrow 0.5\ M_2O_3 + 2\ N_2 + 2\ CO_2 + 8.5\ H_2O + 1.5\ O_2$,

where M stands for Eu or Gd.

The white powder obtained after completing the combustion process was collected. It was either calcined at 550 °C for 3 h or directly used for preparation of supported materials. The latter were synthesized through an impregnation method with a colloidal solution of Rh nanoparticles (NPs). Metal loading was 0.001, 0.01 or 0.03 wt%. Detailed preparation method of metal NPs and catalysts synthesis are described in our previous study.[2]

1.2 *General catalyst characterization*

XRD powder patterns were recorded on a Panalytical X'Pert diffractometer equipped with a Xcelerator detector using automatic divergence slits and Cu kα1/α2 radiation (40 kV, 40 mA; λ = 0.15406 nm, 0.154443 nm). The measurements were performed with a 0.0167° step and 25 s of data collecting time per step. The crystallite size was calculated by applying the Scherrer equation using the integral breadth under the assumption of spherically shaped crystallites.

STEM micrographs were obtained on a probe aberration corrected JEM-ARM200F transmission electron microscope (Jeol Ltd.) at 200 kV. Sampling was done by dry deposition of the catalyst powder on a Cu grid (mesh 300) covered by a holey carbon film, which was then transferred into the microscope.

To investigate catalyst reducibility, temperature-programmed reduction (H_2-TPR) experiments were carried out in an in-house developed setup equipped with eight individually heated continuous-flow fixed-bed quartz reactors. Initially, each catalyst (100 mg) was heated in N_2 flow up to 550 °C (10 $K \cdot min^{-1}$) followed by feed air (10 $mL \cdot min^{-1}$) for 1 h and then cooling down to 40 °C. After flushing with Ar (10 $mL \cdot min^{-1}$, 15 min) the calcined samples were heated in a flow of H_2:Ar = 5:95 (10 $mL \cdot min^{-1}$) to 900 °C with a heating rate of 10 $K \cdot min^{-1}$. The H_2 consumption was quantified using the ratio of H_2/Ar being detected at the atomic mass units of 2 (H_2) and 40 (Ar).

The surface area analysis was carried out by the standard BET technique with N_2 physisorption at –196 °C using a Micromeritics ASAP 2020 setup.

1.3 Temporal analysis of products

Transient studies with O_2, D_2, C_3H_8 or C_3D_8 were performed in the temporal analysis of products (TAP) reactor.[3, 4] For each catalyst (Gd_2O_3 or Rh(0.001 wt%)/Gd_2O_3, 55 mg of catalyst (particle size: 315 – 710 μm) were sandwiched between two layers of quartz (particle size: 250 – 350 μm) in the isothermal zone of an in-house developed micro-reactor made of quartz (d_{in} = 6 mm, L = 40 mm). Prior to the pulse experiments, each catalyst was pretreated as follows: it was initially heated (10 $K \cdot min^{-1}$) in an O_2 flow (5 $mL \cdot min^{-1}$) from room temperature to 550 (for Rh(0.001 wt%)/Gd_2O_3) or 600 °C (for Gd_2O_3). Then, it was flushed at the same temperature in a flow of N_2 (5 mL·min^{-1}) for 5 min and finely treated in a flow of 60 vol% H_2 in N_2 (5 mL·min^{-1}) for 1 h. After completing this treatment, the catalyst was exposed to high vacuum of 10^{-5} Pa.

The number of oxygen vacancies was determined upon pulsing an O_2:Ar = 1:1 mixture over Gd_2O_3 or Rh(0.001 wt%)/Gd_2O_3 at 550 °C. The mixture was prepared using O_2 (Air Liquide, 4.5) and Ar (Linde Gas, 5.0) without additional purification. It was pulsed until no changes were observed in the intensity of O_2 transient responses during at least 30 pulses.

To check catalyst ability for hydrogen activation, a D_2:Ne = 1:1 mixture was pulsed over Gd_2O_3 or Rh(0.001 wt%)/Gd_2O_3 at 550 °C. D_2 (CK special gases limited, N2.8) and Ne (Air Liquide, 4.0) were used for preparing the mixture “as received”.

Mechanistic aspects of propane dehydrogenation over Gd_2O_3 or Rh(0.001 wt%)/Gd_2O_3 were derived from single pulse experiments at 550 °C with C_3H_8:Ar = 1:1 or C_3D_8:Ar = 1:1 mixtures prepared using C_3H_8 (Linde, 3.5), C_3D_8 (ISOTEC INC, 99 atom % D) and Ar (Air Liquide, 5.0).

A quadrupole mass spectrometer (HAL RC 301 Hiden Analytical) was applied for quantitative analysis of the feed components and the reaction products. The following AMUs (atomic mass units) were used for mass-spectrometric identification of different compounds: 52 (C_3D_8), 48 (C_3D_6), 46 (C_3D_6), 44 (C_3H_8), 42 (C_3H_8, C_3H_6), 41 (C_3H_8, C_3H_6), 32 (O_2), 34 (C_3D_8), 29 (C_3H_8), 4 (D_2), 3 (HD), 2 (H_2), 20 (Ne) and 40 (Ar). The concentration of the feed components and the reaction products was determined from the respective AMUs using standard fragmentation patterns and sensitivity factors derived from analyzing mixtures of known composition.

1.4 Catalytic tests

An in-house developed setup consisting of 15 continuous-flow fixed-bed quartz reactors operating at 1 bar in parallel was used for catalytic tests with a C_3H_8:N_2 = 2:3 feed. To determine the rate of propene formation, the degree of propane conversion was kept below 10% for ensuring pseudo differential reactor operation. Catalyst amount (0.05 g, fraction 315 – 710 µm) and total reaction feed flow (40 mL·min^{-1}) were used. Firstly, the catalysts were heated in N_2 flow up to 550 °C and calcined in air flow for 1 h. After flushing with N_2 for 15 min they were pretreated in H_2 flow (H_2:N_2 = 1:1) for 1 h and flushed with N_2 for 15 min again. Finally, the reaction feed was directed to a selected reactor, while other reactors were flushed with N_2. The latter procedure was repeated using different temperatures (T_{red} = 575, 600, 625, 650 °C) of reductive pretreated in H_2 flow (H_2 : N_2 = 1:1), while the temperature of 550 °C was set for calcination in air flow and for dehydrogenation reaction.

To construct selectivity-conversion relationship for propene and other side products including coke, catalytic tests were carried out at 550 °C at different contact times to reach different degrees of propane conversion. The total feed flow was varied between 6 and 60 mL·min^{-1}. The catalysts (0.4 g) were initially heated in N_2 flow up to 550 °C, calcined in air flow for 1 h, heated in N_2 flow up to 600 °C and then pretreated in a flow of H_2 (H_2:N_2 = 1:1) also for 1 h. After cooling down in N_2 flow to 550 °C the selected reactor was treated with reaction feed, while other reactors were flushed with N_2.

The feed components and the reaction products were quantified by an on-line gas chromatograph (Agilent 6890) equipped with flame ionization (FID) and thermal conductivity detectors (TCD).

Equations (1) – (5) were used to calculate the space time yield of propene formation STY(C_3H_6) expressed as kg(C_3H_6)·h^{-1}·m$^{-3}_{cat}$, the rate of propene formation r(C_3H_6) expressed as mmol(C_3H_6)·g$^{-1}_{cat}$ ·min^{-1}, propane conversion X(C_3H_8), selectivity to gas phase products (S_i) and coke S(coke), respectively.

$$\mathrm{STY}\ (\mathrm{C_3H_6})\ =\ \frac{\dot{\mathrm{n}}^{\mathrm{out}}_{\mathrm{C_3H_6}}\cdot M(C_3H_6)\cdot 60}{m_{cat}} \tag{1}$$

$$r(\mathrm{C_3H_6})\ =\frac{\mathrm{STY}(\mathrm{C_3H_6})\cdot 1000}{60\cdot M(\mathrm{C_3H_6})} \tag{2}$$

$$X(\mathrm{C_3H_8})\ =\ \frac{\dot{\mathrm{n}}^{\mathrm{in}}_{\mathrm{C_3H_8}}-\dot{\mathrm{n}}^{\mathrm{out}}_{\mathrm{C_3H_8}}}{\dot{\mathrm{n}}^{\mathrm{in}}_{\mathrm{C_3H_8}}} \tag{3}$$

$$S_{\mathrm{i}}\ =\ \frac{\nu_i}{3}\cdot\frac{\dot{\mathrm{n}}^{\mathrm{out}}_{\mathrm{i}}}{\dot{\mathrm{n}}^{\mathrm{in}}_{\mathrm{C_3H_8}}-\dot{\mathrm{n}}^{\mathrm{out}}_{\mathrm{C_3H_8}}} \tag{4}$$

$$S(\mathrm{coke})\ =1-\sum S_{\mathrm{i}} \tag{5}$$

Where $\dot{n}^{out}_{C_3H_6}$ is the molar flow rate of propene under standard conditions (mol·min^{-1}), $M(C_3H_6)$ is the molar mass of propene (42.02 g·mol^{-1}), m_{cat} is the catalyst amount (g), ρ_{cat} is the density of catalyst (kg·m^{-3}), $\dot{n}^{in}$and $\dot{n}^{out}$ stand for the molar flows of gas phase components at the reactor inlet and outlet respectively (mol·min^{-1}), ν_i is the number of carbon atoms in a product i. N_2 was used as internal standard for taking into account reaction-induced changes in the number of moles.

2 Tables

Table S1 Crystallite size, phase, surface area, pore volume and average pore diameter of Eu_2O_3 and Gd_2O_3 synthesized by different methods.

Catalyst	Crystallite size/ nm	phase	Surface area / $m^2 \cdot g^{-1}$	pore volume/ $cm^3 \cdot g^{-1}$	average pore diameter / nm
Eu_2O_3 [a)]	11	cubic	55	0.44	26
Eu_2O_3_C [b)]	10	cubic	23	0.04	4
Gd_2O_3[a)]	14	cubic	44	0.34	27
Gd_2O_3_C [b)]	11	cubic	10	0.02	5

[a)] M_2O_3 synthesized by glycine-method and calcined at 550 °C for 3 h. [b)] M_2O_3 synthesized by calcination of corresponding nitrate at 550 °C for 3 h.

Table S2 The space time yield of propene formation STY(C_3H_6) of various catalysts from literature and from the present study in the non-oxidative propane dehydrogenation to propene.

Name of the catalyst	X (C_3H_8) / –	T / °C	STY(C_3H_6) /$kg \cdot h^{-1} \cdot kg^{-1}$	Ref.
Ga/Cr-α-ZrP	0.28	550	0.41	[5]
Cr_2O_3/ZrO_2	0.61	550	0.13	[6]
Cr5/SBA-1	0.33	550	0.32	[7]
Cr_2O_3-K_2O/Al_2O_3	0.42	550	0.55	[2]
Cr_2O_3-K_2O/Al_2O_3	0.51	600	2.59	[2]
Cr_2O_3-K_2O/Al_2O_3	0.42	625	3.18	[2]
Ga_2O_3	0.33	600	0.35	[8]
Ga_2O_3/Al_2O_3	0.33	600	0.09	[9]
VO_x/Al_2O_3	0.32	600	0.86	[10]
VO_x/Al_2O_3	0.25	600	1.39	[11]
ZrO_2	0.28	550	1.58	[12]
ZrO_2	0.28	600	2.71	[12]
ZrO_2	0.28	625	3.15	[12]
ZnO/ZSM-5	0.92	600	0.33	[13]
ZnO/Al_2O_3	0.35	600	1.04	[14]
ZnO@NC/S-1	0.55	600	0.40	[15]
Eu_2O_3	0.23	550	0.46	This work
Gd_2O_3	0.23	550	0.56	This work

Table S3 Rh-loading in wt% determined by ICP, temperatures of maximal reduction ($T_{max}(H_2)$) and amounts of H_2 consumed ($n(H_2)$) in H_2-TPR experiments.

Name of the catalyst	wt%	$T_{max}(H_2)$ / °C	$n(H_2)$ / µmol·g^{-1}
Eu_2O_3	–	590	309.05
0.001 wt% Rh Eu_2O_3	n.d.[a)]	590	502.80
0.01 wt% Rh Eu_2O_3	0.01	450; 590	952.54
0.03 wt% Rh Eu_2O_3	0.03	430; 570	831.58
Gd_2O_3	–	580	197.77
0.001 wt% Rh Gd_2O_3	n.d.	590	386.95
0.01 wt% Rh Gd_2O_3	0.01	480; 595	748.95
0.03 wt% Rh Gd_2O_3	0.02	470; 600	838.19

[a)] n.d.= not definable

3 Figures

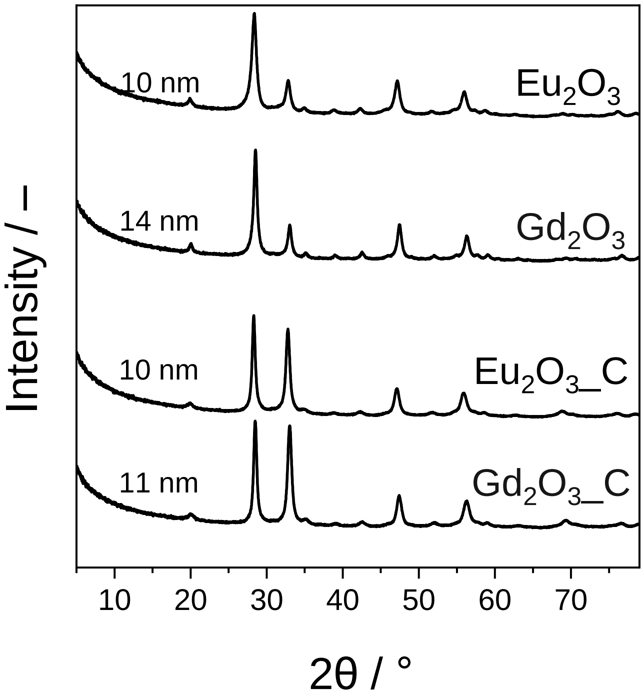

Figure S 1 XRD pattern of Eu_2O_3 or Gd_2O_3 and through calcination preparation method synthesized Eu_2O_3_C and Gd_2O_3_C.

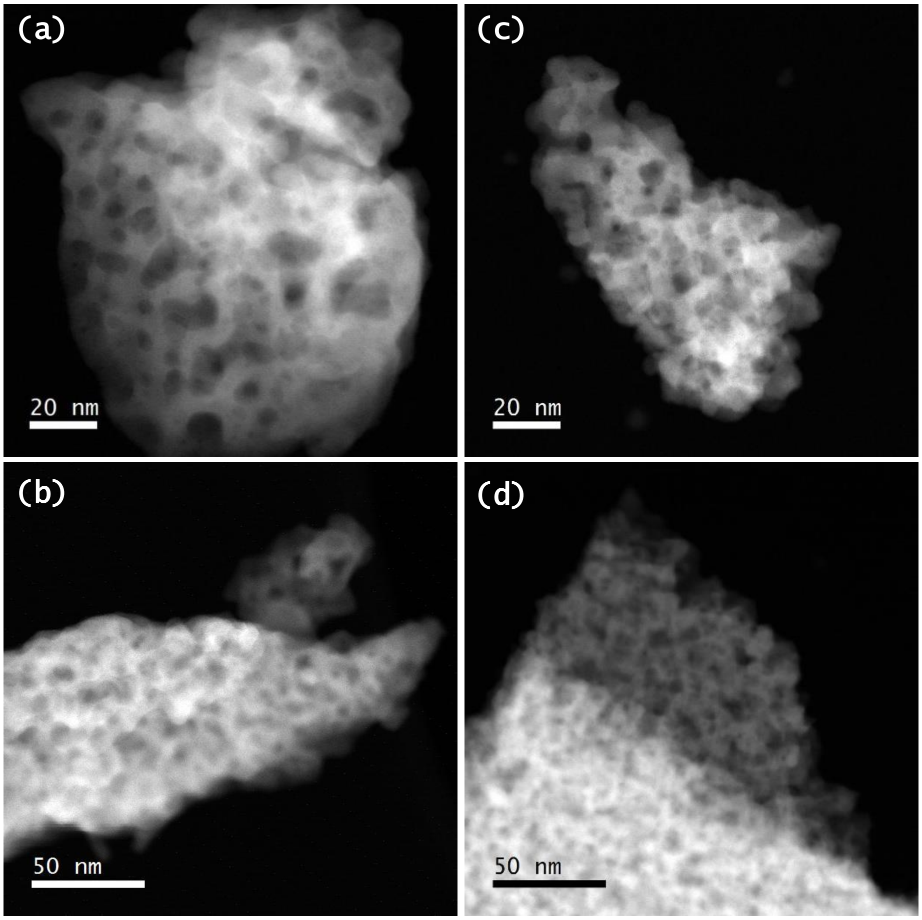

Figure S 2 HAADF-STEM images of Gd_2O_3_C (a, b) and Eu_2O_3_C (c, d) prepared through calcination of the corresponding nitrates at 550 °C for 3 h.

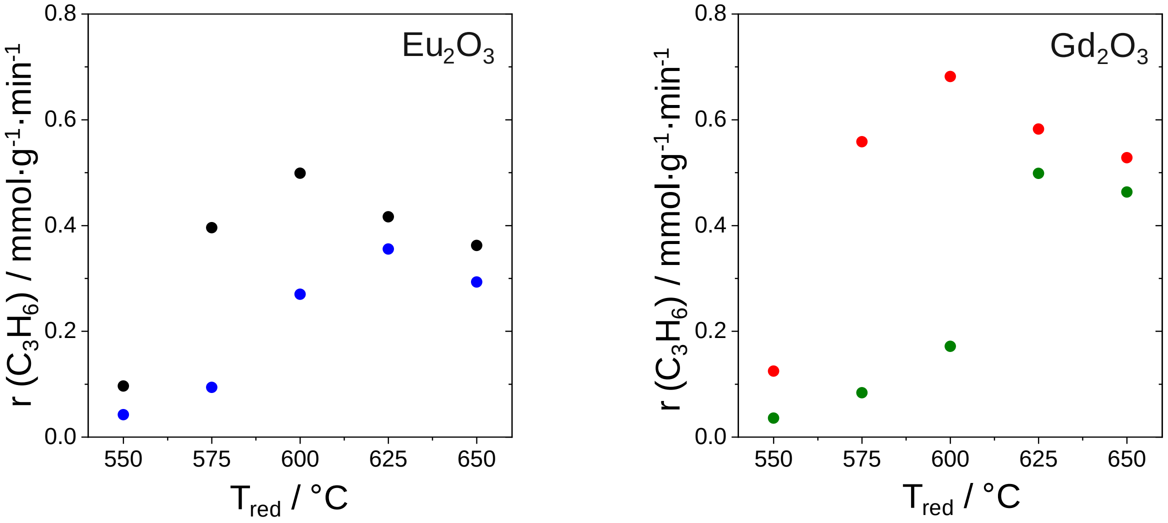

Figure S 3 The rate of propene formation over Eu_2O_3 (●), Gd_2O_3 (●), Eu_2O_3_C (●) and Gd_2O_3_C (●) versus temperature of reductive catalyst pretreatment with H_2 (T_{red}). Reaction condition: 550 °C, $X(C_3H_8) < 0.1$, $C_3H_8:N_2 = 2:3$ feed.

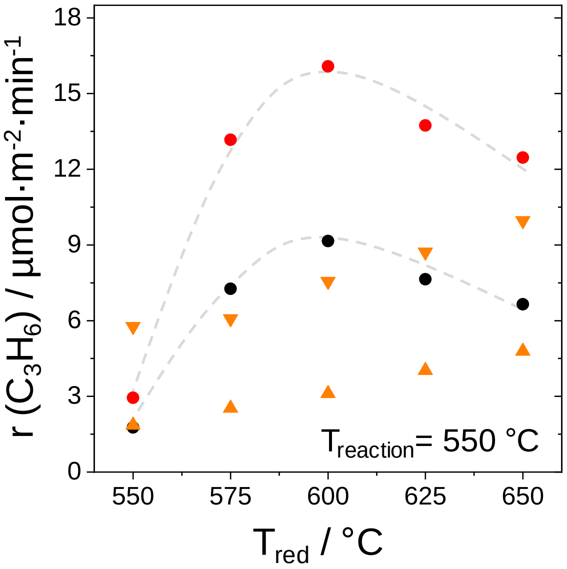

Figure S 4 The rate of propene formation calculated using specific surface area instead of the mass of the catalyst over bare Eu_2O_3 (●), Gd_2O_3 (●) and $LaZrO_x$ (▲) or $YZrO_x$ (▼) from previous study[2] versus temperature of reductive pretreatment with H_2 (T_{red}). Reaction condition: 550 °C, $X(C_3H_8) < 0.1$, $C_3H_8:N_2 = 2:3$ feed.

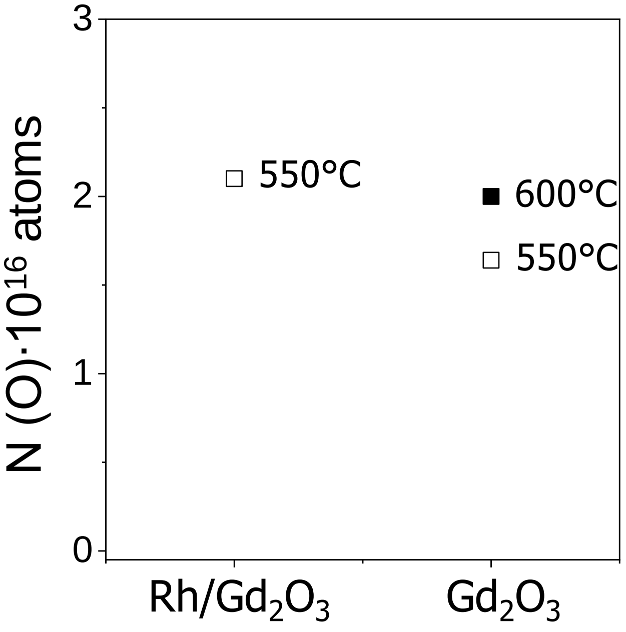

Figure S 5 Amount of consumed oxygen atoms over bare Gd_2O_3 after reductive pretreatment with H_2 at 550 °C or 600 °C and Gd_2O_3 supported with 0.001 wt% Rh (T_{red} = 550 °C).

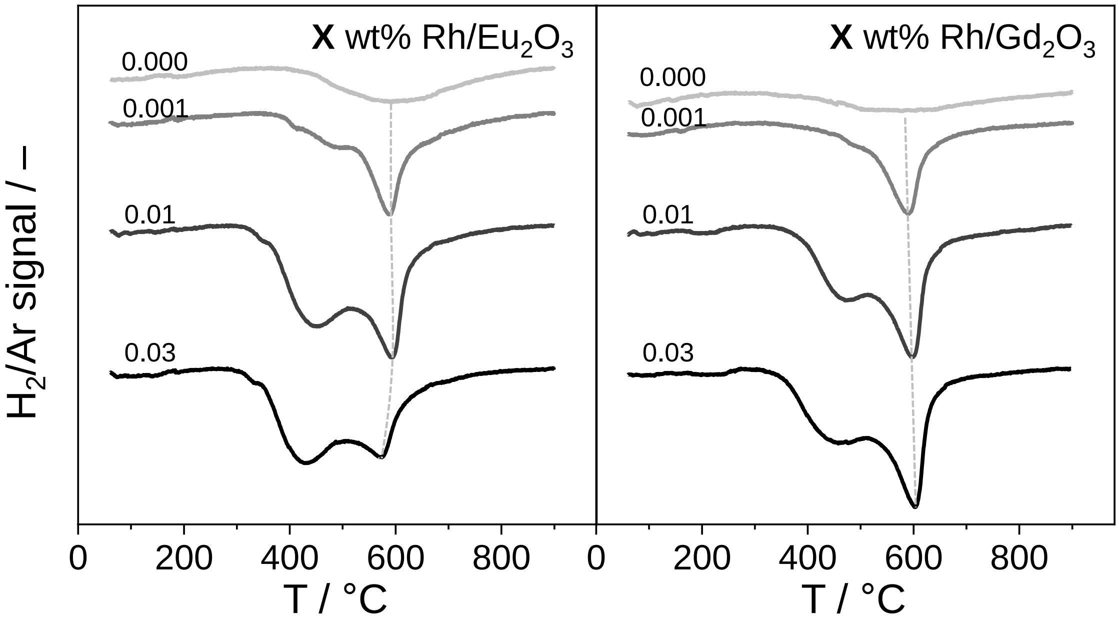

Figure S 6 H_2-TPR profiles of bare Eu_2O_3 or of bare Gd_2O_3, as well as their counterparts with 0.001 wt%, 0.01 wt% or 0.03 wt% Rh.

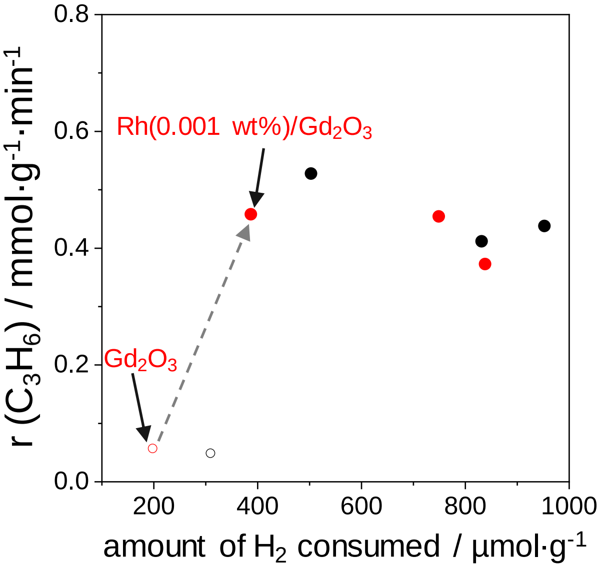

Figure S 7 The rate of propene formation versus the amount of H_2 consumed in H_2-TPR tests with bare Eu_2O_3 (○) and its counterparts with 0.001, 0.01 or 0.03 wt% Rh (●). The corresponding Gd_2O_3-based catalysts are represented by the red symbols. The content of Rh increases from the left-hand side to the right-hand side.

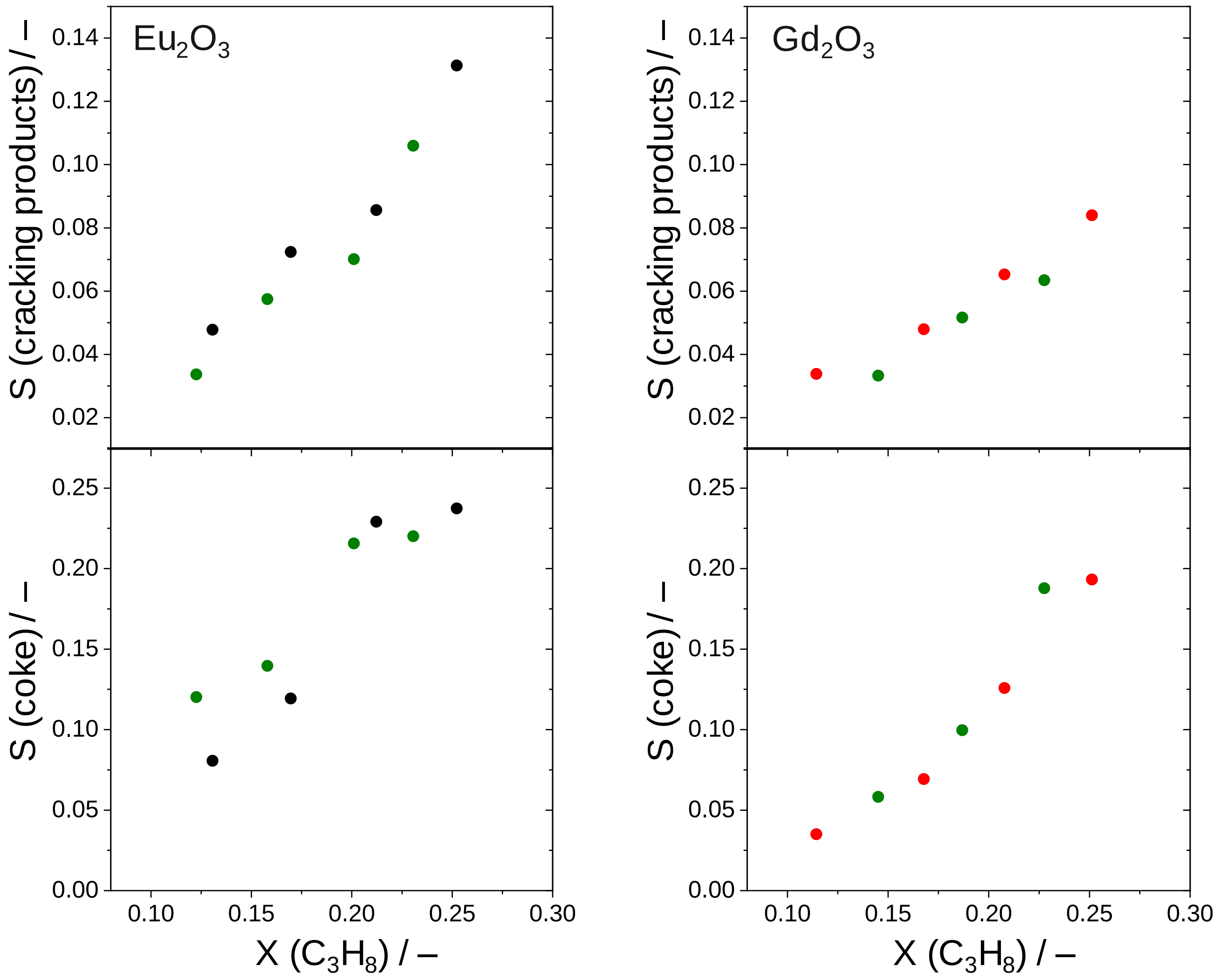

Figure S 8 Selectivity to cracking products or selectivity to coke conversion versus propane conversion over bare Eu_2O_3 (●) or Gd_2O_3 (●) and its counterparts with 0.001 wt% (●) Rh at 550 °C (T_{red} = 600 °C).

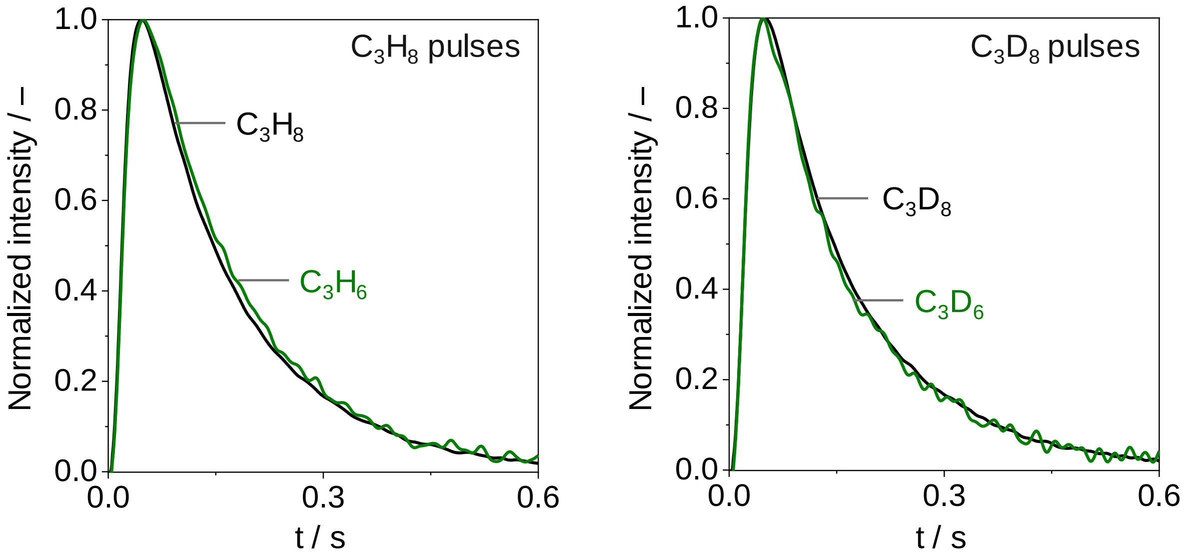

Figure S 9 The height-normalized responses of C_3H_8:C_3H_6 or C_3D_8:C_3D_6 recorded after pulsing of C_3H_8:Ar = 1:1 or C_3D_8:Ar = 1:1 mixtures over Rh(0.001 wt%)/Gd_2O_3 at 550 °C (T_{red} = 550 °C).

4 Reference

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