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**Electronic Supplementary Information (ESI)** 

### Cerium oxide as catalyst for the ketonization of aldehydes: Mechanistic insights and a convenient way to alkanes without consumption of external hydrogen

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Figure S10. Specification of the n-Hexane contribution to the "Others" product group in Table 2. "Total Others" represent the values listed in Table 2 and are the sum of the other two columns, "*n*-Hexane" and "Total Others – *n*-Hexane".

Figure S11. Distribution of alkanes produced in the cascade reaction of heptanal to tridecane.

Scheme S1. McLafferty rearrangement of 7-tridecanone to produce 2-octanone.

Deduction of the equation for the rate determining step of the ketonization of aldehydes over cerium oxide

#### Synthesis of 7-pentadecanone

Heptanoic acid (11.5 mmol, 1.82 g) and nonanoic acid (11.5 mmol, 1.5 g) were passed over 0.50 g of m-ZrO<sub>2</sub> at 450 °C, with a rate of 0.147 mL·min<sup>-1</sup> together with a gas flow of 144 mL·min<sup>-1</sup> at ambient pressure in a fixed-bed, continuous-flow reactor. The liquid product was condensed with an ice bath and analyzed offline by GC and GC-MS. Heptanoic acid and nonanoic acid conversion were 69 and 62%, respectively and the yield of 7-pentadecanona of 33%.

MS: m/z (%) = 226 (2) [M<sup>+</sup>], 43 (100), 71 (81), 58 (69), 57 (67), 113 (67).

## Hydrogenation of the carbon-carbon double bond of the aldol condensation product to the saturated aldehyde.

2-Pentyl-2-nonenal (0.1 g, 0.5 mmol) in pentane (0.65 g) was hydrogenated for 5 min at room temperature in a 2 mL-Pyrex glass reactor equipped with a magnetic stirring bar, using 5 mg of 5% palladium on carbon under  $5 \cdot 10^5$  Pa hydrogen pressure. The mixture was centrifuged to remove the catalyst. The supernatant was separated and the organic solvent evaporated under reduced pressure to characterize the compound by GC-MS and NMR.

<sup>1</sup>H NMR 2-pentyl-nonanal:<sup>1</sup> (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.56 (1H, d, *J* = 3.2 Hz), 2.28-2-20 (1H, m), 1.66-1.59 (4H, m), 1.37-1.21 (16H, m), 0.90-0.87 (6H, m). - <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 205.7 (CH), 52.0 (CH), 31.9 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 27.1 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>). – MS: m/z (%) = 212 (0.4) [M<sup>+</sup>], 57 (100), 96 (80), 41 (59), 43 (57), 81 (56).

#### Hydrogenation of the aldol condensation product by NaBH<sub>4</sub>.<sup>2</sup>

Into on oven-dried, 5-mL flask equipped with a magnetic stirring bar 0.036 g (1 mmol) of sodium borohydride was introduced, and then 2 mL of methanol. To this slurry, 0.1 g (0.5 mmol) of 2-pentyl-2-nonenal was added. The reaction was carried out for 5 min under vigorous stirring. Water (1.5 mL) was added dropwise and cautiously and then, the mixture was filtered and poured into 2 mL of diethyl ether. The ether layer was separated, washed with sodium chloride solution, dried over magnesium sulfate and the solvent evaporated under reduced pressure. The product obtained after evaporation was characterized by GC-MS and NMR.

<sup>1</sup>H NMR 2-pentyl-2-nonen-1-ol: (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 5.42 (1H, t, *J* = 7.2 Hz), 4.04 (2H, s), 2.12-2.01 (4H, m), 1.42-1-30 (14H, m), 0.93-0.88 (6H, m). - <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.1 (C), 127.1 (CH), 67.3 (CH<sub>2</sub>), 32.0 (CH<sub>2</sub>), 31.8 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 28.0 (CH<sub>2</sub>), 27.4 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>). – MS: m/z (%) = 212 (27) [M<sup>+</sup>], 71 (100), 55 (85), 57 (84), 81 (84), 69 (71).

#### Autoxidation of the aldol condensation product.<sup>3</sup>

Oxidation of 2-pentyl-2-nonenal (0.05 g, 0.2 mmol) in methanol (1 mL) was carried out in a 2-mL flask under atmospheric pressure with a continuous flow of oxygen at room temperature for 12 h. The product obtained after evaporation was characterized by GC-MS and NMR.

<sup>1</sup>H NMR 2-pentyl-2-nonenoic acid (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.91 (1H, t, *J* = 7.5 Hz), 2.40-2-18 (4H, m), 1.46-1-31 (14H, m), 0.93-0.88 (6H, m). - <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.8 (C), 145.5 (CH), 131.7 (C), 31.8 (CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>). – MS: m/z (%) = 226 (17) [M<sup>+</sup>], 141 (100), 143 (69), 55 (65), 41 (64), 169 (56).

Figure S1. HRTEM images of nanocrystals of  $CeO_2$  for selected samples: a)  $CeO_2$ -5nm, b) and c)  $CeO_2$ -6nm, d) and e)  $CeO_2$ -11nm.





Figure S2. Weight loss for different CeO<sub>2</sub> materials in the temperature range between 400 and 500 °C measured by thermogravimetric analysis (TG) in air, ordered by a) crystal size and b) BET surface area.

Figure S3. X-ray diffraction patterns of fresh CeO2-11nm catalysts and the used ones in presence of water (700 min) and absence of water (400 min).



Figure S4. Apparent activation energy for the ketonization of heptanal over zirconium oxide. The apparent activation energy for the second step, i.e. for the ketonic decarboxylation of heptanoic acid was also determined experimentally. The different values of heat of formation for heptanal<sup>4</sup> and heptanoic acid<sup>5</sup> were taken from literature and for 7-tridecanone from the Cheméo database (<u>https://www.chemeo.com/cid/56-631-9/7-Tridecanone</u>; calculated by the Joback method<sup>6</sup>)



Figure S5. Napierian logarithm of the initial rate of the ketone formation from heptanal in the presence of CeO<sub>2</sub> (co-feeding water) over the inverse temperature for the calculation of the experimental activation energy. Reaction conditions: heptanal : water molar ratio 1 : 1; heptanal (5 mL, 0.147 mL·min<sup>-1</sup>, 1.5·10<sup>4</sup> Pa partial pressure), water (0.638 mL, 0.019 mL·min<sup>-1</sup>, 1.5·10<sup>4</sup> Pa partial pressure), 118 mL·min<sup>-1</sup> N<sub>2</sub>, 25 mg CeO<sub>2</sub>-11nm; 390, 400, 410, 420, 430, 440 and 450 °C.



Figure S6. Napierian logarithm of the initial rate of the ketone formation from heptanoic acid in the presence of  $CeO_2$  (without co-feeding water) over the inverse temperature for the calculation of the experimental activation energy. Reaction conditions: heptanoic acid (5 mL, 0.147 mL·min<sup>-1</sup>, 1.5·10<sup>4</sup> Pa partial pressure), 144 mL·min<sup>-1</sup> N<sub>2</sub>, 25 mg CeO<sub>2</sub>-11nm; 390, 400, 410, 420, 430, 440 and 450 °C.



Figure S7. Napierian logarithm of the initial rate of the ketone formation from heptanoic acid in the presence of  $CeO_2$  (co-feeding water) over the inverse temperature for the calculation of the experimental activation energy. Reaction conditions: heptanoic acid : water molar ratio 1 : 1; heptanoic acid (5 mL, 0.147 mL·min<sup>-1</sup>, 1.5·10<sup>4</sup> Pa partial pressure), water (0.638 mL, 0.019 mL·min<sup>-1</sup>, 1.5·10<sup>4</sup> Pa partial pressure), 118 mL·min<sup>-1</sup> N<sub>2</sub>, 25 mg CeO<sub>2</sub>-11nm; 390, 400, 410, 420, 430, 440 and 450 °C.



Figure S8. Comparison between experimental and calculated initial reaction rate in heptanal ketonization catalyzed by  $CeO_2$ -6nm in presence of water ( $1.5 \cdot 10^4$  Pa) as a function of heptanal partial pressure (1.5, 3.0, 4.5 and  $6.0 \cdot 10^4$  Pa). The calculated graph was obtained by means of the Origin program (Non-linear fit, Levenberg-Marquardt iteration algorithm, coefficient of determination R2 = 0.998). Reaction conditions: see Figure 6.



Figure S9. Comparison between experimental and calculated initial reaction rate in heptanal ketonization catalyzed by CeO<sub>2</sub>-6nm at heptanal partial pressure of  $1.5 \cdot 10^4$  Pa, in the presence of different amounts of water (0.8, 1.5, 3.0 and  $4.5 \cdot 10^4$  Pa). The calculated graph was obtained by means of the Origin program (Non-linear fit, Levenberg-Marquardt iteration algorithm, coefficient of determination R<sup>2</sup> = 0.998). Reaction conditions: see Figure 7.



Figure S10. Specification of the *n*-Hexane contribution to the "Others" product group in Table 2. "Total Others" represent the values listed in Table 2 and are the sum of the other two columns, "*n*-Hexane" and "Total Others – *n*-Hexane".



Figure S11. Distribution of alkanes produced in the cascade reaction of heptanal to tridecane (except for the main product tridecane). It can be assumed that the  $C_{14}$  derivate (green color) is produced from the aldol condensation intermediate, octane (light red color) from 2-octanone and heptane (light blue color) from non-converted heptanal substrate.



Scheme S1. McLafferty rearrangement of 7-tridecanone to produce 2-octanone.

► OH С -> 7-tridecanone ▶ \_ 2-octanone

# Deduction of the equation for the rate determining step of the ketonization of aldehydes over cerium oxide



 $S_1 - OC(R)O - S_2$ 

Single steps for the dehydrogenation of an aldehyde into the corresponding carboxylic acid on the  $CeO_2$  surface.

Adsorptions:

$$\begin{array}{cccc} H_2O + S_1 & \stackrel{K_1}{\rightarrow} & S_1 - OH_2 & \stackrel{very \, fast}{-H^+} & S_1 - OH & & & & & & & \\ RCHO + S_2 & \stackrel{K_2}{\rightarrow} & S_2 - OC(HR) & & & & & & & & & \\ \end{array}$$
 Water adsorption and proton transfer to the surface (S1)

Adduct formation

$$S_1 - OH + S_2 - OC(HR) \xrightarrow{k_3} S_1 - OC(HR)O(H) - S_2$$
 Adduct formation (S3)

Hydride transfer and hydrogen desorption

$$S_1 - OC(HR)O(H) - S_2 \xrightarrow{k_4} S_1 - OC(R)O - S_2 + H_2$$
  
Hydride transfer to the surface and recombination with a proton (S4)

Carboxylic acid desorption

$$S_1 - OC(R)O - S_2 \xrightarrow{K_5} RCOOH + S_1 + S_2$$
  
Carboxylic acid desorption

(S5)

Blocking of centers by water

$$S_1 - OH + H_2 O \xrightarrow{K_6} S_1 - OH - OH_2$$
 Water adsorption to  $S_1 - OH$  (S6)

 $S_2 + H_2 O \xrightarrow{K_7} S_2 - OH_2$  Water adsorption to  $S_2$  (S7)

It is assumed that the hydride shift from the aldehyde (followed by a quick recombination with a surface proton to form molecular hydrogen) coordinated to a surface hydroxy group is the rate limiting step and so from Eq. S4 the following rate equation can be deduced:

$$-r_{\rm RCHO} = k_4 [S_1 - OC(HR)O(H) - S_2]$$
(S8)

The hydride shift from the aldehyde depends on the concentration of  $S_1$ -OH and  $S_2$ -OC(HR) from the equation (S3), therefore, equation (S8) can be written as:

$$-r_{\rm RCHO} = k_3 k_4 [S_2 - OC(HR)] [S_1 - OH]$$
(S9)

Equilibrium equations:

From Eq. S1 follows:

$$K_1 = \frac{[S_1 - OH]}{[H_2 O][S_1]}$$

 $\Rightarrow$ 

$$[S_1 - 0H] = K_1[H_20][S_1]$$
(S10)

From Eq. S2 follows:

$$K_2 = \frac{[S_2 - OC(HR)]}{[RCHO][S_2]}$$

 $\Rightarrow$ 

$$[S_2 - OC(HR)] = K_2[RCHO][S_2]$$
(S11)

From Eq. S5 follows:

$$K_{5} = \frac{[\text{RCOOH}][S_{1}][S_{2}]}{[S_{1} - \text{OC}(\text{R})\text{O} - S_{2}]}$$

$$[S_1 - OC(R)O - S_2] = \frac{[RCOOH][S_1][S_2]}{K_5}$$

 $\Rightarrow$ 

(S12)

From Eq. S6 follows:

$$K_{6} = \frac{[S_{1} - OH - OH_{2}]}{[S_{1} - OH][H_{2}O]}$$
$$[S_{1} - OH - OH_{2}] = K_{6}[S_{1} - OH][H_{2}O]$$
$$[S_{1} - OH - OH_{2}] = K_{1}K_{6}[H_{2}O]^{2}[S_{1}]$$
(S13)

From Eq. S7 follows:

$$K_7 = \frac{[S_2 - OH_2]}{[H_2 O][S_2]}$$

 $\Rightarrow$ 

 $\Rightarrow$ 

$$[S_2 - OH_2] = K_7[H_2O][S_2]$$
(S14)

Substitution of Eq. S10 and S11 in the velocity Eq. S9:

$$-r_{\rm RCHO} = k_3 k_4 K_1 K_2 [\rm RCHO] [\rm H_2O] [\rm S_1] [\rm S_2]$$
(S15)

Balance of all active sites for  $[S_1]$ :

$$[S_1]_0 = [S_1] + [S_1 - OH] + [S_1 - OC(R)O - S_2] + [S_1 - OH - OH_2]$$
(S16)

Substitution of centers occupied by different molecules in the equation of the balance of sites S16 by the adsorption/desorption equilibria, i.e. Eq. S10, S12 and S13 results in S17:

$$[S_1]_0 = [S_1] + K_1[H_20][S_1] + \frac{[\text{RCOOH}][S_1][S_2]}{K_5[H_20]} + K_1K_6[H_20]^2[S_1]$$
(S17)

$$[S_1]_0 = [S_1] \left[ 1 + K_1[H_2O] + \frac{[\text{RCOOH}][S_2]}{K_5[H_2O]} + K_1K_6[H_2O]^2 \right]$$
(S18)

$$[S_{1}] = \frac{[S_{1}]_{0}}{1 + K_{1}[H_{2}0] + \frac{[\text{RCOOH}][S_{2}]}{K_{5}[H_{2}0]} + K_{1}K_{6}[H_{2}0]^{2}}$$
(S19)

At low conversion product concentration of the carboxylic acid [RCOOH] is zero. Then, Eq. S19 can be transformed into Eq. S20.

$$[S_1] = \frac{[S_1]_0}{1 + K_1[H_2O] + K_1K_6[H_2O]^2}$$

(S20)

Balance of all active sites for  $[S_2]$ :

$$[S_2]_0 = [S_2] + [S_2 - OC(HR)] + [S_1 - OC(R)O - S_2] + [S_2 - OH_2]$$
(S21)

Substitution of centers occupied by different molecules in the equation of the balance of sites S21 by the adsorption/desorption equilibria, i.e. Eq. S11, S12 and S14 results in S22:

$$[S_2]_0 = [S_2] + K_2[RCHO][S_2] + \frac{[RCOOH][S_1][S_2]}{K_5} + K_7[H_2O][S_2]$$
(S22)

$$[S_2]_0 = [S_2] \left[ 1 + K_2 [RCH0] + \frac{[RCO0H][S_1]}{K_5} + K_7 [H_20] \right]$$
(S23)

$$[S_{2}] = \frac{[S_{2}]_{0}}{1 + K_{2}[\text{RCHO}] + \frac{[\text{RCOOH}][S_{1}]}{K_{5}} + K_{7}[\text{H}_{2}\text{O}]}$$
(S24)

At low conversion product concentration of the carboxylic acid [RCOOH] is zero. Then, Eq. S24 can be transformed into Eq. S25.

$$[S_2] = \frac{[S_2]_0}{1 + K_2[\text{RCHO}] + K_7[\text{H}_2\text{O}]}$$

(S25)

Substitution of  $\left[S_{1}\right]$  and  $\left[S_{2}\right]$  from Eq. S20 and Eq. S25 in Eq. S15:

$$-r_{\rm RCHO} = k_3 k_4 K_1 K_2 [\rm RCHO] [\rm H_2O] [\rm S_1] [\rm S_2]$$

$$-r_{\rm RCHO} = \frac{k_3 k_4 K_1 K_2 [\rm RCHO] [\rm H_2O] [S_1]_0 [S_2]_0}{(1 + K_1 [\rm H_2O] + K_1 K_6 [\rm H_2O]^2)(1 + K_2 [\rm RCHO] + K_7 [\rm H_2O])}$$

(S26)

$$-r_{\rm RCHO} = \frac{a[\rm RCHO][\rm H_2O]}{(1 + b[\rm H_2O] + c[\rm H_2O]^2)(1 + d[\rm RCHO] + e[\rm H_2O])}$$
(S27)

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(S15)