## Electronic Supporting Information

# Highly efficient Bi-promoted $ZrO_2$-based materials for non-oxidative propane dehydrogenation

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### *Catalyst preparation*

$ZrO(NO_3)_2 \cdot xH_2O$ (99%, Sigma Aldrich), $Bi(NO_3)_3 \cdot 5H_2O$ (99%, Fluka), $NH_3$ (25% aqueous solution, Roth), $HNO_3$ (65%, VWR), $LaZrO_x$ ($ZrO_2$ doped with 10 wt.% $La_2O_3$, MelChemicals), $SiO_2$ (Aldrich) were used as starting materials.

*a) Bulk catalysts*

For the synthesis of bulk $ZrBiO_x$ catalysts, the required amounts of $ZrO(NO_3)_2 \cdot xH_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in deionized water to obtain a solution with a total cation concentration of 0.5 M ($Zr^{4+}$:$Bi^{3+}$ molar ratio was 98:2, 95:5, and 9:1). An aqueous solution of ammonia was then added dropwise under stirring until pH 9. The precipitate formed was aged overnight, filtered and washed several times with deionized water. The solid was dried at 110°C overnight and calcined at 550°C for 4 hours. The samples were denoted as $Zr_{98}Bi_2O_x$, $Zr_{95}Bi_5O_x$, and $Zr_{90}Bi_{10}O_x$, with the subscript numbers standing for molar fraction of cations. Bare $ZrO_2$ was prepared according to the same procedure.

*b) Supported catalysts*

Supported $Bi_2O_3/LaZrO_x$ and $Bi_2O_3/SiO_2$ catalysts were prepared by impregnation of commercial supports with a required amount of a solution of bismuth nitrate. Firstly, 10 wt.% $HNO_3$ aqueous solution was prepared by dilution of 65 wt.% $HNO_3$ with water. Hereafter, bismuth nitrate was dissolved in a certain amount of obtain solution which can be fully adsorbed by the used amount of supports (about 0.9 g of liquid per 1 g of $LaZrO_x$, 2.5 g of liquid per 1 g of $SiO_2$). The supports were then impregnated with the obtained solutions. The samples were dried at 110°C overnight and calcined at 550°C for 4 hours. The samples were denoted as $0.1Bi_2O_3/LaZrO_x$, $0.2Bi_2O_3/LaZrO_x$, $0.5Bi_2O_3/LaZrO_x$, $0.7Bi_2O_3/LaZrO_x$, $1Bi_2O_3/LaZrO_x$, $5Bi_2O_3/LaZrO_x$, $0.5Bi_2O_3/SiO_2$, with the numbers standing for the nominal weight concentration (in %) of $Bi_2O_3$.

### *Catalyst characterisation*

*ICP analysis* of selected samples was performed on a Varian 715-ES ICP-Emission-Spectrometer to determine actual content of Bi. Approximately 10 mg of the sample were mixed with 8 ml of aqua regia and 2 ml of hydrofluoric acid. The digestion was performed in a microwave-assisted sample preparation system "Multiwave PRO" from Anton Paar at ~ 220°C and ~ 50 bar pressure. The digested solution was filled up to 100 ml with deionized water and measured with ICP-OES. The data analysis was performed on the Varian 715-ES software "ICP Expert".

*XPS analysis* were performed for selected samples ($Zr_{95}Bi_5O_x$ and $0.5Bi_2O_3/LaZrO_x$) with a ESCALAB220iXL (ThermoFisher Scientific) with monochromatic Al Kα radiation (1486.6 eV). For charge compensation low-energetic electrons of 10 eV were used (flood gun). The electron binding energy was referenced to adventitious carbon at 284.8 eV according to the advice of NIST. The peaks were fitted after subtracting a Shirley background with Gaussian-Lorentzian curves. The elemental composition of the near-surface region was determined from the peak area dividing by the elemental-specific Scofield factor and the spectrometer-specific transmission function.

*X-ray diffraction (XRD) measurements* were performed on a Theta/Theta diffractometer X'Pert Pro (Panalytical) with CuKα radiation ($\lambda = 1.5418$ Å, 40 kV, 40 mA) and an X'Celerator RTMS detector. Phase composition of the samples was determined using the program suite WinXPOW (Stoe & Cie) with inclusion of the powder diffraction file PDF2 of the international center for diffraction data.

Specific surface area ($S_{BET}$) of the samples was determined from *nitrogen physisorption experiments* at 77 K using a Belsorp mini II setup (Bel Japan). Desorption isotherms were evaluated according to the BET method.

For the investigating reducibility of selected samples *temperature-programmed reduction (TPR) experiments* were performed by heating the samples (100 or 200 mg for each sample) in a flow of 5 vol.% $H_2$ in Ar (10 $ml \cdot min^{-1}$) up to 900°C with a heating rate of 10 $K \cdot min^{-1}$. The $H_2$ consumption was detected using on-line mass spectrometer (Pfeiffer Vacuum OmniStar GSD 320) using following atomic mass units (AMUs): 2 ($H_2$) and 40 (Ar). Prior to the experiment, all samples were *in situ* calcined in air flow (10 $ml \cdot min^{-1}$) at 550°C for 1 hour, cooled down in air flow to room temperature and purged with Ar flow (10 $ml \cdot min^{-1}$) at room temperature for 15 min.

### ***Catalytic tests***

All catalytic tests were performed at 1 bar in an in-house developed setup consisting of 15 continuous-flow fixed-bed reactors made of quartz. To determine the rate of propene formation, the tests were performed at a degree of propane conversion below 10%. In this case, coke formation is insignificant, and the catalytic reactor can be considered as differential. The catalysts (m=40 mg) were heated in an $N_2$ flow up to 550°C followed by feeding air for 1 hour and purging with $N_2$ for 15 min. After the above treatment, the catalysts were either directly tested for their PDH activity at 550°C (40 vol.% $C_3H_8$ in $N_2$ reaction mixture, total flow of 20 $ml \cdot min^{-1}$) or reduced in a flow of 57 vol.% $H_2$ in $N_2$ at different temperatures (550, 575, 600, 625, 650°C) and then tested for their PDH activity at 550°C. The whole series of tests was performed with the same sample for each catalyst. First oxidized catalysts were tested. After the corresponding PDH test at 550°C was completed, the catalysts were reoxidized at 550°C and then reduced at 550°C followed by performing PDH at 550°C and reoxidation at the same temperature. The order of reduction temperature in the series was 550, 575, 600, 625, and 650°C. Equation (S1) was used to calculate the rate of propene formation ($r(C_3H_6)$).

$$r(C_3H_8) = \frac{F_{feed} \cdot x(C_3H_6)}{60 \cdot V_m \cdot m_{cat}} \tag{S1}$$

Where $F_{feed}$ is a volumetric feed flow rate ($mL \cdot h^{-1}$), $x(C_3H_6)$ is a molar fraction of $C_3H_6$, $V_m$ is molar volume (22400 $mL \cdot mol^{-1}$), mcat is catalyst amount (g).

To determine an overall scheme of product formation in the course of propane dehydrogenation, additional tests were performed at different contact times to achieve different degrees of propane conversion. The contact time was modified by varying total flow (6, 10, 15, 20, 25, 30, 35, and 40 mL/min) of the reaction feed and keeping catalyst amount constant (0.3 g). The tests were carried out at 550°C and at 600°C with the catalysts reduced at 550°C or 600°C in an $H_2$ flow (57 vol.% $H_2$ in $N_2$) for 1 hour.

The propane conversion and the selectivity to gas-phase products were calculated according to equations (S2) and (S3) respectively. Coke selectivity was determined from the difference between unity and the sum of selectivity of all determined gas-phase products (Eq. S4).

$$X(C_3H_8) = \frac{\dot{n}^{in}_{C3H8} - \dot{n}^{out}_{C3H8}}{\dot{n}^{in}_{C3H8}} \tag{S2}$$

$$S(i) = \frac{\beta_i}{\beta_{C3H8}} \times \frac{\dot{n}^{out}_{i}}{\dot{n}^{in}_{C3H8} - \dot{n}^{out}_{C3H8}} \tag{S3}$$

$$S(coke) = 1 - \sum_i S(i) \tag{S4}$$

Where $\dot{n}$ with superscripts “in” and “out” stands for molar flow of gas-phase components at the reactor inlet and outlet respectively, S(i) is the selectivity to a gas-phase product i, and β is the number of C atoms in the product i or in $C_3H_8$. Reaction-induced changes in gas volume were accounted for by using $N_2$ as an internal standard.

To check durability of our most promising catalysts, we performed a series of 10 PDH/regeneration cycles at 550 and 600°C using total flow of $C_3H_8$-$N_2$ mixture of 10 and 30 ml/min, respectively. In these experiments, the amount of each catalyst sample was 300 mg. Before the first PDH stage the catalysts were calcined in a flow of air at 550°C for 30 min, flushed in $N_2$ flow for 15 min and reduced in an $H_2$ flow (57 vol.% $H_2$ in $N_2$) for 1 hour. The PDH stages continued for 1 hour. The regeneration stages consisted of calcination step (air flow, 30 min), flushing step ($N_2$ flow, 15 min) and reduction step ($H_2$ flow, 1 hour). The PDH and regeneration stages were separated by purging with $N_2$ for 15 min. The regeneration stage was performed at the PDH temperature. space time yield of propene was calculated according to equation (S5).

$$STY(C_3H_6) = \frac{\dot{n}_{C_3H_6}^{out} \times M(C_3H_6) \times \rho_{cat} \times 1000 \times 60}{V_m \times m_{cat}} \tag{S5}$$

Where $M(C_3H_6)$ is molar weight of propene (42 g·mol-1), $\rho_{cat}$ is catalyst density (g·mL$^{-1}$).

The feed components and the reaction products were analyzed by an on-line gas chromatograph (Agilent 7890) equipped with PLOT/Q (for $CO_2$), AL/S (for hydrocarbons), and Molsieve 5 (for $H_2$, $O_2$, $N_2$, and CO) columns as well as with flame ionization and thermal conductivity detectors.

# Figures

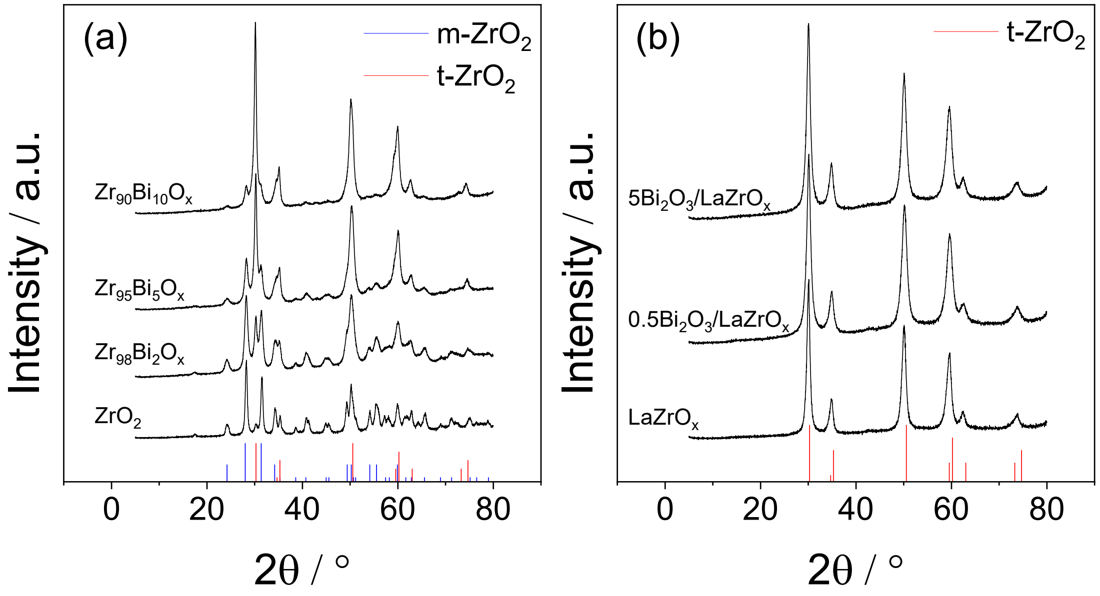

Figure S1 XRD patterns of (a) bare $ZrO_2$ and $ZrBiO_x$ samples as well as (b) calcined bare $LaZrO_x$ and selected $Bi_2O_3/LaZrO_x$ samples. Blue and red bars represent $ZrO_2$ tetragonal (PDF-No. 01-089-7710), $ZrO_2$ monoclinic (PDF-No. 00-005-0543) phases respectively.

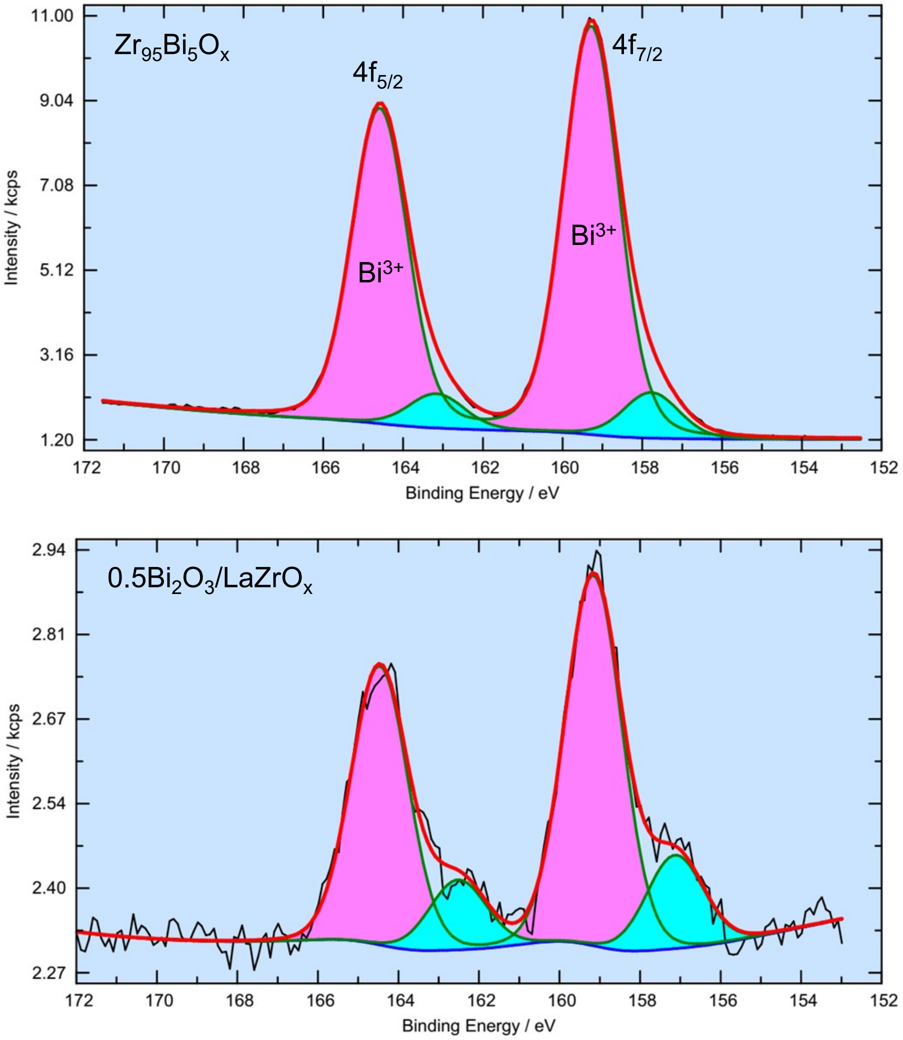

Figure S2 XP spectra of the Bi4f photoelectrons of fresh $Zr_{95}Bi_5O_x$ and $0.5Bi_2O_3/LaZrO_x$.

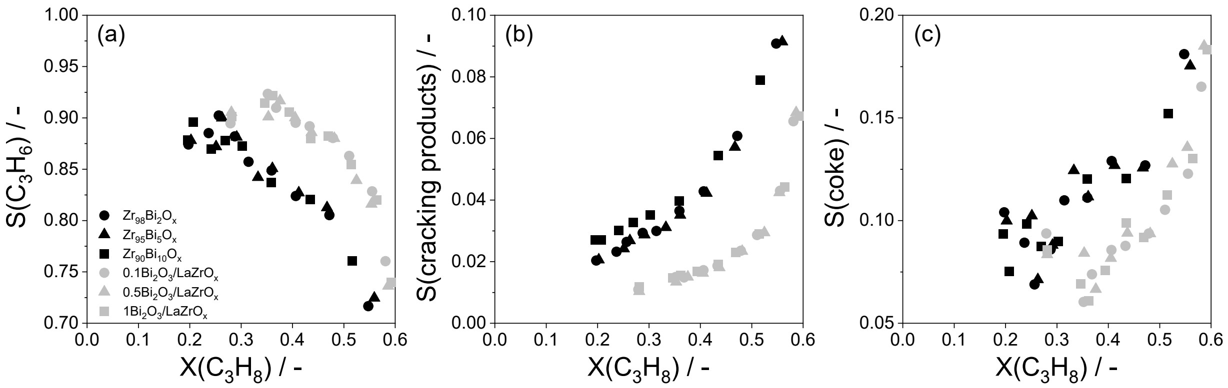

Figure S3 Dependence of selectivity to (a) propene, (b) cracking products ($CH_4$, $C_2H_4$, $C_2H_6$), and (c) coke on propane conversion determined at 600°C over selected $ZrBiO_x$ and $Bi_2O_3/LaZrO_x$ catalysts pre-reduced at 600°C.

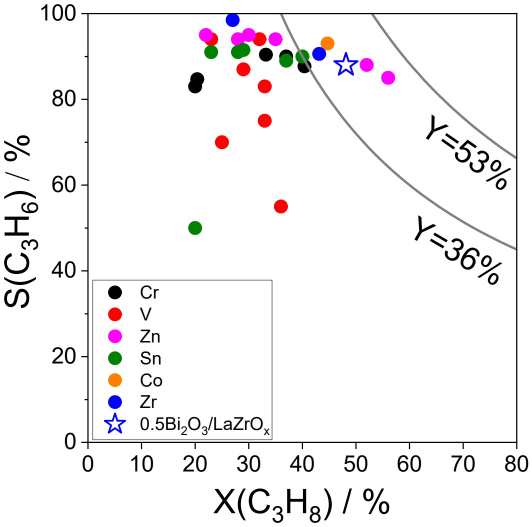

Figure S4 Dependence of selectivity to propene on propane conversion at 600°C for the most perspective metal oxide catalysts according to Ref.[1] (closed circle symbols) and $0.5Bi_2O_3/LaZrO_x$ developed in the current work (open star symbol). The industrially relevant level of propene yield (36 – 53%) is marked with the lines.

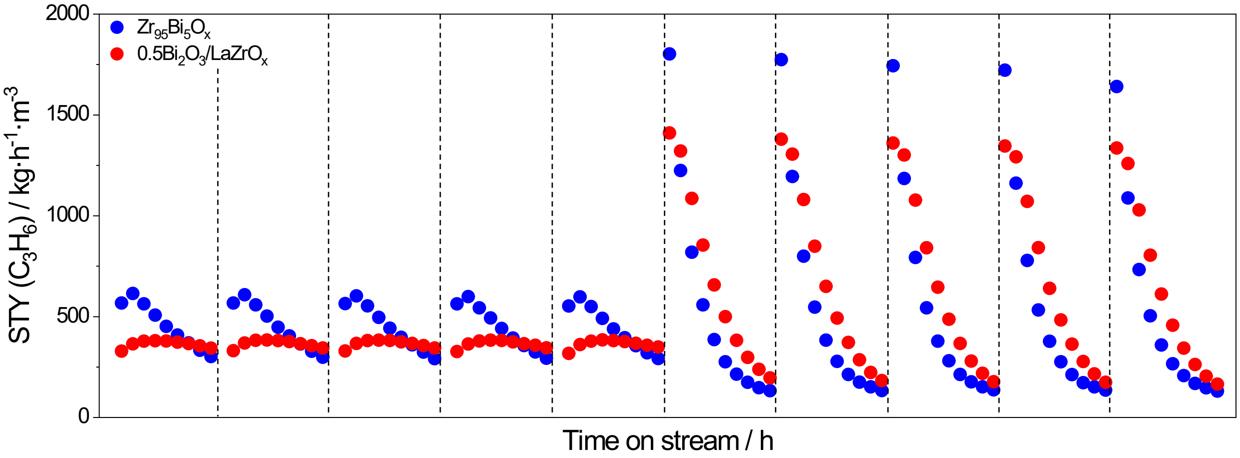

Figure S5 Time-on-stream changes of propene space time yield over $Zr_{95}Bi_5O_x$ and $0.5Bi_2O_3/LaZrO_x$ in each PDH cycle performed at 550°C (first 5 cycles) and 600°C (last 5 cycles).

# Tables

Table S1 Nominal and actual (determined by ICP) weight concentration (in %) of Bi as well as specific surface area of calcined samples.

| Sample | Nominal Bi content, wt% | Actual Bi content, wt% | $S_{BET}$, $m^2 \cdot g^{-1}$ |
|---|---|---|---|
| $ZrO_2$ | 0 | - | 38 |
| $Zr_{98}Bi_2O_x$ | 3.33 | 3.20 | 68 |
| $Zr_{95}Bi_5O_x$ | 8.12 | 8.01 | 64 |
| $Zr_{90}Bi_{10}O_x$ | 15.58 | 15.61 | 68 |
| $LaZrO_x$ | 0 | - | 83 |
| $0.1Bi_2O_3/LaZrO_x$ | 0.09 | n/a* | 116 |
| $0.2Bi_2O_3/LaZrO_x$ | 0.18 | 0.21 | 114 |
| $0.5Bi_2O_3/LaZrO_x$ | 0.45 | 0.56 | 125 |
| $0.7Bi_2O_3/LaZrO_x$ | 0.63 | n/a* | 115 |
| $1Bi_2O_3/LaZrO_x$ | 0.90 | 1.06 | 112 |

* - was not analyzed

# References

[1] T. Otroshchenko, G. Jiang, V. A. Kondratenko, U. Rodemerck, E. V. Kondratenko, *Chem. Soc. Rev.* **2021**, *50*, 473-527.