Electronic Supporting Information

Bulk binary ZrO₂-based oxides as highly active alternative-type catalysts for non-oxidative isobutane dehydrogenation

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Catalyst preparation

 $ZrOCl_2 \cdot 8H_2O$ (>95%, Fluka), $Cr(NO_3)_3 \cdot 9H_2O$ (99%, Aldrich), $Al(NO_3)_3 \cdot 9H_2O$ (>98%, Fluka), $In(NO_3)_3 \cdot 5H_2O$ (99.99%, Alfa Aesar), Ga_2O_3 (99.99%, Aldrich), HCl (37% aqueous solution, Fisher Chemical), NH_3 (25% aqueous solution, Roth) were used as starting materials.

 ZrO_2 was synthesized by precipitation method. Required amount of $ZrOCl_2 \cdot 8H_2O$ was dissolved in deionized water to obtain solution with concentration of Zr^{4+} of 1.0 M. 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 until no more chloride ions were identified in filtrate (reaction with AgNO₃). The solid was dried at 110°C overnight and calcined at 550°C for 4h.

To prepare $Cr_{10}Zr_{90}O_x$, $Cr_5Zr_{95}O_x$, $Cr_2Zr_{98}O_x$, $Al_{10}Zr_{90}O_x$ and $In_{10}Zr_{90}O_x$, required amounts of $ZrOCl_2 \cdot 8H_2O$ and a salt of corresponding doping element were dissolved in deionized water to obtain solution with a total cation concentration of 1.0 M. The next steps of synthesis were the same as for ZrO_2 preparation. $Ga_{10}Zr_{90}O_x$ was synthesized in the same way with using $GaCl_3$ as soluble salt of doping element. $GaCl_3$ was obtained by dissolving Ga_2O_3 in HCl under stirring at 90°C for 3h.

 $CrO_x/La_8Zr_{92}O_x$ was synthesized by impregnation method. To prepare 5 g of the sample, 1.7 g of $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in 4.2 ml of deionized water. Hereafter, 4.7 g of $La_8Zr_{92}O_x$ were impregnated with resulting solution, dried at 70°C overnight and calcined at 550°C for 4h.

Catalyst characterisation

The specific surface area (S_{BET}) of the calcined catalysts was determined from N₂ adsorption isotherms measured at 77 K on BELSORP mini II (BEL, Japan) applying the Brunauer, Emmet and Teller (BET) equation for relative pressure range of 0.05 < p/p0 < 0.30.

To determine phase composition, the samples were measured at room temperature on a theta/theta diffractometer (X'Pert Pro from Panalytical, Almelo, Netherlands) in a 2 theta range 5-80 ° with CuK α radiation ($\lambda = 1.5418$ Å. 40kV, 40 mA) and a X'Celerator RTMS Detector. The alignment was checked by use of a silicon standard.

The phase composition of the samples was determined using the program suite WinXPOW by STOE&CIE with inclusion of the Powder Diffraction File PDF2 of the ICDD (International Centre of Diffraction Data).

For the in situ investigation, the $Cr_{10}Zr_{90}O_x$ catalyst was heated in a MRI temperature chamber (5%H₂/He atmosphere, heating rate 10 K/min), mounted on a theta/theta diffractometer (Empyrean from Panalytical, Almelo, Netherlands), with CuK α radiation ($\lambda = 1.5418$ Å. 40kV, 40 mA) and a PIXcel^{3D} solid state detector.

XPS investigations were performed with a ESCALAB220iXL (ThermoFisher Scientific) with monochromatic Al K α 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.

Catalytic tests

Isobutane DH tests were carried out in an in-house developed setup equipped with 15 continuousflow fixed-bed reactors operating at 1 bar. The catalysts (40 mg) were initially heated in N₂ flow (20 ml·min⁻¹ per reactor) to 550°C. At this temperature they were exposed to a flow of air (10 ml·min⁻¹) for 1 hour and then flushed with N₂ (20 ml·min⁻¹ per reactor) for 15 min. Hereafter, a iso-C₄H₁₀-N₂ (40 vol.% iso-C₄H₁₀) mixture was fed with a total flow of 10 ml/min. In addition, the above catalytic tests were performed with prereduced catalysts. To this end, before the DH reaction, they were treated in a flow of H₂ (57 vol.% H₂ in N₂) for 1 hour followed by flushing with N₂ (20 ml·min⁻¹ per reactor) for 15 min. For a proper comparison of the catalysts in terms of space time yield (STY) of isobutylene formation at an initial isobutane conversion of around 0.4, catalytic tests with oxidized catalysts were carried out at different contact times by varying both catalyst amount and total flow (Figure S4 in ESI).

The concentration of feed components and reaction products was determined by an on-line gas chromatograph (Agilent 6890) equipped with PoraplotQ, HP-PLOT Al_2O_3 "KCl" and Molsieve 5 (for H₂, N₂, CO) capillary columns. Flame ionization and thermal conductivity detectors were used for detection of hydrocarbons and other components, respectively. Equations S1-S3 were used to calculate the isobutane conversion, selectivity to gas-phase products, and STY of isobutylene, respectively.

$$X(iso - C_4 H_{10}) = \frac{\dot{n}_{iso - C_4 H_{10}}^{inlet} - \dot{n}_{iso - C_4 H_{10}}^{outlet} \times \frac{\dot{n}_{N2}^{inlet}}{\dot{n}_{N2}^{outlet}}}{\dot{n}_{N2}^{inlet}}$$
(S1)

$$S(i) = \frac{v_{iso-C_{4}H_{10}}}{v_{i}} \frac{\dot{n}_{i}^{outlet}}{(\dot{n}_{iso-C_{4}H_{10}}^{inlet} - \dot{n}_{iso-C_{4}H_{10}}^{outlet})}{\dot{n}_{iso-C_{4}H_{10}}^{outlet} - \dot{n}_{iso-C_{4}H_{10}}^{outlet})}$$
(S2)

$$STY = \frac{\dot{n}_{N2}}{V_{catalyst}}$$
(S3),

where S(i) is the selectivity to product i, v_i is a stoichiometric factor, $V_{catalyst}$ is catalyst volume in m^3 , $\dot{m}_{iso-C4H8}^{outlet}$ is mass flow of isobutylene in kg/h. \dot{n}_i with superscripts "inlet" and "outlet" stand for molar flow of gas-phase components at the reactor inlet and outlet respectively.

Equation S4 was used to calculate the initial (within the first 9 min on stream) Cr-related rate of isobutane consumption from an overall rate (r(isobutane)) of isobutane conversion (Equation S5) expressed in molecules_{isobutane} $\cdot s^{-1} \cdot m_{catalyst}^{-2}$ and apparent surface chromium density (ω_{Cr} in

 $\text{Cr} \cdot {m_{\text{cataylst}}}^2$). An apparent constant of isobutane consumption (k_{DH}) was determined by integrating the right-hand part of equation S6, which is valid for an integral plug flow reactor.

$$TOF = \frac{r(iso - C_4 H_{10})}{\varpi_{Cr}} = \frac{k_{DH} \cdot p_{iso - C_4 H_{10}}^0}{c_V}$$
(S4)

$$r(iso - C_4H_{10}) = k_{DH} \times p_{iso - C_4H_{10}} - \frac{k_{DH}}{K_{eq}} \times p_{iso - C_4H_8} \times p_{H_2}$$
(S5)

$$\frac{m_{cat}}{F_{iso-C_4H_{10}}^0} = \tau = \int_0^{X_{iso-C_4H_{10}}} \frac{d(X_{iso-C_4H_{10}})}{-r(iso-C_4H_{10})}$$
(S6),

where $p_{iso-C4H10}$, $p_{iso-C4H8}$ and p_{H2} are the partial pressures of isobutane, isobutylene and hydrogen respectively and K_{eq} is the equilibrium DH constant at 550 °C, m_{cat} (g) is catalyst mass, and $F_{iso-C4H10}^0$ (mol_{isobutane}·s⁻¹) is inlet isobutane flow. $P_{iso-C4H10}^0$ stands for the initial partial pressure of isobutane.

Long-term stability of $Cr_{10}Zr_{90}O_x$ Cr-K/Al₂O₃ and Pt-Sn/Al₂O₃ was checked in 30 DH/regeneration cycles at 550 and 600 °C using a feed with 40 vol.% iso-C₄H₁₀ in N₂ at WHSV of 7.75 and 15.5 h⁻¹ respectively. The catalyst amount was fixed to 300 mg. The regeneration was performed in an air flow. The DH and regeneration cycles lasted for 27 and 15 min respectively and were always separated by a phase of flushing with N₂ (10 mLmin⁻¹) lasting for 15 min. Catalytic tests were performed with several catalysts in the same set-up simultaneously. The catalysts were located in the same furnace and were tested in a sequential manner. In other words, when one catalyst was applied for dehydrogenation all other catalysts were flushed in N₂. Catalyst regeneration was performed with all catalysts in parallel.

Figures



Figure S 1 (a) XRD patterns of binary oxides: ZrO_2 tetragonal (PDF-No. 01-089-7710), ZrO_2 monoclinic (PDF-No. 00-005-0543) (b) in-situ XRD measurements of $Cr_{10}Zr_{90}O_x$ in 5% H₂/He atmosphere. Reflections of Pt sample holder are at 2 theta 39.74°, 46.22°, 67.43°.



Figure S 2 Time-on-stream profiles of isobutane conversion over $Cr_{10}Zr_{90}O_x$, $La_8Zr_{92}O_x$, $Ga_{10}Zr_{90}O_x$, and $Y_9Zr_{91}O_x$ at 550°C with iso-C₄H₁₀:N₂=40:60. Catalyst amount and total gas flow were 40 mg and 10 ml/min respectively.



Figure S 3 Background-subtracted spectra of the Zr 3d photoelectrons of the fresh and reduced samples.



Figure S 4 (a) Maximal conversion of isobutane (X(isobutane)) and (b) overall amount of isobutylene formed over $Cr_{10}Zr_{90}O_x$ (•), $Cr-K/Al_2O_3$ (•) and $Pt-Sn/Al_2O_3$ (•) in each dehydrogenation cycle in a series of 30 dehydrogenation/regeneration cycles at 550°C and 600°C with WHSV of 7.75 and 15.5 h⁻¹ respectively. Reaction feed: iso- $C_4H_{10}:N_2=40:60$.



Figure S 5 XRD patterns of fresh $Cr_{10}Zr_{90}O_x$ and $Y_9Zr_{91}O_x$ catalysts and after their testing in a series of 30 DH/regeneration cycles at 550°C and 600°C with WHSV of 7.75 and 15.5 h⁻¹ respectively. Reaction feed: iso-C₄H₁₀:N₂=40:60. Read lines represent reflexes of tetragonal ZrO₂.