Synthesis of hybrid materials containing H-ZSM-5 and CeO₂ for green butadiene production

Loïc Eloi^{a,b}, Ghinwa Fayad^c, Jeroen Poissonnier^b, Jing Ma^c, Ekaterina Makshina^c, Bert F. Sels^c, Maarten K. Sabbe^{a,b}, Joris W. Thybaut^b, and An Verberckmoes^{a,*}

^aIndustrial Catalysis and Adsorption Technology, Ghent University, Valentin Vaerwyckweg 1, 9000 Ghent, Belgium

^bLaboratory for Chemical Technology, Ghent University, Technologiepark 125, 9052 Ghent, Belgium

^cCenter for Sustainable Catalysis and Engineering, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

*Corresponding author. E-mail address: <u>an.verberckmoes@ugent.be</u>

Abstract

Synthesis of hybrid materials combining two or more components with different properties is a commonly used strategy to obtain high-performance materials for a wide range of different applications, including catalytic reactions with a complex reaction network. In this work, two synthesis approaches are investigated to prepare hybrid materials containing two well-defined phases, i.e. H-ZSM-5 and CeO₂. By dispersing nano-sized H-ZSM-5 on CeO₂, and by synthesizing a core-shell catalyst with a nano H-ZSM-5 core and a ceria shell, a high intimacy between H-ZSM-5 and CeO₂ was obtained, while keeping the characteristic properties of each phase. The dehydration of 1,3-butanediol is used as a test reaction to explore the potential of these materials. A ratio between the selectivities of the desired product and intermediates, i.e. 1,3-butadiene (BD), 3-buten-2-ol (3B2OL), and 2-buten-1-ol (2B1OL) to the undesired product propylene (PP) was defined: (BD+3B2OL+2B1OL)/PP. Dispersing H-ZSM-5 zeolites on a CeO₂ surface was the optimal synthesis route to enhance the 1,3-butadiene selectivity, and a (BD+3B2OL+2B1OL)/PP selectivity ratio was obtained (3.9) compared to its parent material (2.1).

Keywords: butanediol dehydration; bio-based butadiene; multifunctional catalysis; biomass conversion; CeO₂; zeolites

1. Introduction

The commercial production of bulk chemicals in today's society is heavily dependent on fossil sources. Transitioning the global economy towards a carbon-neutral and circular one requires a shift towards biomass-derived feedstocks to pave the way towards an environmentally friendly production of both drop-ins and specialty chemicals [1-3]. In this respect, the dehydration of bio-derived alcohols has gained a lot of attention as a sustainable production for olefins, which are considered to be the crucial

building blocks of the organic chemical industry [4]. Current investigations into alcohol dehydration primarily focus on zeolites, more specifically H-ZSM-5, as a catalyst [3, 5-11]. Due to its unique properties, H-ZSM-5 is extensively used in the petrochemical industry, e.g. in fluid catalytic cracking [12], methanol-to-olefins, and aromatization of alkenes [13-16]. Due to its versatile applications, H-ZSM-5 could be essential in the transition towards a sustainable chemical industry.

In the context of catalyst development and alcohol transformation, H-ZSM-5 can be modified by combining the zeolite with another material, thereby generating a hybrid catalyst, to use the advantages/ properties of both materials for a specific application. For instance, de Reviere et al. [8] synthesized a hybrid material for butene production through butanol dehydration by dispersing ZSM-5 on γ -Al₂O₃. The catalyst exhibited a high selectivity towards olefins, related to H-ZSM-5, and a high stability, related to γ -Al₂O₃, resulting in a synergetic effect. Incorporating metals or oxides within the micropore structure of zeolites has been implemented to introduce other types of active sites or to modify their acid strength. Possato et al. [9], for example, impregnated ZSM-5 with V₂O₅ to combine the acid and oxidizing properties to convert glycerol into acrylic acid, while Lari and coworkers [10] converted glycerol to allyl alcohol by incorporating H-ZSM-5 with Ag to hydrogenate acrolein into the corresponding alcohol. Modifying the acid strength of zeolites by incorporating CeO₂ within the pores of MOR has been investigated by Fang et al. [17] for 1,3-butanediol dehydration to butadiene.

The latter process, i.e. butanediol (BDO) dehydration, has received a lot of attention in the past years as an alternative route to produce 1,3-butadiene (BD) [18-27]. Currently, commercial BD is a by-product of naphtha steam cracking, a process focused on ethylene and propylene production [4]. The shift towards lighter feedstocks in naphtha steam cracking, i.e. the shale gas revolution, has resulted in a decrease in BD supply, potentially endangering the industrial needs [1, 5]. Three butanediol isomers, i.e. 1,4-; 2,3- and 1,3-BDO, hold the potential to offer an alternative feedstock for green BD production. Since cyclodehydration of 1,4-BDO and pinacol rearrangement of 2,3-BDO yield tetrahydrofuran and methyl ethyl ketone (MEK) as major products, respectively [28-32], 1,3-BDO becomes an attractive alternative feedstock for the on-purpose BD production. Furthermore, a recent study demonstrates that the bacterium Cupravidus Necator can generate 1,3-BDO through autotrophic fermentation using CO₂ as the sole carbon source [33]. This discovery positions 1,3-BDO as the most pertinent choice for an alternative production route of BD.

The conversion of 1,3-BDO into BD requires two consecutive dehydration steps with unsaturated C4 alcohols (UOLs) as intermediates: 2-buten-1-ol (2B1OL), 3-buten-2-ol (3B2OL), and 3-buten-1-ol (3B1OL) [18]. However, side reactions can occur, such as dehydrogenation of 1,3-BDO, generating methyl vinyl ketone (MVK). Hydrogenation of MVK results in the formation of MEK and 2-butanol. The UOLs, more specifically 2B1OL and 3B1OL, could be hydrogenated, generating 1-butanol, which

could be further dehydrogenated into butanal. Moreover, 3B1OL is susceptible to cracking, forming propylene and formaldehyde [34, 35].

Current investigations on 1,3-BDO dehydration have been focussing on rare earth metal oxides (REOs), mixed metal oxides, silica-supported metal oxides, and acidic zeolites [17-19, 26, 34-41]. REOs, such as CeO₂, Y₂O₃, Er₂O₃, Sc₂O₃, Yb₂O₃ and Lu₂O₃, predominantly form 3B2OL and 2B1OL without further dehydration towards BD [42]. Moreover, it has been reported that WO₃/SiO₂ and especially Y₂Zr₂O₇ possess promising potential for BD production [39, 43]. With respect to acid zeolite catalyst development for the production of BD, investigations have been conducted to get insight into the zeolite parameters and to verify their potential for 1,3-BDO dehydration. Rodriguez and coworkers [41] concluded that Brønsted acid sites are responsible for dehydration, whereas Lewis acid sites promote the inverse Prins reaction of 3B1OL, resulting in propylene formation. However, the presence of strong Brønsted acid sites, which are present in H-ZSM-5, resulted in rapid catalyst deactivation due to coke formation blocking the micropores, and therefore, blocking the access to the acid sites [34]. In addition, Lee et al. [35] investigated the importance of shape-selectivity, highlighting its impact on the dehydration of the UOLs. 3B1OL can form intramolecular hydrogen bonds within ZSM-5 pores, leading to cracking rather than dehydration, which results in a maximum BD yield of 57% for H-ZSM-5 $(Si/Al = 130 \text{ at } 95\% \text{ conversion at } 300^{\circ}C)$ [19]. However, this phenomenon is absent in ZSM-22 and FER, characterized by smaller pores. Consequently, an initial BD selectivity of 62% and 71% was observed for ZSM-22 (Si/Al = 160) and FER (Si/Al = 130), respectively, at complete conversion and 300°C [35].

Given the versatile applications of H-ZSM-5 and its importance in mature and modern technologies, the strategy of developing a hybrid catalyst containing this zeolite could be interesting to explore its potential for sustainable BD production. Therefore, an additional component should be integrated into the catalyst design to steer the first dehydration step towards 2B1OL and 3B2OL, since these UOLs are readily dehydrated to BD on H-ZSM-5. This approach would prevent the cracking of 3B10L into propylene, thereby increasing the BD yield. As mentioned before, REOs are promising for the first dehydration step. Gotoh et al. investigated several REOs and concluded that CeO₂ was the best performing (94% selectivity towards 3B2OL and 2B1OL at 73% 1,3-BDO conversion at 325°C) due to its Ce⁴⁺-Ce³⁺ redox property, and the reaction proceeds via a radical mechanism. The performance of ceria strongly depends on its calcination temperature, because the (111) facet, which is suggested to be the active facet responsible for high selectivity, is predominantly present only on large particles formed after high-temperature treatments [42, 44]. There is limited literature available on synthesis approaches for a hybrid catalyst combining CeO₂ and H-ZSM-5 for dehydration applications. Moreover, these studies investigated one type of synthesis approach, i.e. incorporating CeO₂ within the pores of the zeolite structure [3, 17]. To our knowledge, only Fang et al. [17] investigated the effect of CeO₂ nanoparticles encapsulated in mordenite (MOR) on the BD selectivity. The catalyst was obtained in a

one-pot synthesis and the presence of CeO_2 decreased the acid strength of MOR, resulting in an increase in BD yield from 16% to 46% (Si/Ce = 50). Despite the improved catalytic performance for MOR, no investigations have been made to combine ceria and H-ZSM-5 to asses its catalytic performance for 1,3-BDO dehydration.

In this work, two synthesis procedures are developed to obtain a hybrid catalyst combining CeO₂ and H-ZSM-5. The first strategy involves dispersing nanozeolites on monometallic cerium layered double hydroxide (Ce-LDH), which is either calcined after the addition of the nanozeolites or calcined prior to addition. This catalyst is denoted as CeO₂-X/H-ZSM-5, with X representing the calcination temperature of CeO₂. Monometallic Ce-LDH is used as a precursor since the crystallinity, morphology, and size are easily tuned and because our research group has gained experience with this Ce-LDH material [45, 46]. The second strategy involves dispersing CeO₂ nanoparticles on the surface of nano-ZSM-5, generating a core-shell catalyst with an H-ZSM-5 core and a CeO₂ shell, i.e. H-ZSM-5@CeO₂ [47]. Steering two consecutive reactions, which react on a different active site, could be influenced by a different catalyst design, and thus, a different synthesis approach. Depending on the nature and the proximity of the different active sites, the feedstock and the intermediates could react differently. Therefore, we chose to explore the potential of H-ZSM-5 and its hybrid catalysts in the dehydration reaction of 1,3-BDO. The structural properties are thoroughly evaluated through X-ray diffraction (XRD), N₂ sorption, NH₃ temperature programmed desorption (TPD), Pyridine Fourier Transform Infrared Spectroscopy (Py-FTIR), scanning electron microscopy (SEM), scanning transmission electron microscopy combined with energy dispersive X-rays (STEM-EDX), diffuse reflectance UV-VIS (DR-UV-VIS), inductive coupled plasma optical emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS). All these properties are compared to the parent H-ZSM-5 and a physical mixture of H-ZSM-5 and CeO₂-550. Finally, the catalysts are screened for their potential in the dehydration reaction of 1,3-BDO.

2. Experimental

2.1 Catalyst preparation

In this study, four catalysts are synthesized: (1) nano-sized H-ZSM-5 with a (theoretical) Si/Al of 25, (2) hybrid catalysts containing 50% by weight of nano-sized H-ZSM-5 dispersed in situ onto CeO₂ crystals, (3) a physical mixture of nano-H-ZSM-5 and CeO₂ in a 50/50 weight ratio, and (4) a core-shell catalyst with nano-H-ZSM-5 core and CeO₂ shell, and a theoretical CeO₂ content of 20 wt.%. A schematic overview of these materials and their synthesis approach is given in **Fig.1**.

2.1.1 Materials

Cerium(III)nitrate hexahydrate (Ce(NO₃)₃.6H₂O, 99%), hexamethylenetetramine (HMT, 99%), ammoniumpersulfate (98%), aluminium isopropoxide (Al(O-i-Pr)₃, 98%), tetrapropylammonium hydroxide (TPAOH, 1M in H₂O), tetraethylorthosilicate (TEOS, 99%), polyvinylpyrrolidone (PVP,

40,000 g/mol), and 1,4-dioxane (99.8%) were purchased from Merck Life Science. Ammonium nitrate (NH₄NO₃, >99%), sodium hydroxide (NaOH, >99%), sodium chloride (NaCl, 99.5%), and ethanol (100%) were obtained from Chem-Lab Analytical. 1,3-butanediol (99%) was purchased from Acros Organics. All chemicals in this work were used without further purification steps.



Fig.1: Schematic overview of hybrid materials and their synthesis approaches. Adding Ce-containing solids to the zeolite precursor mixture results in zeolites that are well dispersed onto CeO₂ (CeO₂/H-ZSM-5). Adding zeolites to the precursor mixture of CeO₂ results in a core-shell catalyst with H-ZSM-5 core and CeO₂ shell (H-ZSM-5@CeO₂).

2.1.2 Monometallic Ce-LDH and CeO2 synthesis

The monometallic Ce-LDH was prepared by a modified homogeneous alkalization approach, employing a scaled-up methodology based on the work of Ye et al. [48] and De Saegher et al. [46]. First, 1.75 g of Ce(NO₃).6H₂O, 40 ml 0.5M HMT, 4.8 ml ammonium persulfate and 3.05 g NaCl were added to a 1000 mL round-bottom flask. The resulting solution was diluted with distilled water to achieve a final volume of 500 mL. The flask was then sealed with a septum and purged with nitrogen gas to create an inert atmosphere. Subsequently, the mixture was refluxed at 110°C for 24 hours with continuous stirring at 400 rotations per minute (rpm). The resulting precipitate was recovered via centrifugation, and washed three times with distilled water and once with ethanol. Finally, the material was dried for 48 hours at room temperature. To obtain CeO₂, the monometallic Ce-LDH was calcined under air at 550°C or 800°C for 8 hours under a heating ramp of 2°C/min starting from room temperature.

2.1.3 Nano-ZSM-5 synthesis

The nano-sized H-ZSM-5 zeolites were synthesized via the procedure reported by de Reviere et al. [8]. First, 0.4 g Al(O-i-Pr)₃ was dissolved in 17.5 g TPAOH at room temperature in an ultrasonic bath until a clear solution was obtained. Subsequently, 0.0123 g NaOH and 3.15 g distilled water were added to the solution, followed by the dropwise addition of 10.1 g TEOS under continuous stirring of 800 rpm. The obtained precursor solution was hydrolyzed under continuous stirring (800 rpm) for 24 hours at

room temperature in a closed environment and had an Al/Si/TPAOH/H₂O/NaOH/EtOH molar ratio of 1/25/9/495/0.16/100. Crystallization of the zeolites was performed in Teflon-lined stainless-steel autoclaves of 100 mL at 165°C for 96 hours. The zeolites were then recovered by centrifugation, washed three times with distilled water, dried at 120°C for 20 hours, and calcined under air at 550°C (heating ramp 1°C/min) for 8 hours to remove the template. The Na-ZSM-5 was then ion-exchanged with 1M NH₄NO₃ (10 mL/g zeolite) for 2 hours at 50°C under continuous stirring (200 rpm) and this procedure was repeated three times. The NH₄-ZSM-5 was recovered via centrifugation and washed until the pH of the washing water was neutral. Finally, the zeolites were dried at 120°C for 20 hours and calcined under air at 550°C (heating ramp 1°C/min) for 6 hours to obtain the protonated samples, i.e. nano-H-ZSM-5.

2.1.4 Hybrid catalyst synthesis

In this study, two types of hybrid catalysts were synthesized. The first type, referred to as CeO_2 -X/H-ZSM-5 (or 50/50-hybrid catalyst) with X the calcination temperature of CeO_2 , involved dispersing nano-ZSM-5 zeolites onto CeO_2 . The second type, denoted as H-ZSM-5@CeO₂, is a core-shell catalyst with an H-ZSM-5 core and CeO_2 shell.

The synthesis procedure of the CeO₂-X/H-ZSM-5 catalyst is identical to that of H-ZSM-5, except that Ce-LDH or CeO₂-800 was added under continuous stirring 30 minutes prior to the hydrothermal treatment. The amount of Ce-LDH or CeO₂-800 added was adjusted to achieve a 50/50 weight ratio of CeO₂ and ZSM-5 in the resulting material. The crystallization and post-synthesis procedures were identical to that of H-ZSM-5. Since the hybrid material is calcined at 550 °C, the Ce-LDH is converted to CeO₂, and therefore, CeO₂-550 will be used in further notations. The properties and catalytic performance of CeO₂-550/H-ZSM-5 were compared to a physical mixture of CeO₂-550 and H-ZSM-5 (PM CeO₂-550/H-ZSM-5), which was prepared by mechanically mixing Ce-LDH calcined at 550°C (CeO₂-550) and H-ZSM-5 in a 50:50 weight ratio using a spatula.

The core-shell catalyst was prepared as reported by Di et al. [47]. First, 0.5 g nano-ZSM-5 was dispersed in a 20 mL solution of water and ethanol (1:1 vol/vol%) under continuous stirring (400 rpm) for 30 minutes, followed by 10 minutes of ultrasonic treatment to enhance the dispersion. Subsequently, 1 g of PVP was added under continuous stirring until completely dissolved, after which 0.3 g Ce(NO₃).6H₂O and 0.3 g HMT were added. The mixture was then heated to 60°C and allowed to age for 2 hours while maintaining continuous stirring (400 rpm), followed by statically aging for 3 hours. The material was recovered through centrifugation and washed three times with distilled water. Finally, the catalyst was dried at 100°C for 8 hours and calcined under air at 550°C for 8 hours (heating ramp 1°C/min).

2.2 Catalyst characterization

2.2.1 X-ray Diffraction

Powder X-ray Diffraction was used to identify the crystal structure of the catalyst. The analyses were performed using a Bruker D8 Advance diffractometer with Cu K α radiation (λ =1.54 Å). The XRD patterns were collected between 2 θ of 5° and 90° with a scan rate of 1 °/min and steps of 0.02°. The average crystal sizes of the zeolites and ceria nanoparticles are estimated using the Scherrer equation:

$$d = \frac{\kappa\lambda}{\beta\cos\theta} \tag{1}$$

with d the average crystal size in nanometers, K a dimensionless shape factor with a value of 1, λ the wavelength of the X rays (0.154 nm), β the full-width at half maximum, and θ Bragg's angle [49]. The Scherrer equation is calculated using the reflection at a Bragg's angle θ of 23.2° and 56° for nano-H-ZSM-5 and the CeO₂ nanoparticles, respectively.

2.2.2 Elemental analysis

Inductive coupled plasma optical emission spectroscopy was performed to determine the composition of the nano-H-ZSM-5 zeolite, i.e. the Si/Al ratio. Before analysis, the sample was prepared by fusion in lithium borate. The resulting molten bead is then rapidly digested in nitric acid. The prepared solution was then analyzed using IcaP 7400 ICP-OES (Thermo Scientific). The obtained Si/Al ratio of nano-H-ZSM-5 was 16. The composition of the hybrid materials, more specifically the CeO₂ content in CeO₂-550/H-ZSM-5, CeO₂-800/H-ZSM-5, and H-ZSM-5@CeO₂ is determined by Energy Dispersive X-ray spectroscopy and is 44, 46, and 6 weight percent, respectively.

2.2.3 SEM and STEM-EDX analysis

Scanning Electron Microscopy was performed with a Quanta 200F to determine the morphology of the materials and to compare the dispersion of the nano-sized H-ZSM-5 zeolites on the surface of CeO₂ in both the CeO₂/H-ZSM-5 and the PM CeO₂/H-ZSM-5 catalysts. To further assess the dispersion of CeO₂ on the core-shell catalysts, Scanning Transmission Electron Microscopy Energy Dispersive X-ray spectroscopy (STEM-EDX) was performed. The instrument used for these measurements is a JEOL-2200FS under 200 KV high tension.

2.2.4 XPS

X-ray photoelectron spectroscopy was carried out to determine the presence of both Ce^{3+} and Ce^{4+} , as well as to calculate the Ce^{3+} fraction of the CeO_2 -containing materials. A Surface Science Instruments S-Probe XPS spectrometer with monochromatic Al radiation (1486 eV) was used for the analyses. Calibration was performed using adventitious carbon, and the flood gun was set to 3 eV.

2.2.5 Nitrogen adsorption

 N_2 -adsorption was performed to investigate the surface area and the pore volume of the materials at -196°C using a Micromeritics Tristar II instrument. Before analysis, the samples were degassed at

 300° C overnight under a continuous N₂ flow to remove any adsorped impurities. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. The criteria of Rouquerol were applied to increase the accuracy of the measurements for the microporous materials, i.e. the materials containing H-ZSM-5 zeolites [50]. The micropore area and the micropore volume (V_{micro}) were obtained via the t-plot method for the microporous materials [51], and the total pore volume (V_{tot}) was determined via the single-point adsorption at a relative pressure (p/p°) of 0.95. The Pore Size Distribution (PSD) of the microporous materials was determined via the Non-Local Density Functional Theory (NLDFT) method, assuming cylindrical pore geometries for the zeolites [52, 53].

2.2.6 Diffuse Reflectance UV-VIS spectroscopy

The DR-UV-VIS measurements were performed over the wavelength range of 200-700 nm using a Varian Cary 5000 UV-VIS spectrophotometer and spectralon was used as a background correction for the UV-VIS spectra.

2.2.7 Acidity measurements

Temperature-programmed desorption of NH_3 is performed to determine the amount of acid sites of all the samples. The measurements were performed on a Micromeritics Autochem instrument equipped with a thermal conductivity detector (TCD). Before analysis, the sample (100 mg) was pretreated under a continuous He flow (25 cm³ min⁻¹) at 500°C for 2 hours to remove any adsorbed moisture and gases. The sample was then cooled down to 150°C and a flow of 4% NH₃/He (25 cm³ min⁻¹) was used to completely saturate the sample for 30 min. Subsequently, the physisorbed NH_3 is removed by flushing the sample with He (25 cm³ min⁻¹) for 30 min. Finally, the temperature was increased to 650°C at a heating rate of 10°C min⁻¹ and the amount of desorbed NH₃ molecules was detected with the TCD. To verify the presence of Brønsted and Lewis acid sites, Py-FTIR has been performed on the parent nano-H-ZSM-5. Prior to measurement, around 10-13 mg of sample was pressed (107 Pa) into a wafer and pretreated under vacuum (10-6 torr) at 400°C for 4 hrs. After activation, the wafer was subjected to 2 bar pyridine until saturation at 150°C. Once saturation was reached, the wafer was evacuated at 150°C and the IR spectra were collected. The amount of pyridine adsorbed on Brønsted and Lewis acid sites was determined using the integrated band areas situated at 1545 and 1445 cm⁻¹, respectively, using the following molar extinction coefficients: ε (Brønsted) = 1.67 and ε (Lewis) = 2.22 cm/µmol, as reported in the literature [54].

2.2.8 Thermogravimetric analysis

The quantity of coke present in each catalyst after the reaction was evaluated using thermogravimetric analysis on a Mettler Toledo TGA/DSC 3+ instrument. In a typical experiment, about 20-30 mg of sample was loaded in an alumina crucible and heated from 30 to 800 °C with a heating rate of 10 °C/min under air (90 cm³ min⁻¹).

2.3 Catalytic reaction

The dehydration reactions were carried out in a continuous flow packed-bed reactor (Microactivity-Effi reactor from PID Eng&Tech) under atmospheric pressure. Prior to the reaction, each catalyst (0.5 g) was preheated under N₂ flow (30 cm³ min⁻¹) at 350°C for 2 hours to clean the surface of the catalyst. After cooling the catalyst bed to 300 °C, a reactant feed of 20 wt.% 1,3-BDO in 1,4-dioxane (total liquid-feed flow rate of 1.5 mL h⁻¹) mixed with a N₂ (flow rate of 30 cm³ min⁻¹) was fed over the catalyst bed. The reaction temperature for 1,3-BDO dehydration was set at 300°C in accordance to literature [17, 19, 35], and after preliminary experiments (**Fig. S1**). Light products such as propylene and butadiene were analyzed by an on-line GC (Trace 1300, Thermo Scientific) equipped with a capillary column (PoraPlot Q HT, 0.32mm x 25m) and a flame ionization detector (FID). Heavier products such as the butenol intermediates, butanal, MVK, and 1-butanol were condensed in a cold trap every hour and further analyzed in an off-line GC-FID (HP 6890, Agilent Technologies) equipped with a capillary column (CP-WAX 52 CB, 0.25mm x 30 m) using hexanol as internal standard. A carbon balance exceeding 85% is obtained for all experiments, which is in accordance with reported values in the literature [17, 19, 40].

2.4 Definitions

The weight hourly space velocity (WHSV) was defined as:

WHSV (h⁻¹) =
$$\frac{20\% * F_{tot} * \rho_{1,3-BDO}}{m_{catalyst}}$$
 (2)

With F_{tot} the liquid flow rate (1.5 mL h⁻¹), $\rho_{1,3\text{-BDO}}$ the density of 1,3-BDO (1.01 g mL⁻¹), and $m_{catalyst}$ the mass of the catalyst (0.5 g). The WHSV was fixed at 0.62 $g_{1,3\text{-BDO}}$.h⁻¹.g⁻¹_{catalyst} after preliminary experiments (**Fig. S2**).

The conversion (X) of 1,3-BDO and the selectivities (S) towards the products (i) were defined as follows:

$$X_{1,3-BDO}(\%) = \frac{n_{1,3-BDO}^{\circ} n_{1,3-BDO}}{n_{1,3-BDO}^{\circ}} * 100\%$$
(3)

$$S_{i} = \frac{n_{i}}{n^{\circ}_{1,3-BDO} * X_{1,3-BDO}} * 100\%$$
(4)

Where $n_{1,3-BDO}^{\circ}$ and $n_{1,3-BDO}$ represent the inlet and outlet mole number of 1,3-BDO, respectively.

3. Results and discussion

3.1 Catalyst characterization

Fig. 2 depicts the normalized XRD patterns of the materials studied within this work. The monometallic Ce-LDH exhibits intense diffraction peaks at low angles ($2\theta = 10^{\circ}$ and 17°) which is attributed to

basal-spacing values of 0.838 and 0.419 nm confirming the layered structure [48]. After calcination of Ce-LDH, a reduction in the number of diffraction peaks is observed, including the peak at $2\theta = 10^{\circ}$ which is ascribed to the removal of water and nitrates from the LDH structure [48]. Additionally, new diffraction peaks are detected at $2\theta = 28.5$, 33, 47.5, 56, 59, 69.4, 76.7, 79.1, and 88.6° ($\mathbf{\nabla}$), and are attributed to the (111), (200), (220), (311), (222), (400), (331), (420), and (422) planes of the cubic fluorite structure of CeO₂, respectively. Among these planes, the (111) is crucial for the dehydration mechanism as it contains the oxygen vacancies (OV) that exhibit the preferential adsorption tendency for 1,3-butanediol [44, 55]. These results confirm that after thermal treatment of Ce-LDH, a pure CeO₂ is formed [56, 57]. The XRD patterns of the H-ZSM-5 catalyst exhibit the characteristic diffraction peaks related to the MFI topology between $2\theta = 7.9^{\circ}$ and $2\theta = 22.25^{\circ}$ (*) [58]. No additional peaks associated with impurities are observed. The average crystal size of the zeolites calculated by the Scherrer equation is 108 nm and the Si/Al ratio is 16 according to ICP-OES.



Fig. 2: Normalized XRD patterns of all the catalysts studied in this work: a) H-ZSM-5,
b) CeO₂-550/H-ZSM-5, c) PM CeO₂-550/H-ZSM-5, d) CeO₂-800/H-ZSM-5, e) H-ZSM-5@CeO₂,
f) CeO₂-550, and g) Ce-LDH. The peaks corresponding to the ZSM-5 topology and CeO₂ are indicated with * and ▼, respectively.

The XRD patterns of the hybrid materials (CeO₂-X/H-ZSM-5 and H-ZSM-5@CeO₂) reflect their successful synthesis; both materials contain characteristic peaks corresponding to the ZSM-5 topology and the cubic fluorite phase of CeO₂. Notably, the diffraction peaks related to CeO₂ in the CeO₂-X/H-ZSM-5 catalysts and the physical mixture are sharp and exhibit greater intensity compared

to the diffraction patterns of ZSM-5. Magnified XRD patterns of the CeO₂-X/H-ZSM-5 catalysts and the physical mixture can be found in Fig. S3 The physical mixture and the CeO₂-X/H-ZSM-5 catalysts exhibit an identical XRD pattern without any other impurities, implying that the synthesis of the hybrid catalysts successful. The higher intensity of CeO₂ in CeO₂-X/H-ZSM-5 and was PM CeO₂-550/H-ZSM-5 can be attributed to the presence of micro-scale plates of cerium oxide (as observed in SEM in Fig. 3), while H-ZSM-5 exists at the nanoscale. When comparing the diffraction peaks of ceria in CeO₂-550/H-ZSM-5 and CeO₂-800/H-ZSM-5, sharper peaks with higher intensity are present in the latter. This phenomenon has also been observed by Igarashi et al. [44] and is related to the fact that the (111) facet becomes more predominant when the calcination temperature increases. The mean particle sizes of the zeolites in CeO2-550/H-ZSM-5, CeO2-800/H-ZSM-5, and PM CeO₂₋₅₅₀/H-ZSM-5 are 104 nm, 106 nm, and 109 nm, respectively, and are similar to the parent zeolite. In contrast, the core-shell catalyst features CeO₂ diffraction peaks that are much broader and have a lower intensity than ZSM-5. The smaller and broader diffraction pattern of CeO_2 in the core-shell catalyst can be explained by the presence of CeO₂ nanoparticles (5 nm according to the Scherrer equation) [47].



Fig. 3: SEM images of (a) H-ZSM-5, (b) Ce-LDH, (c) CeO₂, (d) CeO₂-550/H-ZSM-5, e) PM CeO₂-550/H-ZSM-5, (f) CeO₂-800/H-ZSM-5, and (g) H-ZSM-5@CeO₂.

The SEM images of H-ZSM-5, Ce-LDH, CeO₂, CeO₂/H-ZSM-5, and PM CeO₂/H-ZSM-5 are presented in **Fig. 3**. The H-ZSM-5 particles (a) exhibit a cube-like morphology with dimensions ranging from 100

to 180 nm. These particles are composed of smaller zeolite crystals that aggregate together, resulting in these cubes, which aligns with results reported by Song et al. [49]. The monometallic Ce-LDH (b) consists of thin plates with sizes ranging from 1 to 5 μ m (**Fig. S4**) with a thickness between 150 and 200 nm, which is consistent with previously reported dimensions [46, 48]. This observation confirms the successful formation of the LDH structure. Additionally, smaller and irregular particles are observed on the surface of the larger plates. It is assumed that these particles possess a similar composition as the bigger plates [46]. After calcination of Ce-LDH to CeO₂ (c), the material maintains its plate-like structure.

Both CeO₂ and H-ZSM-5 phases are observed in the SEM images of the hybrid materials (d, f) and the physical mixture, but there are notable differences between these materials. The CeO₂-X/H-ZSM-5 hybrid materials show a high degree of intimacy between the plate-like structure of CeO₂ and the cube-like zeolite crystals. The zeolites are consistently and densely distributed both around, between, and on top of the CeO₂ plates (**Fig. S4**), which can be attributed to the reaction between the hydrolyzed TEOS and the surface hydroxyl groups of Ce-LDH or CeO₂ [59].

It is also worth noting that the degree of intimacy between CeO₂ and nano-H-ZSM-5 is more pronounced in the case of CeO₂-550/H-ZSM-5 (**Fig. S4**). The zeolites appear to be more homogeneously distributed on and in between the CeO₂ plates compared to CeO₂-800/H-ZSM-5. This could be explained by a difference in the hydroxyl groups on either Ce-LDH or CeO₂ during the hybrid materials synthesis. Ce-LDH contains solely hydroxyl groups on its surface, whereas these are lost during calcination at 800 °C [46]. However, it is well known that the full or partial restoration of the original LDH structure upon contact with water might happen due to the memory effect but the degree of restoration strongly depends on the temperature applied for the transformation of LDH into oxides phase [60]. Although 800°C is rather a high calcination temperature, we still could assume that the surface of CeO₂-800 is partially re-hydrated in-situ during the synthesis of ZSM-5, and thus, surface hydroxyl groups are available to interact with TEOS. In contrast, the physical mixture displays isolated H-ZSM-5 particles and CeO₂, with no indication of intimate contact. The core-shell catalyst has no difference in morphology or particle size compared to the nano-sized H-ZSM-5. However, no additional phases associated to CeO₂ could be determined on the zeolite crystals with SEM. Therefore, STEM-EDX was performed on the H-ZSM-5@CeO₂ (**Fig. 4**) to evaluate the presence of CeO₂ on this catalyst.

The STEM image confirms the cubic morphology of the zeolites, with dimensions closely matching those calculated using the Scherrer equation, i.e. 116 nm. The intensity of the Ce L α line depicted in the EDX mapping is directly related to both the concentration of CeO₂ and the thickness of the ceria layer. When comparing the edges with the centers of the crystals, a higher intensity of the Ce L α line is noticeable at the edges. This observation confirms the presence of a CeO₂ layer on the facets of the zeolite crystals. The absence of a detectable Ce L α line in the center of H-ZSM-5 indicates that CeO₂ is

not present in the pore structure of the zeolite. Thus, the STEM-EDX image serves as evidence for the formation of a core-shell catalyst composed of an H-ZSM-5 core and a tiny, continuous CeO_2 shell on the facets of H-ZSM-5.



Fig. 4: STEM image of H-ZSM-5@CeO₂ (left) and EDX Ce Lα mapping of H-ZSM-5@CeO₂ (right).

XPS spectra of CeO₂-550, CeO₂-550/H-ZSM-5, PM CeO₂-550/H-ZSM-5, and H-ZSM-5@CeO₂ are depicted in **Fig. 5**. The Ce 3d spectra are deconvoluted into ten peaks: the six U bands and four V bands represent the spin-orbit splitting of Ce $3d_{5/2}$ and Ce $3d_{3/2}$, respectively [61]. The Ce³⁺ 3d spectrum is composed of bands V°, V', U° and U', whereas the Ce⁴⁺ 3d spectrum contains the bands V, V", V"', U, U", and U"'. The Ce³⁺ content ratio can be estimated by calculating the ratio between the areas of the Ce³⁺ bands to the total area of the deconvoluted peaks. The percentage of Ce³⁺ to the total Ce is 45%, 42%, 33%, and 44% for CeO₂-550, CeO₂-550/H-ZSM-5, PM CeO₂-550/H-ZSM-5, and H-ZSM-5@CeO₂, respectively. Since the presence of Ce³⁺ could generate OV on the surface of the catalyst [62], it can be assumed that all materials exhibit a similar amount of OV in the CeO₂, except the physical mixture.

The N₂-sorption isotherms for all the materials studied in this work are depicted in **Fig. 6**. H-ZSM-5, CeO₂-X/H-ZSM-5, PM CeO₂-X/H-ZSM-5, and H-ZSM-5@CeO₂ exhibit a type I isotherm as classified by IUPAC [63]. The isotherms are characterized by a steep N₂ uptake at very low p/p° (type Ia) which is related to the enhanced adsorbent-adsorptive interactions in the narrow micropores. This type of isotherm is related to microporous materials having mainly narrow micropores (widths < 1 nm) [63]. At higher relative pressures (p/p° > 0.8), a small hysteresis is observed which is most pronounced for CeO₂-550/H-ZSM-5. This hysteresis loop can be attributed to the presence of interparticle voids, which are formed due to the agglomeration of the zeolites as can be seen in **Fig. S4** [63, 64]. Consequently, the observed mesoporosity in these materials can be ascribed to interparticle capillary condensation (i.e., secondary mesopores) and is commonly observed in nano-sized zeolites [65-68]. CeO₂ displays a type II isotherm, which is related to non-porous materials [63]. A more detailed nitrogen sorption isotherm



Fig. 5: XPS spectra of Ce 3d region (872 - 932 eV) with peak deconvolution of (a) CeO₂-550, (b) CeO₂-550/H-ZSM-5, (c) PM CeO₂-550/H-ZSM-5 and (d) H-ZSM-5@CeO₂.



Fig. 6: Nitrogen sorption isotherms for all the catalysts used in this study: a) H-ZSM-5, b) H-ZSM-5@CeO₂, c) CeO₂-550/H-ZSM-5, d) PM CeO₂-550/H-ZSM-5, e) CeO₂-800/H-ZSM-5, and f) CeO₂-550.

	Particle size ^d (nm)	N ₂ -adsorption ^a			Acidity, NH ₃ uptake (µmol/g) ^b			Total acidity	Amount of coke
Sample		S_{BET} (m ² /g)	$V_{micro.}$ (cm ³ /g)	V _{tot.} (cm ³ /g)	Weak	Medium	Strong	(µmol/g) ^b	(wt.%) ^c
H-ZSM-5	108^{*}	436	0.17	0.24	141	120	161	422	11.5
PM CeO ₂ -550/H-ZSM-5	109*	224	0.09	0.12	43	82	134	259	14.3
CeO ₂ -550/H-ZSM-5	104^{*}	228	0.08	0.14	44	66	92	202	7.0
CeO ₂ -800/H-ZSM-5	106^{*}	215	0.08	0.11	41	50	85	176	6.7
H-ZSM-5@CeO ₂	107*,5▼	381	0.14	0.19	70	103	132	305	11.1
CeO ₂	-	7	-	0.01	4	13	2	19	-

Table 1: The physicochemical properties of the parent, PM-CeO₂-550/H-ZSM-5, and various hybrid catalysts.

^a Calculated from N₂ adsorption data.

^b Determined from NH₃-TPD measurements.

^c Determined from TGA data after 1,3-BDO dehydration for 24 hours TOS.

^d Particle size related to H-ZSM-5 and CeO₂ are indicated with * and ▼, respectively.

The textural properties of all materials (specific surface area and pore volume) are summarized in **Table 1**. H-ZSM-5 exhibits the highest surface area, followed by H-ZSM-5@CeO₂. CeO₂ exhibits the lowest surface area and contains minimal porosity, whereas CeO₂-X/H-ZSM-5 and PM CeO₂-550/H-ZSM-5 possess intermediate surface areas and pore volumes. This outcome aligns with the expectation, given that these catalysts consist of a 50/50 weight percent combination of H-ZSM-5 and CeO₂. Analysis of the pore size distributions provides more insight into the pore characteristics of the catalysts. The PSD of materials studied in this work are plotted in **Fig. S6**. The NLDFT PSD reveals two peaks in the micropore range: a first distinct peak at approximately 0.5 nm, which corresponds to the pore diameter of the ZSM-5 framework [49], and a second peak in the range of 0.9 to 1.5 nm. Furthermore, a small amount of mesopores is observed around 2 to 3.5 nm.

The UV-VIS spectra of various samples are shown in **Fig. 7**. Usually, the pure CeO₂ exhibits three absorption maxima centered at ~ 255, 285, and 340 nm. The first and second bands can be assigned to O^{2-} Ce³⁺ and O^{2-} Ce⁴⁺ charge transfer transitions, whereas the third band can be attributed to interband transitions [69, 70]. The PM CeO₂-550/H-ZSM-5 catalyst shows a strong absorption band centered at 345 nm, with a small shoulder centered at ~ 265 nm, due to the presence of bulk cerium oxide particles. These two bands are also observed over hybrid catalysts; however, the former one is shifted to a lower wavelength. The shift of absorption maxima towards shorter wavelengths (also called

the blue shift) in UV typically indicates a decrease in particle size [69]. Since the dehydration of 1,3-BDO into unsaturated alcohols over CeO₂ is greatly affected by its particle size, this observation is important for understanding the catalytic results. Igarashi et al. [44], showed that as the calcination temperature of CeO₂ increased, its particle size increased and eventually the most stable (111) facet, which consists of the active sites for the selective dehydration of 1,3-BDO to unsaturated 3B2OL and 2B1OL alcohols, becomes the predominant one, and therefore enhancing the catalytic activity. Among the hybrid catalysts, CeO₂-800/H-ZSM-5 exhibited the lowest shift, suggesting a larger particle size of ceria compared to the core-shell catalyst.



Fig. 7: Diffuse reflectance UV-VIS spectra of a) CeO₂-550/H-ZSM-5, b) CeO₂-800/H-ZSM-5, c) H-ZSM-5@CeO₂, d) PM CeO₂-550/H-ZSM-5, and e) H-ZSM-5 with their corresponding peak maximum.

The total amount and distribution of the acid sites on the parent, PM, and hybrid catalysts are measured by NH₃-TPD. The corresponding TPD profiles are plotted in **Fig. 8**, and a linear-combination fit of three Gaussian peaks is performed to distinguish three types of acid sites related to their peak maxima, i.e. weak (200-230°C), medium (260-290°C), and strong (385-415°C), which is depicted in **Fig. S7**. **Table 1** summarizes the acid properties of all the materials studied in this work. Analysis of **Fig. 8** reveals that all samples, except CeO₂, exhibit two desorption peaks at approximately 220 and 400°C, reflecting the catalysts' weak and strong acid sites, respectively. CeO₂ only displays a single small broad peak at 250°C. Among the catalysts, nano-H-ZSM-5 exhibits the highest number of acid sites, followed by the core-shell catalyst. CeO₂/H-ZSM-5 and the physical mixture exhibit half the acid site content because ZSM-5 comprises half of the catalyst material. CeO₂ has by far the lowest number of acid sites. The presence of Ce-LDH in the precursor solution of ZSM-5 and CeO₂-550 in the physical mixture results in a slight decrease in acid strength, which is reflected by the shift of the high-temperature peak towards lower temperatures. However, this is not the case for CeO₂-800/H-ZSM-5. The amount of Brønsted acid sites (BAS) and Lewis acid sites (LAS) of the nano-H-ZSM-5 is determined by Py-FTIR after evacuation at 150°C and is 120 µmol/g and 26 µmol/g and the corresponding spectrum can be found in **Fig S8**. Since the post-treatment of the CeO₂-X/H-ZSM-5 hybrid catalysts prepared by hydrothermal crystallization is identical to the parent H-ZSM-5, and the same parent material is used to prepare the physical mixture and to synthesize the core-shell catalyst, it can be assumed that BAS are present in all the zeolite materials.



Fig. 8: NH₃-TPD profiles of all the catalysts studied in this work: a) H-ZSM-5, b) H-ZSM-5@CeO₂,
c) PM CeO₂-550/H-ZSM-5, d) CeO₂-550/H-ZSM-5, e) CeO₂-800/H-ZSM-5, and f) CeO₂-550.

3.2 Catalytic results: Dehydration of 1,3-butanediol into butadiene

The potential of the hybrid materials to steer two consecutive reactions has been assessed by screening them for the catalytic dehydration of 1,3-BDO to BD. **Fig. 9** depicts the conversion and product selectivities as a function of time on stream (TOS) during the vapor phase dehydration of 1,3-BDO over the parent H-ZSM-5 and CeO₂. The main products detected over parent H-ZSM-5 were BD, propylene (PP), and 3B1OL, while 2B1OL and 3B2OL were predominantly formed over CeO₂ together with butanol, butanal, and MVK. The presence of 2B1OL and 3B2OL could be explained by the presence of OV in CeO₂. The H of the position-2 methylene group and the OH groups will interact with Ce⁴⁺ and Ce³⁺, respectively, thereby forming a tridentate coordination. Abstraction of the position-2 H by Ce⁴⁺ via a radical mechanism is the initial step of 1,3-BDO dehydration over the OVs in CeO₂ [37]. As can be seen from the graphs, H-ZSM-5 reached 100% conversion which remains constant after 22 hours. Although bulk CeO₂ is less active than H-ZSM-5 under these reaction conditions (20% conversion which remained constant after 22 hours TOS), its influence on H-ZSM-5 is observable in the hybrid materials.

Fig. 10 depicts the conversion and product selectivities as a function of TOS in the vapor-phase dehydration of 1,3-BDO over the physical mixture, as well as over the various hybrid catalysts: CeO₂-X/H-ZSM-5 and H-ZSM-5@CeO₂. As can be seen from this graph and the data of parent H-ZSM-5, full BDO conversion was achieved over all the tested catalysts. After 23 hours TOS, the conversion of all CeO₂-containing materials slightly decreases, while this is not the case for the parent

H-ZSM-5 and could be explained by the presence of more acid sites since the same mass of catalyst is used in each experiment. Although TGA experiments (**Table 1**) confirmed that coke formation occurred on all materials, no claims about deactivation phenomena or a comparative deactivation study could be made, since all materials exhibit full BDO conversion. However, the product distributions of all the catalysts could give us insight into the influence of CeO_2 on the parent H-ZSM-5, which could be used for further optimization of the catalyst design.



Fig. 9: 1,3-BDO conversion and product selectivities as a function of TOS for parent H-ZSM-5 and CeO₂. Reaction conditions: $T = 300^{\circ}$ C, WHSV = 0.62 h-1, 20 wt.% 1,3-BDO in dioxane. Other detected products include butanol, butanal, and MVK.



Fig. 10: 1,3-BDO conversion and selectivity as a function of time for the physical mixture (PM) and various hybrid catalysts. Reaction conditions: $T = 300^{\circ}$ C, WHSV = 0.62 h⁻¹, 20 wt.% 1,3-BDO in dioxane. Other detected products include 2B1OL, butanol, butanol, and MVK.

In all cases, the main detected products were BD, PP, and 3B1OL. As represented in Scheme 1, the reaction mechanism proceeds with a first dehydration step forming the UOLs, followed by either dehydration to form BD or C-C cleavage of the 3B10L intermediate into PP. In the acid-catalyzed dehydration of 1,3-BDO, the secondary alcohol is more favorable to be dehydrated resulting in the formation of the most unsaturated alcohol, i.e. 2B1OL, compared to 3B1OL according to Zaitsev's rule. Therefore, the degree of formation of the UOLs decreases in the order 2B10L>3B10L>3B20L, which is in good agreement with the thermodynamic equilibrium calculated at 300 °C in the study of Makshina and coworkers [18]. The absence of 2B1OL in the reactor effluent could be attributed to its higher reactivity towards butadiene or by isomerization towards 3B2OL in the presence of Brønsted acid sites [39, 40], which could explain the presence of 3B2OL. Cracking of this intermediate can be explained by considering the molecular configuration of the UOL within the zeolite framework. The hydroxyl group of 3B1OL can form hydrogen bonding interactions with the π electrons of the C-C double bond in the 10-ring channels of ZSM-5. Consequently, the hydroxyl group becomes inaccessible for the 1,2-elimination reaction, which alters the reaction pathway towards cracking instead of dehydration [35]. Minor by-products such as butanol, butanal, and MVK resulting from consecutive hydrogenation and dehydrogenation reactions were also detected. Unlike previous studies on 1,3-BDO dehydration [17, 19, 35], no MEK was detected.



Scheme 1: Schematic overview of the consecutive dehydration of 1,3-BDO.

The dehydration of 1,3-BDO generates 3 intermediates and several reaction products, both desired and undesired. To gain more insight into the catalytic behavior, and the influence of CeO₂ on H-ZSM-5, a ratio between the selectivities of the desired product (BD) and intermediates (2B1OL and 3B2OL) to the undesired product (PP) is defined: (BD+3B2OL+2B1OL)/(PP). **Fig. 11** illustrates the selectivity ratio for all the catalysts as a function of TOS. The selectivity ratios of the parent H-ZSM-5 and the physical mixture are similar and remain constant over time (circa 2). All the hybrid catalysts exhibit a selectivity ratio higher than that of H-ZSM-5 and the physical mixture, with CeO₂-550/H-ZSM-5 being the highest (initial 3.9 and slowly declining to 3.6 after 23 hours TOS). However, the selectivity ratios of CeO₂-800/H-ZSM-5 and H-ZSM-5@CeO₂ show a decline over time and converge to a similar value of 2.8.

We noticed a similar product distribution between the physical mixture and parent H-ZSM-5, indicating that if present as a bulk additive, CeO_2 does not exhibit a significant impact on the performance of H-ZSM-5. This became even more obvious in **Fig. 11**, where the (BD+3B2OL+2B1OL)/PP selectivity ratio of the parent H-ZSM-5 and the physical mixture remain similar over the course of 24 hours on stream. On the other hand, over hybrid catalysts a positive effect of CeO_2 doping was observed, especially in terms of the (BD+3B2OL+2B1OL)/PP ratio in the product mixture, i.e. a much lower amount of PP is formed for the same amount of BD compared to the physical mixture and the parent H-ZSM-5.



Fig. 11: (BD+3B2OL+2B1OL)/(PP) selectivity ratio as a function of time on stream over H-ZSM-5, the hybrid materials, and the physical mixture. Reaction conditions: $T = 300^{\circ}$ C, WHSV = 0.62 h⁻¹, 20 wt.% 1,3-BDO in dioxane.

The similar product distribution of H-ZSM-5 and the physical mixture can be explained by the lower activity of CeO₂ and the isolated nature of the zeolites and the metal oxide particles, as visualized in the SEM images (**Fig. 3**). As a consequence, the dehydration of 1,3-BDO can occur arbitrarily on a Brønsted acid site or an oxygen vacancy. In the former scenario, 2B1OL and 3B1OL are formed according to Zaitsev's and anti-Zaitsev's rule, respectively. Isomerization of 2B1OL over Brønsted acid sites could explain the presence of 3B2OL [39]. While 2B1OL and 3B2OL readily dehydrate to BD, 3B1OL is prone to subsequent cracking due to its higher resistance to dehydration in ZSM-5. In the latter scenario, 2B1OL and 3B2OL are formed over an OV of CeO₂, but will not dehydrate to BD since the adsorption of the UOLs is less stable over CeO₂ [37]. However, due to the lower activity of CeO₂, the catalytic performance of the physical mixture is predominantly dependent on H-ZSM-5.

In contrast to H-ZSM-5 and the physical mixture, adding Ce-LDH or CeO₂ to the precursor gel of ZSM-5 results in a higher selectivity ratio, which can be attributed to the intimate contact between the zeolite and the metal oxide. As mentioned before, the hydroxyl groups of Ce-LDH/CeO₂ interact with the hydrolyzed TEOS during synthesis, leading to well-dispersed zeolite crystals on the CeO₂ surface, and a synergistic interaction between both phases which is reflected in the catalytic performance. The close proximity between both phases could enhance the accessibility of the active sites (oxygen vacancies and Brønsted acid sites) which could facilitate the initial adsorption of 1,3-BDO onto CeO₂, followed by the subsequent dehydration towards 2B1OL and 3B2OL, and therefore, increasing the selectivity towards BD. As previously stated, the Ce³⁺ content ratio, which is correlated to the amount of OV, is higher for

the hybrid material (45%) than for the physical mixture (33%). Consequently, the hybrid material can facilitate the first dehydration step due to its increase in OV content.

A higher initial BD yield of 56% is observed for CeO₂-800/H-ZSM-5 compared to CeO₂-550/H-ZSM-5 (50%). The increase in BD yield could be attributed to a higher calcination temperature, resulting in increased particle size of CeO₂ and a more predominant (111) facet [37, 44], as confirmed by UV-VIS and XRD. This could enhance the first dehydration step towards 2B1OL and 3B2OL over CeO₂. However, due to a lower degree of intimacy in CeO₂-800/H-ZSM-5 (**Fig. 3f**), the accessibility between the two active sites is reduced compared to CeO₂-550/H-ZSM-5. Consequently, the first dehydration step might occur more frequently over the acid sites of nano-H-ZSM-5, which results in a higher 3B1OL selectivity, and therefore more propylene formation.

Finally, the core-shell catalyst exhibits a higher selectivity ratio compared to both the physical mixture and the parent H-ZSM-5, which can be attributed to the presence of a tiny CeO₂ shell on the zeolite facets. However, it is worth noting that, despite a similar Ce³⁺ content ratio (44%) to CeO₂/H-ZSM-5 (45%), this catalyst has a lower initial BD yield of 42% compared to the other hybrid materials. This can be attributed to the lower amount of CeO₂, and thus less active sites for the first dehydration step, within the core-shell, resulting in a lower selectivity of 3B2OL and a higher selectivity of 3B1OL. Furthermore, Igarashi et al. [44] have demonstrated that in small particles of CeO₂ other facets such as (100) and (110) are becoming more dominant. Moreover, they observed an increase in the density of surface oxygen defects on CeO₂ with decreasing particle size. They concluded that these two factors played a role in the degradation of 1,3-BDO into methanol and ethanol. Although we did not detect these reaction products in our experiments, the presence of other facets and more surface oxygen defects in the small CeO₂ particles could explain the increased amount of unidentified products.

Based on these results, it is noticeable that the combination of CeO₂ and H-ZSM-5 in a hybrid material has a positive impact on the BD yield. If a higher BD yield is desired with this type of material, further research should consider several factors regarding catalyst design. It is crucial, for instance, that there is a high intimacy between the zeolites and CeO₂, and that the ceria should consist of sufficiently large particles. Thus, it is recommended to opt for a catalyst of the type CeO₂-X/H-ZSM-5, in which the intimate contact could be further promoted by pre-treating Ce-LDH or CeO₂ with TPAOH, analogous to the study of Chu and coworkers [71]. In addition, a higher amount of OV is preferable, as it steers the first dehydration towards 2B1OL and 3B2OL, which could be realized by synthesizing a hybrid material with a higher CeO₂/H-ZSM-5 weight ratio. Another strategy is to introduce Zr in the Ce-LDH lattice during synthesis, as demonstrated by Luo et al. [72], to enhance the OV content. Finally, the acid properties of the zeolites should be taken into account for catalyst development. In this study, H-ZSM-5 had a high number of strong acid sites, while medium acid sites are preferable for BD production [19],

and thus H-ZSM-5 with a higher Si/Al is opted for the optimization of the hybrid catalyst design for the dehydration of 1,3-BDO to BD.

4. Conclusion

Hybrid catalysts composed of CeO₂ and H-ZSM-5 were synthesized for sustainable olefin production by bio-alcohol dehydration. Both when dispersing nano-sized H-ZSM-5 on CeO₂ (CeO₂-X/H-ZSM-5) and when synthesizing a core-shell catalyst with nano-H-ZSM-5 core and ceria shell (H-ZSM-5@CeO₂), a high intimacy between H-ZSM-5 and CeO₂ was obtained, while both phases were isolated in the physical mixture. It was confirmed that the core-shell catalyst contained a continuous shell of CeO₂ nanoparticles (5 nm) on the facets of the zeolite crystals, with a similar Ce^{3+} content (44%) as the CeO₂-550/H-ZSM-5 (45%). The dehydration of 1,3-butanediol to butadiene was used as an application to explore the potential of H-ZSM-5 composed in hybrid catalysts with CeO₂ for alcohol dehydration containing consecutive dehydration steps. The presence of bulk CeO₂-550 did not influence the product distribution as the (BD+3B2OL+2B1OL)/(PP) selectivity ratio remained similar to the parent material (i.e., 2). However, when dispersing H-ZSM-5 on CeO₂-550, the selectivity ratio increased to 3.9, which could be attributed to a higher intimate contact and an increase in Ce³⁺ content in CeO₂. The core-shell catalyst contained less predominant (111) facets of CeO₂ which resulted in a lower selectivity ratio as compared to the hybrid material (3.1). Although an increase in calcination temperature of CeO₂ up to 800 °C resulted in an increase in BD yield by 10% compared to the parent material, the selectivity ratio remained lower (3.6) than over CeO₂-550/H-ZSM-5 (3.9) which could be attributed to a lower degree of intimacy between ceria and the zeolite material. Hence CeO₂-550/H-ZSM-5- outperformed all the other hybrid materials with the highest (BD+3B2OL+2B1OL)/(PP) selectivity ratio, which remained constant over the course of 23 hours TOS. Future work could focus on finetuning the acid density distribution of the hybrid materials, by for example increasing the Si/Al ratio. Further optimizing intimate contact between ceria and the zeolites could be done by for example pretreating CeO₂ with the structure directing agent. Increasing the amount of CeO₂ in CeO₂-550/H-ZSM-5 or introducing Zr in the Ce-LDH structure, and thereby increasing the amount of oxygen vacancies in CeO₂, are two synthesis strategies to steer the reaction pathway towards 2B1OL and 3B2OL, and thus increasing the BD yield.

CRediT authorship contribution statement:

Loïc Eloi: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization. Ghinwa Fayad: Investigation, Visualization, Validation, formal Analysis, Data Curation, Writing – Review & Editing. Jeroen Poissonnier: Validation, Writing – Review & Editing, Project administration. Jing Ma: Investigation (UV-vis), Formal analysis (UV-vis). Ekaterina Makshina: Validation, Writing – Review & Editing, Project administration. Bert Sels: Conceptualization, Supervision, Validation, Resources, Funding acquisition. Maarten K. Sabbe: Writing – Review & Editing, Supervision. Joris W. Thybaut: Writing – Review & Editing, Supervision, Funding acquisition. An Verberckmoes: Conceptualization, Validation, Resources, Writing – Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of generative AI in scientific writing:

During the preparation of this work, Loïc Eloi used ChatGPT to improve readability. After using this tool/service, the author reviewed and edited the content as needed and took full responsibility for the content of the publication.

Acknowledgements:

This work was performed in the framework of the Catalisti clusterSBO project GREEN-B2B (HBC.2020.2606 "Acid catalyzed production of green butadiene from butanediols"), with the financial support of VLAIO (Flemish Agency for Innovation and Entrepreneurship). This Work was also funded by the Special Research Fund of Ghent University (BOF DOC 2021002901). The authors acknowledge Olivier Janssens (Department of Solid State Sciences, Ghent University) for XRD analyses and SEM measurements, Vitaliy Bliznuk (Department of Electromechanical, Systems and Metal Engineering, Ghent University) for STEM-EDX measurements, Pieter Vermeir and Diederik Leenknecht (Department of Green Chemistry and Technology, Ghent University) for ICP-OES analysis, and Els Bruneel (Department of Chemistry, Ghent University) for XPS analysis. E.M. acknowledges internal funding from KU Leuven (Small research infrastructure project – Advanced thermogravimetric analysis (TGA) tools for advanced study of materials and sustainable processes, KA/20/038)

Data availability:

Data will be made available on request.

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