# Ethanol to 1,3-Butadiene Conversion by using ZrZn-Containing MgO/SiO<sub>2</sub> Systems Prepared by Coprecipitation and Effect of Catalyst Acidity Modification

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The conversion of ethanol to 1,3-butadiene (1,3-BD) has been investigated over  $ZrO_2$ - and ZnO-containing magnesia silica oxides prepared by a co-precipitation method at different Mg-to-Si molar ratios. The effect of reaction temperature and ethanol flow rate was investigated. The catalyst acidity was modified through the addition of alkali metals (Na, K and Li) to the final materials. Catalysts were characterised by nitrogen physisorption analysis, X-ray diffraction, scanning electron microsco-

py with energy dispersive X-ray, temperature-programmed desorption of ammonia, infrared spectroscopy and <sup>29</sup>Si/(<sup>7</sup>Li) NMR spectroscopy. The catalytic results showed that the controlled reduction of catalyst acidity allows ethanol dehydration to be suppressed, whilst increasing 1,3-BD selectivity. The best catalytic performance achieved 72 mol% for the combined 1,3-BD and acetaldehyde selectivity.

SEBS).<sup>[2]</sup> 1,3-BD is currently produced from naphtha steam

crackers as a co-product of ethene manufacturing.<sup>[3,4]</sup> Besides

environmental concerns as a result of the use of petroleum-de-

rived hydrocarbons, the need for a new route to 1,3-BD is fur-

ther exacerbated owing to the possible future shortfall in

supply as a result of the changes of feedstock from naphtha to ethane in the U.S.<sup>[5,6]</sup> The catalytic conversion of ethanol into

1,3-BD is an attractive alternative owing to the availability of bioethanol, which is expected to significantly increase over the next few years from the fermentation of sugar-rich waste materials (second generation bioethanol).<sup>[1,5,7,8]</sup> For example, in Brazil alone, 23.4 billion litres of bioethanol were produced in

The route most widely accepted to account for 1,3-BD production from ethanol involves five consecutive reactions.[10-16] Initially, ethanol is dehydrogenated to acetaldehyde. Then, 3-hydroxybutanal is formed from acetaldehyde self-aldolisation. Next, 3-hydroxybutanal dehydrates to crotonaldehyde, which is reduced (Meerwein-Ponndorf-Verley (MPV) reduction) with ethanol to produce crotyl alcohol and acetaldehyde. Finally, crotyl alcohol is dehydrated to afford 1,3-BD. This mechanism was initially suggested and experimentally supported by Quattlebaum et al.,<sup>[17]</sup> who verified that higher 1,3-BD yields were achieved when crotonaldehyde and ethanol were used compared with a feed comprising acetaldehyde and ethanol, with either a SiO<sub>2</sub>-based system or  $Ta_2O_5/SiO_2$  catalyst. With the latter catalyst, the authors also observed that a feed comprising of only acetaldehyde was converted into crotonaldehyde, which was not observed in significant quantities when ethanol and acetaldehyde were passed over the catalyst. This suggests that crotonaldehyde was rapidly converted into crotyl alcohol (presumably by an MPV process) and subsequently to 1,3-BD. However, some reports have recently ruled out the aldol con-

### Introduction

1,3-Butadiene (1,3-BD) is an important starting material used as a monomer for the production of a variety of synthetic polymers.<sup>[1]</sup> The polymerisation of 1,3-BD with itself and with other olefin monomers represents its largest commercial use; examples include the production of styrene-butadiene-rubber (SBR), polybutadiene (PB), styrene-butadiene latex (SBL), acrylonitrilebutadiene-styrene (ABS), adiponitrile, nitrile rubber (NBR), chloroprene and styrene-butadiene block copolymers (SBS and

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	Supporting information for this article can be found under http:// dx.doi.org/10.1002/cctc.201600331.

ChemCatChem 2016, 8, 1–12 Wiley Online Library

These are not the final page numbers! 77

2014.[9]

densation as the main path, suggesting instead that crotyl alcohol is produced through the reaction between an activated form of ethanol and acetaldehyde.<sup>[18,19]</sup>

Owing to the specific features of the catalyst that are required for this cascade reaction, materials with multifunctional properties have been studied, especially MgO/SiO<sub>2</sub> systems.<sup>[2,5]</sup> This is related to the fact that Mg-O pairs might act as Lewis acid/Brønsted basic sites and the silanol moieties as a Brønsted acid, which are necessary for ethanol dehydrogenation,<sup>[20]</sup> acetaldehyde condensation,<sup>[21]</sup> crotonaldehyde reduction and the further crotyl alcohol dehydration to 1,3-BD. However, owing to the presence of acid sites in these systems, ethanol dehydration to ethene and diethyl ether are significant competitive reactions. Efforts have been dedicated to the design of catalysts able to suppress these undesirable parallel reactions. For instance, the addition of metals and/or metal oxides based on Cu, Zr, Zn and Ag to the MgO/SiO<sub>2</sub> system has been shown to be beneficial to the 1,3-BD yield.<sup>[13,21-23,28]</sup> In particular, a synergic effect between ZrO<sub>2</sub> and ZnO has been demonstrated.<sup>[12,23]</sup> ZnO may support ethanol dehydrogenation and ZrO<sub>2</sub> is expected to assist aldol condensation and crotonaldehyde reduction.  $^{\left[12,\,14,\,23,\,28-30\right]}$  Conversely, in addition to catalyst composition, the catalyst preparation method is of paramount importance for 1,3-BD formation, as different acid/basic features may be obtained depending on the synthesis conditions.[18,22,23,31] Owing to this, different optimum Mg-to-Si molar ratios for 1,3-BD formation have been reported, depending on the synthesis procedure employed.<sup>[13, 18, 23]</sup>

Among the catalyst preparation procedures, different methods have been investigated such as physical mixtures of MgO and SiO<sub>2</sub>,<sup>[11,13]</sup> wet-kneading,<sup>[10-13,22,23]</sup> sol-gel,<sup>[18,24]</sup> impregnation<sup>[13]</sup> and co-precipitation.<sup>[22,25,26]</sup> Whereas it has been proven that a physical mixture between precursor oxides is not suitable for 1,3-BD formation, as the resultant catalysts show similar features to single MgO and SiO<sub>2</sub> phases, wet-kneading methods have been the most widely discussed in the literature with less attention being dedicated to sol-gel and co-precipitation methods.<sup>[5]</sup>

In the wet-kneading preparation procedure, MgO and SiO<sub>2</sub> are usually mixed at the desired molar ratio in the presence of water, then dried and calcined. Besides the specific features of the MgO and SiO<sub>2</sub> precursors employed and their molar ratio, the amount of water, time, ageing temperature, drying and calcination procedure represent some of the preparation steps that might alter the catalyst's behaviour.<sup>[5]</sup> As observed by energy-dispersive X-ray (EDX) and TEM analyses, materials prepared by wet-kneading are usually inhomogeneous in their composition and morphology.<sup>[11,22,27]</sup> They are generally constituted of islands of MgO and SiO<sub>2</sub>, and a limited amount of amorphous magnesia hydrosilicate phase.<sup>[22,27]</sup> These unique characteristics are described as the key factor for the conversion of ethanol into 1,3-BD, as an intrinsic basic/acid sites distribution is obtained on these materials.<sup>[22,27]</sup>

By using a sol-gel method, Ochoa et al.<sup>[18]</sup> observed that the Mg/Si molar ratio affected the number, strength and distribution of the basic/acid sites, the surface area and the crystalline structure of the catalysts, impacting the product distribution. A comparison between wet-kneading and a co-precipitation method, at the same Mg/Si ratio, has pointed to the former as more suitable for ethanol conversion into 1,3-BD.<sup>[22,27]</sup> However, the co-precipitation method may be an efficient preparation procedure to produce catalysts with homogeneous properties throughout their surface, therefore increasing the potential of controlling the physical and chemical properties of the catalyst and facilitating the determination of structure–activity relation-ships. Despite that, a rigorous study using the co-precipitation method has not been reported.

Herein, we report for the first time an extensive investigation using the co-precipitation method for the synthesis of magnesium silica oxide catalysts with different Mg-to-Si (Mg/Si) molar ratios for ethanol conversion into 1,3-BD. The materials were used as supports for ZnO and ZrO<sub>2</sub> doping and the Mg/Si molar ratio effect of materials containing ZrO<sub>2</sub> and ZnO was also evaluated. The effect of reaction temperature and ethanol flow rate was also studied. In particular, the ethanol flow rate was investigated to assess catalyst performance regarding 1,3-BD productivity (in  $g_{BD}g_{cat}^{-1}h^{-1}$ ), a variable usually neglected<sup>[18,22,32,33]</sup> but that is important for industrial applications. As it is well-known that the acidic/basic features play a key role for this process, we have modified the catalyst acidity through the addition of alkali metals (Na, K and Li) to the final materials. The catalyst preparation method was further optimised by modification of the number of calcination steps. As a result, it is shown that the co-precipitation method is suitable to prepare MgO/SiO<sub>2</sub> systems that, after ZrO<sub>2</sub> and ZnO addition, produce 1,3-BD productivities as high as those obtained by using expensive Ag-containing systems.<sup>[2, 14]</sup> Besides this, the catalyst acidity modification through the alkali metal doping was successful for the suppression of ethanol dehydration, allowing the combined 1,3-BD and acetaldehyde selectivity to be increased up to 72%. Catalysts were characterised by nitrogen physisorption, X-ray diffraction, scanning electron microscopy with energy dispersive X-ray, temperature-programmed desorption of ammonia, infrared spectroscopy and <sup>29</sup>Si/(<sup>7</sup>Li) NMR spectroscopy.

#### **Results and Discussion**

#### The effect of the Mg/Si molar ratio

Magnesium silica oxide catalysts prepared at different Mg/Si molar ratios were evaluated at 325 °C, by using an ethanol weight hourly space velocity (WHSV) of 0.62  $h^{-1}$ . At this condition, ethanol conversion was typically lower than 20%, allowing clear observation of the different catalytic properties among the catalysts samples.

Figure 1 shows the selectivity profile of the main carboncontaining products, obtained after 3 h of time on stream (TOS), as a function of the Mg/Si molar ratio for (a) MgO/SiO<sub>2</sub> systems and (b) MgO/SiO<sub>2</sub> systems containing a fixed amount of ZrO<sub>2</sub> and ZnO, which has previously shown to be optimum for SiO<sub>2</sub> and acts as a comparison with our previous work.<sup>[12,23]</sup> The profiles observed for ethene, diethyl ether (DEE) and acetaldehyde (AcH) show the same general trend as a function of



**Figure 1.** Mg/Si molar ratio effect on the main carbon-containing reaction products for a) MgO/SiO<sub>2</sub> systems and b) MgO/SiO<sub>2</sub> systems containing ZrO<sub>2</sub> and ZnO (T=325 °C, TOS=3 h, WHSV=0.62 h<sup>-1</sup>, contact time=4 s).

the Mg/Si molar ratio. Whereas ethene and DEE selectivities decreased as the Mg/Si molar ratio was increased, AcH selectivity showed a sharp increase, from less than 10% with the 1:1 species to over 40% with higher amounts of MgO. The decrease in the ethanol dehydration along with the increase in the ethanol dehydrogenation as the Mg/Si molar ratio was increased is in agreement with a reduction in the catalyst acidity, as expected when the Mg/Si increases.<sup>[10, 18]</sup>

On the other hand, interestingly, the effect of the Mg/Si molar ratio on 1,3-BD selectivity was different between MgO/SiO<sub>2</sub> systems and MgO/SiO<sub>2</sub> systems containing ZrO<sub>2</sub> and ZnO. Although a smooth rise in 1,3-BD selectivity was verified as the Mg/Si molar ratio increased for pure MgO/SiO<sub>2</sub> samples, Figure 1 (a), the same trend was not observed for catalysts containing ZrO<sub>2</sub> and ZnO, Figure 1 (b). Instead, a maximum in the 1,3-BD selectivity was obtained for the catalyst with the Mg/Si molar ratio equal to one.

We have previously studied the effect of the Mg/Si molar ratio for Zn<sup>II</sup>- and Zr<sup>IV</sup>-containing MgO/SiO<sub>2</sub> systems, using the wet-kneading method for the MgO/SiO<sub>2</sub> preparation.<sup>[12]</sup> In line with results presented in Figure 1, MgO/SiO<sub>2</sub> systems prepared by the wet-kneading method have shown a different 1,3-BD selectivity behaviour upon the addition of ZrO<sub>2</sub>/ZnO to the catalyst. However, although a maximum in the 1,3-BD selectivity was observed at a Mg/Si molar ratio equal to 3:1 for the pure MgO/SiO<sub>2</sub> systems, an increase in 1,3-BD selectivity was observed as the Mg/Si molar ratio was increased for the systems prepared by incipient wetness.<sup>[12]</sup> These results are in contrast with those reported here, in Figure 1, emphasising that the coprecipitation preparation procedure has dramatically changed the physicochemical properties of the catalyst compared with the wet-kneading procedure.

Regarding the textural properties, samples with higher Mg/Si molar ratios showed lower surface areas compared with the 1:1 and 25:75 ratios, which may indicate the formation of MgO particles in the pores of the samples, Table S1 in the Supporting Information.<sup>[13,23]</sup> Diffraction patterns indicated samples with amorphous features, the MgO periclase phase being observed only in the MgO/SiO<sub>2</sub> (95:5) sample (peaks at Bragg angles of  $37.0^{\circ}$ ,  $43.0^{\circ}$ ,  $62.4^{\circ}$ ),<sup>[2]</sup> Figure S1. In particular, the ZrZn/MgO-SiO<sub>2</sub>-1 system presented broad peaks (at 25-30°, 33–39 $^{\circ}$  and 58–62 $^{\circ}\text{)}\text{, characteristic of magnesium silicate hy$ drates.<sup>[34,35]</sup> As samples containing ZrO<sub>2</sub> and ZnO have shown similar PXRD patterns compared to the initial MgO/SiO<sub>2</sub> support, ZrO<sub>2</sub> and ZnO should be dispersed into the -Mq-O-Si- network or their small loading was undetectable by PXRD. These results highlight the effect of the preparation method on the catalyst properties, as the MgO phase was observed even for a Mg/Si molar ratio equal to 1 by using a sol-gel technique.<sup>[18]</sup>

A clear modification of silicon environments as a function of the Mg/Si molar ratio was suggested by <sup>29</sup>Si{<sup>1</sup>H} CP MAS NMR experiments, Figure S2 (in the Supporting Information). Catalysts with higher amounts of MgO, that is, the MgO/SiO<sub>2</sub> (95:5) and MgO/SiO<sub>2</sub> (75:25) samples, presented a single resonance with maxima around -71 ppm, indicating a high concentration of Q<sup>1</sup> species. Conversely, as the Mg/Si molar ratio was decreased, MgO/SiO<sub>2</sub> (1:1) and MgO/SiO<sub>2</sub> (25:75) samples, resonance maxima were shifted down field, to approximately -87 and -94 ppm, indicating an increase in  $Q^2$  and  $Q^3$  species.<sup>[2, 34, 36]</sup> In comparison with the wet-kneading method,<sup>[23]</sup> Q<sup>2</sup> and Q<sup>3</sup> species were observed at a Mg/Si molar ratio equal to 75:25, and Q<sup>2</sup>, Q<sup>3</sup> and Q<sup>4</sup> species were observed at a Mg/Si molar ratio equal to 1. Thus, the co-precipitation method used in this work seems to be more efficient in the formation of Mg-O-Si linkages. These results are in agreement with a general uniform distribution of elements inside catalyst particles as verified for the ZrZn/MgO-SiO<sub>2</sub>-1 sample by scanning electron microscopy with energy dispersive X-ray, Figure S3 (in the Supporting Information). Even though a residual amount of Na was observed from catalyst preparation, as will be more detailed in the catalyst characterisation section, these Na traces did not significantly affect catalyst activity.

As the synergistic effect of  $ZrO_2$  and ZnO on the MgO/SiO<sub>2</sub> system was more beneficial to 1,3-BD formation at the Mg/Si molar ratio equal to one, this catalytic system, labelled as ZrZn/MgO-SiO<sub>2</sub>-1, was selected for further investigation.

#### **Reaction temperature and WHSV effect**

Initially, the reaction temperature and the WHSV effect were investigated to evaluate catalyst performance and afford more insights into the kinetic mechanism. Mass transfer limitations were excluded by the apparent activation energy estimation,<sup>[37]</sup> Figure S4 (in the Supporting Information).





Figure 2. WHSV and reaction temperature effect on a) ethene and b) DEE selectivities  $(ZrZn/MgO-SiO_2-1, TOS = 3 h)$ .



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Figure 3. WHSV and reaction temperature effect on a) AcH and b) 1,3-BD selectivities ( $ZrZn/MgO-SiO_2-1$ , TOS = 3 h).

The effect of reaction temperature and WHSV on ethanol dehydration products is shown in Figure 2. It should be noted that, in this work, higher WHSV conditions correspond to a higher ethanol molar fraction in the gas phase and lower contact times.

As expected, an increase in reaction temperature increased ethene selectivity, Figure 2(a), and decreased DEE selectivity, Figure 2(b), as ethanol dehydration to ethene is endothermic and to DEE it is exothermic.<sup>[7, 38]</sup> Even though the mechanism of DEE formation is still being discussed in the literature, for instance, regarding whether it involves acid/base pairs,<sup>[39,40]</sup> Brønsted acid sites and/or Lewis acid sites,<sup>[40]</sup> it is understood that DEE formation should involve the reaction of the two nearest chemisorbed ethanol moieties.<sup>[41]</sup> On the other hand, ethene formation should occur through a concerted mechanism, where the methyl hydrogen of the ethoxide species, chemisorbed on a Lewis<sup>[41]</sup> or Brønsted acid site,<sup>[42]</sup> is abstracted by the adjacent Brønsted basic site. Indeed, by using an alumina catalyst, Arai et al.<sup>[41]</sup> verified a rise in DEE formation as the concentration of surface ethoxide was increased, while ethene formation was suppressed. Therefore, the effect of WHSV on ethene and DEE selectivities observed in this work suggests an increase in the concentration of chemisorbed ethanol species on the catalyst surface with a concurrent increase in WHSV, as higher ethanol molar fractions were fed at higher WHSV conditions.

Figure 3 shows the effect of reaction temperature and WHSV on AcH and 1,3-BD selectivities. AcH shows a selectivity increase for both reaction temperatures as the WHSV was raised, Figure 3 (a). As ethanol dehydrogenation to AcH should involve Brønsted basic sites and Lewis acid sites,<sup>[20,43]</sup> verified tendencies suggest a high concentration of active sites for ethanol dehydrogenation on the catalyst surface.

The further AcH transformation involves 3-hydroxybutanal formation and its subsequent dehydration to crotonaldehyde.<sup>[5,12]</sup> Whereas the aldol coupling is an endergonic reaction in the temperature range studied, which becomes more endergonic as reaction temperature increases,<sup>[5]</sup> 3-hydroxybutanal dehydration to crotonaldehyde is favourable in this temperature range and becomes more favourable as the temperature increases.

Thus, as ethanol dehydrogenation to AcH is favoured thermodynamically as the reaction temperature increases,<sup>[5]</sup> an excess of acetaldehyde in the system might contribute to further AcH condensation, explaining its lower selectivities at 375 °C.

The 1,3-BD selectivity behaviour presents different tendencies as a function of reaction temperature and WHSV, Figure 3 (b). At the higher temperature, the increase in 1,3-BD selectivity as WHSV increased might be related to an excess of AcH in the system, whereas at the lower temperature, the contact time appears to affect 1,3-BD formation more dramatically. This same effect of residence time was observed by Sushkevich et al.,<sup>[14]</sup> who evaluated the WHSV effect by using an Ag/ZrO<sub>2</sub>/ SiO<sub>2</sub> system at 320 °C. In addition, additional experiments varying the WHSV at 375 °C and using the same ethanol molar fraction (the amount of catalyst remained constant and the gas flow and ethanol feed rate were both varied), indicated the

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same general tendency observed at 325 °C, Figure S4(c). This implies that the extra ethanol present in the higher WHSV processes facilitates the full conversion to 1,3-BD, as observed previously.<sup>[12]</sup>

Butene selectivity (1-butene, cis- and trans-2-butene) decreased smoothly as the WHSV was increased at both reaction temperatures, Figure 4. The formation of butene from ethanol



Figure 4. WHSV and reaction temperature effect on butene selectivity (ZrZn/ MqO-SiO<sub>2</sub>-1, TOS = 3 h).

is thought to occur through deoxygenation of butanal produced from crotyl alcohol isomerisation.<sup>[5]</sup> Other studies suggest butene as a butanol dehydration product, butanol being produced from the hydrogenation of butanal, which, in turn, might be obtained from the hydrogenation of the C=C double bond of crotonaldehyde.<sup>[16,25]</sup> However, no traces of butanal or butanol were observed in this work and butene may be a product of 1,3-BD hydrogenation. Thus, the reduction in butene selectivity with WHSV can be explained by a reduction in contact time of 1,3-BD in the reactor.

Other minor products observed were ethane, acetone, propene and propane, their combined selectivities did not achieved more than 7% in all experiments. Traces of ethyl acetate, C5 (pentadienes and its isomers) and C6 (hexadienes) compounds were also identified in the output stream.

Regarding ethanol conversion, an increase was observed as reaction temperature increased, whereas an ethanol conversion drop was observed as WHSV was raised, Figure 5. The higher WHSV increases the ethanol molar fraction in the gas stream, at the same time shortening the contact time, factors that might help to explain the reduced conversion.

Figure 6 shows the effect of reaction temperature and WHSV on the yield of the main carbon-containing reaction products. Firstly, it is worth noting that the ethanol conversion increase resulting from the temperature rise has boosted the 1,3-BD yield from 9–16% at 325  $^\circ\text{C}$  to 27–30% at 375  $^\circ\text{C},$  within the same range of WHSV between 0.3 and 1.2  $h^{-1}$ .

Moreover, even though the increase in WHSV has reduced ethanol conversion, Figure 5, 1,3-BD yield has only reduced slightly. Thus, a linear increase in BD productivity (in  $g_{BD}g_{cat}^{-1}h^{-1}$ ) was obtained with WHSV, Figure 7.

As discussed by Makshina et al.,<sup>[13]</sup> catalytic data is usually reported at low ethanol concentrations and 1,3-BD productivi-



375 °C

– 325 °C

50

40

30 %

10

4

x 20



Figure 6. Effect of WHSV on the yield of the main carbon-containing products at a) 325 °C and b) 375 °C. (ZrZn/MgO-SiO<sub>2</sub>-1, TOS = 3 h).



Figure 7. Effect of WHSV and reaction temperature on 1,3-BD productivity  $(g_{BD}g_{cat}^{-1}h^{-1})$  on ZrZn/MgO-SiO<sub>2</sub>-1 catalyst (TOS = 3 h).

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1.2

ΔcH

DFF



ties are usually too low to be industrially relevant. The 1,3-BD productivity values achieved in this work suggest that the ZrZn/MgO-SiO<sub>2</sub>-1 material prepared by co-precipitation is a promising catalyst for 1,3-BD production, as it presents high productivity with reasonable 1,3-BD selectivity compared with other catalytic systems.<sup>[13,30]</sup> For instance, Janssens et al.<sup>[2]</sup> reported productivity equal to 0.15  $g_{BD}g_{cat}^{-1}h^{-1}$  over a catalyst based on Ag/MgO-SiO<sub>2</sub>, at 400 °C and WHSV = 1.2 h<sup>-1</sup>. Using a lower temperature (320 °C), but much higher WHSV (10.3 h<sup>-1</sup>), Sushchevich et al.<sup>[14]</sup> observed 0.23  $g_{BD}g_{cat}^{-1}h^{-1}$  over a Ag/ZrO<sub>2</sub>/SiO<sub>2</sub> system.

Based on these results, we conclude that our ZrZn/MgO-SiO<sub>2</sub>-1 catalyst has shown a suitable performance for ethanol to 1,3-BD conversion. However, ethanol dehydration occurred in significant quantities and, thus, we aimed to modify the acidic features of this system through the addition of the alkali metals Na, K and Li.

#### **Catalyst acidity modification**

The effect of added  $Na_2O$  content on selectivity for the main carbon-containing products is shown in Figure 8(a). The increase in  $Na_2O$  content decreased the selectivities to ethene and diethyl ether, while increasing the selectivities to 1,3-BD



**Figure 8.** a) Effect of catalyst Na content on the selectivity of the main carbonaceous products and b) selectivities comparison with ethanol conversion. ( $T = 375 \text{ }^\circ\text{C}$ , WHSV = 0.62 h<sup>-1</sup>, TOS = 3 h).

and AcH. Conversely, no significant change was observed to the butene selectivity, which fluctuated around 10%.

A positive linear relation was verified when 1,3-BD and AcH selectivities were considered as a function of Na<sub>2</sub>O content, Figure 8 (b), achieving 66% for the combined 1,3-BD and AcH selectivities for the sample with the highest Na content. Also, a negative linear relation was obtained when the ethene and DEE selectivities were considered as a function of catalyst Na<sub>2</sub>O content, Figure 8 (b).

Moreover, a reduction in ethanol conversion was observed as a function of Na content, Figure 8(b), resulting in lower 1,3-BD yields and productivities, Table 1, entries 1–4. These tendencies were confirmed by using a lower WHSV equal to  $0.3 h^{-1}$ , entries 5–7, Table 1. However, it should be emphasised that avoiding ethanol dehydration is the most important step to attain high 1,3-BD yields, as ethene is the most thermodynamically stable product.<sup>[5]</sup> The thermodynamics of the reaction mixture in the case where ethanol dehydration occurs together with ethanol to 1,3-BD conversion was discussed by Makshina et al.,<sup>[5]</sup> who have shown that the thermodynamic yield of 1,3-BD is considerably lower when ethanol dehydration is present.

The suppression of acid sites through Na doping was recently studied on  $Zn_xZr_yO_z$  mixed metal oxides in the ethanol to 1,3-BD conversion.<sup>[30]</sup> An increase in the AcH and 1,3-BD selectivity and a decrease in ethene selectivity were observed for Na<sub>2</sub>O-containing samples. The catalytic results were rationalised through a reduction in the number of strong acid sites as a result of Na doping, which was verified by temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD).

In this work, the acidity of the catalyst samples was investigated through ammonia adsorption followed by TPD experiments and IR measurements. Gases released during TPD experiments were monitored by MS, Figure S5 (in the Supporting Information). A dramatic reduction in the m/z signal attributed to NH<sub>3</sub>, on going from the ZrZn/MgO-SiO<sub>2</sub>-1 system to samples impregnated with sodium, was verified, indicating a large reduction in the number of acidic sites. A minor reduction in the number of acidic sites as the quantity of sodium was increased in the samples was also indicated by NH<sub>3</sub>-TPD experiments, Table S2 (in the Supporting Information). Furthermore, sodiumcontaining samples presented peaks with maximum intensity at temperatures around 380  $^\circ\text{C},$  Figure S5(b), whilst the ZrZn/ MgO-SiO<sub>2</sub>-1 system exhibited peak maximum intensity around 520 °C. Therefore, the addition of sodium resulted in a reduction in the concentration and strength of the acid sites.

IR measurements after NH<sub>3</sub> adsorption supported the NH<sub>3</sub>-TPD conclusions, presenting a clear reduction in the NH<sub>3</sub> stretching intensity as the Na content was increased in the samples, Figure S6 (in the Supporting Information). In particular, a weaker NH<sub>3</sub> signal was observed for the precursor MgO-SiO<sub>2</sub>-1 material, indicating that the ZrO<sub>2</sub> and ZnO addition increased the acidity on going from the MgO-SiO<sub>2</sub>-1 to the ZrZn/ MgO-SiO<sub>2</sub>-1 system. Thus, the sodium addition should have deactivated the Lewis acid sites associated with ZrO<sub>2</sub> and ZnO, as will be discussed more later, contributing to the reduction of the ethanol dehydrated fraction and ethanol conversion.

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Entry	Catalyst	WHSV	Х	Selectivity [mol %]			1,3-BD yield <sup>[d]</sup>	1,3-BD productivity		
			[%]	1,3-BD	AcH	Ethene	DEE	Butene	[mol%]	$[g_{BD}g_{cat}^{-1}h^{-1}]$
1	ZrZn/MgO-SiO <sub>2</sub> -1	0.62	40	35.9	8.3	32.2	9.8	9.2	30.4	0.13
2	0.8-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	26	39.1	14.2	22.9	5.1	11.5	18.1	0.08
3	1.2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	24	46.5	13.1	18.7	4.6	10.9	17.3	0.07
4	2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	24	48.5	17.3	15.5	3.6	9.8	13.7	0.06
5	ZrZn/MgO-SiO <sub>2</sub> -1	0.31	52	31.8	7.0	34.7	5.6	14.6	27.6	0.06
6	1.2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.31	35	49.3	11.8	16.3	4.4	12.4	25.4	0.05
7	2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.31	36	50.6	16.9	13.8	3.4	9.9	17.4	0.03
8	Water/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	46	32.5	6.6	34.9	10.4	10.6	26.8	0.11
9 <sup>[a]</sup>	1.2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	28	52.2	20.0	10.5	2.7	10.2	19.6	0.09
10 <sup>[b]</sup>	ZrZn/MgO-SiO <sub>2</sub> -1	0.62	32 <sup>[c]</sup>	44.6	8.2	24.2	6.6	10.8	41.4	0.17
11 <sup>[a,b]</sup>	1.2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	6.9 <sup>[c]</sup>	44.7	34.1	5.8	1.2	9.9	25.4	0.10
12	1.2-K/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	22	51.6	13.7	17.4	5.2	7.5	21.1	0.09
13	1.2-Li/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	18	44.3	20.5	16.2	4.4	8.7	11.4	0.05
14 <sup>[e]</sup>	ZrZn/MgO-SiO <sub>2</sub> -1	0.62	44	26.2	6.3	43.6	12.7	7.5	24.6	0.11
15 <sup>[a,e]</sup>	1.2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	19	49.5	22.8	11.3	3.2	9.0	22.2	0.10
16 <sup>[a,e]</sup>	1.2-K/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	26	55.1	17.1	12.2	3.5	7.9	27.1	0.12
17 <sup>[a,e]</sup>	1.2-Li/ZrZn/MgO-SiO <sub>2</sub> -1	0.62	19	47.7	17.0	13.4	2.6	13.7	15.9	0.07
18 <sup>[a,e,f]</sup>	1.2-K/ZrZn/MgO-SiO <sub>2</sub> -1	0.31*	44	57.8	12.9	10.3	2.5	10.3	37.2	0.07
19 <sup>[a,e,f]</sup>	1.2-K/ZrZn/MgO-SiO <sub>2</sub> -1	0.62*	35	55.9	19.2	10.2	2.78	7.5	20.1	0.09
20 <sup>[a,e,f]</sup>	1.2-K/ZrZn/MgO-SiO <sub>2</sub> -1	1.24*	26	44.6	30.9	7.5	2.36	5.0	13.1	0.12

As expected, however, besides acidity, the sodium addition modified the samples' textural properties as well. Although no significant change in pore structure was indicated by  $N_2$  adsorption–desorption isotherms, Figure S7 (in the Supporting Information), the surface area was reduced with Na content, Table S3 (in the Supporting Information), probably owing to Na<sub>2</sub>O particle formation in the catalyst pores.<sup>[13,23]</sup> Thus, the ethanol conversion reduction should be associated, mainly, with the deactivation of acid sites and to the smaller access to the active sites as a result of surface area reduction.

The effect of Na<sub>2</sub>O on the catalytic properties was confirmed by an additional experiment in which the process of Na addition was imitated by using only water, entry 8, Table 1. The catalytic performance was similar to that obtained for the ZrZn/ MgO-SiO<sub>2</sub>-1 (entry 1, Table 1) system. Thus, the additional calcination step involved in the Na addition process, which is illustrated in the Figure S8 (in the Supporting Information) as *Calcination 3*, does not appear to have affected the catalyst activity, and therefore, the effect of the removal of this calcination step was investigated, entry 9, Table 1. A slight increase in the 1,3-BD selectivity, yield and productivity (compare entries 3 and 9) was obtained. However, there is a difference in the surface area, (219 versus 333 m<sup>2</sup>g<sup>-1</sup>) of the two materials, which may contribute to the difference in performance.

In an attempt to further improve the catalytic data, the effect of acetaldehyde in the feed was evaluated by using an ethanol-to-acetaldehyde feed ratio equal to 8:2, as this condition has resulted in better catalytic performances in the literature.<sup>[12]</sup> Catalytic data is shown in Table 1, entries 10–11. As expected, the addition of AcH in the feed increased the amount of 1,3-BD produced (compare yields and productivities of entries 1 and 10, and between entries 9 and 11, Table 1). More-

over, ethanol dehydration to ethene and DEE was further suppressed upon AcH addition, this suppression being more pronounced for the catalyst containing  $Na_2O$ .

The acidity modification of the ZrZn/MgO-SiO<sub>2</sub>-1 system was also investigated by using two other alkali metals, K and Li, entries 12 and 13, Table 1. Both systems were effective in the suppression of ethanol dehydration, presenting lower selectivities to ethene and DEE compared with the starting ZrZn/MgO-SiO<sub>2</sub>-1 material. A similar catalytic performance was observed between samples doped with Na and K (compare entries 3 and 12). Conversely, the 1.2-Li/ZrZn/MgO-SiO<sub>2</sub>-1 sample presented a lower 1,3-BD yield and productivity, which is in line with its lower Brunauer–Emmett–Teller (BET) surface area, equal to  $81 \text{ m}^2\text{g}^{-1}$ , compared with the surface area of 1.2-Na/ZrZn/MgO-SiO<sub>2</sub>-1 and 1.2-K/ZrZn/MgO-SiO<sub>2</sub>-1 samples, which are equal to 219 and 243 m<sup>2</sup>g<sup>-1</sup>, respectively.

Finally, the effect of calcination step removal before Zr and Zn addition was investigated, entries 14-17. The removed calcination step is illustrated in Figure S8 as Calcination 1. Regarding the ZrZn/MgO-SiO<sub>2</sub>-1 system, a slight enhancement of the ethene and diethyl ether selectivities was observed upon the removal of the calcination step (compare entries 1 and 14, Table 1), suggesting an increase in the acidity of the catalyst and/or an improvement in the access to active acid sites, as the BET surface area changed from 323 to 416  $m^2g^{-1}$  for the ZrZn/MgO-SiO<sub>2</sub>-1 system prepared with and without the calcination step before Zr and Zn addition, respectively. For samples containing Na<sub>2</sub>O, K<sub>2</sub>O and Li<sub>2</sub>O, the removal of the calcination step was beneficial to the 1,3-BD yield and productivity (compare entries 3 and 15 for Na<sub>2</sub>O, entries 12 and 16 for K<sub>2</sub>O and entries 13 and 17 for Li<sub>2</sub>O containing samples). As observed for the ZrZn/MgO-SiO<sub>2</sub>-1 system, 1.2-K/ZrZn/MgO-SiO<sub>2</sub>-



1 and 1.2-Li/ZrZn/MgO-SiO<sub>2</sub>-1 samples also presented an increase in the surface area as a result of the initial calcination step removal, Table S4 (in the Supporting Information).

These results suggest a clear relationship among 1,3-BD formation, acidic/basic concentration and its distribution on catalyst surface, as 1,3-BD yield and productivity were strongly correlated with catalyst surface area for samples containing alkali metals, Figure 9.



**Figure 9.** Relationship between surface area, 1,3-BD yield (left) and 1,3-BD productivity (right) for 1.2-Na/ZrZn/MgO-SiO<sub>2</sub>-1, 1.2-K/ZrZn/MgO-SiO<sub>2</sub>-1 and 1.2-Li/ZrZn/MgO-SiO<sub>2</sub>-1 samples. Reactions performed as entries 3, 12, 13, 15–17, Table 1.

The effect of calcination step removal was further investigated through <sup>7</sup>Li MAS NMR spectroscopy. Figure S9 (a) (in the Supporting Information) shows the spectra for samples 1.2-Li/ZrZn/MgO-SiO<sub>2</sub>-1 and 1.2-Li/ZrZn/MgO-SiO<sub>2</sub>-1 prepared with only one calcination step after ZrO<sub>2</sub> and ZnO addition. Even though a similar chemical shift was observed between the samples, the different lineshape, broader in the half width for the sample with higher number of calcination steps, Figure S9 (b), and the different intensities of the spinning sideband distribution indicated a modification in the local environment of the lithium

nuclei. Thus, the reduction of the number of calcination steps, besides largely affecting surface area, in agreement with other studies,<sup>[44]</sup> also produces different structural ordering between samples.

The catalyst 1.2-K/ZrZn/MgO-SiO<sub>2</sub>-1 was further investigated regarding WHSV effects, entries 18–20, Table 1. A similar kinetic behaviour to the ZrZn/MgO-SiO<sub>2</sub>-1 system at 325 °C was observed, as higher contact times (obtained at lower WHSVs) were beneficial to 1,3-BD selectivity and yield.

Therefore, the acidity modification of the ZrZn/MgO-SiO<sub>2</sub>-1 system prepared by co-precipitation, through the addition the alkali metals, specially by using K<sub>2</sub>O, seems to be a promising—and cheap—catalyst preparation method to maximize 1,3-BD formation from ethanol conversion. Firstly, ethanol dehydration might be avoided, which is a thermodynamic requirement to achieve higher 1,3-BD yields. In addition, unconverted ethanol and the acetaldehyde produced might be recycled in the process, overcoming the lower ethanol conversion obtained with these systems.

#### Catalyst characterisation

The elemental dispersion of selected samples at specific locations on the catalyst particles was investigated through scanning electron microscopy with energy dispersive X-ray analysis. Table 2 shows the average values determined. A general uniform distribution of Mg, Si, Zr, Zn and Na was observed.

However, a higher measurement scattering was observed for Zr, Zn and Na (compare standard deviations, Table 2), which may be due to a less uniform distribution of these compounds and/or related to a lower analysis sensitivity associated with the smaller concentration of these species. Moreover, the Na doping was confirmed by analyses, which highlight the different Na<sub>2</sub>O content among samples. The residual amount of Na observed in the ZrZn/MgO-SiO<sub>2</sub>-1 catalyst might be a result of an incomplete removal of Na during catalyst washing.

Element distribution on the catalysts surface was further evaluated through EDX mapping analysis. Figure 10 shows the element distribution for the 1.2-Na/ZrZn/MgO-SiO<sub>2</sub>-1 catalyst, emphasising the homogeneous chemical distribution of elements.

Element distribution for samples  $0.8-Na/ZrZn/MgO-SiO_2-1$  and  $2-Na/ZrZn/MgO-SiO_2-1$  is shown in Figures S10–S11 in the Supporting Information. The dispersion homogeneity was further verified by an additional analysis by using a higher magnification, Figure S12 (in the Supporting Information).

Table 2. Elemental dispersion of catalyst samples in wt%.							
Sample	Mg	Si	Zr	Zn	Na		
ZrZn/MgO-SiO <sub>2</sub> -1 0.8-Na/ZrZn/MgO-SiO <sub>2</sub> -1 1.2-Na/ZrZn/MgO-SiO <sub>2</sub> -1 2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	$\begin{array}{c} 32.1 \pm 0.5 \\ 31.8 \pm 1.0 \\ 31.5 \pm 0.9 \\ 31.8 \pm 0.4 \end{array}$	$59.6 \pm 2.2 \\ 56.7 \pm 2.0 \\ 55.8 \pm 0.5 \\ 56.7 \pm 0.5$	$\begin{array}{c} 6.3 \pm 2.0 \\ 7.6 \pm 2.5 \\ 7.2 \pm 0.3 \\ 6.5 \pm 0.7 \end{array}$	$\begin{array}{c} 1.4 \pm 0.4 \\ 1.7 \pm 0.4 \\ 1.9 \pm 0.6 \\ 1.9 \pm 0.3 \end{array}$	$\begin{array}{c} 0.6 \pm 0.2 \\ 2.2 \pm 0.2 \\ 3.7 \pm 0.5 \\ 3.2 \pm 0.1 \end{array}$		
[a] Values of Mg, Si, Zr, Zn and Na were normalised to 100 and represent a dispersion measure only							

The metal loadings were confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Na loadings of 0.98 and 1.96, Zn loadings of 0.39 and 0.37, and Zr loadings of 1.13 and 1.07 wt% were observed for samples 1.2-Na/ZrZn/MgO-SiO<sub>2</sub>-1 and 2-Na/ZrZn/MgO-SiO<sub>2</sub>-1, respectively.

Figure S13 (in the Supporting Information) shows the PXRD patterns for MgO/SiO<sub>2</sub> and the metal-doped variants. Similar PXRD patterns were observed for K<sub>2</sub>O- and Li<sub>2</sub>O-containing samples, Figure S14 (in the Supporting Information), for the 1.2-Na/ZrZn/MgO-SiO<sub>2</sub>-1 sample prepared with no calcination after Na doping, Figure S15 (in the Supporting Information), and for samples prepared with no calcination step before Zr and Zn addition, Figure S16 (in the Supporting Information). Thus, samples presented a common amorphous structure with the three broad peaks (at 25–30°, 33–39° and 58–62°) characteristic of magnesium silicate hydrates.<sup>[34,35]</sup>

The local environment of the silicon atoms on the catalyst surface was investigated through <sup>29</sup>Si MAS NMR spectroscopy, Figure S17 (in the Supporting Information). Figure S17 (a)

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Figure 10. Elemental mapping of the 1.2-Na/ZrZn/MgO-SiO<sub>2</sub>-1 catalyst.

shows the spectra for catalysts i) MgO-SiO<sub>2</sub>-1, ii) ZrZn/MgO-SiO<sub>2</sub>-1, iii) 0.8-Na/ZrZn/MgO-SiO<sub>2</sub>-1, iv) 1.2-Na/ZrZn/MgO-SiO<sub>2</sub>-1 and v) 2-Na/ZrZn/MgO-SiO<sub>2</sub>-1. Spectra are in agreement with the PXRD patterns, the two broad resonances with maxima around -87 and -95 ppm suggest the presence of -Mg-O-Si-linkages. Moreover, the lack of signal at -110 indicates the absence of silica in the catalyst structure, or the presence of an amount too small to be detected.<sup>[34]</sup> Similar signals with chemical shift between -85 and -89 ppm and between -92 and -99 ppm were already reported for magnesium silicate systems and they were attributed to Q<sup>2</sup> and Q<sup>3</sup> species, respectively, as Si\*(OMg)(OSi)<sub>2</sub>(OH) and Si\*(OMg)(OSi)<sub>3</sub>.<sup>[2, 34, 36]</sup> <sup>29</sup>Si MAS spectra were confirmed by cross-polarization (CP) experiments, Figure S17 (b). A shoulder at ca. -80 ppm was observed for all samples, which might be related to Q<sup>1</sup> species.

<sup>29</sup>Si MAS spectra were fitted by a function containing two Gaussian distributions to compute spectra areas and obtain the relative proportion of each silicon environment, the data being summarised in Table 3. Only subtle differences were observed between the relative proportion of  $Q^2$  and  $Q^3$  species, which are probably due to the intrinsic experimental analysis fluctuation. This data indicates that the catalytic results are not explained through the interaction of Na species with surface Brønsted acidic silanol moieties.

Furthermore, basicity features of the catalyst samples were investigated through IR measurements from  $CHCI_3$  adsorp-

 Table 3. Summary of <sup>29</sup>Si MAS NMR data. Numbers represent the relative proportion of each silicon environment.

Catalyst sample	Q² (-87 ppm)	Q <sup>3</sup> (-95 ppm)
i) MgO-SiO <sub>2</sub> -1	21.9	78.1
ii) ZrZn/MgO-SiO <sub>2</sub> -1	27.4	72.6
iii) 0.8-Na/ZrZn/MgO-SiO <sub>2</sub> -1	28.6	71.4
iv) 1.2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	27.0	73.0
v) 2-Na/ZrZn/MgO-SiO <sub>2</sub> -1	26.3	73.7

tion,<sup>[45,46]</sup> Figure S18 (in the Supporting Information). Subtle differences in the CHCl<sub>3</sub> stretching intensities were observed among samples. A comparison with MgO suggested that samples containing higher alkali metal content (1.2 and 2 wt%) may have a slightly higher basicity compared with the precursor MgO/SiO<sub>2</sub> and the ZrZn/MgO-SiO<sub>2</sub> system.

Therefore, the main effect of alkali metal doping may be related to their interaction with Lewis acid sites associated with  $ZrO_2$  and ZnO species, as also suggested by NH<sub>3</sub>-TPD experiments and IR measurements from NH<sub>3</sub> adsorption.

#### Conclusions

In this work, the effect of the Mg-to-Si molar ratio was investigated in the synthesis of magnesia silicate oxides prepared by co-precipitation for the ethanol to 1,3-butadiene conversion. Catalysts were used as support for ZrO<sub>2</sub> and ZnO and the ethanol conversion was studied in a wide range of WHSVs by using two reaction temperatures. <sup>29</sup>Si MAS NMR data suggested that the co-precipitation method was more efficient in the formation of Mg-O-Si linkages compared with the traditional wetkneading. The Mg/Si molar ratio equal to 1 was more suitable to 1,3-BD formation, whereas higher Mg/Si molar ratios produced more acetaldehyde. High 1,3-BD productivities (in  $g_{BD}g_{cat}^{-1}h^{-1}$ ) were obtained with the ZrZn/MgO-SiO<sub>2</sub>-1 system, results that might be associated with the homogeneity of the catalyst properties. Catalytic results supported the usual kinetic route of ethanol to 1,3-BD conversion involving acetaldehyde condensation. The catalyst acidity was modified through the addition of alkali metals (M = Na, Li and K) to the final materials. This process resulted in a decrease in the fraction of ethanol dehydrated, boosting 1,3-BD selectivity. A positive linear relation was obtained for the combined 1,3-BD and acetaldehyde selectivities as a function of the catalyst Na content. Further catalyst optimisation was performed through the reduction of calcination steps in the catalyst preparation, resulting in higher surface areas, 1,3-BD yields and productivities. In particular, a strong correlation between surface area, 1,3-BD yield and productivity was observed for 1.2-M/ZrZn/MgO-SiO<sub>2</sub>-1 samples. Thus, efforts should be dedicated to increasing the surface area of these systems, keeping the acid/basic site distribution constant. The best catalytic results were obtained with the 1.2-K/ZrZn/MgO-SiO<sub>2</sub>-1 material, achieving 72 mol% for the combined selectivity of 1,3-BD and acetaldehyde, at a reasonable 1,3-BD yield and productivity level. Therefore, as unconverted ethanol and acetaldehyde may easily be recycled in the



process, the *x*-K/ZrZn/MgO-SiO<sub>2</sub>-1 system prepared by co-precipitation is a promising material that deserves more investigation to maximize 1,3-BD production. Catalyst acidity modification was further confirmed by NH<sub>3</sub>-TPD and IR measurements from NH<sub>3</sub> adsorption, but <sup>29</sup>Si MAS NMR data indicated that the role of the alkali metal in the catalyst structure was not related to its interaction with Brønsted acidic silanol moieties. As IR measurements from CHCl<sub>3</sub> adsorption indicated only subtle differences between catalyst basicity, the main effect of alkali metal doping should be associated with a selective deactivation of Lewis acid sites related to ZrO<sub>2</sub> and ZnO.

#### **Experimental Section**

#### **Catalyst preparation**

In a typical synthesis, catalysts with the Mg/Si molar ratios equal to 25:75, 50:50, 75:25 and 95:5 were prepared by co-precipitation. For the 50:50 material, SiO<sub>2</sub> (9.01 g, Sigma-Aldrich, 99.8%) was dissolved in NaOH solution (100 mL of 1.2 M, Sigma-Aldrich, 99%). The mixture was heated to between 60 and 80  $^\circ\text{C}$  under vigorous stirring until complete SiO<sub>2</sub> dissolution, the solution was cooled and Na<sub>2</sub>CO<sub>3</sub> (42.4 g, Sigma–Aldrich, 99.9%) added. Α Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution (Sigma-Aldrich, 99%) was added dropwise into this mixture whilst stirring at 25 °C (38.85 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 200 mL). The pH was maintained at 10.5 by adding appropriate quantities of 1.2 M NaOH solution and, at the end of the process, the solution volume was adjusted to 600 mL with deionized water. The resultant mixture was stirred for 2 h before ageing for 22 h at 25°C. Finally, the mixture was filtered and washed with 7.5 L of hot water. The precipitate was dried in static air at 80°C for 24 h before grinding. Materials were calcined in air at 500 °C for 4 h, using a heating rate of 5 °C min<sup>-1</sup>.

To produce materials with 1.5 wt% and 0.5 wt% of  $Zr^{IV}$  and  $Zn^{II}$ , respectively,  $ZrO(NO_3)_2$ ·H<sub>2</sub>O (0.57 g, Sigma–Aldrich, 99%) and  $Zn(NO_3)_2$ ·G H<sub>2</sub>O (0.24 g, Sigma–Aldrich, 98%) were dissolved in water (50 mL), and the solution was added to 10 g of the MgO/SiO<sub>2</sub> system. This was stirred until the mixture was completely dry. Finally, the solid was calcined in air at 500 °C for 5 h. For the Na doping, the appropriate volume of 1.2 m NaOH solution was added to the final catalyst drop-wise. The mixture was kept under stirring for 1 h at 25 °C before drying at 80 °C for 5.5 h and finally calcined at the same previous condition. KOH (Sigma–Aldrich, 90%) and LiOH·H<sub>2</sub>O (Alfa Aesar, 99%) were used instead of NaOH for comparison. The catalyst preparation procedure is illustrated in the Scheme 1 in the Supporting Information. Samples were labelled as *y*-M/ZrZn/MgO-SiO<sub>2</sub>-*x*, where *y* denotes the content of the alkali metal M in wt% and *x* represents the Mg/Si molar ratio.

#### **Catalyst characterisation**

SEM images and SEM/EDX mapping were carried out with a JEOL6480LV at 5–25 kV. Energy-dispersive X-ray spectroscopy (EDX) was carried out in situ during SEM analysis. At least five different spots were selected throughout the images, to evaluate the homogeneity of elements within catalyst particles. Measurements of static adsorption of N<sub>2</sub> at -196 °C were obtained by using a Micromeritics 3Flex instrument. Samples were degassed at 150 °C under vacuum for 2 h prior to analysis. Powder X-ray diffraction (PXRD) was performed with a BRUKER D8-Advance diffractometer using CuK<sub>α</sub> ( $\lambda = 1.5406$  Å) radiation. Intensities were measured with a 0.02° step size and a measuring time of 0.3 s per point. <sup>29</sup>Si solid-

state magic angle scattering (MAS) NMR spectroscopy was performed by using a Varian VNMRS 400 MHz spectrometer, operating at a resonance frequency of 79.44 MHz with a spinning rate of 6 kHz. 1000 scans were accumulated with a recycle time of 60 s, the pulse length being 4.5 µs. The <sup>29</sup>Si{<sup>1</sup>H} CP MAS NMR spectra were recorded with the same spectrometer. 4000 scans were accumulated with a recycle time of 1 s. The CP contact time was 3.0 ms. The  $^{\rm 29}{\rm Si}$  chemical shifts are referenced to tetramethylsilane. The acidity of the samples were determined by temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) with a Setsys Evolution TGA Setaram system coupled with an in-line mass spectrometer, OmniStar™ Pfeiffer Vacuum Quadrupole, for the measurement of the outgas composition. The release of ammonia (m/z = 15) was monitored. The signal m/z equal to 15 was used to avoid interference by the fragmentation of water molecules. Samples were exposed to NH<sub>3</sub> for 48 h at room temperature before the TPD experiments. Pure argon, 100 mLmin<sup>-1</sup>, was used as the sweep gas. Before starting the analysis, the analytical chamber was purged of ambient air by using an argon flow at 200 mLmin<sup>-1</sup> for 40 min. The NH<sub>3</sub>-TPD analyses were started by heating the sample at 10°Cmin<sup>-1</sup> from room temperature to 700°C and maintaining that temperature for 0.5 h, under argon. In situ IR spectra were recorded with a PerkinElmer Frontier spectrometer. Measurements were performed by accumulating 15–30 scans at a resolution of 4 cm<sup>-1</sup>  $CHCl_3$  was used as a molecular probe for the basicity evaluation.<sup>[45]</sup> Samples were exposed to CHCl<sub>3</sub> at 20 °C. MgO (Sigma–Aldrich) was evaluated for comparison.

#### **Catalytic reactions**

The catalytic tests were carried out in a flow quartz packed-bed reactor at atmospheric pressure. Argon was used as the carrier gas (8 mLmin<sup>-1</sup>). The ethanol weight hourly space velocity (WHSV) was varied within 0.3–2.4 h<sup>-1</sup> through the modification of the ethanol flow rate, keeping the catalyst mass and carrier gas flow rate fixed. The WHSV range investigated corresponded to ethanol molar fractions between 0.41 and 0.85. The contact time (calculated as the ratio between the catalyst volume and the total gas flow at the reaction temperature) ranged from 1.3 to 5.5 s. The reaction temperature was within 325-375 °C. The exhaust gases were analysed after 3 h of time on stream (TOS) by GC-MS with an Agilent 7890A instrument with a HP-PLOT/Q, 30 m long, 0.53 mm diameter column equipped with FID/MS detectors. The GC was calibrated as detailed elsewhere.<sup>[13]</sup> Carbon balances were typically better than 80%. Carbon balances and reaction conditions are summarized in the Table S5 (in the Supporting Information).

Ethanol conversion (X), selectivity (S) and yield were computed as in Equations (1), (2) and (3), respectively, where  $N_{EtOH,in}$  and  $N_{EtOH,out}$ represent the number of mols of ethanol that were added and collected, respectively,  $N_i$  denotes the number of mols of the product *i*,  $N_P$  is the total number of products and *r* is the ratio between the number of carbons of the product *i* and of ethanol. For 1,3-BD, for instance, *r* is equal to 2.

$$X(\%) = \frac{N_{\text{EtOH,in}} - N_{\text{EtOH,out}}}{N_{\text{EtOH,in}}} \times 100$$
(1)

$$S_i(\%) = \frac{N_i}{\sum_{i=1}^{N_p} N_i} \times 100$$
<sup>(2)</sup>

$$yield(\%) = \frac{r \cdot N_i}{N_{\text{EtOH,in}}} \times 100$$
(3)

ChemCatChem 2016, 8, 1-12

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#### Acknowledgments

The authors thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) for supporting this research and providing scholarships. We wish to thank the EPSRC Solid-state NMR facility in Durham (Dr David Apperley). We thank the Universities of Bath and Cardiff for involvement in the GW4 partnership.

Keywords: 1,3-butadiene · ethanol · green chemistry · heterogeneous catalysis · silica magnesia catalyst

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Received: March 23, 2016 Revised: May 9, 2016 Published online on

www.chemcatchem.org

ChemCatChem 2016, 8, 1-12

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Ethanol to 1,3-Butadiene Conversion by using ZrZn-Containing MgO/SiO<sub>2</sub> Systems Prepared by Co-precipitation and Effect of Catalyst Acidity Modification



**Ethanol to 1,3-butadiene**: The role of catalyst acidity of ZrZn-containing silica magnesia oxides prepared by a co-precipitation method has been investigated. Catalyst acidity control is found to be the key step to increase butadiene selectivity.

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