



Cite this: *Green Chem.*, 2024, **26**, 7869

## Catalyst screening for dehydration of primary alcohols from renewable feedstocks under formation of alkenes at energy-saving mild reaction conditions†

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Among current challenges for the chemical industry is the shift of the raw material basis from fossil feedstocks to renewable sources, which is also of relevance for the field of the industrial product class of alkenes with a chain length of  $C_6$  or more. A process concept based on  $CO_2$  and renewable energy is the conversion of 1-hexanol, being accessible from such renewable sources, to hexene sources. In this contribution, the dehydration of 1-hexanol catalyzed by Lewis acids such as metal triflates is presented. The prioritized catalysts have been also applied for the dehydration of  $C_7$ – $C_{12}$  primary alcohols.  $Hf^{(IV)}$  and  $Ti^{(IV)}$  triflates have shown the highest conversions in comparison to 13 other metal triflates, leading to high alkene yields of more than 70%. Furthermore, this study revealed a process running at energy-saving conditions and the so far lowest reaction temperatures for a chemocatalytic dehydration of primary alcohols being in the range of 140–180 °C only.

Received 29th February 2024,  
Accepted 14th March 2024

DOI: 10.1039/d4gc01038h  
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### 1 Introduction

The change of raw materials from fossil feedstocks to renewable raw materials is a key challenge for the chemical industry and of high urgency.<sup>1</sup> Nearly 80% of the energy consumption are accounted by nonrenewable resources,<sup>2</sup> yet these sources are destined to run out.<sup>3</sup> Therefore, renewable resources such as cellulose from biomass or directly  $CO_2$  from air represent attractive feedstocks for the future.<sup>4</sup> Today the major class of required industrial organic compounds in terms of mass are alkenes.<sup>5</sup> While ethylene and propylene are the compounds with the largest production volumes and numerous applications for plastics, higher homologues such as hexene are of utmost importance as well and serve as indispensable intermediates for manufacturing a broad range of diverse specialty chemicals. A typical production route to hexenes is through crude oil refining processes. An alternative approach, which enables the use of renewable raw materials, is based on the dehydration of 1-hexanol. Since recently, 1-hexanol has been produced on technical scale by means of the Siemens–Evonik process starting from carbon dioxide and water by combining artificial photosynthesis with microbial fermentation.<sup>6</sup>

Otherwise, the formation of such hydrocarbons starting from syngas is typically done by, *e.g.*, Fischer–Tropsch synthesis.<sup>7</sup> Though, Fischer–Tropsch-synthesis is accompanied by challenges, such as high temperatures,<sup>8</sup> low catalyst stability<sup>9</sup> and low activity as well as selectivity of the catalyst.<sup>8,10</sup>

However, while 1-hexanol as starting material originates from a “green” source and on the first glance this simple-looking reaction of 1-alkanol dehydration appears like “standard” textbook chemistry, surprisingly this reaction is far from being well studied. Typically, the reaction conditions are very harsh with extremely high temperatures being needed, which makes such processes very energy intensive, thus leading to an unfavored carbon footprint. For example, the dehydration of primary alcohols by boric acid requires the use of a stoichiometric amount of catalyst under rather harsh conditions (350 °C).<sup>11</sup> In addition, isomerization of the alkenes takes place under these conditions. For example, if the reaction undergoes an E1 elimination, a carbocation is formed which can then yield an internal alkene through Wagner–Meerwein-rearrangement.<sup>12</sup>

Thus, in order to make use of the advantages of such a potentially environmentally friendly access to hexenes, dehydration conditions at much lower temperatures are needed. In fact, however, just a very few examples are known to proceed at lower temperature and energy-saving milder conditions.

Typically, Brønsted acid-based catalysts such as sulfuric acid or solid catalysts like zeolites,<sup>13</sup> alumina<sup>14</sup> or zirconia<sup>15</sup> are used for the dehydration reaction. However, Brønsted acids are associated with limitations, such as low selectivity, low

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4gc01038h>



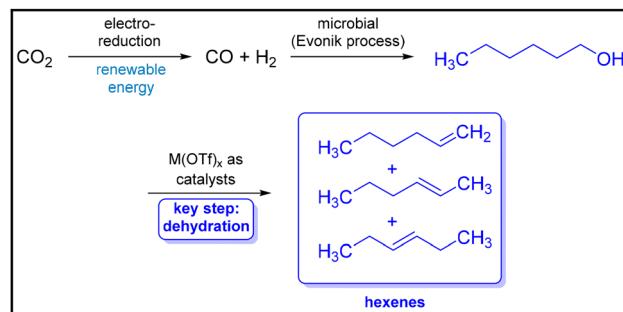
functional group tolerance and corrosiveness.<sup>16</sup> Additionally, the use of Brønsted acids requires neutralization of the acid residues which in turn increases the waste.<sup>4</sup>

Preliminary work utilizing metal-type Lewis acid catalysts has been reported by Laali *et al.*, who noted within their studies on dehydration of a range of alcohols with Cu(OTf)<sub>2</sub> that also a primary alcohol can be dehydrated, which was exemplified by one experiment with 1-hexanol as substrate.<sup>17</sup> In this experiment the resulting hexenes were obtained in a total yield of 38% by means of an *in situ*-removal of the alkenes *via* distillation, but an experimental protocol with the detailed temperature for dehydration of this primary alcohol substrate was not provided. Recently, within an intensive study of the dehydration of metal triflates on secondary alcohols reported by Repo *et al.*, the authors also described two experiments on the dehydration of 1-octanol.<sup>18</sup> These reactions run at a temperature of 180 °C. In the presence of the metal triflates Fe(OTf)<sub>3</sub> and Hf(OTf)<sub>4</sub> as catalysts, the resulting octenes were obtained in total yields of 2% and 65%, respectively. These initial attempts and proof-of-concepts<sup>17,18</sup> illustrate the promising potential of metal triflates as catalysts for this purpose of primary alcohol dehydration although temperatures of at least 180 °C are needed. A further very recent study by Vorholt *et al.* demonstrated that reaction temperatures below 200 °C, can be achieved also with Brønsted acids.<sup>19</sup> In detail, the Vorholt group used phosphoric acid in stoichiometric amount and succeeded in dehydrating 1-octanol at 190 °C mainly to the ether but also in lower amounts to the alkenes.

The high industrial interest in efficient dehydration strategies is also reflected by numerous patent applications filed in this field. Most of these patent applications focus on the use of heterogeneous catalysts as reusability of catalysts plays a major role and reactions are most of the time carried out in the gas phase, thus enabling high space-time yields.

The most common dehydration catalysts are those based on alumina. While Ziehe *et al.* described the dehydration of C<sub>4</sub>–C<sub>14</sub> alcohols at a very high reaction temperature of 280–320 °C and with a feed of 2 mL min<sup>-1</sup>,<sup>20</sup> a further patent application reported the dehydration and etherification of fatty alcohols such as NACOL® 16-99. At an, however, again very high reaction temperature of 260 °C and by means of 10 kg h<sup>-1</sup> NACOL®, the etherification is mentioned to proceed with almost quantitative yields.<sup>21</sup> In a more recent example from 2022, Koo *et al.* describes the use of barium oxide modified alumina supports for the dehydration of 1-octanol, which is conducted at a reaction temperature of 300–400 °C and resulted in yields of >60% and selectivities of >50%.<sup>22</sup> The reported substrate range comprises C<sub>4</sub>–C<sub>20</sub> alcohols.

The whole concept of our study towards a sustainable production of hexenes with minimized energy demand is based on the combination of an initial Siemens–Evonik process,<sup>6</sup> which converts carbon dioxide with sunlight and by means of water-splitting through artificial photosynthesis into syngas, followed by microbial conversion to 1-hexanol and a subsequent metal triflate-catalyzed dehydration. The overall process concept is shown in Scheme 1. The work is part of the ongoing EU-Japan-funded research project being entitled 4AirCRAFT, aiming on



**Scheme 1** Overall process concept for producing hexenes from CO<sub>2</sub>, water and renewable energy such as sunlight and wind in a chemoenzymatic cascade with metal triflate dehydration as a key step.

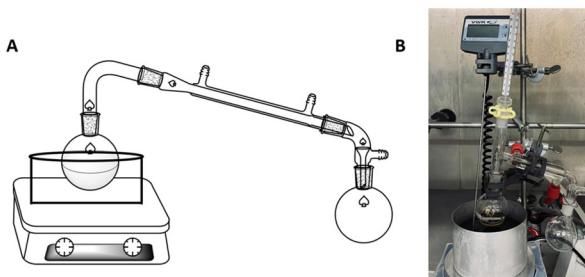
the development of aviation fuels from renewable sources.<sup>23</sup> Until 2040 at least 30% of total transportation fuels should be replaced by renewable fuel sources.<sup>24</sup> In the work described in this contribution, we explored the catalyst potential of metal triflates for such a low temperature and energy-saving dehydration of primary alcohols with a focus on 1-hexanol. In particular our goal was to identify the lowest possible reaction temperature for still conducting the dehydration with reasonable reaction rate, thus minimizing energy demand of this endothermic reaction. We further aimed on getting insight into the reaction mechanism and a detailed catalyst-activity relationship.

## 2 General process concept and reaction set-up

Since the dehydration of primary alcohols is thermodynamically unfavored, very harsh conditions are typically needed. To reduce the needed energy, the equilibrium is shifted towards the desired alkene products by distillative *in situ*-removal of these easily vaporizable products.

In principle, starting from the primary alcohol, first either an ether or alkene is formed whereby the ether formation is favored since it is slightly exothermic.<sup>25,26</sup> On the other hand, the dehydration towards the alkene is endothermic and unfavored.<sup>27,28</sup> However, either the ether or alcohol can be converted under formation of the alkene. The activation energy for the C–O-cleavage of the ether under alkene formation is lower compared to the one for the alcohol, which results in the overall mechanism described in more detail below in chapter 7.<sup>29</sup> Thus, in accordance with literature we hypothesize that at first, in a condensation reaction under release of water, the ether is formed, which is then subsequently cleaved to furnish the corresponding alkene and alcohol. In order to achieve this "formal" dehydration under moderate temperatures, the reactions were carried out under distillation and, thus, *in situ*-removal of the formed alkene fraction.

To avoid any distillation of the substrate 1-hexanol, the reactions were first carried out under reduced temperature at 150 °C for 1.5 h as the model substrate 1-hexanol has a boiling point of 157 °C. Afterwards, the oil bath was heated to 180 °C.



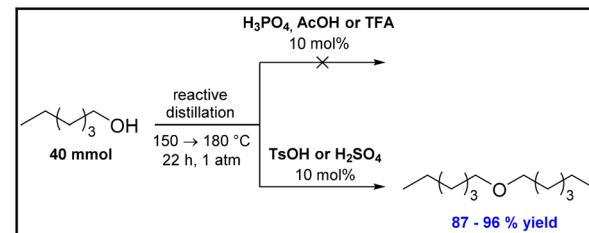
**Fig. 1** Reaction set-up for the dehydration of primary alcohols by *in situ*-removal of the formed products to shift the equilibrium to the product side. On the left side a schematic drawing (A) and on the right side a photo of the reaction set-up (B) are given. The schematic drawing has been drawn by the program "ChemDraw 19.1" from PerkinElmer Informatics.

However, *in situ*-measurements showed that the reaction already takes place at 150 °C, which, to best of our knowledge, is the lowest reaction temperature ever reported for a chemocatalytic dehydration of a primary aliphatic alcohol. The reactions were carried out at a reaction time of 6–22 h. Typically, the end of the reaction was recognised by the fact that no further product was distilled. The real reaction set-up (B) and the schematically drawn one (A) are shown in Fig. 1.

### 3 Dehydration by Brønsted acids

In classic textbook chemistry, elimination of alcohols under formation of alkenes *via* dehydration typically is exemplified by catalysis with strong Brønsted acids. This approach has been studied intensively. However, very high temperatures are typically needed and mostly in literature reaction temperatures around or above 200 °C are mentioned when it comes to the dehydration of primary alcohols. In order to get a "benchmark" for our work using metal triflates as catalysts, we became interested to evaluate these typical Brønsted catalysts with respect to their potential to conduct this challenging transformation of converting 1-hexanol as a model substrate for a primary alcohol to hexene. Such a dehydration of 1-hexanol was investigated by means of various typical Brønsted acids, *e.g.*, phosphoric acid and sulfuric acid. In order to shift the equilibrium to the product side, these endothermic reactions were performed, as described above in chapter 2, under *in situ*-removal of the hexene products by means of distillation. In a typical set-up the dehydration was conducted on a 40 mmol scale of 1-hexanol. To avoid distillation of the substrate, the reactions were first performed at 150 °C which was afterwards heated to 180 °C oil bath temperature.

It is noteworthy that in case of phosphoric acid ( $pK_a = 2.1$ ) no conversion to either the ether or corresponding alkenes was observed. On the first glance this result appears to be in contrast to the dehydration study done by Vorholt *et al.* who obtained a formation of alkenes from primary alcohols with phosphoric acid as a catalyst.<sup>19</sup> However, higher reaction temperatures (190–200 °C) as well as much higher catalyst loadings (1 eq.) were used in their work.<sup>19</sup> Likewise, no conversion was



**Scheme 2** Attempts for dehydration of 1-hexanol by several Brønsted acids showing that only with TsOH and sulfuric acid ether formation was observed. In neither case, the alkenes were formed.

achieved when acetic acid ( $pK_a = 4.8$ ) or trifluoracetic acid ( $pK_a = 0.23$ ) were used as further acidic catalysts.

In the presence of the much stronger acids tosylic acid ( $pK_a = -2.8$ ) or sulfuric acid ( $pK_a = -3$ ) at least the ether was formed and isolated in 96% and 87% yield, respectively (Scheme 2). This improved reactivity found when using TsOH or sulfuric acid can be rationalized by a higher  $pK_a$ , which facilitates the elimination of water from 1-hexanol and, thus contributes to a better conversion. By means of <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopy, however, only the formation of the linear ether di-*n*-hexyl ether was identified. In neither case, the alkene was formed.

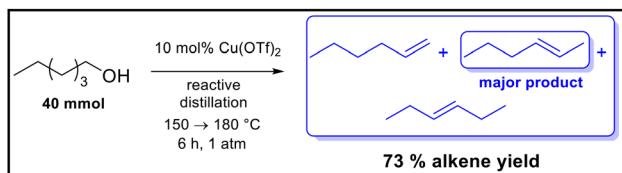
### 4 Dehydration by Lewis acids

Since the dehydration of 1-hexanol by Brønsted acids only lead to the formation of the ether within the desired "lower temperature window" the dehydration under such temperature conditions was investigated with Lewis acids. The literature-known dehydration under similar conditions, which was reported by Laali *et al.* based on the use of Cu(OTf)<sub>2</sub>, served as a starting point for our study.<sup>17</sup> However, under the originally described conditions no conversion of the primary alcohol 1-hexanol towards the alkenes nor to the ether was observed. Therefore, the dehydration process was then optimized by slowly increasing the temperature to a still relatively moderate temperature in order to enable formation of the alkenes. Since the boiling point of 1-hexanol is at 157 °C, the temperature was first set to 150 °C, followed by an increase to 180 °C to initiate the dehydration without distillation of the substrate. To our surprise, under such conditions now the desired alkene fraction was formed with an already high crude yield of 81% and an alkene purity of 90%, thus corresponding to an alkene yield of 73% (Scheme 3).

When the reaction was repeated using a two-necked flask equipped with a thermometer (Fig. 2), a temperature of 150 °C was recorded when the distillation of the product occurred. Also in this case, a similar alkene yield was obtained. As far as these authors are aware, this is the lowest reaction temperature described so far for the dehydration of primary alcohols in the presence of a chemocatalyst.

In the next step, the catalyst loading was reduced to 2 mol% while the reaction time was prolonged to 22 h. However, under these conditions the alkene yield was reduced to 64%.





**Scheme 3** Dehydration of 1-hexanol by Cu(OTf)<sub>2</sub> at 150–180 °C oil bath temperature. Alkenes were formed whereas 2-hexene was the major product. In traces the ether was detected.



**Fig. 2** Set-up for the determination of the temperature inside the flask during the dehydration of 1-hexanol.

In order to investigate the influence of the anion component of the metal catalysts, the dehydration was carried out with CuCl<sub>2</sub> (10 mol%). Conditions remained identical to the ones of the previous experiments. Interestingly, when CuCl<sub>2</sub> was used, no alkene formation was observed, whereas the ether was formed in a low yield of 19%. As a side-product with a yield of 4% hexyl chloride was formed. Thus, these results suggest that the counter anion plays an essential role in the catalytic activity. The use of triflate anion results in an increased Lewis acidity of the metal, which leads to improved catalytic activity.

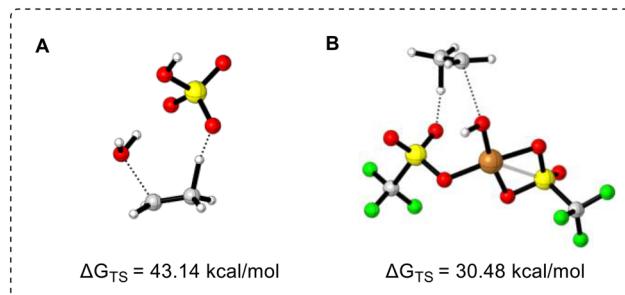
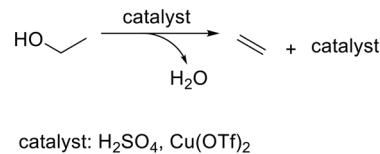
## 5 Computational design

### Brønsted acid- vs. Lewis acid-catalyzed alcohol dehydration

We became interested to rationalize the interesting finding that even “classic” strong Brønsted acids do not lead to the formation of the desired hexenes when applying the envisaged moderate and energy-saving temperature range of 150–180 °C while in case of Cu(OTf)<sub>2</sub> such a transformation proceeds efficiently. To identify the reason for these findings, we calculated the free Gibbs energies for the dehydration step as an indication about the catalytic suitability of Cu(OTf)<sub>2</sub> for the desired elimination reaction compared to the one when utilizing strong Brønsted acids (exemplified for sulfuric acid).

In detail, by means of density functional theory (DFT), we calculated the transition state for the dehydration of ethanol as a structurally very simple primary alcohol and compared the catalytic efficiency when using H<sub>2</sub>SO<sub>4</sub> as Brønsted acid and Cu(OTf)<sub>2</sub> as Lewis acid for  $\beta$ -elimination of 1-ethanol as a model reaction in the gas phase (Fig. 3).

It is noteworthy that we found a strong difference in the activation of ethanol when using the Brønsted acid H<sub>2</sub>SO<sub>4</sub> and



**Fig. 3** DFT studies at the PBE0 D3BJ def2-TZVP def2/J level of theory. Determination and comparison of transition states for  $\beta$ -elimination of 1-ethanol by utilizing H<sub>2</sub>SO<sub>4</sub> (A) or Cu(OTf)<sub>2</sub> (B) as a catalyst.

the Lewis acid Cu(OTf)<sub>2</sub> as catalysts for this dehydration. The free Gibbs energy for the transition state in the direct dehydration with H<sub>2</sub>SO<sub>4</sub> was calculated to be 43.14 kcal mol<sup>-1</sup>, thus being much less favourable than the one with Cu(OTf)<sub>2</sub>, which was 30.48 kcal mol<sup>-1</sup>. These calculations are in good agreement with the experimental observation that activation of 1-hexanol and the dehydration reaction proceeds under energy-saving conditions with a temperature range around 150–180 °C only in case of Cu(OTf)<sub>2</sub> but not with H<sub>2</sub>SO<sub>4</sub>. Thus, as a next step, based on this result, various metal triflates were investigated to achieve the best-performing catalyst.

## 6 Catalyst screening for the dehydration of 1-hexanol

However, when using Cu(OTf)<sub>2</sub> a decomposition of the catalyst was observed. Thus, in order to find more active metal triflates as catalysts, which additionally avoid catalyst decomposition, 14 further metal triflates were investigated. Since different reaction rates were obtained with these catalysts when an *in situ*-removal of the product was done, the reaction time was adjusted within a range of 6–22 h depending on the metal component. Only seven of the screened metal triflates, which are Hf(IV), Ti(IV), Al(III), Fe(III), Sc(III), Cu(II) and Ag(I), showed moderate to high alkene formation. For Sc(III) only a low percentage of alkene was formed. The main product was the ether.

Interestingly, for all other triflates based on lanthanoid metals no conversion was observed, neither to the ether nor to the alkenes. For the other studied transition metal triflates, either the dehydration to the alkene or ether as main products was observed. The triflates with Hf(IV) and Ti(IV) gave the highest activities in terms of dehydration to the alkene. For Al(III) triflate, the alkenes were formed within a moderate reaction time of 12 h. For the triflates based on the non-coordinating and weak Lewis acidic alkali metals Na(I) and K(I), as



expected, no conversion was observed. This indicates that the dehydration is strongly dependent on the coordination to a metal ion serving as a Lewis acid catalyst.

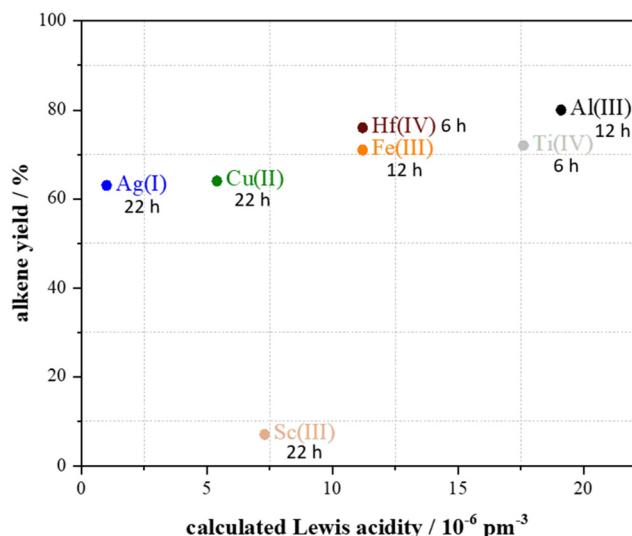
To find out the reasons for the observed differences in alkene yields when using the 15 metal triflates, the obtained yields were plotted against the Lewis acidity and oxophilicity of the metals (Fig. 4 and 5). In previous work of Repo *et al.*, who investigated the dehydration of the secondary alcohol 2-octanol, for secondary alcohols a dependency on the oxophi-

licity was found while the Lewis acidity did not influence the reaction as strongly (Table 1).<sup>18</sup>

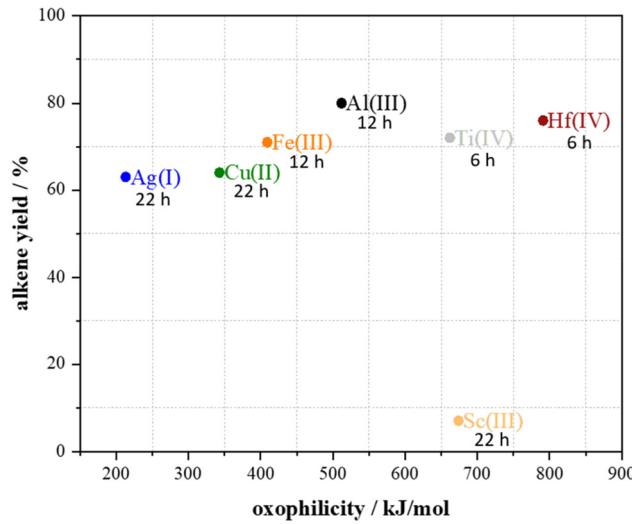
Since only for seven out of the 15 investigated metal triflates formation of alkene was observed, the alkene yields of these catalysts in the dehydration of 1-hexanol were plotted against their Lewis acidity and oxophilicity (Fig. 4 and 5). Typical yields in the range of 60–80% were obtained but the reaction time strongly differs depending on the type of metal ion. Since the product needs to be removed from the reaction to shift the equilibrium to the product side by distillation, only the alkene yields were plotted. A plot of the conversion was not possible by means of the described synthetic method. Similar to the previously reported dehydration of secondary alcohols, no correlation between the Lewis acidity and alkene yield was observed (Fig. 4).<sup>18</sup> However, for the dehydration of the primary alcohol 1-hexanol, there seems to be a correlation between the oxophilicity and alkene yield. Except for Sc(III) triflate, the higher the oxophilicity of the respective metal in the metal triflate is, the higher the yields are and the shorter the reaction time becomes (Fig. 4).

Since Hf(IV) and Ti(IV) showed the highest activities for the dehydration of 1-hexanol (taken into account the obtained yield and the needed reaction time), further experiments were conducted with these two catalysts to also dehydrate C<sub>7</sub>–C<sub>12</sub> primary alcohols in order to gain insight into the substrate scope. In addition, Cu(OTf)<sub>2</sub> was included as a further catalyst in this study since reasonable activities were obtained before and since this catalyst is also economically attractive. In this case, however, the catalyst loading of Cu(OTf)<sub>2</sub> was increased to 10 mol% to have a similar reaction time compared to Hf(OTf)<sub>4</sub> and Ti(OTf)<sub>4</sub>, which are more reactive and have been used with a catalyst loading of 2 mol%. The resulting results are summarized in Table 2.

For the resulting C<sub>8</sub>–C<sub>12</sub> alkene products, a reduced pressure was used for the *in situ*-product removal in order to avoid any decomposition at the boiling point of the produced alkenes at ambient pressure. For example, in the dehydration of 1-octanol under reduced pressure the alkene yield was increased from 57% to 69% when Hf(OTf)<sub>4</sub> was used as a catalyst. A much higher difference in alkene yield has been observed in case of 1-nonanal with an increase of the yield from 9 at 1 atm to 62% under reduced pressure (350–400 mbar). For C<sub>6</sub>–C<sub>8</sub> alkenes, comparable yields were found, and with Hf(OTf)<sub>4</sub> as a catalyst the highest yields were observed. With increasing number of carbon atoms of the primary alcohol, the yield decreased drastically, which can be rationalized by either an increase of the activation energies, a more difficult *in situ*-product removal by distillation or a lowered solubility of the catalyst in the alcohol component.



**Fig. 4** Plotting of alkene yield and calculated Lewis acidity ( $z/r^3$ ) for the dehydration of 1-hexanol catalyzed by 15 different metal triflates whereas only the metal triflates with detected alkene formation are shown: Ag(I), Cu(II), Sc(III), Fe(III), Al(III), Hf(IV) and Ti(IV). For Na(I), K(I), Mn(II), Y(III), Yb(III), Er(III) and La(III) no conversion was observed.



**Fig. 5** Plotting of alkene yield and oxophilicity for the dehydration of 1-hexanol catalyzed by 15 different metal triflates whereas only the metal triflates with detected alkene formation are shown: Ag(I), Cu(II), Sc(III), Fe(III), Al(III), Hf(IV) and Ti(IV). For Na(I), K(I), Mn(II), Y(III), Yb(III), Er(III) and La(III) no conversion was observed.

## 7 Investigating the mechanism of the dehydration catalyzed by metal triflates

An experimental study with different hexanols, which underlines the need for a dramatically higher activation to dehydrate

**Table 1** Dehydration of 1-hexanol catalyzed by 2 mol% metal triflates under an oil bath temperature of 150–180 °C. The Lewis acidity was calculated by  $z/r^3$ .<sup>30</sup> The effect of the anion was not included in the calculation. Oxophilicity was determined by the M–O dissociation energies of the respective metals.<sup>30</sup> Also, in this case the influence of the anion was not considered

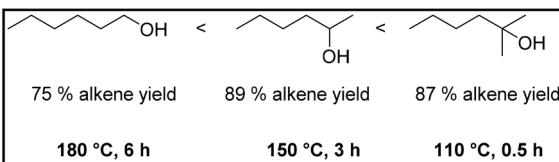
Entry	Metal triflate	Time/h	Oxophilicity/kJ mol <sup>-1</sup>	Lewis acidity/10 <sup>-6</sup> ppm	Main product	Alkene yield/%
1	Hf(IV)	6	791	11.2	Alkene	76
2	Ti(IV)	6	662	17.6	Alkene	72
3	Al(III)	12	512	19.1	Alkene	80
4	Fe(III)	12	409	11.2	Alkene	71
5	Sc(III)	22	674	7.3	Ether	7
6	La(III)	22	799	2.7	—	0
7	Dy(III)	22	611	1.3	—	0
8	Er(III)	22	611	4.1	—	0
9	Yb(III)	22	380	4.3	—	0
10	Y(III)	22	715	4.6	—	0
11	Cu(II)	22	343	5.1	Alkene	64
12	Mn(II)	22	402	6.6	—	0
13	Ag(I)	22	213	1	Alkene	63
14	Na(I)	22	257	0.94	—	0
15	K(I)	22	239	0.38	—	0

**Table 2** Dehydration of C<sub>6</sub>–C<sub>12</sub> primary alcohols catalyzed by metal triflates: Cu(II), Ti(IV) and Hf(IV) at an oil bath temperature of 180 °C

Entry	Substrate	C-number	Pressure	Alkene yield/%		
				Cu(II) <sup>a</sup>	Ti(IV) <sup>b</sup>	Hf(IV) <sup>c</sup>
1	1-Hexanol	6	1 atm	73	72	75
2	1-Heptanol	7	1 atm	71	74	84
3	1-Octanol	8	1 atm	57	n.d. <sup>d</sup>	57
4	1-Octanol	8	550–600 mbar	74	62	69
5	1-Nonanol	9	1 atm	26	n.d. <sup>d</sup>	9
6	1-Nonanol	9	350–400 mbar	61	50	62
7	1-Decanol	10	250–300 mbar	64	52	70
8	1-Undecanol	11	180–200 mbar	54	28	44
9	1-Dodecanol	12	100–120 mbar	52	22	32

<sup>a</sup> 10 mol% Cu(OTf)<sub>2</sub>. <sup>b</sup> 2 mol% Hf(OTf)<sub>4</sub>. <sup>c</sup> 2 mol% Ti(OTf)<sub>4</sub>. <sup>d</sup> not determined.

primary alcohols in comparison to secondary and tertiary alcohols is shown in Fig. 6 and ESI Table 6.† Accordingly, lower reaction temperatures as well as shorter reaction times can be applied in the latter cases compared to the dehydration of 1-hexanol. These findings are in accordance with the well-known elimination tendency of alcohols following the sequence tertiary > secondary > primary alcohols. In addition, dehydration of secondary and tertiary alcohols is in literature described as a direct elimination reaction with the formation of a more stable carbocation as an intermediate (E1) and therefore requiring less energy.<sup>31</sup>



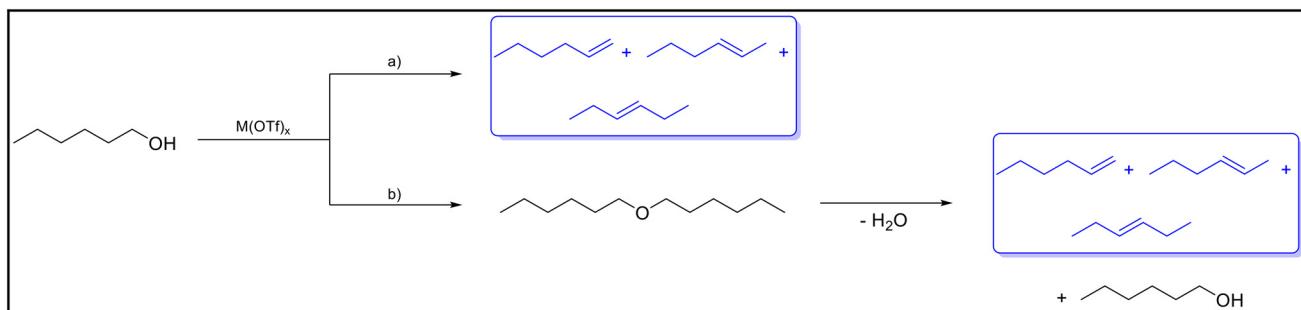
**Fig. 6** Order of reactivity for the dehydration of primary, secondary and tertiary alcohols using Hf(OTf)<sub>4</sub>.

However, still the question of the mechanism for the dehydration of primary alcohols, *e.g.*, 1-hexanol as our substrate of choice, remains open. For primary alcohols, the E1-mechanism can be ruled out as the formation of primary carbocations is less likely,<sup>32</sup> and, thus, other mechanisms have to be taken into consideration.

In general, two different mechanisms are presented in literature for the dehydration of alkanols under formation of alkenes, which in principle could also serve as an explanation for the studied dehydration of 1-hexanol. First, a direct dehydration of 1-hexanol could give the corresponding hexene with water as a by-product. Second, alternatively one 1-hexanol molecule is attacked by a second one, thus forming di-*n*-hexyl ether under removal of water, and subsequently then the ether is cleaved under formation of the desired hexene and the substrate molecule 1-hexanol. These two proposed mechanisms are shown in Scheme 4. To investigate which of the two mechanisms is responsible for the dehydration of primary alcohols catalyzed by these metal triflates at temperatures of 150–180 °C, various experiments were done. Since in the dehydration of alcohols either directly the alkenes or at first the ether can be formed it was investigated if the ether can be directly dehydrated by the metal triflates towards the alkenes. In addition, we studied if another intermediate, namely 1-hexyltriflate is formed and, under these conditions, can undergo elimination to the alkenes. In order to evaluate if di-*n*-hexyl ether could serve as an intermediate, this compound was treated under identical conditions as in the dehydration of 1-hexanol. Since this ether represents a dimer of the alcohol, double as much of the amount of the catalyst was used to have comparable catalyst loading related to the amount of hexenes, which could be formed. In the publication of Repo *et al.* the dehydration of the ether was already described but it was postulated that 1 eq. of water was needed to initiate the reaction.<sup>18</sup> Therefore, we also investigated the impact of water.

In our experiments we found that in each case, with Cu(OTf)<sub>2</sub> as well as Hf(OTf)<sub>4</sub>, the ether was cleaved to the alkenes, respectively. Furthermore, similar yields as for the de-





**Scheme 4** Postulated mechanism for the dehydration of 1-hexanol by metal triflate through: (a) direct dehydration without the formation of an intermediate and (b) by the formation of the ether which is followed by an elimination to form the alkenes and 1 eq. of 1-hexanol.

hydration of 1-hexanol were obtained when di-*n*-hexyl ether was used as a substrate. In our study, water (0.5 eq.) as an additive did not influence the reaction much, since in both cases the alkene was formed, and quite similar yields were obtained.

In addition we synthesized 1-hexyltriflate following the reaction procedure of Cibulka *et al.*<sup>33</sup> to investigate if 1-hexyl triflate is an intermediate in the dehydration of 1-hexanol. In detail, 1-hexyltriflate was synthesized by using 1-hexanol with triflic anhydride and pyridine as a base in 88% yield. In the next step, the elimination to the alkenes starting from 1-hexyl triflate was tested under various conditions: (a) without any catalyst, (b) with  $Cu(OTf)_2$  as a catalyst and (c) using EtOH as a solvent. In each case, however, the alkenes were not formed. In case without the catalyst and  $Cu(OTf)_2$  only decompositions products were found while in case of EtOH as a solvent the non-symmetric ether, namely ethyl hexyl ether, was formed, which is a plausible product since the triflate group is an excellent leaving group. Yet, the alkenes were not formed also in this case. Thus, it can be concluded that 1-hexyl triflate is not an intermediate in the dehydration reaction.

Since 1-hexyl triflate was ruled out as a possible intermediate the dehydration of 1-hexanol is expected to follow one of the two pathways shown in Scheme 4: (a) direct dehydration or (b) indirect dehydration. In (a) 1-hexanol is dehydrated to the alkenes without the formation of an intermediate while in (b) first the ether is formed, which in a second step is converted to the corresponding alkenes (Scheme 4). When carrying out experiments at reaction temperatures below 150 °C, we observed that even with the catalytically very active metal triflates no hexenes are formed from 1-hexanol, but di-*n*-hexyl ether. In addition, ether formation is known to be thermodynamically favored and, thus, exothermic according to literature while the dehydration is an endothermic step.<sup>25–29</sup> These findings support the mechanism according to hypothesis (b). However, it would have to be shown that the ether can be cleaved under the applied temperature range of 150–180 °C. Thus, we conducted studies using di-*n*-hexyl ether as a substrate in the presence of  $Cu(OTf)_2$  and  $Hf(OTf)_4$  as catalysts to proof that the ether could be cleaved under such conditions, thus leading to the hexene products. For comparison, we also conducted this study in parallel using 1-hexanol as a substrate. The results, which are shown in Table 3, show that also when using the ether as a substrate, the desired

**Table 3** Dehydration of di-*n*-hexyl ether catalyzed by  $Cu(OTf)_2$  and  $Hf(OTf)_4$

Entry	Catalyst	Catalyst loading/mol%	Substrate	Substrate loading/mmol	Alkene yield/%
1	$Cu(II)$	10	1-Hexanol	40	73
2		20	Di- <i>n</i> -hexyl ether	22	68
3		20	Di- <i>n</i> -hexyl ether	22	71 <sup>a</sup>
4	$Hf(IV)$	2	1-Hexanol	40	75
5		4	Di- <i>n</i> -hexyl ether	22	66
6		4	Di- <i>n</i> -hexyl ether	22	67 <sup>a</sup>

<sup>a</sup> 0.5 eq. of water was used to enhance the reaction.

hexene products are formed in yields being comparable to the ones obtained when using 1-hexanol as a substrate. In contrast to the often proposed direct dehydration according to Scheme 4, route (a),<sup>18,22</sup> our findings suggest that the reaction mechanism proceeds through a two-step process, which consists of an initial, exothermic formation of the di-*n*-hexyl ether from 1-hexanol, followed by a decomposition of di-*n*-hexyl ether under formation of the hexene products (Scheme 4, route (b)). Thus, even if the overall process represents a “formal” dehydration, according to such a reaction mechanism no direct elimination of water, as described in many articles and textbook chemistry, occurs. Accordingly, not the primary alcohol serves as the “real” substrate in the elimination key step, which is furnishing the alkene product, but the *in situ*-formed ether, which was described in previous work<sup>18</sup> as a side-product. Our proposed mechanism for the formation of 1-hexene is also supported by various literature reports. Based on the findings of, *e.g.*, Busca *et al.*<sup>34a</sup> and Yu *et al.*<sup>34b</sup> it can be expected that route (b) is the preferred route at the applied reaction temperature of 150–180 °C, as it was shown that at milder temperatures route (b) is preferred, while at higher temperatures route (a) is favored. In contrast, high temperature dehydration methods, *e.g.*, the one reported by Koo *et al.*<sup>22</sup> running at 300–400 °C, are more likely to proceed *via* route (a).

## 8 Reusability of $Hf(OTf)_4$

Taking into account the price differences of (at least most) catalysts and commodity chemicals, in general recycling and

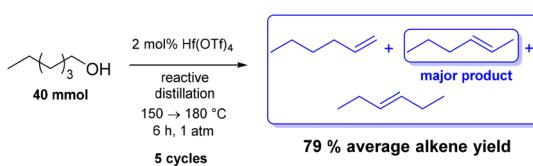


reusability of the catalyst is crucial for an industrial application in this field. Accordingly, also in our work on the metal triflate-catalyzed dehydration process we became interested in the recyclability of the catalyst. An elegant method was reported by Cullen *et al.* already in 2009.<sup>35</sup> By simple aqueous extraction and subsequent removal of water under reduced pressure and elevated temperatures, the catalyst was recycled while still maintaining its activity for three cycles.<sup>35</sup>

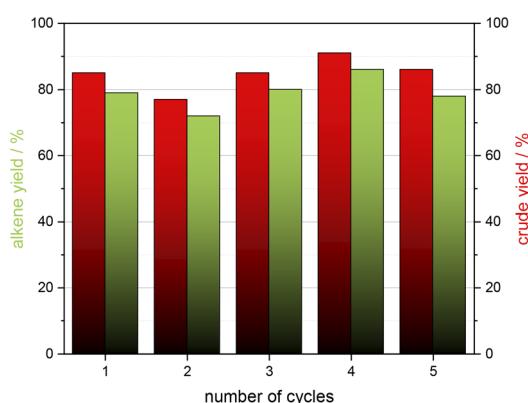
However, as the product is continuously removed in our case, we envisioned that the extraction step can be fully avoided by ensuring reusability simply by adding fresh substrate to the reactor, which is at the same time the distillation flask. As  $\text{Hf}(\text{OTf})_4$  showed the highest yields, this catalyst was chosen for our reusability study. Reaction conditions were identical to previous reaction where only one cycle was performed. In the recycling study, then additional substrate was added after completion of the previous reaction cycle in order to start the next reaction cycle (Scheme 5).

We were pleased to find that high alkene yields of in average 79% were obtained in each cycle (Fig. 7). The slight increase in some of the cycles can be rationalized by distillation of some of the product from the previous cycle, which remained in the distillation flask.

By means of this *in situ*-product removal by distillation as the only work-up step, an effective and efficient way to reuse the catalyst without the need of further unit operation steps was found. Thus, this process concepts also fully avoids the use of solvents for extraction and, thus, effectively contributes to minimizing waste production.



**Scheme 5** Reusability of  $\text{Hf}(\text{OTf})_4$  (2 mol%) for the dehydration of 1-hexanol.



**Fig. 7** Reusability of  $\text{Hf}(\text{OTf})_4$  (2 mol%) for the dehydration of 1-hexanol. In red the crude yield is shown while in green the alkene yield.

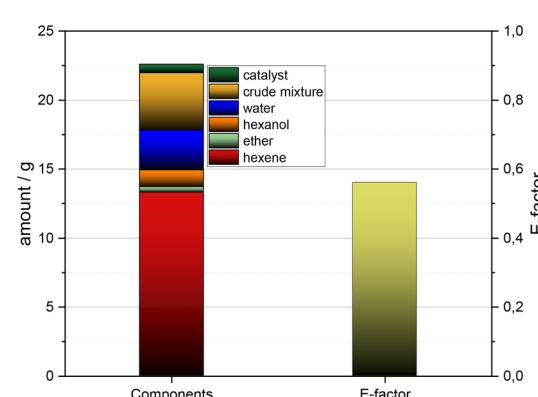
Besides the distillation fraction containing the desired hexene products, the crude mixture of the reaction flask was also analyzed as in average 85% crude yield is obtained and therefore 15% remains in the flask. Interestingly, neither 1-hexanol nor di-*n*-hexyl ether were found in the remaining crude mixture. Only hydrocarbons were found according to NMR and GC measurements. Main products included hexene and its oligomers whereby the  $\text{C}_{12}$  dimers were the main components. The accumulation of such  $\text{C}_{12}$  dimers can be rationalized by their high boiling point and represents an interesting finding because such  $\text{C}_{12}$  compounds are also of interest in terms of utilization as jet-fuels or intermediates thereof.

## 9 Sustainability metrics

After having been able to demonstrate the recyclability of the catalyst, which is a key criteria for an economic process, next we became interested in an initial evaluation of this process in terms of sustainability metrics data. Ahead of the results from such calculations it should be added that the complete avoidance of any solvent utilization and the straightforward work-up by simple distillation of the product during the reaction as an *in situ*-product removal represent advantages also in terms of sustainability.

Conducting the process under neat conditions and the avoidance of any solvent utilization, neither at the stage of the reaction nor at the stage of the work-up, substantially contributes to the very attractive *E*-factor, which has been calculated to be 0.57, thus being in a very low range (Fig. 8). It should be added that this *E*-factor calculation is based on the recycling experiment with five reaction cycles under recycling of the catalyst  $\text{Hf}(\text{OTf})_4$ . Besides the *E*-factor, also the PMI turned out to be in a low range and in detail, a PMI-value of 1.51 was calculated.

Besides such quantitative sustainability metrics data, three further facts should be added which makes this process attractive from the perspective of sustainability: first, the dehydration of 1-hexanol only gives water as an environmentally friendly by-product. Second, even the remaining 15% of mass, which is related to non-hexene fractions and consists of a large



**Fig. 8** Amount of products and waste including *E*-factor for five cycles.



fraction of C<sub>12</sub> dimers, are of potential interest for industrial applications (Fig. 8). Third, the starting material is obtained in a process being highly attractive also from the perspective of sustainability. In detail, the starting material 1-hexanol has been recently reported to be produced from CO<sub>2</sub> and water within the Siemens–Evonik-process that combines an artificial photosynthesis using solar energy with a microbial fermentation step.<sup>6</sup> Thus, the starting material is accessible from renewable carbon sources as well as green energy and consequently avoids the utilization of fossil feedstocks.

## 10 Computational details

All computations were completed by utilizing ORCA 5.0.3 software.<sup>36</sup> The geometries of all minima and transition states were optimized and characterized at the PBE0 D3BJ def2-TZVP def2/J level of theory in the gas phase.<sup>37,38</sup> This method has showed good results for thermochemical approach and is suggested as an efficient tool for the DFT-calculations.<sup>37–39</sup> All reported free energies were performed with entropy corrections at 298.15 K and 1 atm. The transition states were obtained by full geometry optimization, verified by vibrational frequency (imaginary mode), and subsequently validated with Intrinsic Reaction Coordinate (IRC) calculations. The alkyl chain of alcohol was simplified in the calculations. Avogadro<sup>40</sup> and CYLview<sup>41</sup> as software were applied for the visualization of 3D-optimized structures.

## 11 Conclusion

This study describes the use of specific metal triflates as catalysts for the dehydration of primary alcohols, exemplified for 1-hexanol, under formation of the hexene products. This route turned out as a highly efficient way to dehydrate primary alcohols under relatively mild conditions with a reaction temperature of 150–180 °C in case of 1-hexanol. Within the catalyst screening, 15 different metal triflates were screened for the dehydration of 1-hexanol, and among them seven metal triflates have yielded the alkenes. Ti(IV) and Hf(IV) triflates have shown the best properties with respect to high alkene yields, which exceeded 70%. By plotting the Lewis acidity and oxophilicity against the alkene yield it was shown the Lewis acidity is not influencing the reaction while the oxophilicity did. Furthermore, the substrate scope was investigated with the prioritized Cu(OTf)<sub>2</sub>, Ti(OTf)<sub>4</sub> and Hf(OTf)<sub>4</sub> catalysts for the dehydration of C<sub>6</sub>–C<sub>12</sub> primary alcohols, whereby a yield of 69–84% was obtained for C<sub>6</sub>–C<sub>8</sub>. In case of longer carbon chains, however, the alkene yield decreased with prolonged chain length. In addition, the reaction mechanism was studied, and experimental data indicates that the dehydration proceeds through a two-step process with an initial formation of di-*n*-hexyl ether and subsequent cleavage under formation of hexene products. Due to the superior catalytic activity of Hf(OTf)<sub>4</sub>, this catalyst was chosen for reusability studies where at

least five cycles were performed with no loss of activity. Lastly, several sustainability metrics were calculated whereby an *E*-factor as small as 0.56 was obtained for Hf(OTf)<sub>4</sub>. Comparable to previous studies, which run at very high reaction temperatures in the range of 260–400 °C in the gas phase and in the presence of fixed-bed reactors,<sup>20–22</sup> in our process the dehydration is performed in liquid phase with a homogeneous catalyst at a dramatically decreased reaction temperature of 150–180 °C in combination with an *in situ*-product removal through distillation.

Current research activities are focusing on process intensification and scale-up of this process technology. A further task of future work will center on the design of further improved catalysts. Among various conceivable concepts, synergistic effects of combined Brønsted and Lewis acids properties in such catalysts will be explored (as suggested by one of the reviewers of this article).

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

The authors acknowledge financial support from the European Union (EU) within the Horizon 2020 research and innovation programme for the funded project “4AirCRAFT” (grant agreement 101022633). We gratefully acknowledge the computing time provided to them on the high-performance computers [noctua 1] at the NHR Center PC2, which are funded by the Federal Ministry of Education and Research of Germany and the state governments participating on the basis of the resolutions of the GWK for the national high-performance computing at universities (<https://www.nhr-verein.de/unser-partner>). The authors are grateful for having received the suggestion for the development of further catalysts by combining Brønsted and Lewis acids functionalities in synergistic manner, which was made by one of the reviewers of this article and will be subject of future work. The authors also thank Tibor Schumski and James Kamtsikis for technical assistance.

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