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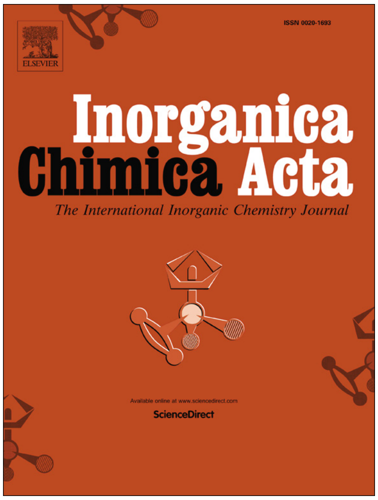

Metal-containing TUD-1 mesoporous silicates as versatile solid acid catalysts for the conversion of bio-based compounds into valuable chemicals

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Metal-containing TUD-1 mesoporous silicates as versatile solid acid catalysts for the conversion of bio-based compounds into valuable chemicals

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Abstract

Three-dimensional mesoporous silicates of the TUD-1 family were synthesised with different metals (Zr, Hf and Sn) incorporated in the framework of the material. The mesoporosity of the prepared TUD-1s was confirmed by X-ray diffraction (XRD), nitrogen physisorption and TEM. The incorporation of the metals in the silicate structure was investigated by FT-IR and UV-Vis spectroscopy. All three TUD-1 materials present a combination of Lewis and mild Brønsted acid sites, as determined by TPD-FT-IR of pyridine adsorption. The metal-containing TUD-1 materials were tested as solid acid catalysts for the conversion of three bio-based compounds into valuable chemical products. In the conversion of dihydroxyacetone into ethyl lactate, complete selectivity towards the desired lactate product was achieved with Zr-, Hf- and Sn-TUD-1. The three heterogeneous catalysts displayed similar activity, with Hf-TUD-1 reaching the highest conversion and metal-based turnover number. Sn-TUD-1 also displayed high activity and selectivity in two acetalisation reactions, *i.e.* the synthesis of solketal from acetone and glycerol and the reaction of vanillin with propylene glycol. The catalytic performance of these TUD-1 materials is ascribed to the high accessibility of their active sites and to the suitable combination of acid sites. The catalysts were successfully reused in consecutive runs and did not suffer from leaching.

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1. Introduction

The discovery of ordered mesoporous silicates, such as MCM-41, MCM-48, HMS-1 and SBA-15 [1], opened new possibilities in the field of catalysis, particularly when metal atoms that can act as catalytic

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sites are introduced in the framework [2,3]. The advantage of these mesoporous catalysts compared to their microporous counterparts (such as zeolites) lies in the larger pore size that provides increased accessibility to the active sites, which is of particular importance for reactions involving large molecules. TUD-1 is a relatively new type of mesoporous silicate with large and tuneable pore size, which can be prepared by a surfactant-free, one-pot synthesis route [4]. The incorporation of a large set of heteroatoms including transition metals into the silica framework of TUD-1 was reported [5-8]. These materials outperformed other metal-containing mesoporous silicates in various relevant catalytic applications. In this work, we demonstrate that Zr-, Hf- and Sn-TUD-1 are highly active, selective and reusable heterogeneous catalysts for the conversion of three bio-based compounds (dihydroxyacetone, glycerol and vanillin) to valuable products.

Glycerol is an important bio-based feedstock, which can be converted into different valuable chemicals [9-11]. The availability of glycerol as renewable feedstock is connected to the increasing interest in biodiesel, which is an economically and environmentally attractive alternative to conventional fossil fuels [12]. Biodiesel is typically synthesised by esterification of vegetable oils or animal fats, yielding approximately 10 wt% of glycerol as the major co-product [13]. The growing production of biodiesel during the last years led to an oversupply of glycerol, causing a significant drop in its commercial value. Therefore, glycerol is becoming increasingly available as a starting material for the synthesis of other valuable chemicals. Glycerol can be converted into trioses, *i.e.* dihydroxyacetone (DHA) and glyceraldehyde (GLY) either by fermentation or catalytic partial oxidation [14-17]. The trioses can be converted to lactic acid or lactates through a multi-step catalytic route involving dehydration and rearrangement reactions (Scheme 1.a) [18-25]. Lactic acid can be used for the synthesis of poly(lactic acid), which is an important biodegradable polymer with a wide range of applications, whereas alkyl lactates can be used as green solvents [26,27]. Moreover, lactic acid and lactates are employed in food, cosmetic and pharmaceutical industries [28]. The catalytic route from dihydroxyacetone has been proposed to be a greener and more efficient method for the synthesis of lactic acid/lactates compared to the conventional method based on the fermentation of glucose [29]. Another interesting use of glycerol is in the acetalisation reaction of acetone to produce 2,2-dimethyl-1,3-dioxolane-4-methanol, better known as solketal (Scheme 1.b), which is a valuable chemical with potential applications as fuel additive, solvent, surfactant and low-temperature heat-transfer fluid [30,31]. The third reaction studied in this work is another acetalisation, involving the conversion of vanillin (4-hydroxy-3-methoxybenzaldehyde) by reaction with propylene glycol (Scheme 1.c) [32]. The obtained acetal is utilised as vanilla flavour and fragrance in the food and cosmetic industry [32,33]. This reaction is commercially performed in the presence of homogeneous Brønsted acid catalysts such as HCl, *p*-toluensulphonic acid or H_3PO_4 [28,34,35]. However, the

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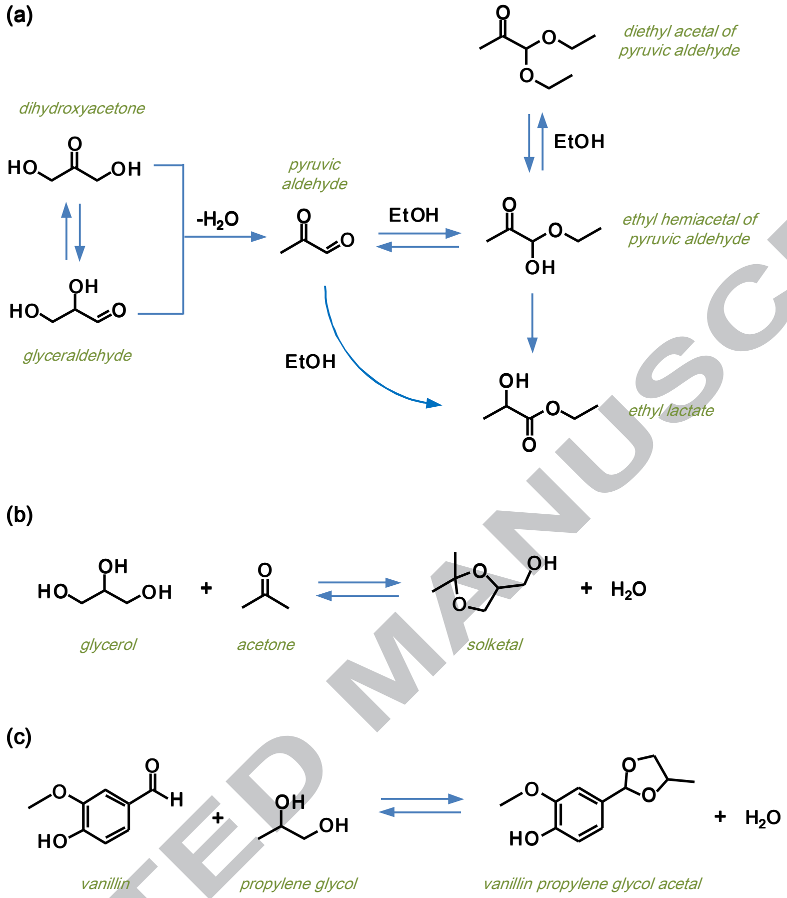
development of heterogeneous catalysts is desirable to simplify the process and to make it more environmentally friendly.



Scheme 1. (a) Conversion of dihydroxyacetone into ehtyl lactate. (b) Acetalisation of acetone with glycerol yielding solketal. (c) Acetalisation of vanillin with propylene glycol.

Recently, we reported the use of Zr- and Hf-TUD-1 as efficient heterogeneous catalysts for the reaction of glycerol with acetone to produce solketal [36]. These catalysts display a combination of mild Brønsted acid sites and Lewis acid sites. This feature is promising for application in the conversion of dihydroxyacetone to lactates: previous work has shown that the initial dehydration of dihydroxyacetone (or glyceraldehyde) to pyruvic aldehyde is catalysed by mild Brønsted acid sites, whereas Lewis acid sites catalyse the conversion of pyruvic aldehyde into the desired lactates (Scheme 1.a) [19,20]. It has been proposed that for Sn-silicates, the dehydration is the rate determining step of the reaction [37]. Strong Brønsted acidity favours the formation of side-products and should be avoided [19]. Besides investigating the catalytic performance of Zr- and Hf-TUD-1 in the conversion of dihydroxyacetone to ethyl lactate, in

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this work we studied also the catalytic performance of Sn-TUD-1. The choice of this tin-based catalyst stems from previous reports in which it was shown that Sn-MCM-41 mesoporous silicates are active and selective heterogeneous catalysts both for the conversion of trioses and for the synthesis of solketal from glycerol and acetone [20,36]. Sn-TUD-1 is expected to display similar active sites and larger pores compared to Sn-MCM-41 and, therefore, high activity in these reactions. The versatility of the catalyst was further evaluated in the acetalisation of a larger substrate as vanillin with propylene glycol.

2. Experimental

2.1. Synthesis of the TUD-1 catalysts

Sn-, Zr- and Hf-TUD-1 were prepared via a synthesis method based on those developed for metal-containing TUD-1 materials [5,8]. Triethanolamine (TEA) was used as chelating and templating agent in a one-pot sol-gel procedure employing a synthesis mixture with the following molar composition: 1 Si : 0.02 M : 0.5 TEAOH : 1 TEA (with M = Sn, Zr or Hf). Tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), zirconium (IV) propoxide ($Zr(OCH_2CH_2CH_3)_4$ (70 wt% in 1-propanol), and hafnium (IV) chloride ($HfCl_4$) were used as metal precursors. A pre-mixed solution of $1.6 \cdot 10^{-3}$ mol of metal precursor in 15 ml of 2-propanol was added to 16.9 g of tetraethyl orthosilicate (TEOS) and vigorously stirred for 10 min. Then, a mixture of 12.3 g of triethanolamine and 16.0 g of deionised water (TEA : H_2O = 1:11) was added, followed by addition of 16.8 g of tetraethyl ammonium hydroxide solution (TEAOH, 35 wt.%, aqueous) under vigorous stirring. The gel obtained after these steps was aged statically at room temperature for 24 h and then dried at 98 °C in air for 24 h. The obtained solid was gently ground and transferred into a Teflon-lined stainless steel autoclave to undergo thermal treatment at 178 °C for 24 h. Finally, the solid was calcined in air at 600 °C for 10 h (heating rate: 1 °C min^{-1}). Before the catalytic tests, the materials were dried at 60 °C overnight. It should be noted that the method presented here for the synthesis of Sn-TUD-1 is different from the one previously reported in literature for this type of material [6].

2.2. Characterisation

Powder X-ray diffraction (XRD) was recorded on a STOE Stadi P diffractometer with CuKα1 radiation (λ = 1.54056 Å) and equipped with a Ge (111) monochromator. Nitrogen adsorption-desorption isotherms were measured at 77K on a Micromeritics Tristar 3000. The Brunauer-Emmett-Teller (BET) method was used to calculate the surface area of the samples [38]. The pore size distributions were obtained from the adsorption isotherm using the Barrett-Joyner-Halenda (BJH) method [39]. Transmission electron

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microscopy (TEM) was performed on a Philips FEG CM 200 operating at 200 kV. Prior to the TEM analysis, the samples were dispersed in ethanol and deposited on 300-mesh carbon-coated copper grids. Solid state UV-Vis spectra were measured on a Varian Cary 5 spectrophotometer in the 200-600 nm range. The samples were not treated before the measurement and the spectra were recorded in air. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 730 FT-IR spectrometer using KBr self-supported wafers. The chemical composition of Sn-, Zr- and Hf-TUD-1 was determined by dissolving 50 mg of each sample in a mixture of 0.5 ml of aqua regia and 3 ml of 40% aqueous HF. The obtained solutions were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Jobin Yvon Ultima instrument. Thermogravimetric analysis (TGA) was performed with a heating rate of 10 °C min^{-1} in the range 35–500 °C under N_2 flow using TGA Q500 from TA Instruments. The detailed procedure used to estimate the number of water molecules adsorbed per nm^2 of surface of the material can be found in previous reports [36]. The type and amount of acid sites was studied by adsorption and temperature programmed desorption (TPD) of pyridine monitored by FT-IR spectroscopy. The infrared spectra were recorded on a Nicolet 6700 spectrometer equipped with a DTGS detector (128 scans, 2 cm^{-1} resolution). A self-supporting wafer of the sample (about 10-15 mg) was evacuated in a vacuum infrared cell with in-house built ZnSe windows. The sample was dried at 400 °C for 1 h under vacuum to remove the adsorbed water. During cooling down of the sample to 50 °C, reference spectra were recorded at 350, 250, 150 and 50 °C. The dried sample at 50 °C was saturated with 25 mbar of pyridine vapour for 10 min and then was evacuated again for 30 min to remove all the physisorbed pyridine. The evacuated sample was subjected to TPD at 150, 250 and 350 °C for 30 min, with heating rate of 4 °C min^{-1}. FT-IR spectra were recorded in situ at each of these temperatures. The amount of acid sites at 150, 250 and 350 °C was determined from the integral intensity of the corresponding bands (1450 cm^{-1} for Lewis acid sites and 1545 cm^{-1} for Brønsted acid sites) in the FT-IR spectra using the molar extinction coefficients of Emeis [40]. The reference spectra were subtracted from those containing bands from adsorbed pyridine at the corresponding temperatures.

2.3 Catalytic tests

Catalytic tests were carried out in a multiple-well parallel reaction block [41]. In a typical test for the conversion of dihydroxyacetone (DHA) to ethyl lactate, a mixture of 1,3-dihydroxyacetone dimer (0.180 g, $2.00 \cdot 10^{-3}$ mol) and decane (0.0215 g, $1.50 \cdot 10^{-4}$ mol, as GC internal standard) in 5 ml ethanol (3.92 g, as solvent and reactant) was pre-heated at 45 °C for 30 min to fully dissolve the dimer and convert it into DHA. The selected amount of catalyst (50, 100 or 200 mg) was introduced into the pre-heated solution, the glass vial containing the reaction mixture was capped and then stirred vigorously at 90 °C for the selected

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reaction time. At the end of the test, the catalyst was separated by centrifugation and the reaction solution was analysed by gas chromatography (GC) on a Trace GC Ultra from Interscience (RTX-5 column, 5 m, 0.25 mm) [20]. The recyclability of the catalysts was evaluated by separating the solid from the reaction mixture by centrifugation at the end of the test. Next, the solid catalyst was washed five times with ethanol and dried overnight in an oven at 100 °C. In an alternative recycling approach, after the five washings with ethanol the material was thermally treated in an oven at 300 °C for 5 h in air (heating rate: 1 °C min^{-1}). The catalyst was then reused in a new test following the procedure described before. Leaching tests were performed by removing the catalyst (100 mg) after 30 min of reaction: the sample was first centrifuged and then filtered through a 0.2 μm filter while at the reaction temperature. The filtrate was allowed to react for further 5 h 30 min. The conversion and product yields after 30 min and at the end of the hot filtration test were determined by GC analysis (*vide supra*) and compared.

The catalytic tests for the synthesis of solketal were performed in tightly closed glass vials loaded with 25 mg of catalyst and a solution containing 0.921 g of highly purified glycerol ($1.00{\cdot}10^{-2}$ mol) or 1.15 g of a mixture of 80 wt.% glycerol and 20 wt.% water (aqueous glycerol) ($1.00{\cdot}10^{-2}$ mol of glycerol), 0.581 or 1.162 g of acetone ($1.00{\cdot}10^{-2}$ or $2.00{\cdot}10^{-2}$ mol), 0.132 g of 1,4 dioxane ($1.50{\cdot}10^{-3}$ mol, as internal standard) and 1.48 g of *tert*-butanol ($2.00{\cdot}10^{-2}$ mol, as solvent) [36]. The tests were carried out at 80 ºC for 6 h with continuous and vigorous stirring. At the end of the test, the sample was centrifuged to separate the catalyst from the reaction solution, which was analysed on a Trace GC Ultra from Interscience (PH POR-Q column, FT-3, 10 m, 0.25 mm).

The acetalisation reaction of vanillin with propylene glycol was performed under vigorous stirring in a round bottom flask equipped with a Dean-Stark apparatus to remove the water formed during the reaction. Vanillin (250 mg, $1.64{\cdot}10^{-3}$ mol) and propylene glycol (250 mg, $3.28{\cdot}10^{-3}$ mol) were added to 8 ml of toluene together with 19 mg of Sn-TUD-1 (7.5 wt.% relative to vanillin) and heated to 115ºC [32]. After the desired reaction time, the sample was allowed to cool down and centrifuged to separate the catalyst from the reaction solution, which was analysed on a Trace GC Ultra (RTX-5 column, 5 m, 0.25 mm) with 1,4-dioxane as internal standard added after the catalytic test.

In all the studied reactions, he identity of the products was confirmed by gas chromatography-mass spectrometry (GC-MS) performed on an Agilent 6890 N gas chromatograph (WCOT fused silica column, 30 m, 0.25 mm) coupled with an Agilent 5973 MSD mass spectrometer.

3. Results and discussion

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The three metal-containing mesoporous silicates Sn-, Zr- and Hf-TUD-1 were prepared using a surfactant-free synthesis method at room temperature in which triethanolamine (TEA) acts as mesopore directing agent and as chelating agent for the silicon and metal species [5]. The physicochemical properties of the synthesised materials were investigated by using a combination of techniques. The mesoporous nature of the materials was proven by N_2-physisorption analysis, which showed a type IV isotherm for all three TUD-1s [37, 42], with a relatively narrow pore size distribution in the mesopore range and high BET surface area (Table 1 and Fig. 1.a). The XRD patterns of the three materials display a broad peak at low $2\theta^{\circ}$ values (Fig. 1.b), which is typical of disordered mesoporous materials and is in agreement with previous reports on TUD-1 [43]. No evidence of crystalline metal oxide clusters was observed in the diffractograms, suggesting a good incorporation of the metal atoms within the silica framework in all three materials. The mesoporosity of the materials was further confirmed by TEM (Fig. 2), which evidences the disordered mesopores that are encountered in the sponge-like 3-D network characteristic of TUD-1 [36]. The Si/M (M = Sn, Zr or Hf) ratios of the solids obtained after calcination, determined by ICP-OES elemental analysis, are remarkably close to those in the synthesis gel (Table 1), confirming the efficiency of the synthesis protocol [8,42]. The successful incorporation of the metals into the TUD-1 material is a necessary but not sufficient condition for generating the desired catalytic sites. In general, the active sites in metal-containing silicates consist of metal atoms that isomorphously substitute Si atoms in the silicate framework, and thus present tetrahedral coordination. The configuration of the metal atoms in Sn-, Zr- and Hf-TUD-1 was investigated by means of solid state UV-Vis spectroscopy (Fig. 3). Sn-TUD-1 showed an absorption peak at around 208 nm (Fig. 3.a), which indicates the presence of Sn atoms in tetrahedral coordination [44-46]. The broad absorption around 300 nm is assigned to hexacoordinated polymeric Sn-O-Sn type species [44,46]. These results reveal that the majority of the tin atoms are incorporated in the desired tetrahedral framework sites, but that extra-framework tin oxide species are also present. The absence of any signal due to crystalline SnO_2 in the XRD patterns suggests that the tin oxide domains are small and amorphous [6]. Zr-TUD-1 displayed a broad peak centred around 250 nm (Fig. 3.b), which is assigned to a charge transfer between O^{2-} and Zr^{4+} and can generally be ascribed to isolated Zr atoms and/or to small Zr_xO_y domains in the framework [47]. The absence of the absorption at around 300 nm observed in commercial ZrO_2 [47] confirms the good dispersion of zirconium in the silica framework. The UV-Vis spectrum of Hf-TUD-1 presents a peak at around 230 nm, with a tail extending to higher wavenumbers (Fig. 3,c). Although there is a lack of studies about Hf atoms tetrahedrally incorporated in silicate frameworks, the position of this absorption band is similar to that observed in the UV-Vis spectra of Zr- and Ti-TUD-1[43,47], suggesting the efficient incorporation of Hf atoms in isolated tetrahedral sites. This assignment is also in line with the large population of Lewis acid sites in Hf-TUD-1 determined by FT-IR analysis of adsorbed pyridine (Table 2) [36]. However, it should be noted that HfO_2 only weakly absorbs in the UV-Vis range [48, 49]

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and the presence of oxide domains in the Hf-TUD-1 sample cannot be excluded simply on the basis of the UV-Vis spectrum [50]. The FT-IR spectra (Fig. 4) of the TUD-1s skeletal region show the typical bands at 1093 cm^{-1} and 1220 cm^{-1} due to asymmetric stretching vibrations of Si-O-Si. The band at 798 cm^{-1} is generated by the symmetric stretching vibration of Si-O-Si [51]. No peak can be clearly distinguished in the region where the Si-O-M stretching vibrations [44,52-54] and/or those of terminal silanol groups (Si-OH) [52] are observed (*i.e.* around 960 cm^{-1}). The signal due the presence of the metal atoms might be masked by the stronger absorptions due to Si-O-Si species, which are much more abundant in these TUD-1 having Si/M ratio around 50.

Table 1: Physicochemical properties of the synthesised TUD-1 mesoporous materials.

Sample	**Si/M ratio**		**S_{BET} (m^2/g)^b**	**Mesopore volume (cm^3/g)^b**	**Average pore size (nm)^b**	**$n_{H_2O} \cdot$ nm^{-2}**
	Synthesis gel	Product^a				
Sn-TUD-1	50	51	843	0.6	3.2	5.6
Zr-TUD-1^c	50	51	651	0.8	13	5.2
Hf-TUD-1^c	50	53	715	0.6	4.0	7.1

^{a} From ICP-OES analysis (M = metal).

^{b} From nitrogen physisorption analysis.

^{c} Data taken from ref. [36]

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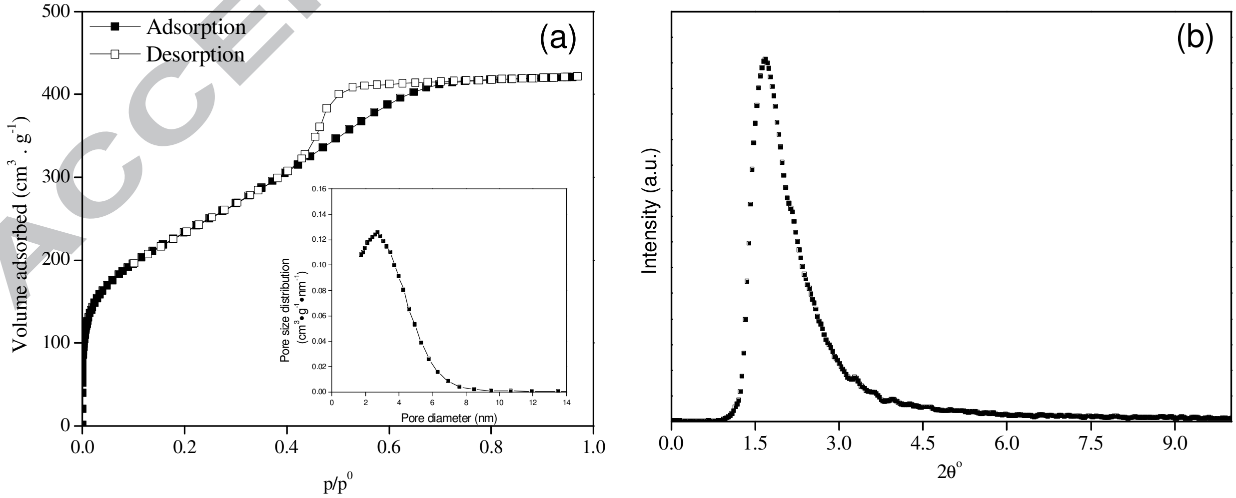

Figure 1. (a) Nitrogen adsorption-desorption isotherms (inset: pore size distribution) of Sn-TUD-1, displaying the typical hysteresis loop due to mesoporosity. (b) Diffractogram of Sn-TUD-1 in the low-angle region. Note: the N_2 adsorption-desorption isotherms and the XRD patterns of Zr- and Hf-TUD-1 were reported before and can be found in ref. [36].

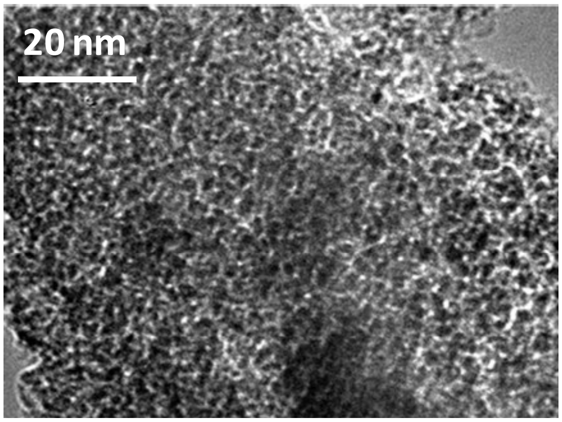

Figure 2. TEM image of Sn-TUD-1. The corresponding images for Zr- and Hf-TUD-1 can be found in ref. [36].

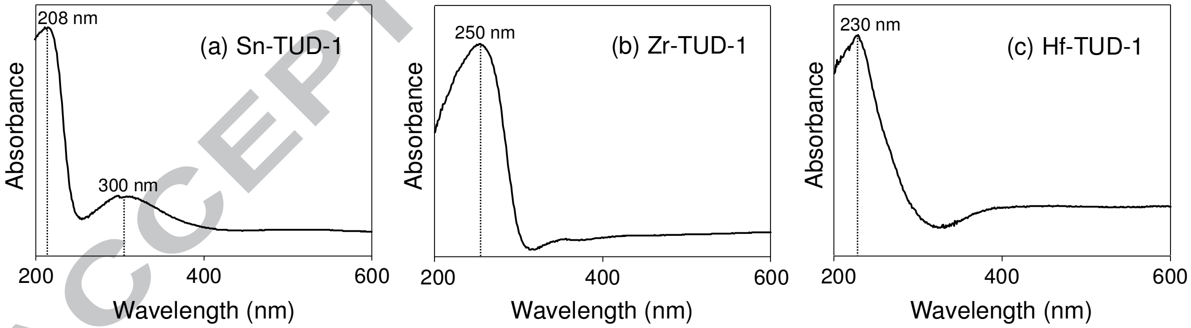

Figure 3. Solid state UV-Vis spectra of Sn-, Zr- and Hf-TUD-1 in the 200-600 nm range.

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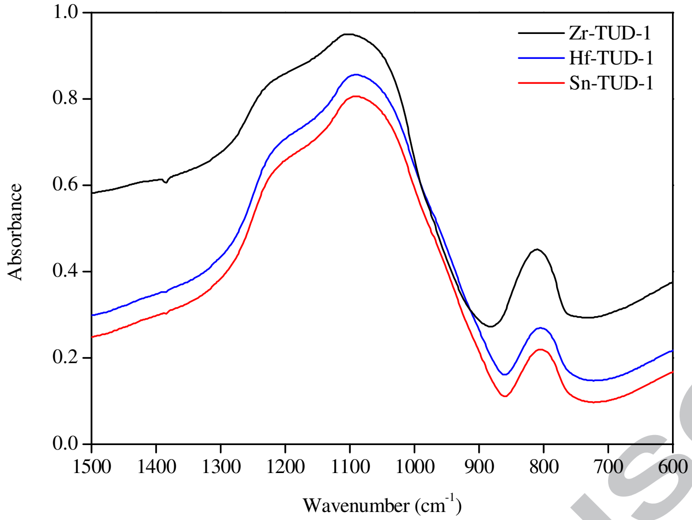

Figure 4. Skeletal FT-IR spectra of Zr-, Hf-and Sn-TUD-1.

FT-IR studies of temperature programmed desorption (TPD) of adsorbed pyridine were performed to assess the type and strength of the acid sites present at the surface of Sn-TUD-1 and to complement similar data previously obtained for Zr- and Hf-TUD-1 [36]. The spectrum of Sn-TUD-1 after pyridine desorption at 150 °C (Fig. 5) exhibits characteristic bands at 1450 and 1620 cm^{-1} (strong Lewis acid sites bound to pyridine), 1575 cm^{-1} (weak Lewis acid sites), 1545 and 1639 cm^{-1} (Brønsted acid sites) and 1492 cm^{-1} (both Brønsted and Lewis acid sites) [55]. All three TUD-1s display mainly Lewis acidity (Table 2), in line with the expected nature of Sn, Zr and Hf atoms in tetrahedral sites in the silicate framework [36, 56]. All materials also present a population of Brønsted acid sites, which is generally ascribed to surface silanols located in the proximity of the Lewis acid metal sites [57,58]. The relatively mild nature of these Brønsted acid sites is indicated by the weaker adsorption of pyridine on these sites compared to the Lewis acid sites, as demonstrated by the increase in the Lewis/Brønsted ratios as a function of the temperature at which the spectrum of the adsorbed pyridine is measured (Table 2). Among the three M-TUD-1 materials, Hf-TUD-1 displays the highest amount of acid sites (Lewis and Brønsted).

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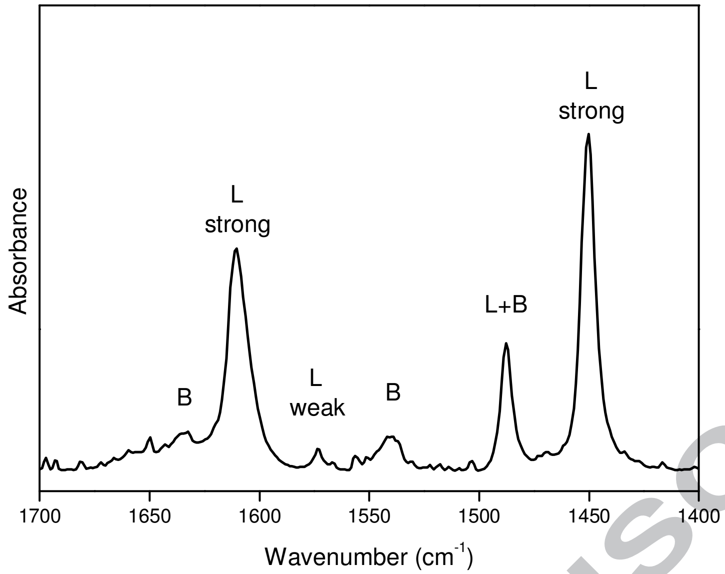

Figure 5. FT-IR spectrum of pyridine adsorbed at 150 °C on Sn-TUD-1. Signals attributed to pyridine adsorbed on Brønsted acid sites are labelled with B and on Lewis acid sites with L.

Table 2. Type and amount of surface acid sites and Lewis/Brønsted (L/B) acidity ratios of the TUD-1 catalysts, as determined by TPD-FT-IR with pyridine as probe molecule.

Catalysts	**Lewis acidity [mmol/g]**			**Brønsted acidity [mmol/g]**			**L/B ratio**		
Temperature:	150 °C	250 °C	350 °C	150 °C	250 °C	350 °C	150 °C	250 °C	350 °C
Sn-TUD-1	0.079	0.014	0.001	0.012	0.002	0.000	6.6	7.0	(∞)
Zr-TUD-1[a]	0.093	0.033	0.004	0.025	0.005	0.001	3.7	6.6	6.8
Hf-TUD-1[a]	0.157	0.059	0.006	0.043	0.007	0.001	3.6	9.0	10.0

[a] Data taken from ref. [36]

Sn-, Zr- and Hf-TUD-1 were investigated as catalysts in the conversion of dihydroxyacetone into ethyl lactate. All three materials display high activity in this reaction, reaching full conversion with complete selectivity towards the desired ethyl lactate product after 12 h of reaction at 90°C (Fig. 6). The selectivity towards ethyl lactate increases as the reaction proceeds because the formation of the hemiacetal and acetal of pyruvic aldehyde side-products is reversible, and their concentration tends to decrease with increasing reaction time [19,25]. Accordingly, these side-products are only observed at shorter reaction time and if the reaction is carried with lower catalyst loading (Fig. 6 and Table 3). The high activity and excellent selectivity displayed by these catalysts originates from their combination of Lewis acid sites and mild

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Brønsted acid sites, as determined by pyridine TPD-FT-IR. The catalytic performance of these metal-containing TUD-1 materials is similar to that of the previously reported Sn-MCM-41 [20]. When comparing the three catalysts at low reaction time (*e.g.* after 2 h at 90°C with 100 mg of catalyst, see Fig. 6) or with lower catalyst loading (*i.e.* 50 mg of catalyst, 6 h at 90°C, see Table 3, entries 1-3), it is concluded that Hf-TUD-1 displays the highest catalytic activity in this reaction, followed by Zr-TUD-1 and Sn-TUD-1 (though the differences are not major). This trend correlates well with the trend in the amount of acid sites in the three catalysts (Table 2). The analysis of the turnover numbers (TON) provides further insight into the catalytic properties of these materials. When the TON are calculated on the basis of the number of metal sites, the values for the three catalysts are in the same range and follow the trend of activity Hf-TUD-1 > Zr-TUD-1> Sn-TUD-1 (Table 3). Turnover numbers can be calculated also on the basis of the number of Brønsted and Lewis acid sites, remembering that the former promote the initial dehydration of dihydroxyacetone, and the latter catalyse the successive rearrangement into ethyl lactate (Scheme 1.a). When the catalysts are compared based on turnover numbers derived from the amount of acid sites, either Brønsted or Lewis, the trend is reversed and Sn-TUD-1 displays the highest TON, followed by Zr-TUD-1 and finally by Hf-TUD-1 (Table 3). These data indicate that the acid sites in Sn-TUD-1 are the most active in catalysing the conversion of dihydroxyacetone to ethyl lactate. On the other hand, not all Sn atoms present in the catalyst are in isolated tetrahedral surface sites that can act as Lewis acids, as suggested by the presence of the absorption band at around 300 nm in the UV-Vis spectrum of this material (*vide supra*). It can be concluded that Sn-TUD-1 contains the most suitable active sites for this reaction, but Hf-TUD-1 is a more active catalyst because it contains a large number of acid sites, as a consequence of a more efficient incorporation of hafnium atoms as tetrahedral single sites at the surface of the material.

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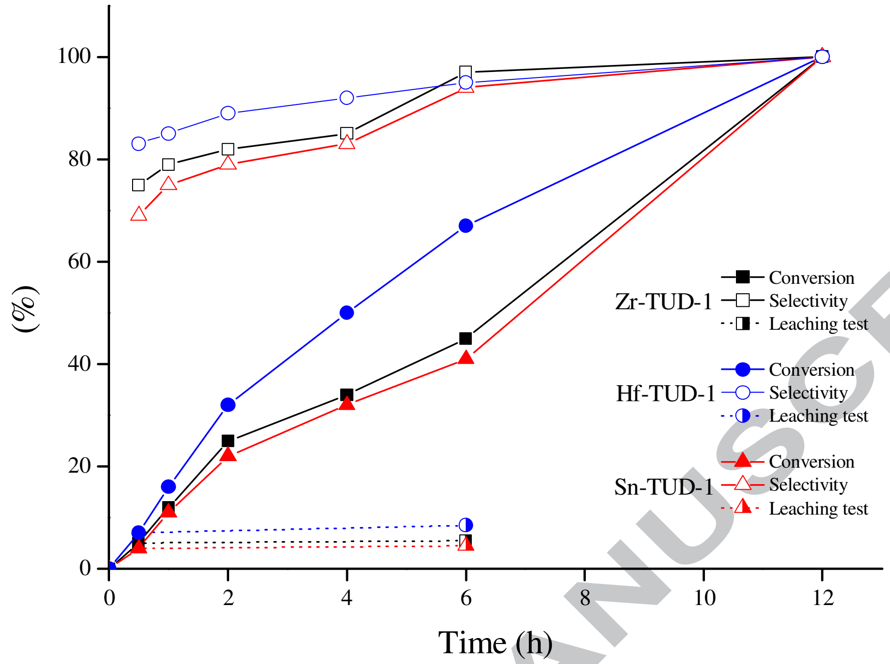

Figure 6. Kinetic study on the conversion of dihydroxyacetone over metal-containing TUD-1 catalysts. Reaction conditions: 5 ml of 0.4 M DHA, 100 mg of catalysts, 90°C. Leaching test results are presented with half-filled symbols.

Table 3. Catalytic conversion of dihydroxyacetone into ethyl lactate over Sn-, Zr- and Hf-TUD-1.[a]

Entry	**Catalyst**	X_{DHA} [%][b]	$Y_{lactate}$ [%]	$Y_{hemiacetal}$ [%]	Y_{acetal} [%]	$S_{lactate}$ [%]	**TON**		
							Based on number of metal sites [c]	Based on number of B. acid sites [d]	Based on number of L. acid sites [e]
1	Sn-TUD-1	30	27	2	1	90	38	1000	137
2	Zr-TUD-1	31	28	2	1	91	39	496	120
3	Hf-TUD-1	33	31	1	1	94	42	307	79
4	Hf-TUD-1[f]	>99	>99	0	0	>99	127	930	255
5	Hf-TUD-1[g]	>99	>99	0	0	>99	127	930	255

[a] Reaction conditions: 5 ml of 0.4 M DHA, 50 mg of catalyst, 90 °C, 6 h; [b] calculated as the sum of the yields of ethyl lactate, hemiacetal and acetal of pyruvic aldehyde [19,20]; [c] TON defined as mol of dihydroxyacetone converted per mol of metal atoms; [d] TON defined as mol of dihydroxyacetone converted per mol of Brønsted acid sites, as determined by pyridine TPD-FT-IR at 150 °C (Table 2). [e] TON defined as mol of dihydroxyacetone converted into ethyl lactate per mol of Lewis acid sites, as determined by pyridine TPD-FT-IR at 150 °C (Table 2). [f] Reaction conditions: 5 ml of 0.4 M DHA, 200 mg of catalysts, 90 °C, 6 h. [g] Reaction conditions: 5 ml of 0.4 M DHA, 100 mg of catalysts, 90 °C, 12 h.

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The reusability of Sn-, Zr- and Hf-TUD-1 as catalysts for the conversion of dihydroxyacetone to ethyl lactate was tested in several consecutive cycles. Before each successive test, the catalyst was washed with ethanol and dried at 100°C overnight. The activity (and thus the selectivity) of the catalysts gradually decreased upon recycling but could be fully restored by thermal treatment in air at 300 °C for 5 h (Fig. 7). This behaviour is similar to that observed for Sn-MCM-41 [20,25], suggesting that the deactivation of the catalysts is due to residues that poison the active sites and can be removed only upon thermal treatment. When such relatively mild treatment at 300 °C was performed after each test, the catalytic activity was maintained in successive runs (Fig. 7). The truly heterogeneous nature of the three TUD-1 catalysts was demonstrated by performing hot filtration leaching tests. The catalysts were separated from the reaction mixture after 30 min by centrifugation and filtration at the reaction temperature, then the filtrate was allowed to react for further 5 h 30 min at 90°C. The negligible increase in the conversion of dihydroxyacetone at the end of 6 h of reaction of the filtrate, compared to that after 30 min (Fig. 6), indicates that virtually no leaching of active species occurred.

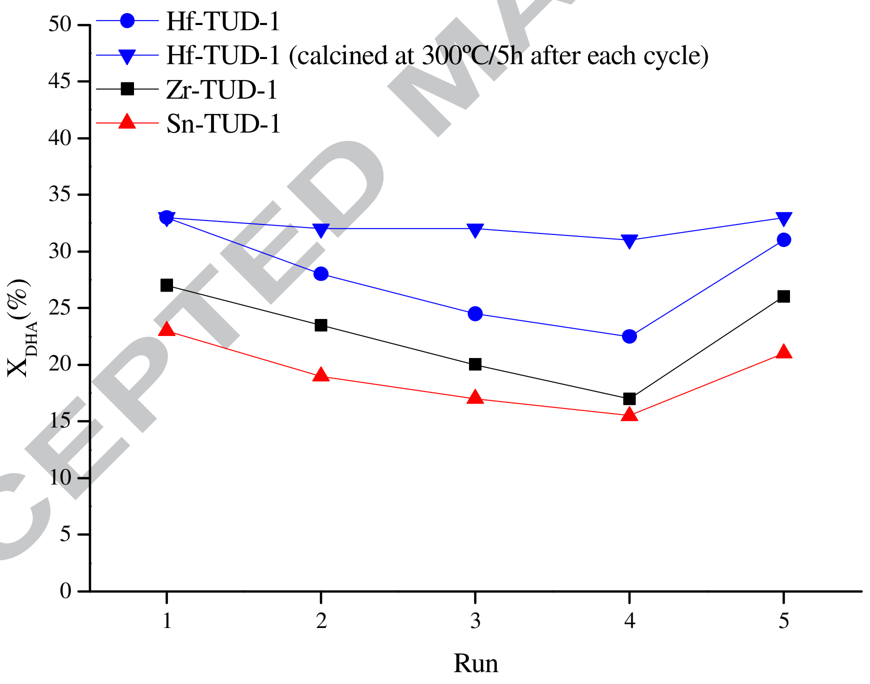

Figure 7. Recycling tests for the conversion of dihydroxyacetone into ethyl lactate over metal-containing TUD-1 catalysts. Reaction conditions: 5 ml of 0.4 M DHA, 50 mg of catalyst, 90 °C, 6 h. The catalysts were subjected to thermal treatment (300 ºC for 5h) after the 4th run.

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Sn-TUD-1 was also tested in the synthesis of solketal through the acetalisation of acetone with glycerol (Fig. 8), and its catalytic performance was compared to that previously observed with Zr- and Hf -TUD-1 (Table 4) [36]. In the reaction of acetone with pure glycerol in 1:1 ratio, Sn-TUD-1 reaches a conversion of 44% with complete selectivity towards the five-membered-ring solketal product. Increasing the acetone-to-glycerol ratio to 2:1 leads to an increase in the conversion to 64%, while the complete selectivity towards solketal is retained. The catalyst was tested also using aqueous glycerol (80 wt.% in glycerol) as substrate, to mimic the characteristics of crude glycerol. Under these conditions, solketal was still the only product but a lower conversion of glycerol was achieved (19 %), as expected considering that water is one of the products of the acetalisation reaction (Scheme 1.b), which implies that a higher concentration of water in the reaction mixture favours the hydrolysis of the formed solketal and thus limits the degree of conversion of glycerol [36]. It has been proposed that the main factors determining the activity of heterogeneous catalysts in this reaction are the number of accessible acid sites and the hydrophobicity of the surface of the catalytic materials [31,36]. A relatively hydrophobic surface can promote the removal of water from the active site region, thus reducing the probability of the hydrolysis of solketal. The hydrophobicity of Sn-TUD-1 was estimated on the basis of the degree of H_2O adsorption on its surface by means of TGA analysis and was found to be intermediate between that of Zr- and Hf-TUD-1 (Table 2), which were reported to have a relatively hydrophobic surface [36]. The slightly lower activity of Sn-TUD-1 compared to Zr- and Hf-TUD-1 is thus ascribed to its lower number of acid sites. This is a similar trend to that observed in the synthesis of ethyl lactate from dihydroxyacetone (*vide supra*). Also the turnover numbers follow the same trend as in the conversion of dihydroxyacetone, with Hf-TUD-1 displaying the highest TON based on metal sites and Sn-TUD-1 reaching the highest TON based on number of acid sites (Table 4). Recycling tests performed for Sn-TUD-1 showed that the activity gradually decreases if the recycling is carried out by simply washing the catalyst, and that the original activity can be completely restored by means of a thermal treatment (*data not showed*). This behaviour is analogous to that observed for Zr- and Hf-TUD-1 in this reaction [36], and is also similar to what found in this work for recycling of the TUD-1 catalysts for the conversion of dihydroxyacetone into ethyl lactate (*vide supra*).

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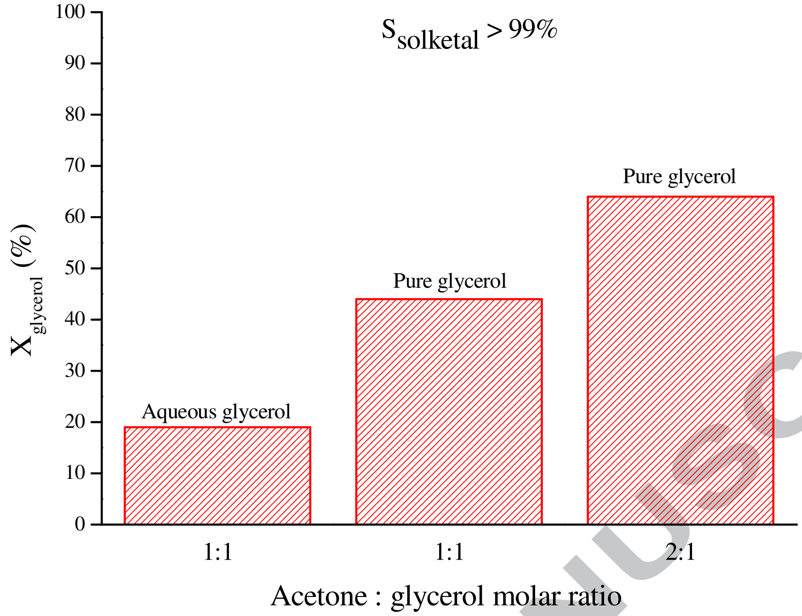

Figure 8. Conversion of glycerol in the synthesis of solketal catalysed by Sn-TUD-1. Reaction conditions: $1.00 \cdot 10^{-2}$ mol glycerol, $1.00 \cdot 10^{-2}$ mol acetone ($2.00 \cdot 10^{-2}$ mol acetone in the last test), *tert*-butanol ($1.00 \cdot 10^{-2}$ mol) as solvent, 25 mg of catalyst, 80 ºC, 6h.

Table 4. Catalytic conversion of glycerol into solketal over Sn-, Zr- and Hf-TUD-1.[a]

Entry	**Catalyst**	**X_{glycerol} [%]**	**S_{solketal} [%]**	**TON**	
				Based on number of metal sites [b]	Based on number of acid sites [c]
1	Sn-TUD-1	44	> 99	565	1955
2	Zr-TUD-1	46 [d]	> 99 [d]	570	1559
3	Hf-TUD-1	52 [d]	> 99 [d]	705	1040

[a] Reaction conditions: $1.00 \cdot 10^{-2}$ mol glycerol, $1.00 \cdot 10^{-2}$ mol acetone, $1.50 \cdot 10^{-3}$ mol of 1,4 dioxane (as GC internal standard), *tert*-butanol ($1.00 \cdot 10^{-2}$ mol) as solvent, 25 mg of catalyst, 80 ºC, 6h; [b] TON defined as mol of glycerol converted per mol of metal atoms; [c] TON defined as mol of glycerol converted per mol of acid sites, as determined by pyridine TPD-FT-IR at 150 °C (L+B in Table 2); [d] data taken from ref. [36]

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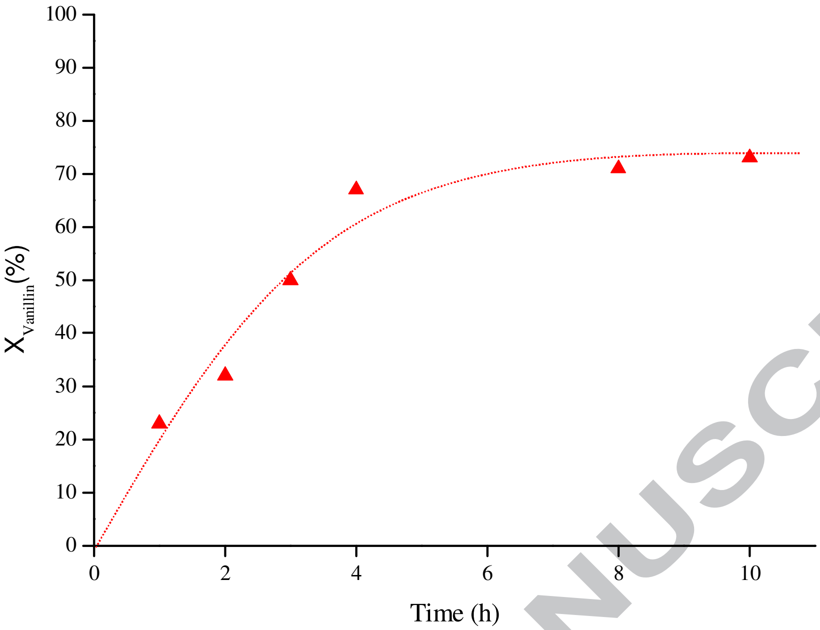

Figure 9. Kinetic curve for the acetalisation of vanillin with propylene glycol. Reaction conditions: 19 mg of Sn-TUD-1, 115ºC, $1.64 \cdot 10^{-3}$ mol vanillin, $3.28 \cdot 10^{-3}$ mol propylene glycol, 8 ml of toluene. The reaction was carried out using a Dean-Stark apparatus to remove the water formed during the reaction.

Finally, Sn-TUD-1 was tested as heterogeneous catalyst for the acetalisation of vanillin with propylene glycol, which is an industrially significant reaction to produce a vanillin-flavoured fragrance used in food and cosmetic industries. Although acetalisation reactions are generally catalysed by Brønsted acids, catalysts presenting mainly Lewis acidity, such as Sn-, Zr- and Hf-TUD-1, outperformed heterogeneous catalysts presenting mainly Brønsted acid sites, such as zeolite USY and Al-TUD-1, in the acetalisation of acetone with glycerol [36]. Therefore, these metal-containing TUD-1 materials are promising candidates also for other acetalisation reactions, as that of vanillin with propylene glycol. Indeed, Sn-TUD-1 showed a good activity in the production of the propylene glycol acetal of vanillin reaching a 70% conversion of vanillin with complete selectivity towards the desired product (Fig. 9). The plateau in the conversion of vanillin suggests that the reaction is limited by the presence of residual water. An optimisation of the water removal procedure is expected to allow reaching higher conversion in this reaction [32].

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4. Conclusions

Metal-containing mesoporous silicates of the TUD-1 family - namely Sn-, Zr- and Hf-TUD-1 - were studied as heterogeneous catalysts for three reactions involving the conversion of a bio-based compound into a valuable product: (1) the conversion of the triose sugar dihydroxyacetone into ethyl lactate; (2) the acetalisation of acetone with glycerol yielding solketal; (3) the acetalisation of vanillin with propylene glycol. High activity and complete selectivity towards the desired product were observed in all reactions. The catalytic behaviour of the TUD-1 materials could be correlated to their type and number of acid sites determined by TPD-FT-IR analysis of adsorbed pyridine. The TUD-1 catalysts could be efficiently reused without loss of activity if the samples were subjected to a mild thermal treatment after each test. A hot-filtration leaching test confirmed the truly heterogeneous nature of these catalysts. These results demonstrate the versatility of Sn-, Zr- and Hf-TUD-1 as heterogeneous catalysts for the conversion of renewable feedstock into relevant products.

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[49] A sample of HfO_2 was prepared by basic hydrolysis of $HfCl_4$ in aqueous ammonia, followed by calcination of the precipitate at 850ºC for 6h (3ºC min^{-1}). Powder XRD showed that the sample is crystalline monoclinic hafnium oxide. The UV-Vis spectrum of this material (not shown) presents a very weak absorption at around 215 nm. The intensity of this peak is much lower compared to the absorption at around 230 nm in Fig. 3.c, implying that even if hafnium oxide was present in the Hf-TUD-1 sample, its identification would be difficult.

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- Zr-, Hf- and Sn-TUD-1 are versatile solid acid catalysts.
- Zr-, Hf- and Sn-TUD-1 are active in the conversion of bio-based compounds into valuable chemicals.
- The activity stems from the highly accessible Lewis and Brønsted acid sites.
- Zr-, Hf- and Sn-TUD-1 display high selectivity towards the desired product in all reactions.
- The catalysts are truly heterogeneous and can be successfully reused in consecutive runs.

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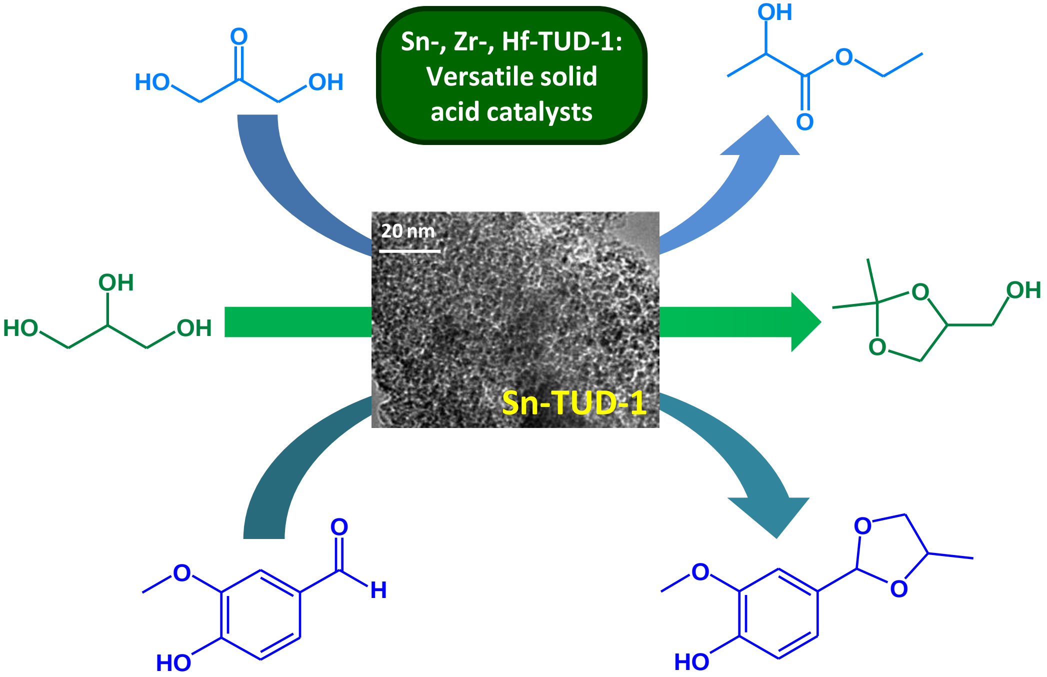

Sn-, Zr-, Hf-TUD-1:
Versatile solid
acid catalysts