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Al-SBA-15 catalysed cross-esterification and acetalisation of biomass-derived platform chemicals

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Al-SBA-15 exhibited excellent catalytic activities in acid-catalysed glycerol transformation including esterification and acetalisation reactions. Quantitative conversion and good selectivities to mono- and diacetylglycerides could be obtained in the esterification of glycerol with levulinic acid. The catalyst also proved to be very effective in the acetalisation of glycerol with aldehydes and acetone, with an interesting selectivity switch from the 6-membered acetal (using paraformaldehyde as an aldehyde source) to a 5-membered acetal (when benzaldehyde or furfural was employed). Al-SBA-15 materials were also proved to be highly stable and reusable in most glycerol transformations under the investigated reaction conditions.

1. Introduction

Biomass valorization has been increasingly recognized to be the way forward in order to provide future alternatives for the production of energy and chemicals from sustainable resources.[1,2] Biomass as widely available and renewable feedstock can in principle provide access to similar chemical entities, energy and materials to those currently obtained from crude oil. A number of biomass deconstruction strategies have been proposed in recent years to break down complex feedstocks into useful starting compounds (*e.g.* platform molecules). The chemistries of such biomass-derived platform chemicals will play a major future role in terms of a better understanding in biomass transformations. In 2004, the US Department of Energy (DOE) provided a number of key biomass-derived molecules for further transformations,[3] recently revisited by Bozell and Petersen.[4] These platform chemicals include sugars (glucose, xylose), polyols (sorbitol, xylitol, glycerol), furans (furfural, 5-hydroxymethylfurfural) and acids (succinic, levulinic, lactic acids), which will be key to provide routes towards useful chemicals, fuels and materials from renewable resources.

Glycerol, generally synthesized from propylene oxide derived from fossil fuel resources,[5] can be obtained from renewable resources as a by-product from soap manufacture, biodiesel production[5,6] and/or microbial fermentation.[7] With glycerol having low value as a by-product, its conversion into value-added chemicals is of great industrial importance due to the large production of glycerol derived from the biodiesel industry.[8,9]

Comparatively, levulinic acid (LA) is another biomass-derived key platform chemical which is repeated in both lists[3,4] due to its possibilities to be produced from lignocellulosic feedstocks at low cost. LA is a versatile building block for the synthesis of various organic chemicals including levulinate esters, γ-valerolactone, acrylic acid, 1,4-pentanediol, β-acetylacrylic acid, methyl THF and δ-amino levulinic acid.[10,11] Several of these levulinic acid derivatives have been used as monomers for the synthesis of different polymers including levulinic acid–glycerol oligomers.[12]

Furfural has also been considered as a promising chemical which can be derived from sugar dehydration (*e.g.* hemicelluloses) and further converted into fuel additives, monomers and intermediates for fine chemistry such as 2-methylfuran and 2,5-dimethylfuran.[13]

With the advent of green chemical technologies for more sustainable processes, researchers have attempted a shift from the use of toxic heavy metals and stoichiometric quantities of reagents to novel, benign, and recyclable heterogeneous catalysts for different processes. As part of our research endeavors towards the utilization of greener catalysts for industrially relevant transformations, we report herein the utilization of highly active, stable and versatile Al-SBA-15 in a series of glycerol transformations to valuable compounds including esterification with levulinic acid and acetalisation with furfural and a range of carbonyl compounds.

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2. Experimental

2.1. Materials

Pluronics (P123), sodium metasilicate, tetraethyl orthosilicate (TEOS), aluminium isopropoxide, glycerol, levulinic acid, formaldehyde, benzaldehyde, furfural, acetone, deuterium oxide, hexane, diethyl ether and ethanol employed in this work were purchased from Aldrich, Scharlau and Panreac. All chemicals were used without further purification, except for furfural which was purified by column chromatography.

2.2. Preparation of Al-SBA-15

The catalysts were prepared according to a previously reported methodology.[14] Around 20 g of the P123 template, 700 mL of HCl solution and the desired quantity of the Al precursor (aluminium isopropoxide, in order to reach a Si/Al 30 ratio in the synthesis gel) were added (pH 1.5) and then mixed until all P123 was dissolved. The silica precursor (TEOS) was then added dropwise to the solution. The mixture was then stirred for 24 hours at 100 °C (aging) until a white solid was formed. The material was then filtered off, dried in the oven and eventually calcined for 24 h at 550 °C under air.

2.3. Preparation of Zr-SBA-16

Zr-SBA-16 materials were synthesized according to a previous literature report.[15] In a typical synthesis, 16 g 10% aqueous solution P123 ($EO_{106}PO_{70}EO_{106}$,), 26 g distilled water and 4.71 g sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) were stirred together at 40 °C until the formation of a clear solution. 13.6 g HCl (35%) with the target amount of zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$, to achieve a Si/Zr ratio of 25 in the gel) were subsequently added under vigorous stirring. The molar composition of the gel mixture was $1.0SiO_2 : xZr : 3.17 \times 10^{-4}$ $P123 : 6.68HCl : 137.9H_2O$. The solution was continuously stirred for 120 min (optimum conditions)[15a] and subsequently microwave-irradiated in a microwave digestion system (Milestone Corporation, ETHOS-1) for 120 min at 100 °C. The solid product was eventually filtered off, dried at 120 °C overnight and calcined at 500 °C. The material was prepared with a Si/Zr ratio of 25 and denoted as Zr-SBA-16 (25).

2.4. General procedure for catalytic experiments

2.4.1. Esterification of glycerol with levulinic acid. In a typical experiment, the catalyst (0.025 to 0.05 g), levulinic acid and glycerol (4 : 1 molar ratio) were placed inside an ampoule and the mixture was then heated at different temperatures (100, 120 or 140 °C) under continuous stirring for 8 h. Upon reaction completion, the resulting mixture was filtered, extracted with ethanol and subsequently analyzed by GC-MS. The products mono-, di- and tri-acetylglycerides were identified by GC-MS (and their corresponding ratios). The response factors of the starting material and products were determined using naphthalene as an external standard.

2.4.2. Glycerol acetalisation with aldehydes

2.4.2.1. Formaldehyde (source: paraformaldehyde). In a typical acetalisation reaction, the catalyst (0.005–0.01 g) was suspended in a mixture of glycerol (1 mmol) and paraformaldehyde (1 mmol) inside an ampoule under stirring at 100 °C for 8 h. The resulting mixture was then filtered, ethanol-extracted and analyzed by GC-MS. The reaction products including 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane were identified by GC-MS.

2.4.2.2. Benzaldehyde. In a typical acetalisation reaction with benzaldehyde, the catalyst (0.05–0.1 g) was suspended in a mixture of glycerol (1 mmol) and benzaldehyde (1 mmol) inside an ampoule under stirring at 100 °C for 8 h. Upon reaction completion, the resulting mixture was then filtered off, extracted using ethanol and analyzed by GC-MS. Several reaction products could be observed including (2-phenyl-1,3-dioxolan-4-yl)methanol and 2-phenyl-1,3-dioxan-5-ol using GC-MS and ^1H NMR (D_2O) studies.

2.4.2.3. Furfural. The reactions were carried out as in the case of benzaldehyde described above, but the time of reaction for this particular process was 12 h. The reaction products included (2-(furan-2-yl)-1,3-dioxolan-4-yl)methanol and 2-(furan-2-yl)-1,3-dioxan-5-ol and were again identified by GC-MS and ^1H NMR (D_2O).

2.4.3. Glycerol acetalisation with acetone. The formation of solketal from glycerol (1 mmol) and acetone (1 mmol) was carried out in an ampoule at 100 °C for 8 h under continuous stirring. Products (2,2-dimethyl-1,3-dioxolan-4-yl)methanol and 2,2-dimethyl-1,3-dioxan-5-ol and their ratios were identified by GC-MS.

2.5. Recyclability tests

To determine the stability of the catalysts under the investigated conditions, recyclability studies were performed. The catalysts were reused upon reaction completion by simple centrifugation, separation and vacuum drying, followed by subsequent washing (three times) with ethanol and drying prior to their reuse in another catalytic run.

2.6. Analytical methods

Upon reaction completion, the quantitative analysis of products was performed by GC-MS. Chromatograms were recorded on a GS-MS turbo system (5975–7820A) model equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm), under the following conditions:

Esterification and acetalisation (benzaldehyde and furfural): injector temperature 230 °C, detector temperature 250 °C, 50 °C ramp 10 °C min^{-1} until 230 °C (held 20 min).

Retention times (levulinic acid): peak at 6.73 min levulinic acid, at 12.50 min naphthalene, at 12.66 min monoacetylglyceride, at 19.61 min diacetylglyceride and at 32.21 min triacetylglyceride.

Retention times (benzaldehyde): peak at 5.20 min benzaldehyde, at 12.66 and 12.89 min two diastereomers of (2-phenyl-1,3-dioxolan-4-yl)methanol, and at 13.54 min the two diastereoisomers of 2-phenyl-1,3-dioxan-5-ol.

Retention times (furfural): peak at 3.48 min furfural, at 10.32 and 10.60 min the two diastereomers of (2-(furan-2-yl)-1,3-

dioxolan-4-yl)methanol, at 10.39 and 11.32 min the other two diastereomers of 2-(furan-2-yl)-1,3-dioxan-5-ol.

Acetalisation (paraformaldehyde and acetone): injector temperature 230 °C, detector temperature 250 °C, oven temperature program: 40 °C (10 min) ramp 5 °C min^{-1} until 100 °C and another ramp 9 °C min^{-1} until 200 °C.

Retention times (paraformaldehyde): peak at 1.54 min aldehyde, at 10.54 min 4-hydroxymethyl-1,3-dioxolane, at 11.40 min 5-hydroxy-1,3-dioxane and at 22.90 min glycerol (broad peak).

Retention times (acetone): at 14.75 min (2,2-dimethyl-1,3-dioxolan-4-yl)methanol, at 16.26 min 2,2-dimethyl-1,3-dioxan-5-ol and at 22.90 min glycerol (broad peak).

NMR spectra were registered using a Varian Mercury 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm and were measured relatively by the internal referencing to the D_2O (^1H).

3. Results and discussion

Al-SBA-15 (Si/Al 30 ratio) possessed typical textural and structural properties as compared to previously reported analogous materials.[14] The material possessed a surface area of 720 m^2 g^{-1}, a pore size of *ca.* 8 nm and a pore volume of 0.8 mL g^{-1}. Surface acidity measurements by means of titration with pyridine (PY) and 2,6-dimethylpyridine (DMPY) showed that the catalyst contained a good balance between Lewis and Brønsted acid sites (Table 1), in good agreement with previous surface acidity results.[14] Relatively similar results were found for Zr-SBA-16, although a higher total acidity and larger proportion of Lewis acid sites were determined in this material (Table 1). Structural characteristics of analogous mesoporous Al-SBA-15 materials (XRD, TEM and N_2 physisorption) have also been previously reported.[14]

In view of such measured acidity, Al-SBA-15 materials have a promising potential as solid acid catalysts for various acid-catalysed processes. The catalytic activity of Al-SBA-15 was subsequently investigated in a range of esterification and acetalisation processes for glycerol valorization to useful polymer-intermediates and fuel oxygenated additives.

3.1. Esterification of glycerol with levulinic acid

Traditionally, mineral acids have been used as catalysts in the esterification of glycerol to prepare mono-, di- and triglycerides that find a number of applications in the food industry.[16] However, heterogeneous catalysts have various advantages in terms of simple recovery and/or recycling, with structures or textural properties potentially influencing reaction selectivities (*e.g.* porous network). Different solid acids including zeolites and acidic mesoporous materials have been recently reported in glycerol esterification[17–20] which can render a range of value-added products including pharmaceutical intermediates, foodstuffs, plasticisers and insecticides.[21–23]

The esterification of glycerol with levulinic acid was carried out using Al-SBA-15. The effect of various parameters in the reaction including temperature and catalyst loading was studied to optimize the reaction conditions (Table 2). Blank runs (in the absence of a catalyst) provided negligible glycerol conversion even at temperatures above 120 °C and longer times of reaction (Table 2). Al-SBA-15 exhibited a good conversion to products at 120 °C, with high selectivity to monoacylglycerides (Table 2, entry 2). Diacylglycerides became the major products at a reaction temperature of 140 °C, with quantitative conversion of the starting material (Table 2, entry 3). Interestingly, product selectivity remained unchanged at high conversion values when decreasing catalyst loadings in the esterification reaction (Table 2, entry 4). A higher catalytic activity was comparably obtained for Zr-SBA-16 (Table 2, entry 5). Clearly, Zr-SBA-16 possesses a superior Lewis acidity as compared to Al-SBA-15 (*i.e.* the DMPY-PY value is a rather accurate measure of Lewis acidity; this was found to be 65 for Al-SBA-15 as compared to 200 for Zr-SBA-16). These findings therefore suggest that the proposed esterification reaction was largely promoted by Lewis acid sites.

3.2. Acetalisation of glycerol with aldehydes

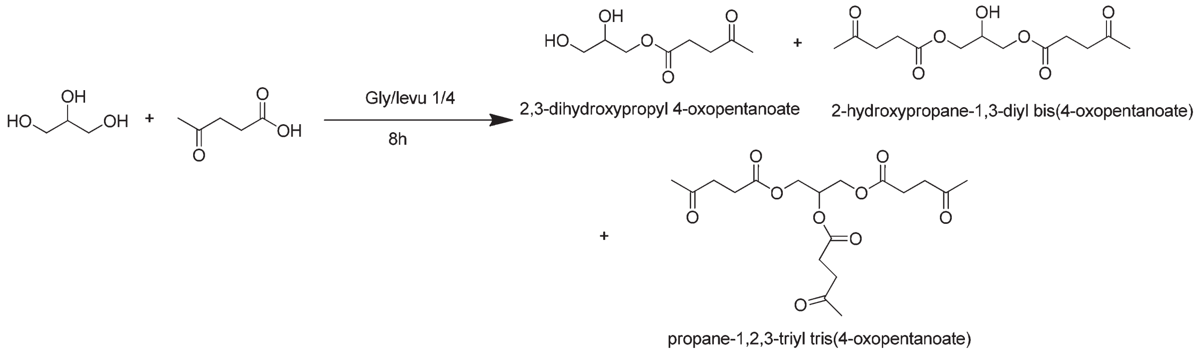
The acetalisation of glycerol is an important reaction for the synthesis of six- and five-membered cyclic products that find a wide range of industrial applications. Glycerol acetals and ketals have been extensively utilized as additives fuels, binders as well as in formulations of water-based inks.[24–26] A variety of heterogeneous catalysts have been studied in glycerol acetalisation including exchanged resins,[27] heteropolyacids,[28] mesoporous materials,[20,29] and zeolites.[30]

3.2.1. Paraformaldehyde. The results obtained in the acetalisation of glycerol with paraformaldehyde have been summarised in Table 3. The reaction conditions (molar ratio of glycerol to formaldehyde, temperature and time) were selected based on our experience and results obtained by Ruiz *et al.*[30] The condensation of glycerol with paraformaldehyde, as aldehydes generally lead to the formation of a six-membered cyclic acetal as a stable product (Table 3), is even more remarkable for Al-SBA-15 as compared to Zr-SBA-16 (Table 3, entry 4).

Table 1 Textural and surface acid properties of Al-SBA-15 and Zr-SBA-16 materials

Catal.	Surface area (m^2 g^{-1})	Pore size/volume (nm/mL g^{-1})	Surface acidity at 300 °C (μmol g^{-1}) PY (total acidity)	DMPY (Brønsted acidity)	Lewis acidity
Al-SBA-15 (30)	720	8.0/0.8	140	75	65
Zr-SBA-16 (25)	>600	6.0/0.6	233	33	200

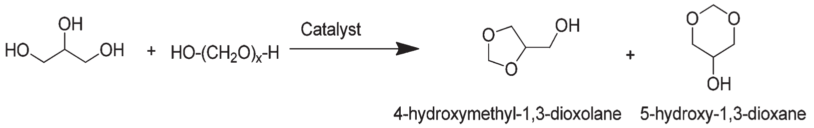
Table 2 Esterification of glycerol with levulinic acid using mesoporous solid acid catalysts[a]



Entry	Catalyst	μmol of acid groups per mmol of glycerol	Mono/di/tri selectivity (mol %)	Temperature (°C)	Conversion (%)
Blank	—	—	—	140	<10
1	Al-SBA-15	7	—	100	—
2	Al-SBA-15	7	94/5/1	120	78
3	Al-SBA-15	7	0/85/15	140	>99
4	Al-SBA-15	3.5	6/85/9	140	85
5	Zr-SBA-16 (25)[b]	5.82	77/23/0	100	70

[a] Reaction conditions: 1 mmol glycerol, 4 mmol levulinic acid, catalyst, solventless, 8 h. [b] Zr-SBA-16 (Si/Zr 25 ratio).

Table 3 Catalytic activity of Al-SBA-15 and Zr-SBA-16 (25) in the acetalisation of glycerol with paraformaldehyde[a]

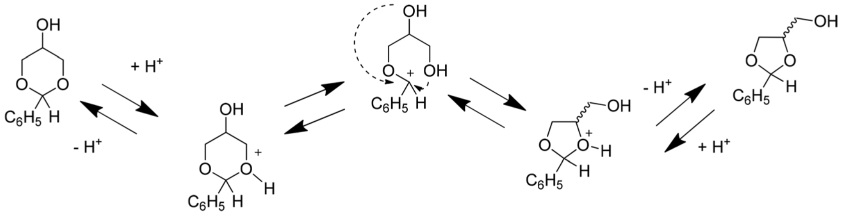


Entry	Catalyst	μmol of acid groups per mmol of glycerol	Selectivity (dioxolane/dioxane)	Conversion (%)
1	Al-SBA-15	2.8	34/66	96
2	Al-SBA-15	1.4	36/64	93
3	Al-SBA-15	0.7	31/68	43
4	Zr-SBA-16 (25)[b]	23.3	26/74	44

[a] Reaction conditions: 1 mmol glycerol, 1 mmol paraformaldehyde, solventless, 100 °C, 8 h. [b] Zr-SBA-16 (Si/Zr 25 ratio).

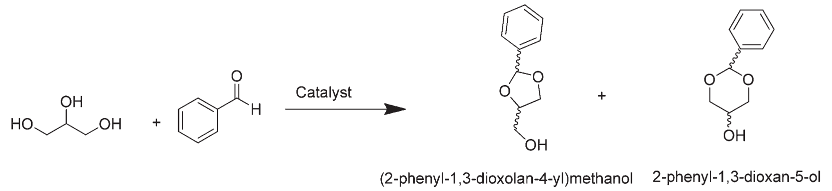
Results seem to point to a Brønsted-acid promoted reaction taking into account the low Brønsted acidity of Zr-SBA-16 compared to Al-SBA-15, which was proved to be highly active even at low catalyst loadings (Table 3, entries 1–3).

3.2.2. **Benzaldehyde.** The selectivity comparably changes from dioxane to dioxolane (from a 6-membered ring to a 5-membered ring) in the acetalisation of glycerol with benzaldehyde, in good agreement with literature results.[27,31] However, the evolution of five- to six-membered rings at longer times of reaction was reported by Deustch *et al.*[27] To further prove the stability of the dioxolane product under the investigated reaction conditions (Scheme 1), the reaction mixture was



Scheme 1 Acid-catalysed equilibrium between C6 and C5 products obtained in glycerol acetalisation with benzaldehyde.

Table 4 Catalytic activity of Al-SBA-15 in the acetalisation of glycerol with benzaldehyde[a]

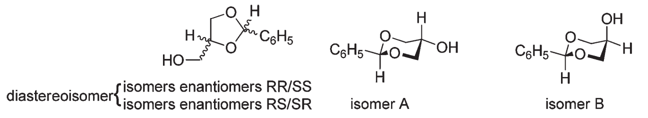


Entry	Catalyst	μmol of acid groups per mmol of glycerol	Selectivity (dioxolane/dioxane)	Conversion (%)
1	Al-SBA-15	7	83/17	72
2	Al-SBA-15	14	83/17	82

[a] Reaction conditions: 1 mmol glycerol, 1 mmol benzaldehyde, solventless, 100 °C, 8 h.

subsequently reacted overnight. After 24 h+ reaction, the five-membered ring was still preferentially obtained as a major reaction product, in contrast to results obtained by Deustch *et al.* The effect of Al-SBA-15 loading on glycerol conversion was subsequently investigated (Table 4). Catalytic experiments were conducted by varying the catalyst amount (0.05 and 0.1 g, 7 and 14 μmol of acid groups in the catalyst per mmol of glycerol, respectively) under identical reaction conditions. No significant improvements on glycerol conversion or selectivity were observed as evidenced in Table 4.

The synthesised product mixture contained two pairs of diastereomers, each of which is formed by two C5 diastereomers and two C6 isomers (Scheme 2) as identified by GC-MS and ^{1}H-NMR.



Scheme 2 Conformational isomers of (2-phenyl-1,3-dioxolan-4-yl) methanol and 2-phenyl-1,3-dioxan-5-ol.

Chromatograms showed three distinctive products, with mass spectra revealing C5 diastereomers (first two peaks) and C6 isomers (third peak, Fig. 1A). ^{1}H NMR spectra exhibited four peaks corresponding to OC*H*(C_6H_5)O, C5 [5.82 and 5.71 ppm] and C6 [5.58 and 5.45 ppm] (Fig. 1B). All chemical shifts were found to be in agreement with literature results.[27]

3.2.3. Furfural. Similar product and catalytic activity trends could be observed in the acetalisation of glycerol with furfural as an aldehyde source. The reaction was found to be kinetically controlled, with the catalytic formation of five-membered cyclic acetals proceeding at a higher rate with respect to those of the six-membered cyclic acetals. Such behavior might be attributed to the increasing torsional effect in 6-membered rings with cyclic and aromatic substrates.

Table 5 summarises results for the acetalisation reaction of glycerol with furfural. Good conversions in the systems (*ca.* 70%) could be achieved at 100 °C after 12 h reaction, in agreement with literature reports.[32,33] Importantly, an increase in catalyst loading did not significantly influence the conversion under the investigated reaction conditions.

Different 5- and 6-membered stereoisomers were again obtained as depicted in Scheme 3. Product identification by GC-MS pointed to the presence of four peaks (Fig. 2), further

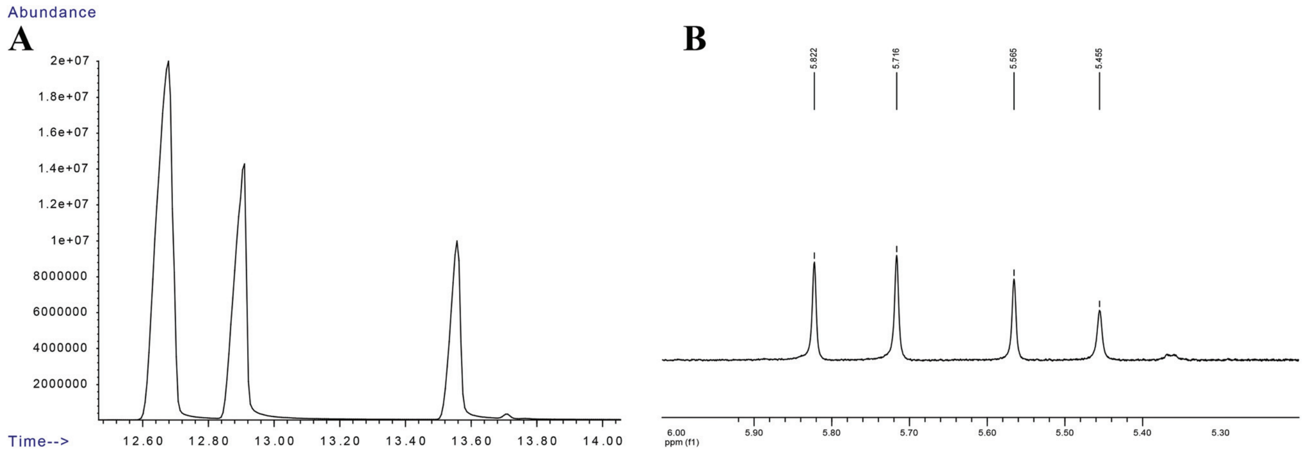
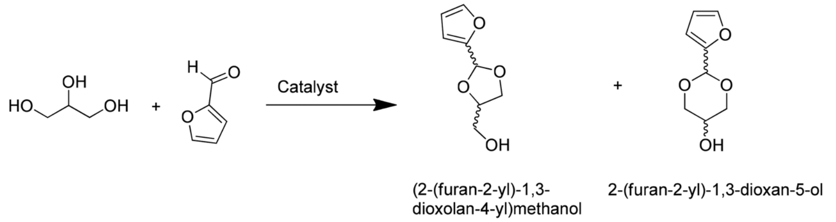


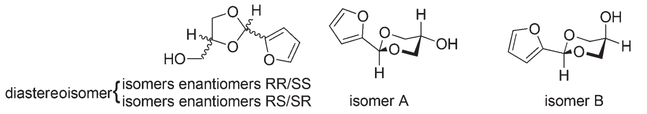
Fig. 1 Product mixture from glycerol acetalisation with benzaldehyde. (A) GC chromatogram. (B) ^{1}H NMR spectrum.

Table 5 Catalytic conversion of glycerol and furfural to cyclic acetals[a]



Entry	Catalyst	μmol of acid groups per mmol of glycerol	Selectivity (dioxolane/dioxane)	Conversion (%)
1	Al-SBA-15	7	67/33	69
2	Al-SBA-15	14	68/32	74

[a] Reaction conditions: 1 mmol glycerol, 1 mmol furfural, solventless, 100 °C, 12 h.



Scheme 3 Conformational isomers of (2-(furan-2-yl)-1,3-dioxolan-4-yl)methanol and 2-(furan-2-yl)-1,3-dioxan-5-ol.

confirmed by mass spectrometry as two C5 and C6 isomers, respectively. The mixture was subsequently purified by column chromatography using a silica column (eluted with 1 : 2 hexane–diethyl ether[32]) and attempted to identify individual products by GC-MS and ^{1}H-NMR. A 2-(furan-2-yl)-1,3-dioxan-5-ol diastereomer could be isolated as a pure compound.

3.3. Acetalisation of glycerol with acetone

The acetalisation of glycerol with acetone is another relevant process for glycerol valorization to produce solketal (2,2-dimethyl-1,3-dioxolan-5-ol) (Table 6). This molecule constitutes an excellent product as an additive in gasoline formulations as well as diesel and biodiesel fuels. The catalyst loading was found to be critical in the conversion of the systems (Table 6, entries 1 *vs.* 2), with Al-SBA-15 exhibiting comparable activities to those previously reported using Amberlyst-15.[27]

3.4. Reusability of Al-SBA-15

The reusability and stability of the catalyst are crucial features of catalysts besides the activity and selectivity for practical applications. The possibility to reuse Al-SBA-15 in all conducted reactions (esterification and acetalisation) was subsequently explored, with results discussed in Fig. 3–7.

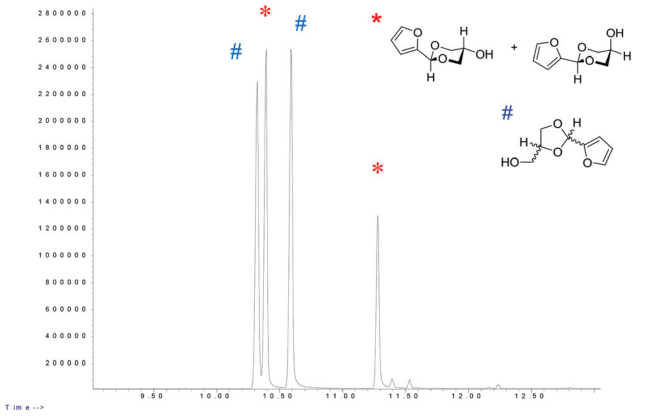
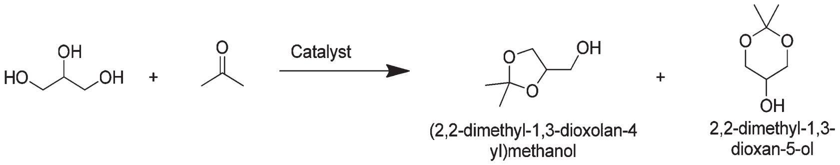


Fig. 2 Chromatogram reaction with Al-SBA-15, 1 mmol glycerol, 1 mmol furfural, 8 h, 100 °C (selectivity 68/32).

Table 6 Acetalisation of glycerol with acetone catalyzed by Al-SBA-15[a]



Entry	Catalyst	μmol of acid groups per mmol of glycerol	Selectivity (dioxolane/dioxane)	Conversion (%)
1	Al-SBA-15	7	99/1	6
2	Al-SBA-15	14	99/1	75

[a] Reaction conditions: 1 mmol glycerol, 1 mmol acetone, solventless, 100 °C, 8 h.

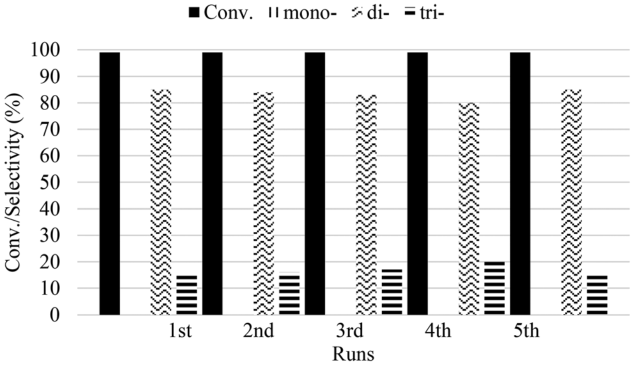


Fig. 3 Reusability of Al-SBA-15 in the esterification of glycerol with levulinic acid. Reaction conditions: 1 mmol glycerol, 4 mmol levulinic acid, 0.05 g catalyst (7 μmol of acid groups in the catalyst per mmol of glycerol), solventless, 140 °C, 8 h reaction.

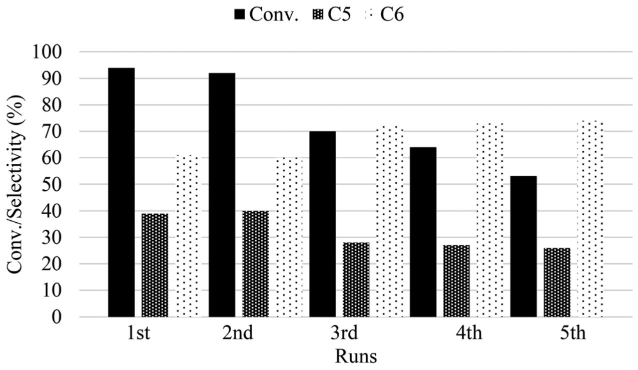


Fig. 4 Experiments of catalyst recycling in the acetalization of glycerol with paraformaldehyde. Reaction conditions: 1 mmol glycerol, 1 mmol paraformaldehyde, 100 °C, 0.01 g catalyst (1.4 μmol of acid groups per mmol glycerol), solventless, 8 h reaction.

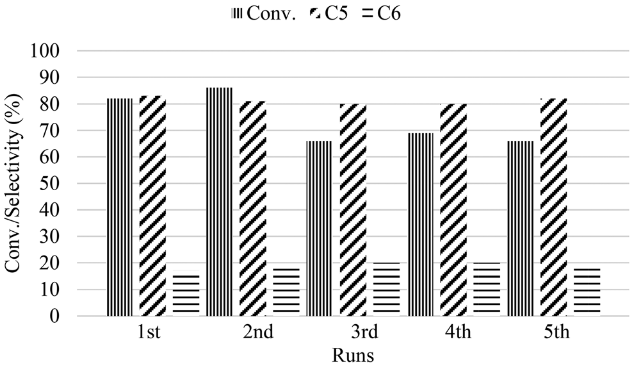


Fig. 5 Al-SBA-15 recycling experiments in the acetalisation of glycerol with benzaldehyde. Reaction conditions: 1 mmol glycerol, 1 mmol benzaldehyde, 100 °C, 0.1 g catalyst (14 μmol of acid groups per mmol glycerol), solventless, 8 h reaction.

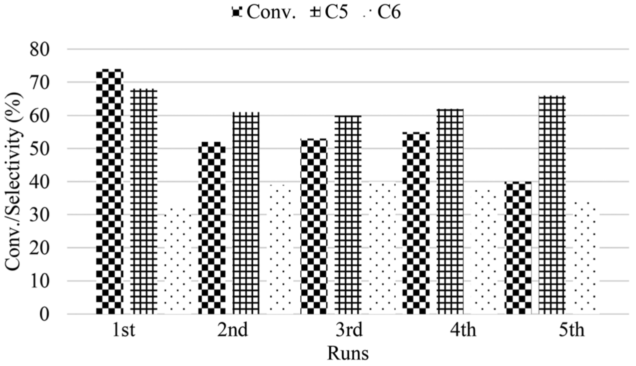


Fig. 6 Reuse experiments for Al-SBA-15 in the acetalisation of glycerol with furfural. Reaction conditions: 1 mmol glycerol, 1 mmol furfural, 100 °C, 0.1 g catalyst (14 μmol of acid groups per mmol glycerol), solventless, 12 h reaction.

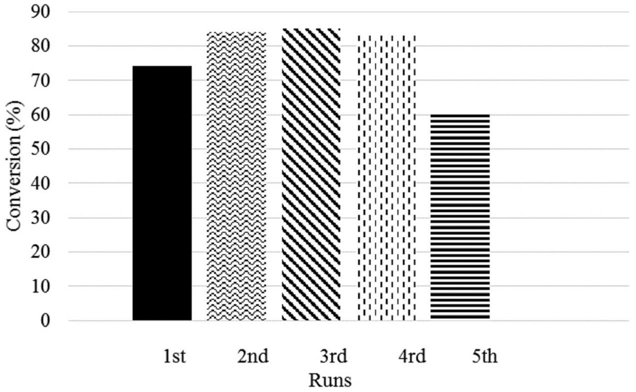


Fig. 7 Reusability study for the acetalisation of acetone with glycerol using Al-SBA-15 as a catalyst. Reaction conditions: 1 mmol glycerol, 1 mmol acetone, 100 °C, 0.1 g catalyst (14 μmol of acid groups per mmol glycerol), solventless, 8 h reaction.

Al-SBA-15 was fairly stable and reusable in most cases, preserving most initial catalytic activities after several uses. In the case of esterification of glycerol with levulinic acid, results from Fig. 3 prove the high stability and the possibility to recycle the catalyst up to five uses without any noticeable decrease in its activity. The selectivity was also preserved in the reused Al-SBA-15 material.

Fig. 4 comparably shows that Al-SBA-15 exhibited a poor reusability in the acetalisation of glycerol with paraformaldehyde. The activity was preserved in the first reuse but over 40% of its initial activity was already lost after three reuses (Fig. 4). Interestingly, the observed significant drop in activity was also accompanied by a change in selectivity towards a favoured production of 6-membered acetal products. The observed reduction may be caused by the formation of physisorbed species and/or carbonaceous deposits on the surface of the catalyst.

In contrast with glycerol acetalisation using paraformaldehyde, Al-SBA-15 was found to also lose activity in the acetalisation of glycerol with benzaldehyde (around 20% of initial activity, Fig. 5) but only after the first reuse. Subsequent reuses of the catalyst provided essentially identical activities, with also analogous selectivities to the major C5 cyclic product (Fig. 5). A similar behaviour was also observed in the acetalisation of glycerol with furfural (Fig. 6). The observed activity drop after the first run could be due to deactivation of strong Brønsted acid sites in the reaction (*i.e.* by coking) in a similar way to that observed in the acetalisation of glycerol with paraformaldehyde (Fig. 4). Selectivity remained unchanged after several reuses, with a preferential formation of 5-membered acetal products.

An interesting recycling behavior was observed for Al-SBA-15 in the acetalisation of glycerol with acetone (Fig. 7). The stability of the catalyst was remarkably improved as compared to previous acetalisation with paraformaldehyde, benzaldehyde or furfural up to 4 cycles. Interestingly, the activity significantly dropped after the fourth cycle (70% of the initial activity) which could be related to a partial deactivation of the catalyst due to the formation of carbonaceous deposits. Solketal was selectively obtained in all runs as a major product.

4. Conclusion

A highly stable, recyclable and efficient Al-SBA-15 catalyst was utilized as a heterogeneous catalyst in two important industrial reactions (esterification and acetalisation). Both Al-SBA-15 and Zr-SBA-16 exhibited very good conversions to monoacetylglycerides, with a reaction promoted by Lewis acid sites. Comparably, Al-SBA-15 provided improved yields to products in acetalisation reactions promoted by Brønsted acid sites. Interestingly, the use of linear chain aldehyde precursors tend to favor the preferential production of 6-membered ring isomers, while the use of cyclic substrates lead to the formation of 5-membered isomers. The simplicity of the methodology and the catalyst make this protocol potentially useful to related glycerol and polyol chemistries with advanced functional materials (*e.g.* supported nanoparticles on Al-SBA-15) to be reported in due course.

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