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Selective glycerol transformations to high value-added products catalysed by aluminosilicate-supported iron oxide nanoparticles

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Abstract

Conversion of glycerol to cyclics acetals (with paraformaldehyde, benzaldehyde, furfural and acetone) and to mono-, di- and triacetylglicerides (with levulinic acid) was investigated using an supported iron oxide nanoparticle system of a mesoporous aluminosilicate heterogeneous catalyst (Fe/Al-SBA-15). The effect of various parameters on the reaction, temperature, mol% catalyst or ratio glycerol/substrate were studied. An optimization of the reaction conditions carried out with glycerol by means of experimental design methodology showed that a very high glycerol conversion (99%) and high combined selectivity toward di- and triacetylglycerides could be obtained under optimized conditions. All the acetalisation reactions carried out at 100ºC also gave good to excellent conversions and selectivities to target products, illustrating the potential of Fe/Al-SBA-15 as highly active, stable and reusable heterogeneous catalyst in glycerol acid-catalysed transformations.

Keywords: solvent-free syntheses, glycerol, glycerol oxygenates, esterification, acetalisation, iron.

1. Introduction

Rapid consumption of fossil fuels and increasing energy demand have forced the mankind to seek for a renewable and sustainable energy source.[1,2] In this consequence, biomass-derived fuels have attracted the attention as alternatives to fossil fuels due to their environmentally benign and renewable nature.[3,4] Significant number of platform chemicals have been derived from biomass in the past few years for the production of commodity chemicals and fuels.[5,6,7,8,9,10,1112] Glycerol is one of the most abundant platform chemicals for the production of fine chemicals and fuel additives.[13,14] Since glycerol is a by-product in the processes of saponification of triglycerides in biodiesel and soap industries it can be utilized as an inexpensive precursor for the production of commercially-valued fuel blends. Glycerol itself cannot be added directly to fuel because at high temperature it polymerizes and thereby blocks the engine and furthermore, it is partly oxidized to toxic acrolein. Another major concern of using glycerol as fuel is that, being a polyol it is very hygroscopic in nature and thus has a great tendency to be contaminated with water. On the other hand, glycerol oxygenate derivatives are reported as excellent fuel additives on the basis of their antidetonant and octane-improving properties. Glycerol can be converted to various fuel units through different routes such as etherification,[15-17] esterification,[18,19] transesterification[20,21] and hydrogenolysis.[22,23] The transformation of glycerol into fuel oxygenates by etherification and esterification methods are of special interest since they are economically beneficial to the production of glycerol by-product and biodiesel process.

Esterification of glycerol is generally carried out over conventional acids as homogeneous catalysts.[24] But these catalytic processes are usually accompanied by several technical and environmental drawbacks such as the catalyst separation, product purity, reactor corrosion, and the effluent disposal. So the challenge was to replace them by solid acid catalysts which are easier to separate from the products, stable at high temperature and less toxic. There are some solid acid catalysts that are reported in the literature for the esterification and acetalisation of glycerol which include amberlyst,[25] heteropolyacids,[26] zeolites[27] and others. However, solid acid catalysts such as ion exchange resins (e.g. Amberlyst) exhibit drawbacks like poor thermal stability, poor selectivity under certain conditions, poor regeneration ability and low specific surface area.[28] Supported heterpolyacids (HPAs) have nearly comparable efficiency for a series of acid-catalyzed reactions to sulfuric acid in liquid phase.[29] Due to their high solubility in polar media, it is often difficult to separate them from the reaction products, which is problematic in industrial processes. Thus, a water–tolerant solid acid catalyst with high conversion ability and selectivity is essential for the esterification and acetalisation of glycerol, where the active components of the catalyst will remain intact even in highly polar reaction mixture at elevated temperature.

Recently we reported mesoporous Zr-SBA-16 catalyst for the esterification and acetalisation of glycerol and the catalyst was shown to be very effective in solvent-free protocols.[30] Accordingly in the present work, we report aluminosilicate supported iron oxide catalyst for the valorization of glycerol into its fuel oxygenates *via* esterification and acetalisation reactions in solvent-free condition. Fe incorporation was previously reported to significantly improve the acid properties (both in terms of Brönsted and/or Lewis acidity) of Al-SBA-15 materials[31]. Hence, improved acidity (and higher number of acid sites) has been correlated with better catalytic performance in both acetalisation[25] and esterification reactions.[32] The synthesis procedure and detailed characterization of Fe/Al-SBA-15 used in this work has been previously discussed in detailed in earlier reports.[33,34](see also Experimental section). Reaction conditions were optimized for the conversion of glycerol and the role of active metal oxide nanoparticles on product distribution was emphasized. Finally, catalyst recyclability studies were performed for both esterifications and acetalisations of glycerol to prove its excellent stability and reusability properties.

2. Experimental

2.1. Synthesis of Al-SBA-15 and supported Fe/Al-SBA-15.

The catalysts were prepared according to a previous reported methodology.[34] 20 g of P123 template was coated around the sides of a plastic bottle. 700 mL of HCl solution and the desired quantity of Al precursor (aluminium isopropoxide, in order to reach a Si/Al 30 ratio in the synthesis gel) was added (pH of 1.5) and then mixed until all P123 was dissolved. The silica precursor used in the study (TEOS) was then slowly introduced to the solution. The mixture was then left for at least 24 hours at 100ºC (aging) until a white solid was formed. The material was then filtered off, dried in the oven and eventually calcined at 550ºC for 24 h.

A typical preparation of the supported iron catalyst was performed as follows: Al-SBA-15 (0.2 g) was suspended in an ethanol solution (2 mL) containing previously dissolved $FeCl_2 \cdot 4H_2O$ (100 mg). The mixture was heated in a microwave at 200 W for 15 min (average temperature 100ºC, 120ºC maximum temperature reached). The solid was then filtered off, washed with an excess of ethanol and acetone and dried overnight at 100ºC. Fe/Al-SBA-15 final catalyst was obtained after calcination of the dried material under air at 400ºC for 2 h.

2.2. Typical procedure for catalytic experiments

Glycerol was employed in the various investigated reactions. In a typical esterification reaction, 10 mmol glycerol, 40 mmol levulinic acid and the catalyst (0.025-0.050 g) were placed in an ampoule with continuous stirring (1200 rpm) for 8h at different temperatures. The resultant mixture was filtered off, extracted using ethanol and the products mono-, di-(1,2-diacetylglyceride) and triacetylglycerides were identified by GC-MS and their ratios also. The response factors of the starting material and products were determined using naphthalene as external standard. In the acetalisation with aldehydes, 1 mmol glycerol, 1 mmol aldehyde and the catalyst (0.1-0.01 g, depends on the aldehydes) were placed inside an ampoule under stirring (1200 rpm) at 100ºC for 8h (in the case of furfural 12h). The resultant mixture was then filtered off, extracted using ethanol and the products were identified by GC-MS and their ratio. For benzaldehyde and furfural, the products were also identified by ^{1}H NMR (D_2O). The formation of solketal from glycerol (1 mmol) and acetone (1 mmol) was carried out in an ampoule at 100 ºC for 8h under continuous stirring (1200 rpm), over catalysts (0.1-0.05 g). (2,2-dimethyl-1,3-dioxolan-4-yl)methanol and 2,2-dimethyl-1,3-dixan-5-ol were identified as products by GC-MS.

2.3. *Recyclability tests*

This test methodology is used in recycling all reactions; the catalyst was reused upon reaction completion by simple centrifugation and separation followed by subsequent washing three times with ethanol and drying prior to reutilization in the target process.

2.4. *Analytical methods*

Upon reaction completion, the quantitative analysis of products was performed on GC-MS. Chromatograms were recorded on a GS-MS turbo system (5975-7820A) model equipped with a HP-5MS capillary column (30 m x 0.25 mm x 0.25 μm). NMR spectra were recorded using Varian Mercury 300 spectrometer. Chemical shifts (δ) are reported in ppm and were measured relative by the internal referencing to the D_2O (^1H).

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

Retention times (levulinic acid): peak at 9.66 min. levulinic acid, at 12.50 min. naphthalene, at 15.99 min. monoacetylglyceride, at 23.07 min., diacetylglyceride and at 36.17 min. triacetylglyceride.

Retention times (benzaldehyde): peak at 5.20 min. benzaldehyde, at 12.66 and 12.89 min. the diastereoisomer 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 diastereoisomers of (2-(furan-2-yl)-1,3-dioxolan-4-yl)methanol and at 10.39 and 11.32 min. the other two diastereoisomers of 2-(furan-2-yl)-1,3-dioxan-5-ol.

Acetalisation (paraformaldehyde and acetone): injector temperature 250˚C, detector temperature 230˚C, oven temperature program: 40˚C (10 min.) ramp 5˚C/min. until 100˚C and another ramp 9˚C/min. until 200˚C.

Retention times (paraformaldehyde): peak at 1.54 min. formaldehyde, 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 14.99 min. 2,2-dimethyl-1,3-dioxan-ol and at 22.90 min. glycerol (broad peak).

2.5. Materials

Glycerol (99%), levulinic acid (98%), paraformaldehyde (powder, 95%) and furfural (99%), employed in this work were purchased from Aldrich. Benzaldehyde (99%) was purchased from Panreac. Acetone, hexane, diethyl ether and ethanol were purchased from Scharlaub. Deuterium oxide was purchased from Euriso-top. All chemicals were used without further purification, except furfural which was purified by column chromatography. Textural and surface acid properties of materials synthesized in this work have been summarized in Table 1.

Table 1. Textural properties [surface area (m^2 g^{-1}), pore size (nm) and pore volume (mL g^{-1})], surface acidity and metal loading (wt.%) are listed in the literature[31] and the following table:

Catal.	**Metal loading wt.%**	**Surface area** (m^2 g^{-1})	**Pore size/volume (nm/mL)**	**Surface acidity at 300ºC/μmolg^{-1}**	
				PY (total acidity)	**DMPY (Brönsted acidity)**
Al-SBA-15	3 (Al)	747	8.0/0.65	82	61
Fe/Al-SBA-15	0.63(Fe)	688	7.8/0.63	104	88

3. Results and Discussion

Fe/Al-SBA-15 and its respective parent support were characterised for textural and surface acidic properties as summarized in Table 1. The most interesting feature for Fe/Al-SBA-15 related to its increase in Brönsted acidity upon Fe incorporation even at a very low Fe quantities (0.63 wt.%, as measured by ICP/MS). In view of the surface acid properties of both parent Al-SBA-15 and Fe/Al-SBA-15, the increase in acidity does not seem to be particularly significant but the catalytic properties of the Fe-containing materials clearly differ from those of the Al-SBA-15 support as previously reported by our group.[31, 34] Hence, the possibility to investigate changes in catalytic activity of these systems in glycerol transformations was considered and subsequently explored in this work.

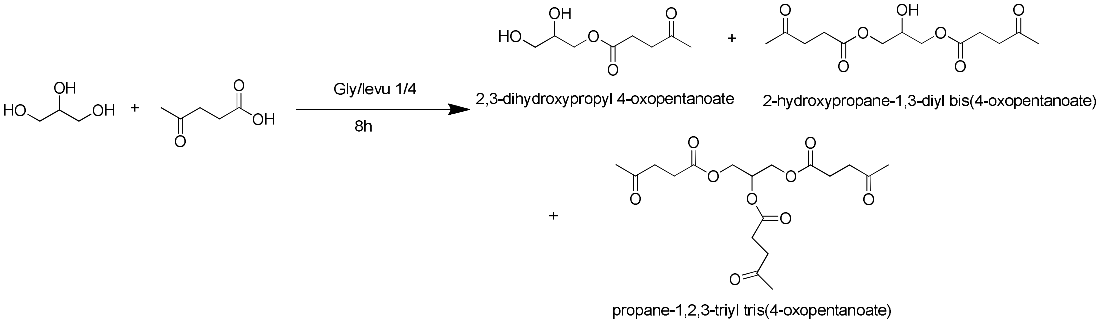
3.1. Esterification of glycerol

The esterification reaction of glycerol was carried out with levulinic acid, which is also a biomass derived chemical. Results are summarized in Table 2. Three products can be formed in the reaction, namely mono-, di- and tri-acetylglycerides. Due to the equal activity of two terminal alcoholic groups, the mono-acetylglycerides was not observed. Di-acetylglycerides was found to be the major product under investigated reaction conditions, with the exception of the use of Al-SBA-15 as catalyst (in this case, Al-SBA-15 was less reactive and also more selective to the mono-glyceride). As the proposed esterification is a sequential reaction (going through mono-, di- and triglyceride), the observed preferential selectivity to di-glyceride can be in principle attributed to the lower activity of the central alcoholic group. Since it is attached to the secondary carbon and after formation of di-acetylglycerides, this –OH group becomes electron deficient which essentially prevents a further esterification to tri-acetylglycerides. Preliminary experiments were conducted at 100 °C, but the catalyst did not show any conversion at this temperature (Table 2, entry 1).

Almost quantitative conversion was achieved in the systems with di- and tri-acetylglycerides ratios of 71:28 (Table 2, entry 2) when the reaction temperature was raised to 120 °C. A further increase to 140 °C did not have any effect in the systems, with only a slight selectivity change (Table 2, entry 5). This selectivity change could be due to the lower thermal stability of tri-acetylglycerides at this temperature. At lower catalyst concentration (25 mg catalyst per mmol glycerol), the reaction was strongly affected and no conversion was observed (Table 2, entry 3).

Blank runs (in the absence of catalyst) gave negligible conversion in the systems under identical conditions even at 140ºC. Comparably, reduced conversions (<80%) were obtained for the parent Al-SBA-15 support, with a remarkable selectivity change (Table 2, entry 4). Mono-acetylglycerides was almost exclusively obtained under comparable conditions to those of Fe/Al-SBA-15. (Table 2, entry 2 vs 4).

Table 2. Esterification of glycerol with levulinic acid using Fe/Al-SBA-15.[a]



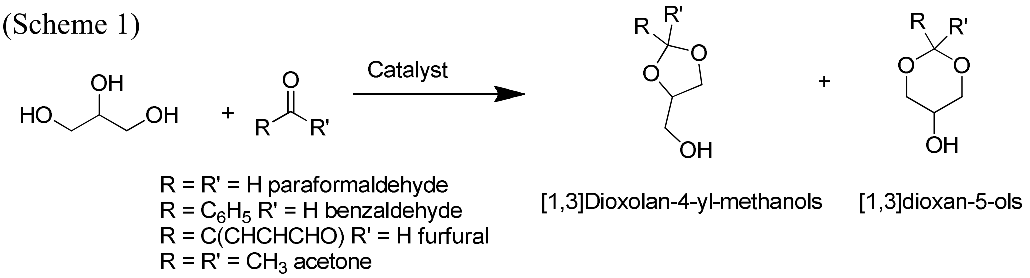
Entry	Catal.	Catal./Gly. (mg/mmol)	mono/di/tri	T (ºC)	Conv. (%)
1	Fe/Al-SBA-15	50/1	-	100	-
2	Fe/Al-SBA-15	50/1	0/71/28	120	>99
3	Fe/Al-SBA-15	25/1	-	120	-
4	Al-SBA-15	50/1	94/5/1	120	78
5	Fe/Al-SBA-15	50/1	0/80/20	140	>99

[a] Reaction conditions: 1 mmol glycerol, 4 mmol levulinic acid, catalyst, solventless, 8h.

3.2. Acetalisation of glycerol with aldehydes and acetone.

Acetalisation of glycerol was carried out with different carbonyl compounds including formaldehyde, benzaldehyde, furfural and acetone in the presence of

Fe/Al-SBA-15. The catalyst was found to be catalytically active and produced the cyclic acetals, dioxolane (five-membered) and dioxane (six-membered). Interestingly, the six-membered acetal was formed with higher selectivity, although six-membered acetal is the thermodynamically favored product, not always it was the major product. (Scheme 1)



Scheme 1. Cyclic acetals formed in the condensation of glycerol with aldehydes or acetone.

Acetalisation of glycerol with formaldehyde was performed at 100 °C for 8 h in neat conditions. From results shown in Table 3, 90% conversion was achieved for a catalyst loading of 20 mg/mmol of glycerol, with a selectivity dioxolane/dioxane of 34:66. Quantitative conversion was obtained when formaldehyde concentration was increased to 1:2 (glycerol/formaldehyde) and the selectivity of six-membered acetal was increased as well. Similar to the esterification reaction, the lower catalyst loading also impeded the acetalisation reaction, giving only 11% conversion. Interestingly, the acetalisation of glycerol with formaldehyde using the parent Al-SBA-15 as catalyst provided significantly improved conversions (Table 3, entry 3) with respect to Fe/Al-SBA-15 (Table 3, entry 2). The observed reduced activity for the Fe-based system may be attributed to partial Al acidic site covering and/or pore blocking by iron nanoparticles, with the reaction only catalysed at the external surface. There was in fact no significant improvement in Lewis acidity upon Fe incorporation, while Brönsted acidity increased by 25-30%. However, this is a very minor issue, because conversion in the systems could reach 90% at increasing quantities of catalyst, an improvement which is obviously related to the availability of a larger number of active sites. (Table 3, entry 1). Blank reactions (in the absence of catalyst) provided no conversion under the investigated reaction conditions.

The acetalisation of glycerol with benzaldehyde was subsequently conducted under optimized conditions. In this case, the reaction needed a slightly higher quantity of catalyst under similar reaction conditions as compared to those using formaldehyde in order to drive the reaction to completion (Table 4). Blank runs (in the absence of catalyst) gave a maximum 25% conversion under optimized conditions. Conversions were comparatively lower to those obtained in the reaction with formaldehyde. Both five- and six-membered ring products, with five-membered dioxolane predominantly formed as major product. The use of Al-SBA-15 provided essentially analogous activities in the reaction under comparable reaction conditions (Table 4, entries 1 vs 2). No change in conversion and selectivity was observed by increasing the catalyst amount.

Table 3. Catalytic activity of Fe/Al-SBA-15 in the acetalisation of glycerol with paraformaldehyde.[a]

Entry	**Catalyst**	**Catal./Gly (mg/mmol)**	**Selectivity (dioxolane/dioxane)**	**Conv.(%)**
1	Fe/Al-SBA-15	20/1	34/66	90
2	Fe/Al-SBA-15	10/1	36/64	11
3	Al-SBA-15	10/1	36/64	93
4	Fe/Al-SBA-15	20/1	24/76	100[b]

[a] Reaction conditions: 1 mmol glycerol, 1 mmol paraformaldehyde, solventless 100ºC, 8h. [b] Ratio gly:aldehyde 1:2

Table 4. Fe/Al-SBA-15 as catalyst in the acetalisation of glycerol with benzaldehyde.[a]

Entry	Catalyst	Catal./Gly (mg/mmol)	Selectivity (dioxolane/dioxane)	Conv.(%)
1	Fe/Al-SBA-15	50/1	84/16	70
2	Al-SBA-15	50/1	83/17	72
3	Fe/Al-SBA-15	100/1	84/16	71

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

Almost similar trends were found in the acetalisation of glycerol with furfural (Table 5). Blank runs gave a maximum of 20 % of conversion. The six-membered dioxolane ring was obtained as major product, but the ratio between the two products was decreased (Table 4, entry 1 *vs.* Table 5, entry 1). An increase in catalyst loading could push conversions to a maximum of 56%, with no significant changes in selectivity (Table 5, entry 3). The most important effect on conversion was related to increased furfural concentrations. An increase in furfural/glycerol ratio from 1 to 1.5 provided a significant boost in activity (95% conversion obtained) with an identical product distribution.

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

Entry	Catalyst	Catal./Gly (mg/mmol)	Selectivity (dioxolane/dioxane)	Conv.(%)
1	Fe/Al-SBA-15	50/1	61/39	44
2	Fe/Al-SBA-15	50/1	60/40	>95[b]
3	Fe/Al-SBA-15	100/1	53/47	56
4	Al-SBA-15	100/1	68/32	74

[a] Reaction conditions: 1 mmol glycerol, 1 mmol furfural, solventless 100ºC, 12h. [b] Ratio gly:furfural 1:1.5

Al-SBA-15 exhibited a higher activity in the acetalisation of glycerol with benzaldehyde and furfural as compared to its Fe-containing counterpart, but again the observed differences in conversion cannot be considered as very significant with respect to the acetalisation reaction of glycerol with paraformaldehyde. In this cases, the reason is only related to the use of larger quantities of catalyst (an increasing number of active sites are present for a 100/1 catalyst/glycerol ratio) as no differences could be observed when the catalyst/glycerol ratio was 50/1 (comparing Fe/-Al-SBA-15 vs Al-SBA-15).

For both benzaldehyde and furfural, acetalisation resulted into two pairs of isomers for each product (five- and six-membered) (Figure 1) which were identified from proton signals of –OC*H*(R)O– in ^{1}H NMR and GC-MS studies. The chemical shift values (δ) are provided in Table 6.

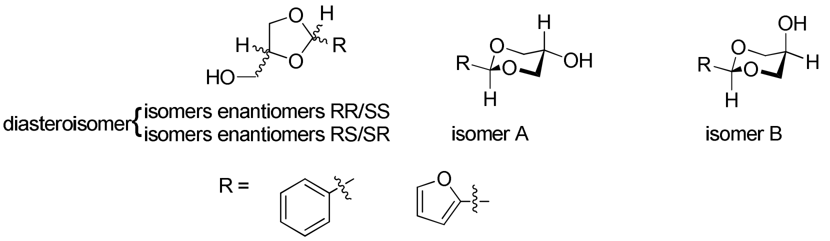


Figure 1. Conformational isomers of cyclic acetals from benzaldehyde and furfural.

The acetalisation of glycerol with acetone showed relatively lower conversion than the aldehydes, which is probably due to the lower electron withdrawing effect of ketone carbonyl groups compared to that of aldehydes. Another plausible explanation may relate to a partial deactivation of acid sites with fully miscible water contained in acetone. Five-membered dioxolane was found to be the major product with very high selectivity (99%), as already reported in the literature.[27,36,37] Higher catalyst loading resulted in a slight increase in conversion (58%, Table 7, entry 1 *vs.* 2). Importantly, the presence of iron oxide nanoparticles in Fe/Al-SBA-15 was proved to be critical in this particular acetalisation process, in which the parent support gave almost negligible conversion under identical reaction conditions (Table 6, entries 1 and 2).

Table 6. The cyclic acetals from acetalisation of glycerol with benzaldehyde or fufural and characteristic proton signals OC*H*(R)O.[a]

Aldehyde	Products	Chemical shift (ppm)
Benzaldehyde	(2-phenyl-1,3-dioxolan-4-yl)methanol **A** and **B** 2-phenyl-1,3-dioxane-5-ol.	5.79 (s), 5.68 (s) 5.53 (s), 5.41 (s)
Furfural	(2-(furan-2-yl)-1,3-dioxolan-4-yl)methanol **A** and **B** 2-(furan-2-yl)-1,3-dioxan-5-ol.	5.93 (s), 5.81 (s) 5.65 (s), 5.55 (s)

Table 7. Acetalisation of glycerol with acetone over Fe/Al-SBA-15.[a]

Entry	Catalyst	Catal./Gly (mg/mmol)	Selectivity (dioxolane/dioxane)	Conv.(%)
1	Fe/Al-SBA-15	50/1	99/1	51
2	Al-SBA-15	50/1	99/1	6
3	Fe/Al-SBA-15	100/1	99/1	58

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

3.3. Catalyst reusability study

To check the regeneration ability of the catalyst, it was recycled in all reactions under optimized conditions.

3.3.1. Esterification of glycerol with levulinic acid

Fe/Al-SBA-15 could be easily recovered from the reaction mixture, reaction conditions glycerol/levulinic acid 1:4, solventless 120ºC for 8 h and used five times without any significant loss of activity (Figure 2).

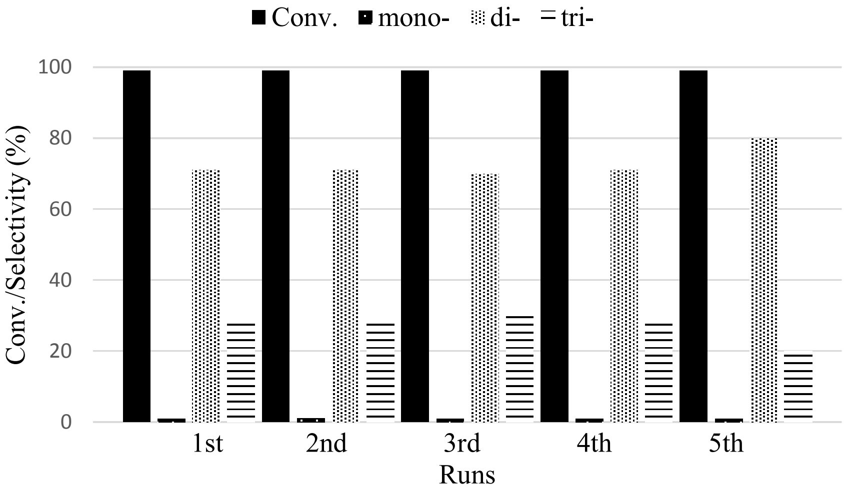


Figure 2. Reusability of Fe/Al-SBA-15 in the esterification of glycerol with levulinic acid.

2.5.1. Acetalisation of glycerol with aldehydes and acetone

Fe/Al-SBA-15 also showed a remarkable stability and activity up to five consecutive cycles (Figure 3). Product distribution ratios were also measured for each set of studies and observed to be almost identical for all catalytic runs.

The preparation of cyclic acetals using acids catalysts has previously been reported in the literature (Table 8). In general, (Fe)/Al-SBA-15 catalysts exhibited comparable activities to those previously reported in the literature, under however different conditions. Results from this work cannot be strictly compared to literature reports as those have been carried out under different reaction conditions including 1) the use of organic solvents (Table 8, entries 1, 6, 11 and 17; as compared to our solventless reaction); 2) an excess of the aldehyde/ketone substrate (with respect to 1:1 ratio in this work); 3) the use of expensive catalysts (Table 8, entries 1, 2 and 21; e.g. $AuCl_3$, oxorhenium compounds, etc.) as well as generally no reutilization studies reported for most literature reports on glycerol acetalisation.

Table 8. A comparison of catalytic activities of different protocols and catalysts in the acetalisation with all the carbonyl group.

Entry [ref.]	Carbonyl group	Reactions conditions [mmol gly:mg catal]	Solvent	T (°C)	Time (h)	Conv. (%)
1 [35][a]	-CHO	AuCl$_3$, 5 mol %	Dioxane	80	4	93
2 [35][a]	-CHO	AuCl$_3$, 5 mol %	-	80	4	83
3 [35][a]	-CHO	PTSA [13:25]	-	100	10	80
4 [35][a]	-CHO	Beta(F)-50 [13:25]	-	100	10	60
5 [35][a]	-CHO	Amberlyst-36 [13:25]	-	100	10	60
6 [24][a]	-CHO	Amberlyst-36 [11:50]	Chloroform	60	6	77
7 [26][b]	-CHO	Amberlyst-15 [1:65]	-	70	1	59
8 [29][a]	-CHO	Zr-SBA-16(100) [1:100]	-	100	8	77
9 This work[a]	-CHO	Al-SBA-15 [1:10]	-	100	8	93
10 This work[a]	-CHO	Fe/Al-SBA-15 [1:10]	-	100	8	11
11 [24][c]	CO(CH$_3$)$_2$	Amberlyst-36 [11:50]	DCM[d]	40	8	88
12 [26][b]	CO(CH$_3$)$_2$	Amberlyst-15 [1:65]	-	70	0.6	>99
13 [36][e]	CO(CH$_3$)$_2$	Ar-SBA-15 [1:5]	-	70	2	80
14 [37][c]	CO(CH$_3$)$_2$	Nb$_2$O$_5$-343	-	70	6	80
15 This work[a]	CO(CH$_3$)$_2$	Al-SBA-15 [1:50]	-	100	8	6
16 This work[a]	CO(CH$_3$)$_2$	Fe/Al-SBA-15 [1:50]	-	100	8	51
17 [24][a]	PhCOH	Amberlyst-36 [11:10]	Chloroform	60	4	94
18 [38][f]	PhCOH	RSASO$_3$H [1:150]	-	100	8	70
19 This work[a]	PhCOH	Al-SBA-15 [1:50]	-	100	8	72
20 This work [a]	PhCOH	Fe/Al-SBA-15 [1:50]	-	100	8	70
21 [39][g]	CHOC(OCH)$_2$	Oxorhenium (V) oxazoline [1:1246,62]	-	100	4	77
22 This work[a]	CHOC(OCH)$_2$	Al-SBA-15 [1:50]	-	100	8	72
23 This work[a]	CHOC(OCH)$_2$	Fe/Al-SBA-15 [1:50]	-	100	8	70

Reaction conditions: [a] 1 mmol glycerol, 1 mmol carbonyl substrates. [b] 1 mmol glycerol, 1.2 mmol organic compound. [c] 1 mmol glycerol, 1.5 mmol organic compound. [d] DCM; dichloromethane [e] 1 mmol glycerol, 2 mmol organic compound. [f] 2 mmol glycerol, 1 mmol organic compound. [g] 1 mmol glycerol, 4 mmol organic compound.

Conclusions

The esterification and acetalisation reactions of glycerol with levulinic acid and paraformaldehyde were found to be successfully catalysed by a heterogeneous Fe/Al-SBA-15 in good to excellent yields to products. Acetalization of glycerol with benzaldehyde, furfural and acetone were carried out with good conversions in the presence of Fe/Al-SBA-15. Under optimum esterification conditions (molar ratio of glycerol/levulinic acid of 1:4, 120 ºC, 8h reaction time), glycerol could be completely converted to a final product containing a mixture of 71% di- and 28% triacetylglycerides, respectively. The catalyst was proved to be highly stable and reusable under the investigated optimum conditions up to five consecutive cycles. Product distribution ratios measured for each set of studies were unchanged for all catalytic runs.

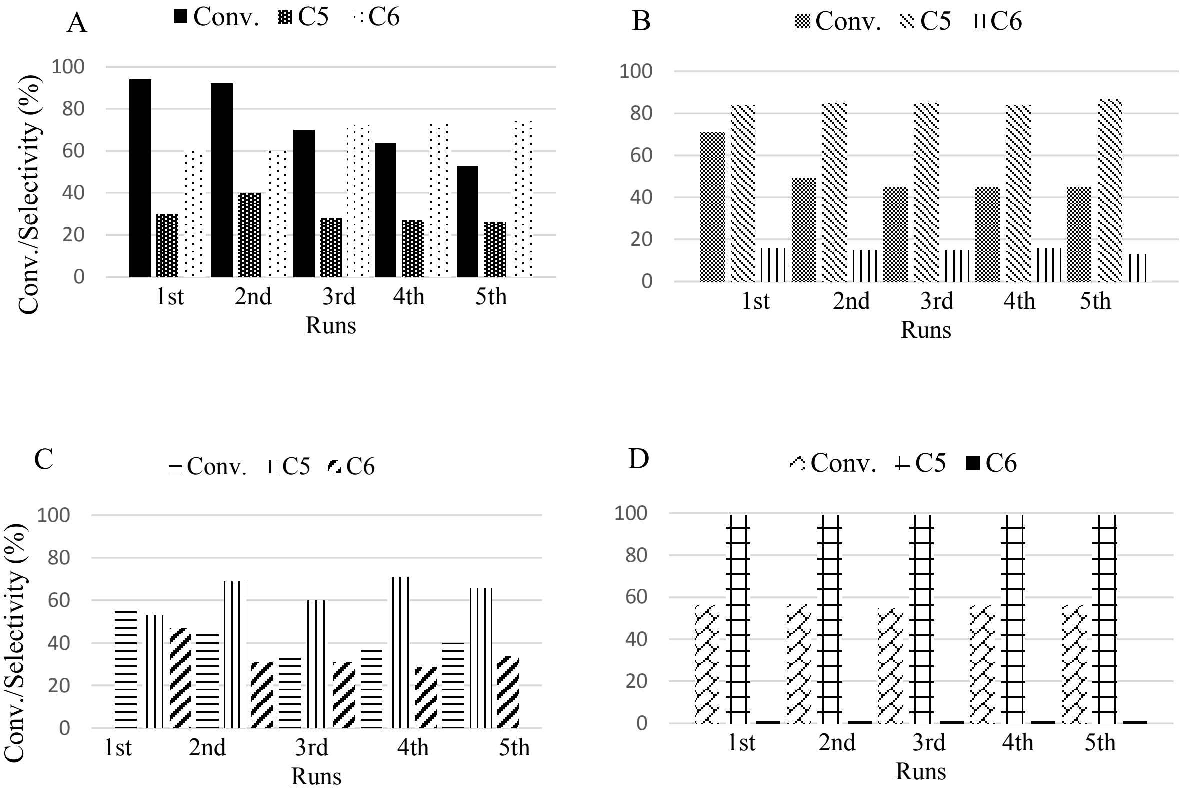


Figure 3. Reusability of Fe/Al-SBA-15 in the acetalisation of glycerol with (A) formaldehyde, (B) benzaldehyde, (C) furfural and (D) acetone.

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