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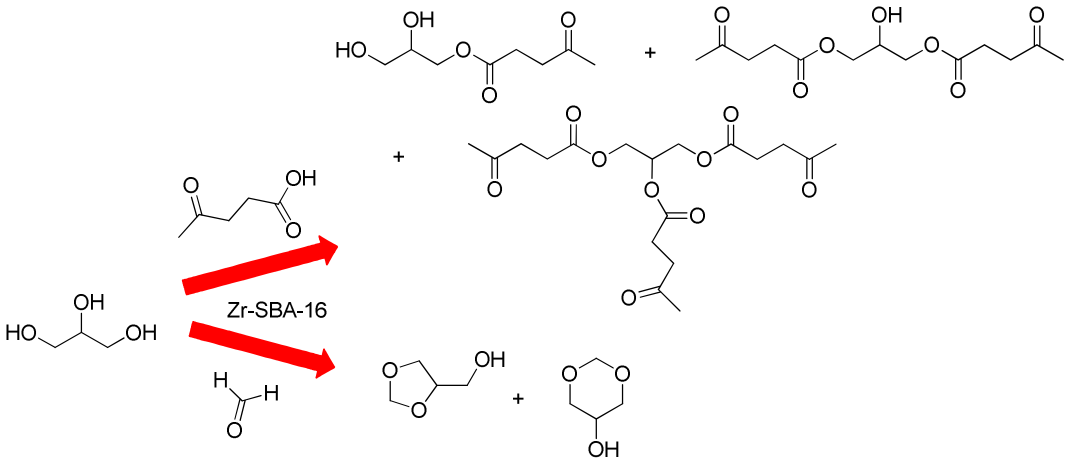

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Mesoporous Zr-SBA-16 catalysts for glycerol valorization processes: towards biorenewable formulations

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Abstract

Zr-containing SBA-16 materials were utilized in glycerol valorization for the production of esters (via reaction with levulinic acid) and glycerol formal (GF) via acetalisation with paraformaldehyde. Materials were found to be highly active and selective for the production of valuable compounds from glycerol using benign by design solventless protocols which employ mild reaction conditions. Certain materials were also found to be highly reusable and stable under the investigated conditions.

Keywords: SBA-16, glycerol, esterification, acetalisation, levulinic acid

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Introduction

Glycerol is an abundant renewable resource considered as relevant platform chemical for the production of chemicals, materials (e.g. polymers) and biofuels/fuel additives.[1,2]. This polyol attracted a significant attention in recent years due to the large volumes of crude glycerol as byproduct (ca. 10%) generated from biodiesel production[2, 3]. Finding applications in the pharmaceutical, personal care and food industry, a number of strategies have been recently developed in order to convert glycerol into important derivatives including propylene glycol, acrolein and triacetin among others[4]. Catalytic transformations of glycerol to such valuable compounds have been extensively reported in the literature in recent years both under batch and continuous flow conditions.[3-9]

Glycerol esterification is a relevant transformation based on the added-value of potential derivatives.[10, 11] As example, triacetin possesses suitable properties as fuel blender in gasolines, improving parameters such as cold point and viscosities. Other esters and related derivatives find important uses as pharmaceutical intermediates, foodstuffs, explosives, plasticisers, insecticides, etc.[12-14] In some cases, acid catalysed condensation of glycerol with carboxylic acids (e.g. levulinic acid) may generate low molecular weight ketal-ester oligomers, providing a new scenario for renewable biopolymer formulations.[15]

Generally, esterification processes have been traditionally promoted by strong mineral acids including HCl and H_2SO_4 as well as other strong acidic systems (e.g. *p*-toluenesulfonic acid, PTSA). In recent years, solid acids including zeolites, acidic mesoporous materials and related catalysts have replaced homogeneous systems in esterification protocols as recent research endeavors have been aimed to switch to more environmentally sound protocols.[4, 8, 9, 16]

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Glycerol acetalisation with aldehydes or ketones for the formation of cyclic oxygenated compounds is another important process considered in glycerol valorization strategies. The reaction between glycerol and formaldehyde is particularly interesting leading to the so-called glycerol formal (GF). GF comprises a mixture of a 5 and 6-membered oxygenated rings (compounds 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane) and finds important applications as low-toxic solvent for pharmaceutical syntheses (anti-parasite veterinary pharmaceuticals, sulfomethoxazal, sulfonamide preparations, tetracycline-based products are injected into GF), binder (cold box), in the synthesis of insecticides, for controlled solvent evaporation in insecticide delivery systems, as well as in formulations of water-based inks.[17] GF preparation has thus far been mostly reported under homogeneous catalytic conditions employing mineral acids such as H_2SO_4 (with and without solvent)[18] or PTSA.[19] Solid acid catalysts have been rarely employed in this particular reaction due to catalyst stability issues under the proposed conditions, with few available reports which employed Amberlyst-36[20] and Al-modified zeolites.[21]

In continuation with our research endeavors devoted to the development of simple, efficient and greener heterogeneous catalytic protocols for biomass-derived molecules, herein we report preliminary catalytic activity results of previously reported highly ordered Lewis acidic mesoporous Zr-containing SBA-16 materials with varying Si/Zr ratios[22, 23] in the esterification of glycerol with levulinic acid (LA). LA is another biomass-derived platform chemical which can be concomitantly obtained with formic acid (FA) from hexoses dehydration or cellulose deconstruction from a range of lignocellulosic materials. [8, 24, 25] Zr-SBA-16 were also investigated as catalysts in the acetalisation of glycerol with formaldehyde for the production of GF.

Experimental

Materials

Pluronics, sodium metasilicate, zirconyl chloride, glycerol, levulinic acid, formaldehyde solution (37 wt. % in H_2O, formalin) and formaldehyde employed in this work were purchased from Aldrich and utilised without further purification.

Catalyst preparation

Zr-SBA-16 materials were synthesized according to a previous literature report.[22, 23] In a typical synthesis, 16 g of a 10 % aqueous solution of Pluronics ($EO_{106}PO_{70}EO_{106}$, Mav = 12,600), 26 g of distilled water and 4.71 g of sodium metasilicate (Na_2SiO_3•$9H_2O$) were stirred together at 40ºC by until clear dissolution. 13.6 g of HCl (35%) with the target amount of zirconyl chloride ($ZrOCl_2$•$8H_2O$) to achieve the different Si/Zr ratios were subsequently added under vigorous stirring to obtain a gel. The molar composition of the gel mixture was 1.0 SiO_2: x Zr: $3.17 \cdot 10^{-4}$ pluronics: 6.68 HCl: 137.9 H_2O. The solution was continuously stirred for 120 min (optimum conditions)[22] and subsequently microwave-irradiated in a microwave digestion system (Milestone Corporation, ETHOS-1) for 120 min at 100ºC. The solid product was eventually filtered, dried at 120ºC overnight and calcined at 500ºC. Three different materials were prepared with Si/Zr ratios of 100, 50 and 25, respectively. These samples have been denoted as Zr-SBA-16(100), Zr-SBA-16(50) and Zr-SBA-16(25).

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Materials possessed similar textural properties to those included in previous work (e.g. high surface areas >600 m^2 g^{-1}, pore sizes over 6 nm and pore volumes >0.6 mL g^{-1}).[22, 23]

Characterisation of surface acidity

Pyridine (PY) and 2,6-dimethylpyridine (DMPY) titration experiments were conducted at 300 ºC via gas phase adsorption of the basic probe molecules utilising a pulse chromatographic titration methodology. Briefly, small amounts of probe molecules (typically 1-2 μL) were injected (to approach conditions of gas-chromatography linearity) into a gas chromatograph through a microreactor in which the solid acid catalyst was previously placed. Basic compounds are adsorbed until complete saturation from where the peaks of the probe molecules in the gas phase are detected in the GC. The quantity of probe molecule adsorbed by the solid acid catalyst can subsequently be easily quantified. In order to distinguish between Lewis and Brönsted acidity, the assumption that all DMPY selectively titrates Brönsted sites (methyl groups hinder coordination of nitrogen atoms with Lewis acid sites) while PY titrates both Brönsted and Lewis acidity in the materials was made. Thus, the difference between the amounts of PY (total acidity) and DMPY (Brönsted acidity) adsorbed should correspond to Lewis acidity in the materials.

Catalytic experiments

Esterification of glycerol with levulinic acid

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In a typical esterification, the catalyst (0.1-0.2 g) was suspended in a mixture of glycerol (1 mmol) and levulinic acid (5 mmol). The reaction was carried out under continuous stirring inside an ampoule at 140 ºC for 8h. Upon reaction completion, the resultant mixture was filtered off, extracted using ethanol and subsequently analyzed by GC-MS. The products mono-, di-(1,2-diacetylglycol) and triacetin were identified by GC-MS and their ratios were also worked out by means of ^{1}H NMR. The response factors of the starting material and products were determinated using naphthalene as external standard.

Glycerol acetalisation with formaldehyde sources

In a typical acetalisation reaction, the catalyst (0.02-0.1 g) was suspended in a mixture of glycerol (1 mmol) and paraformaldehyde (5 mmol). The reaction was carried out inside an ampoule under stirring at 100ºC for 8h. The resultant mixture was then filtered off, extracted using ethanol and analyzed by GC-MS. 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane were identified as products by GC-MS and their ratio worked out also using ^{1}H NMR.

Catalyst testing, recyclability tests and product analysis

Upon reaction completion, the catalyst was washed with ethanol and then filtered off through a silica plug. Product mixtures were analyzed using GC-MS. Chromatograms were recorded on a GS-MS turbo system (5975-7820A) model equipped with a HP-5MS capillary column (30m x 0.25 mm x 0.25 µm), under the following conditions:

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Esterification: 50˚C ramp 5˚C/min. until 100˚C, another ramp 10˚C/min. until 175˚C and the last ramp 10˚C/min. until 230˚C held 20min. Retention times: peak at 9.66 min. levulinic acid, at 15.99 min. monoacetylglycerol, at 23.07 min., diacetylglycerol and at 36.17 min. triacetylglycerol.

Acetalization: injector temperature 250˚C, detector 150˚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: 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).

In recycle studies, 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.

Results and discussion

Zr incorporation has an important effect in developing acidity in silicate materials, as in the case of SBA-16. The acidity of the materials was found to significantly increase at increasing Zr content in the materials, in particular Lewis acidity (Table 1)[22, 23], while all textural and surface properties remained very similar for the three acidic mesoporous materials as previously reported literature data.

Esterification of glycerol

Three samples of SBA-16 with Si/Zr ratios of 25, 50 and 100 were studied. Blank runs (in the absence of catalyst) provided almost negligible or very low activities to products even at high temperatures (>140ºC, Tables 2 and 3). The screening and optimization of reaction conditions pointed out that Zr-SBA-16 materials gave very low

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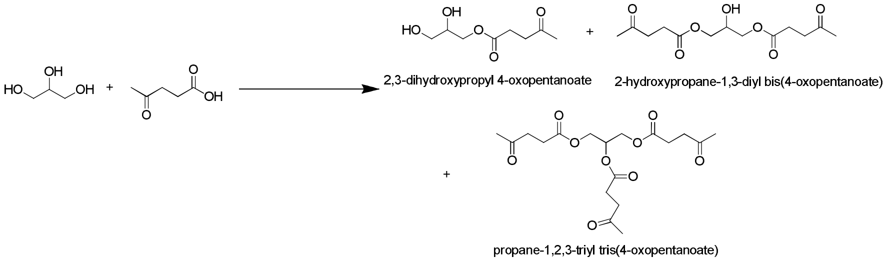
activity at temperatures under 140ºC and for reactions conducted with lower quantities of catalyst to those included in Table 2.

Table 1. Acid properties of Zr-SBA-16 materials as measured by PY and DMPY titration

Materials	Total acidity (μmol PY g^{-1})	Brönsted acidity (μmol DMPY g^{-1})	Lewis acidity (μmol g^{-1})
Zr-SBA-16 (100)	40	28	12
Zr-SBA-16 (50)	116	36	80
Zr-SBA-16 (25)	233	33	200

Table 2. Comparison of catalyst conversion and selectivity for the esterification of glycerol with levulinic acid using Zr-SBA-16 materials.



Entry	Catalyst	Catal./Gly	Selectivity (mono/di/tri, mol%)	Conversion[a] (mol%)
1	Zr-SBA-16(100)	200 mg/1 mmol	71/29/0	40
2	Zr-SBA-16(50)	100 mg/1 mmol	83/16/0	65
3	Zr-SBA-16(25)	25 mg/1 mmol	77/23/0	70

[a] Reaction conditions: 1 mmol glycerol, 5 mmol of levulinic acid, catalyst, solventless, 100 ºC, 15h reaction.

Reaction runs under solventless conditions (as compared to the addition of solvents including acetonitrile, toluene, etc.) also led to a cleaner and improved

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separation workup even at low temperatures of reaction (<100ºC). Results from Table 2 clearly demonstrate that only moderate conversion could be achieved for all materials at 100ºC even after 15 h reaction. Selectivities obtained at this temperature (70-83%) favored a significant production of monoacetylglycerides. Performed reactions employed different quantities of catalysts to study the normalised activity per active Zr site. A temperature increase to 140ºC was subsequently attempted in order to push the reaction to quantitative yields as activities were only slightly increased at temperatures between 100-140ºC. Normalised results (per active Zr site) included in Table 3 proved that reaction completion could be achieved after 8h, with interesting selectivities towards the production of the diester (ca. 65-70%).

Table 3. Optimised results for the esterification of glycerol with levulinic acid using Zr-SBA-16 materials.

Entry	**Catalyst**	**Catal./Gly**	**Selectivity (mono/di/tri, mol%)**	**Conversion[a] (mol%)**
1	No catalyst	-	4/66/30	20
2	Zr-SBA-16(100)	200 mg/1 mmol	11/64/25 (0/50/50)[b]	>99
3	Zr-SBA-16(50)	100 mg/1 mmol	12/64/24 (0/61/38)[b]	>99
4	Zr-SBA-16(25)	25 mg/1 mmol	4/68/28 (0/62/37)[b]	>99

[a]Reaction conditions: 1 mmol glycerol, 5 mmol of levulinic acid, catalyst, solventless, 140 ºC, 8h reaction. [b] Values in brackets correspond to selectivities to products after 15 h reaction under identical conditions.

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Longer times of reaction (15 h) only possessed a minor influence in the selectivity of the systems, with slightly improved values towards the production of tri-ester (37-50 mol%), at the expense of mono-esters (Table 3, entries 2 to 4).

Taking into account optimization results obtained for the reaction (Tables 2 and 3), Zr-SBA-16(25) seemed to provide the optimum activity in the reaction for which this catalyst was selected for reusability tests. The catalyst was proved to be highly reusable under the investigated conditions (Table 4), with fully preserved initial activity even after 4 uses under identical reaction conditions. Interestingly, the di/tri ratio in the reused materials was also identical in all cases, with almost identical selectivities to those of the fresh catalyst.

Table 4. Reusability study in the esterification of glycerol with levulinic acid using Zr-SBA-16(25) as catalyst.[a]

Run	Selectivity (mono/di/tri, mol%)	Conversion (mol%)
1	0/62/37	>99
2	0/54/46	>99
3	0/52/48	>99
4	0/53/47	>99

[a] Reactions conditions: 50 mg catalyst, 1 mmol glycerol, 5 mmol levulinic acid, 140 ºC, 15 h reaction.

Glycerol Acetalization

Zr-SBA-16 materials were also tested in the acetalisation of glycerol with formaldehyde for the preparation of GF. Several parameters were investigated in the proposed reaction, starting with the formaldehyde source and solvenless/solvent

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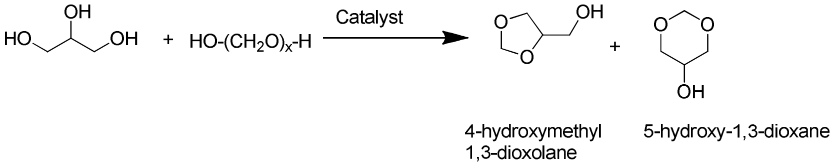
containing systems. Results have been summarised in Tables 5 and 6. Blank runs (in the absence of catalyst) gave no conversion after long times of reactions and high temperatures. Reactions using formaline as formaldehyde source provided very low conversion in the systems under the investigated conditions. Similarly, reaction runs in the presence of paraformaldehyde and polar solvents (e.g. water) gave negligible conversion in the systems even after 15 h reaction. Interestingly, quantitative yields to products could be obtained in the solventless acetalisation of glycerol with paraformaldehyde as formaldehyde source (Table 5, entry 3).

The proposed reaction was recently attempted by Ruiz *et al.*[21] using hydrophobic zeolites and gold-based systems in which the authors did not find a direct correlation between acidity and activity in the systems (i.e. materials with large number of/stronger acid sites were not necessarily most active).

Table 5. Glycerol acetalization catalysed by Zr-SBA-16(25) using different formaldehyde source systems.[a]



Aldehyde source	Conversion (%)
Formalin (solventless)	8
Paraformaldehyde (water)	-
Paraformaldehyde (solventless)	>99

[a]Reaction conditions: 1 mmol glycerol, 1 mmol of aldehyde, Zr-SBA-15(25) (20 mg), 100 ºC, 15h reaction.

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Results summarized in Table 6 compare the catalytic performance of different Zr-SBA-16 materials in the selected reaction after 8 h reaction. Interestingly, Zr-SBA-16(100) provided an unexpectedly optimum activity among all three materials under the investigated reaction conditions, with a conversion of 60% (Table 6, entry 1 vs 2 and 3). Selectivities to the two main C5 and C6 cyclic products in the reaction (4-hydroxymethyl 1,3-dioxolane and 5-hydroxy 1,3-dioxane) followed the expected thermodynamically favored trend towards cyclic C6 product formation in the approximate order ca. 75/25.[21] Results pointed to an increase in catalytic activity with an increase in the quantity of catalyst, which however does not seem to correlate with the acidity in the materials, in good agreement with results from Ruiz *et al*.[21]

Table 6. Catalytic activity of Zr-SBA-16 materials in the acetalisation of glycerol with paraformaldehyde.

Entry	**Catalyst**	**Catal./Gly**	**Selectivity (dioxolane/dioxane)**	**Conversion[a] (%)**
1	Zr-SBA-16(100)	50 mg/ 1 mmol	29/71	60
2	Zr-SBA-16(50)	50 mg/ 1 mmol	24/76	29
3	Zr-SBA-16(25)	50 mg/1 mmol	23/77	30
4	Zr-SBA-16(100)	100 mg /1 mmol	24/76	77
5	Zr-SBA-16(50)	100 mg /1 mmol	27/73	48
6	Zr-SBA-16(25)	100 mg /1 mmol	26/74	44

[a] Reaction conditions: 1 mmol glycerol, 1 mmol paraformaldehyde, 100ºC, 8h reaction.

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Optimised activities for the best performing system in this work were subsequently compared to differently literature reported acid catalysts. Gratifyingly, Zr-SBA-16(100) exhibited improved catalytic activities at shorter times of reaction with respect to most literature reported solid acid heterogeneous catalysts as well as almost comparable activities to those of homogeneous catalysts (Table 7).

Table 7. A comparison of catalytic activity of different protocols and catalysts in the acetalisation of glycerol with paraformaldehyde.[a]

Entry [ref.]	Reaction conditions [mmol gly:mg catal.]	Solvent	T (ºC)	Time (h)	Conversion (%)
1 [21]	$AuCl_3$, 5 mol%	Dioxane	80	4	93
2 [21]	$AuCl_3$, 5 mol%	-	80	4	83
3 [21]	PTSA, [13: 25]	-	100	10	80
4 [21]	Beta(F)-50, [13: 25]	-	100	10	60
5 [21]	Amberlyst-36 [13: 25]	-	100	10	60
This work	Zr-SBA-16(100) [1:100]	-	100	8	77

[a] Reaction conditions: 1 mmol glycerol, 1 mmol paraformaldehyde.

In view of these premises, the recyclability studies were conducted for all materials in order to establish an activity/deactivation comparison between the different Zr-containing SBA-16. Results are depicted in Figure 1. Figure 1A clearly shows Zr-SBA-16(100) exhibited a rather poor reusability, losing over 60% of its initial activity after 3 uses. Rapid deactivation of acid sites in this material seemed to be coincidental to results reported by Reddy *et al.*[26]

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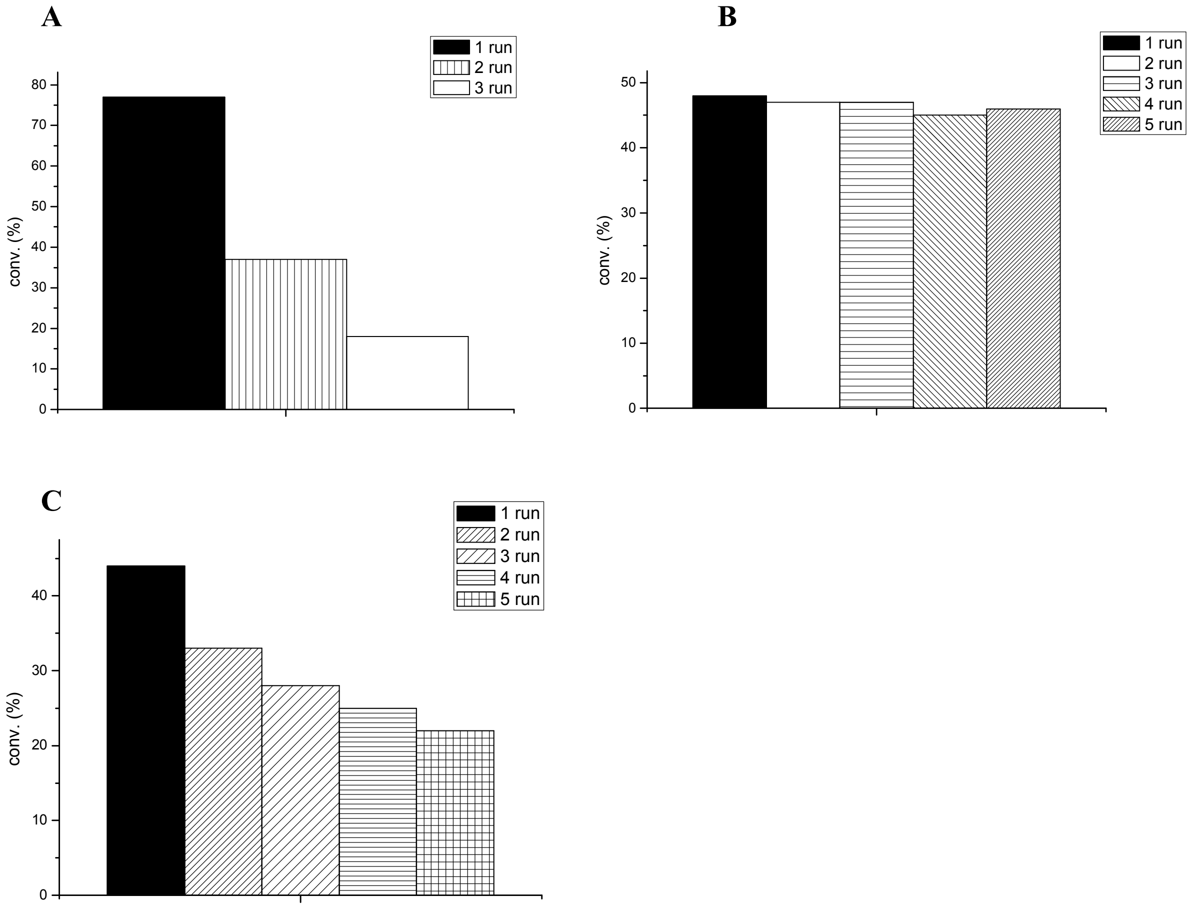

Figure 1. Experiments of catalyst recycling in the acetalization of glycerol with paraformaldehyde. 1 mmol glycerol, 1 mmol paraformaldehyde, 100 mg catalyst, solventless, 100ºC, 8h.

Comparatively, Figure 1C illustrates a rather steady decrease in activity and deactivation through subsequent reuses for Zr-SBA-16(25), which in any case lost almost 50% of its initial glycerol acetalisation activity after 5 uses (Figure 1C). Gratifyingly, Zr-SBA-16(50) could be succesfully reused up to five times under identical reaction conditions, without any noticeable decrease in activity. These results clearly improved those previously reported in the literature,[21] constituting an unprecedented example of an active, stable and highly reusable solid acid in glycerol acetalisation with formaldehyde. A gold complex was reported to provide better yields

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to products in a solvent-mediated protocol, being reusable under the investigated conditions. However, such gold-based catalyst is comparably more expensive and required a significant reaction work-up (i.e. precipitation + filtration) as compared to reusable and easily separable Zr-containing mesoporous materials under solventless conditions.

Conclusions

Preliminary results for Zr-SBA-16 materials with varying Si/Zr ratios indicated that these mesoporous solid acids can have excelling activities in acid catalysed reactions with biomass-derived platform molecules, namely glycerol and levulinic acid. Quantitative conversion was achieved in the esterification of glycerol with levulinic acid with moderate selectivites to diacetylglycerides, being Zr-SBA-16(25) most active in the reaction as expected by its large concentration of acid sites. Comparably, Zr-SBA-16(100) exhibited optimum activities under optimized conditions in the acetalisation of glycerol with paraformaldehyde as formaldehyde source. Investigated catalysts were generally highly stable and reusable under the investigated conditions, with a particularly outstanding recyclability of Zr-SBA-16(50) in glycerol acetalisation.

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