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Gold catalysts and solid catalysts for biomass transformations: Valorization of glycerol and glycerol–water mixtures through formation of cyclic acetals

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ABSTRACT

The valorization of pure glycerol and glycerol in water has been achieved by reaction with aldehydes to form valuable acetals. While soluble PTSA is more active than solid Brønsted acids such as zeolites and resins when reacting with pure glycerol, the synthesis of a hydrophobic zeolite with the adequate ratio of polarity/acidity leads to a better catalyst when reacting with glycerol–water mixtures. Best results (up to 94% yield) were obtained with gold as Lewis acid catalysts under very mild reaction conditions. The preparation of a recoverable and reusable gold catalyst allows to achieve high turnover numbers.

1. Introduction

The production of biodiesel by transesterification of vegetable oils or animal fats with methanol or ethanol is responsible for an increase in the production of glycerol. The yields of glycerol obtained in the transesterification process vary with the fatty ester and, for instance, 1–5 or 12–13 wt.% yield of glycerol is produced from fish and jojoba oils or from coconut oil, respectively. It is then of interest to find processes that can convert glycerol into products with higher added value [1]. With this objective in mind, there is a reaction, such as the acetalization of glycerol with formaldehyde to give glycerol formal (GF), which can be of interest. The product, GF, is a mixture of two cyclic ether compounds: 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane (60:40) (see Scheme 1), which is a viscous colorless liquid with very little odor and soluble in water, chloroform and low molecular weight alcohols and ketones. GF finds applications as low-toxic solvent for various injectable preparations (anti-parasite veterinary pharmaceuticals, sulfomethoxazal, sulfonamide preparations, tetracycline-based products), for binder (cold box), composites made from silica and polyurethane resins, epoxy–SO_2, in the synthesis of insecticides, for controlled solvent evaporation in insecticide delivery systems, in formulation of water-based inks, as solvent for paints and for plastifying agents.

The direct acetalization of glycerol with formaldehyde can be catalyzed by homogeneous acids such as H_2SO_4, with or without solvent (benzene reflux) [2] or by *p*-toluenesulfonic acid (PTSA) [3], giving a 40:60 composition of dioxane and dioxolane. On the other hand, the transacetalization with dimethyl formal in the presence of PTSA and LiBr gives a mixture of dioxane:dioxolane of 94:6, being therefore the transacetalization especially selective toward the dioxane derivative [4].

The preparation of GF in the presence of different soluble Lewis and Brønsted acid catalysts gives a large spectrum of yields [5], being 84% the highest yield reported up to now, with a ratio dioxane:dioxolane of 72:23. Recently, the use of heterogeneous acid catalysts for the acetalization of different carbonyl compounds with glycerol has been reported [6], and the best yield of GF (77%) was obtained with Amberlyst-36 after 6-h reaction time at reflux of chloroform.

In this work, we present a comparative study of the direct acetalization of glycerol and glycerol plus water with formaldehyde using three types of acid catalysts: (1) heterogeneous Brønsted acid (zeolites and organic resins), (2) homogeneous Lewis catalysts, especially those based on gold salts, and (3) a reusable gold complex. In addition, acetalization of *n*-heptanal with glycerol has also been performed.

2. Results and discussion

2.1. Acetalization of formaldehyde with glycerol using Brønsted solid acid catalysts

The acetalization of glycerol was performed in absence of solvent at 373 K with trioxane, with equimolecular amounts of

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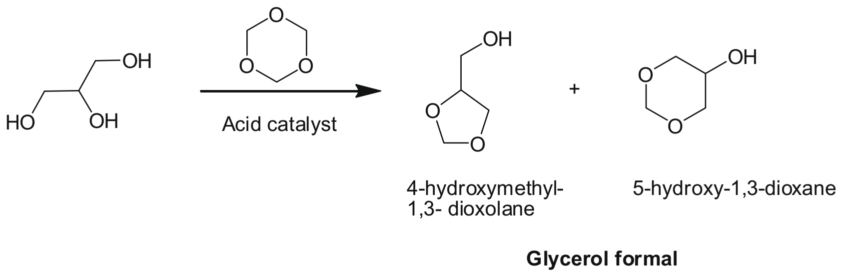


Scheme 1. Synthesis of glycerol formal (GF) using trioxane as source of formaldehyde.

glycerol and formaldehyde. A commercial tridimensional zeolite (Beta-1) and Amberlyst-36 (3 wt.% with respect to glycerol) were used as the starting catalysts. For comparison, the reaction was also performed using PTSA (1 wt.% with respect to glycerol) and the results are presented in Fig. 1. Kinetic results show that the maximum yield (78%) of GF is achieved with the homogeneous catalyst within 2 h and no improvement in the yield is observed for longer reaction times. The results may indicate that under these reaction conditions, catalyst deactivation occurs possibly due to an esterification process between glycerol and the PTSA. With the two solid catalysts, a faster deactivation occurs that is more important for the zeolite. In the three cases, the analysis of products showed the presence of both isomers of GF (see Scheme 1).

In order to establish the reaction scheme, the yields of the different isomers were measured at different levels of conversion with PTSA as catalyst, in order to avoid any masking of the primary chemical selectivity because of geometrical constrains within the micropores of the zeolite. The results displayed in Fig. S1 indicate that both isomers are primary products, but the dioxolane isomer has a clear primary plus secondary character. This corresponds very well with the primary and unstable behavior of the dioxane isomer, indicating that the six-membered ring dioxane isomerizes to give the five-membered ring dioxolane. According to this, a reaction scheme (Scheme 2) can be written that is compatible with the experimental results given in Fig. S1.

In the case of Amberlyst-36 (Fig. S2) in where the acid sites for the reaction are easily accessible at the external surface of the catalyst, the selectivity results toward the two isomers are practically the same that those with PTSA. However, this is not the case for the microporous zeolite catalyst (Fig. S3), in where the isomerization reaction is strongly limited, resulting in a ratio of dioxane to dioxolane sensibly lower than with PTSA or Amberlyst-36. While the molecular dimensions of the two isomers are similar, the intermediate carbocation given in Scheme 2 is ~0.3 Å larger. Taking into account the pore dimensions of zeolite Beta [7], it appears that geometrical restrictions for the formation of the intermediate carbocation (see Scheme 2) can occur and this will explain the larger dioxane/dioxolane ratio observed with Beta zeolite.

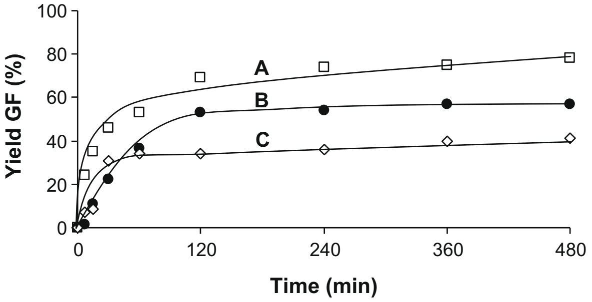
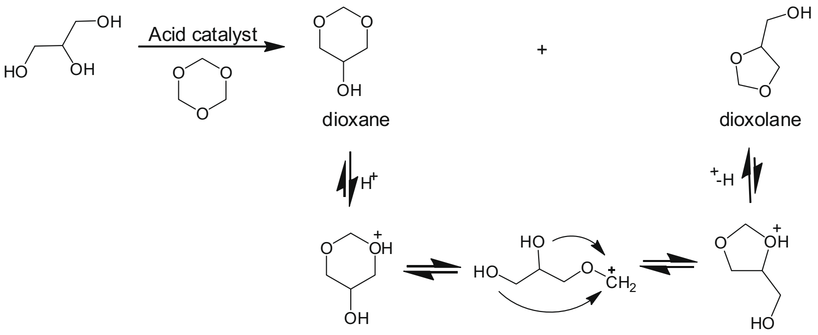


Fig. 1. Kinetic study of the acetalization reaction to give GF. Reaction conditions: solid catalyst (25 mg) or PTSA (12 mg), glycerol (1.225 g), trioxane (400 mg) without solvent, 100 °C. (A) PTSA, (B) Amberlyst-36, (C) Beta-1 was used as catalyst.

2.1.1. Influence of the zeolite polarity

As it can be deduced from Fig. 1, deactivation is observed for the solid catalysts and more specifically for Beta zeolite. The deactivation could be attributed to a strong adsorption of products on the catalyst surface. If this is so, catalyst deactivation should decrease when using a polar solvent to help desorption of the polar compounds from the active sites. This is indeed observed (Fig. S4) when dioxane is used as a solvent, and the influence of the solvent on catalyst deactivation suggests that the key issue for avoiding catalyst decay is to favor desorption of polar products from the catalyst surface. The effect could be achieved not only using an adequate solvent, as was shown previously, but also by modifying the catalyst surface polarity. In other words, the extent of adsorption of the most polar compounds should diminish when making the surface of the catalyst less polar (more hydrophobic), then decreasing the rate of catalyst deactivation. To do this, we have taken two actions. On one hand, the Beta zeolite has been synthesized in fluoride media since it is known that with this synthesis procedure the number of structural defects (internal silanol groups), and consequently the polarity of the zeolite, decreases [8]. On the other hand, and following the fluoride synthesis route, we have prepared samples with different Si/Al molar ratios since the higher the ratio the smaller the number of acid sites and the lower the polarity will be. With this in mind, we expect that an optimum between polarity and number of active sites can exist at a certain zeolite framework Si/Al ratio that will maximize the ratio activity/decay. Thus, four samples of Beta with Si/Al ratios of 15, 30, 50, and 100 were prepared in fluoride media [Beta(F)]. These samples were tested for the acetalization of formaldehyde with glycerol using trioxane as a source of formaldehyde, in absence of solvent, at 100 °C. The results from Fig. 2 show a maximum in activity for the sample with Si/Al ratio of 50 and a lower deactivation rate for any of the fluoride synthesized zeolite than for the regular Beta zeolite (Fig. S4). Moreover, the optimum [Beta(F)] zeolite (Si/Al ~ 50) could be reused with only a slight decrease in the activity (<10%). It should be noticed that, despite the concentration of acid sites on the sample with Si/Al ratio of 50 is lower than for samples with Si/Al ratio 15 and 30 (see Table S1), the former gives a higher activity. In other words, a larger number of acid sites in the zeolites do not necessarily guaranty a higher catalytic activity, and adsorption effects should also be considered.

The effect of the zeolite polarity on reactivity can be better seen when using formalin (35 wt.% aqueous solution of formaldehyde) as a source of formaldehyde and the activity of hydrophobic Beta(50) zeolite, Amberlyst-36, and PTSA are compared. Figs. 3 and 4 show the different kinetic behavior of the three catalysts as function of the formaldehyde source. Thus, with trioxane, PTSA, and Beta(F)-50 give similar initial reaction rates, although Beta zeolite deactivates faster, while Amberlyst-36 resulted to be the



Scheme 2. Possible reaction pathway according to results in Fig. S1.

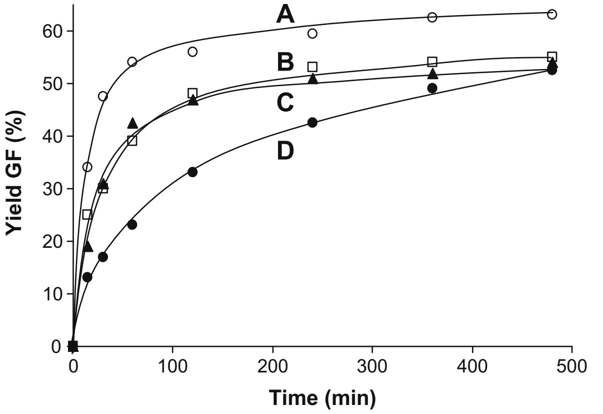


Fig. 2. Comparison of the kinetic of reaction using Beta(F) with different Si/Al ratios as catalysts. Reaction conditions: Beta(F)-(Si/Al ratio) (25 mg), glycerol (1.225 g), trioxane (400 mg), without solvent, 100 °C. (A) Beta(F)-50, (B) Beta(F)-100, (C) Beta(F)-30, (D) Beta(F)-15.

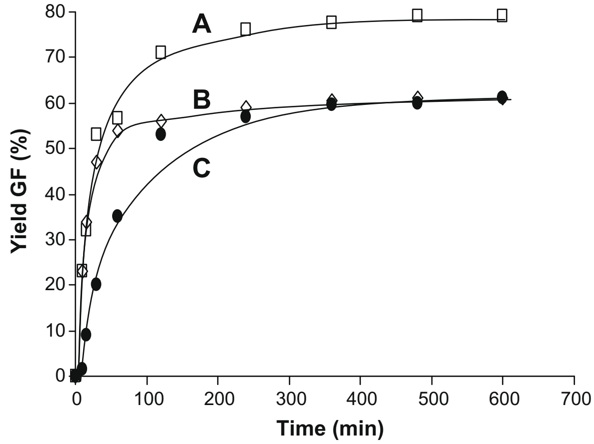


Fig. 4. Kinetic study of the acetalization reaction using trioxane as a formaldehyde source. Reaction conditions: Beta(F)-50 (25 mg), glycerol (1.225 g), trioxane (400 mg), without solvent, 100 °C. (A) PTSA, (B) Beta(F)-50, (C) Amberlyst-36.

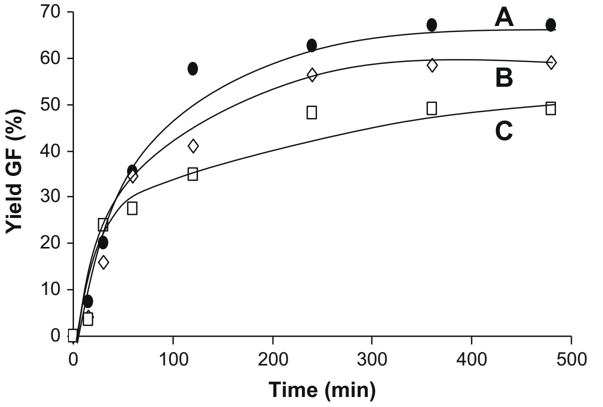


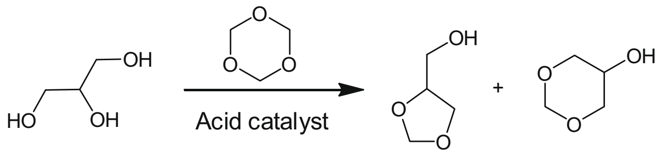
Fig. 3. Kinetic study of the acetalization reaction using formalin as a formaldehyde source. Reaction conditions: formalin (1.115 g, 13.6 mmol), glycerol (1.220 g, 13.4 mmol), solid catalysts (25 mg) or PTSA (12 mg), 100 °C, without solvent. (A) Beta(F)-50, (B) PTSA, (C) Amberlyst-36.

less active catalyst (Fig. 4). However, in Fig. 3, it can be seen that when using formalin, the three catalysts show similar initial reaction rates but lower than in the case of trioxane. This behavior is expected and can be explained taking into account that a significant amount of water is added as formalin solution (31 wt.% of water with respect to the total amount of reactants, 32 wt.% respect to glycerol), and water can compete for adsorption on the strong acid sites, as well as to shift the equilibrium toward acetal hydrolysis. The most interesting feature from Fig. 3 is that the hydrophobic Beta zeolite exhibits the lowest deactivation rate. This behavior should be related with the hydrophobicity of the surface since when water concentration increases in the reaction media, the hydrophobic character of the catalyst should play a positive role for decreasing the water adsorption and therefore the deactivation rate. As a result, with Beta(F)-50 catalyst, similar performances toward the formation of glycerol formal can be achieved by working in absence or in presence of water, at least at the H_2O concentration levels we have been working here. Nevertheless, the yield of acetal obtained either with Beta(50) or with Amberlyst-36 is still not satisfactory, and we have studied the possibility to increase the yield of acetal using a series of Lewis acid catalysts.

2.2. Acetalization of formaldehyde with glycerol using homogeneous Lewis acid catalysts

The preparation of GF from glycerol and formaldehyde using Lewis acids has previously been reported by Marton et al. [5]. The reaction occurs under mild conditions in the presence of the highly toxic $BuSnCl_3$ with a yield of 84% and a dioxane:dioxolane ratio 77:23. Herein, we have studied the formation of GF with a variety of Lewis acid catalysts (Table 1). The reaction was carried out using

Table 1
Acetalization reaction of formaldehyde with glycerol using Lewis and Brønsted acid soluble catalysts.



Entry[a]	Catalyst	Catalyst amount (mol%)	T (°C)	Time (h)	Yield (%)	Ratio (dioxane:dioxolane)
1	$AuCl_3$	5	80	4	93 (83)[b]	63:37
2	$AuCl_3$	2	80	7	92	66:34
3[c]	$AuCl_3$	2	80	1.5	93	72:28
4[c]	$AuCl_3$	2	60	3	50	74:26
5[c]	$AuCl_3$	2	100	0.5	80	75:25
6	$NaAuCl_4$	5	100	16	94	64:36
7	PTSA	5	80	9 (24)	80 (94)	64:36
8	AuCl	5	80	4	52	75:25
9[c]	$AuClPPh_3$	2	100	24	–	–
10	$AgBF_4$	5	100	24	40	83:17
11	$ZnCl_2$	5	100	24	–	–
12	LaOTf	5	80	24	–	–
13	$AlCl_3$	5	80	21	9	75:25
14[d]	$AlCl_3$/HCl	5	80	24	39	61:39

[a] Reaction conditions: glycerol (1 mmol), trioxane as a source of formaldehyde (1 mmol), and dioxane as solvent.
[b] The reaction was carried out without solvent.
[c] 3 eq. of formaldehyde were used.
[d] HCl (5 mol%) was added to form $AlHCl_4$ *in situ*.

trioxane as a source of formaldehyde and dioxane as solvent. As shown in Table 1, $AuCl_3$ was an efficient catalyst for this reaction giving 93% of GF in 4 h (entry 1). The reaction can also be run in the absence of solvent. A decrease in the $AuCl_3$ amount from 5 to 2 mol% gave identical yield but 7-h reaction time was required to complete the reaction (entry 2). In both cases, the dioxane:dioxolane ratio was ~65:35 (Fig. S5). When the molar ratio of glycerol to formaldehyde was increased, the yield of GF also increased (entry 3), being 80 °C the optimum temperature for the reaction (see entries 3–5).

Higher temperatures and longer reaction times were required to obtain similar yields of GF with $NaAuCl_4$ catalyst (entry 6). Nevertheless, the yields obtained using gold catalysts were in all cases higher (~93%) than when using zeolites (~70%) and Amberlyst-36 (~77%). In order to compare the gold Lewis acids with soluble Brønsted acids, the reaction was performed using PTSA under similar conditions than that with $AuCl_3$. Longer reaction times were needed with PTSA (compare entries 1 and 7 in Table 1), and kinetic results shown in Fig. 5 indicate a much higher initial rate with Au(III) than with Au(I) or PTSA (see also entries 8 and 9 in Table 1). Gold(I) compounds were less effective catalysts than the gold(III) salts (entries 8–9).

The catalytic properties of other Lewis acids (Ag, Zn, and Al) have also been studied. In all cases, conversions were significantly lower than those with gold catalysts (compare entries 1 and 6 to entries 10–14) or even no reaction was observed in some cases (entries 10–12). The combination of Lewis and Brønsted acid sites, i.e., HCl + $AlCl_3$, was also tested (entry 14). In this case, the yield to GF was practically the same that with $AlCl_3$.

Although some reports [4] show that the dioxolane is the major product when using Lewis acids as catalysts, other publications, [5,6] as well as our own results (see Table 1), clearly show a higher yield of the six-membered cyclic acetal (dioxane). The result is not surprising since the formation of the dioxane adduct should be usually favored because of the easier disponibility of the primary hydroxyl groups to react when compared to the secondary hydroxyl group.

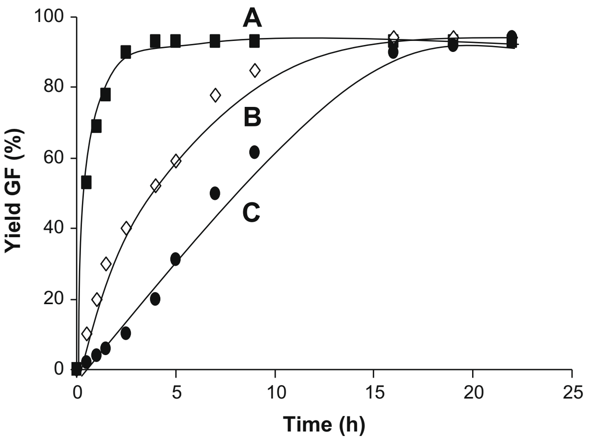


Fig. 5. Kinetic results for GF production using different soluble Lewis acid catalysts. (A) $AuCl_3$, (B) PTSA, (C) $NaAuCl_4$.

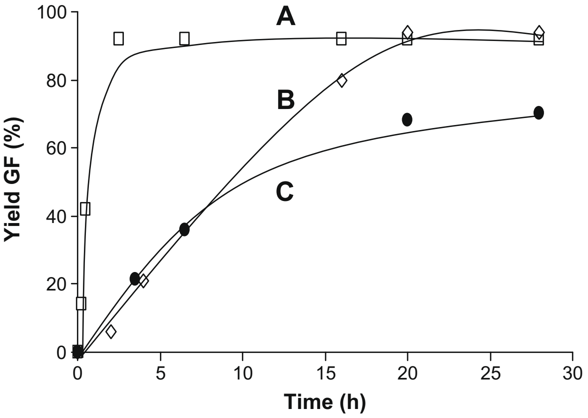
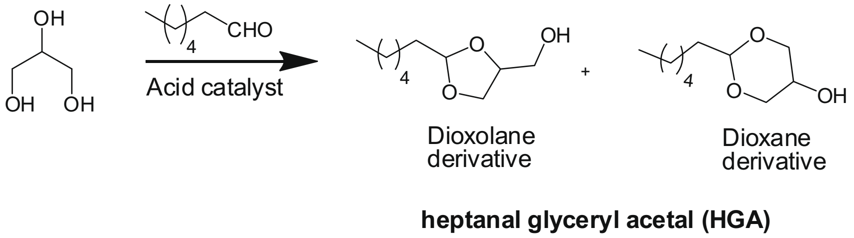


Fig. 6. Kinetic results for glycerol formal production using $NaAuCl_4$, HCl or a combination of both as catalysts in the presence of water (see entries 3, 5 and 6 in Table S2 for conditions). (A) $NaAuCl_4$ + HCl, (B) $NaAuCl_4$, (C) HCl.

Table 2
Acetalization reaction with *n*-heptanal and glycerol/water mixtures using Lewis and Brønsted acid catalysts.



Entry[a]	Catalyst	H_2O (wt.%)	*T* (°C)	Time (h)	Yield (%)	Ratio (dioxane:dioxolane)
1	$AuCl_3$	–	25	0.50	93	34:66
2	$AuCl_3$	25	80	0.50	85	46:54
3	$AuCl_3$	40	80	0.50	80	42:58
4	$NaAuCl_4$	–	80	0.17	86	45:55
5	$NaAuCl_4$	25	80	0.50	86	43:58
6	LaOTf	–	80	3	85	33:67
7	LaOTf	25	80	2	73	24:76
8	HCl (15%)	25	80	0.25	75	40:60
9	HCl (25%)	25	80	0.5	75	43:57

[a] Reaction conditions: *n*-heptanal (1 mmol), glycerol (1 mmol), catalyst (5 mol%), water, and dioxane as solvent (1 mL).

2.2.1. Reactions with glycerol/water mixtures

The glycerol from biodiesel is obtained in many cases mixed with water. Valorization of the cheaper aqueous solutions of glycerol could be done by forming glycerol formal, or other insoluble acetal (for instance from *n*-heptanal) that could be separated, hydrolyzed, and recycled while leaving water-free glycerol [9]. Accordingly, we have performed the reaction of formaldehyde with glycerol/water mixtures (25–40 wt.% of water respect to glycerol), using dioxane as solvent.

As it can be seen in Table S2, gold(III) catalysts were equally efficient in the presence or absence of water (compare entries 1–3 in Table S2 to entries 1 and 6 in Table 1). As observed previously, Brønsted acids lead to slightly lower yields (compare entries 1–3 and 4–5 in Table S2). However, kinetic experiments (Fig. 6) show that the combination of gold (Lewis) and HCl (Brønsted) catalysts improves dramatically the acetalization reaction.

When working with $AuCl_3$ in the presence of water, the hydrolysis of the salt occurs, decreasing the pH within the reaction media. To make as certain that was not the Brønsted acidity generated by hydrolysis of $AuCl_3$ the responsible of the observed catalytic activity, a comparative experiment was performed with the same reactant concentrations, except that $AuCl_3$ was substituted by the amount of HCl required to give the lowest pH observed during the reaction with $AuCl_3$. Results from Table S2 (entry 7) show a lower yield of acetal with HCl than with $AuCl_3$ (entry 1).

For the sake of comparison, all the results obtained in this work and in previous reports for the acetalization reaction of formaldehyde with glycerol using different Brønsted and Lewis acids cata-

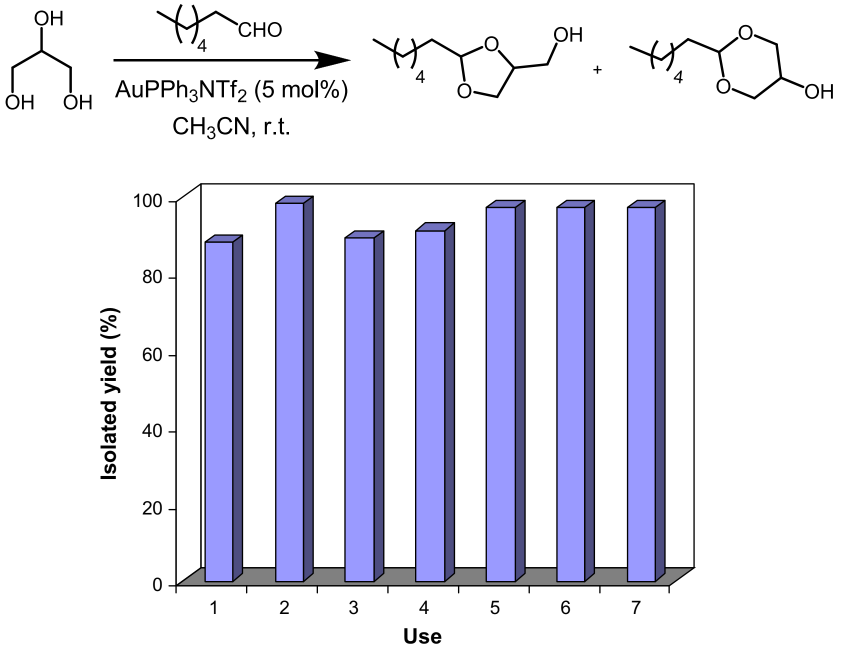


Fig. 7. Reusability study for the acetalization of *n*-heptanal with glycerol using $AuPPh_3NTf_2$ as catalyst.

lysts have been summarized in Table S3 and it can be seen the beneficial role of gold compared to other catalysts.

3. Acetalization of *n*-heptanal with glycerol/water mixtures using homogeneous acid Brønsted and Lewis catalysts

As it was mentioned before, obtaining an extractable hydrophobic acetal of glycerol would be of interest [10]. Thus, we have studied the acetalization reaction of glycerol with *n*-heptanal in dioxane (Table 2). This aldehyde is a product of biomass, obtained by thermal cracking of the castor oil methyl ester and can be used to extract glycerol from glycerol–water mixtures [9].

As it can be seen in Table 2, a high yield of acetal was obtained when $AuCl_3$ was used as catalyst at room temperature, leading to an acetal mixture of heptanal glyceryl acetal (HGA) with a ratio of 34:66 (dioxane:dioxolane, entry 1). The addition of different amounts of water (25–40 wt.% respect to glycerol, entries 2 and 3) and the use of $NaAuCl_4$ (both without and with water, entries 4 and 5) required an increase in temperature in order to achieve similar conversions. LaOTf gave a similar yield than $NaAuCl_4$, with or without water, although longer reaction times were required (entries 6–7). The use of a Brønsted acid as HCl gave again a lower yield than $AuCl_3$ (75 instead of 93%) even when 25% of HCl was used as catalyst (entries 8–9).

We have seen up to now that gold catalysts give good results for the formation of acetals of glycerol with both aldehydes, formaldehyde and *n*-heptanal. However, the price of gold can limit its use. Therefore, we have studied the possibility of using recoverable gold catalysts. Firstly, gold supported on TiO_2 [11], CeO_2 [12], and Fe_2O_3 [11] were tested and, unfortunately, it was found that they were not active as catalyst when reacting with trioxane and glycerol. Alternatively, we used a cationic gold complex, $AuPPh_3NTf_2$, which takes advantage of being soluble in the reaction mixture and can precipitate when *n*-hexane is added at the end of the reaction, allowing in this way its recovery and recycling [13]. Indeed, when reacting with *n*-heptanal and glycerin, ~90% yield of acetal (dioxane to dioxolane ratio 44:56) was obtained (Fig. 7). The complex was reused up to seven times without any observable decrease in the acetal yield. ICP of the extracted products indicates that the amount of gold leached at the end of the seven cycles was less than 0.6% of the original amount.

The evolution of the gold(I) complex was followed during the reuses by ^{31}P NMR spectroscopy (Fig. S6). It was found that a new signal at 45 ppm appears, corresponding to the diphosphine complex $[Au(PPh_3)_2]NTf_2$. This complex was prepared (see experimental) and showed no catalytic activity for the reaction, indicating that all the activity comes from the remaining original $AuPPh_3NTf_2$ complex.

4. Conclusion

Valorization of pure glycerol and glycerol in water has been done by reaction with aldehydes to form valuable acetals. Solid Brønsted acids such as zeolites (Beta) and resins (Amberlyst) were used and compared with soluble acids such as *p*-toluenesulfonic acid (PTSA). It has been found that in absence of water, PTSA and resins are much more active than Beta zeolite. However, when water is present (up to 31 wt.% H_2O), a hydrophobic Beta zeolite gives better results than either PTSA or Amberlyst. Nevertheless, the best results with the aforementioned catalysts never exceeded 80%. However, a soft Lewis acid such as $AuCl_3$ allows achieving up to 94% yield of acetal under very mild reaction conditions. The gold catalyst has been made recoverable by preparing a cationic Au(I) complex that can be separated and reused up to seven times with >90% yield of acetal.

5. Experimental section

5.1. Catalysts

Beta-1 zeolite in the acidic form was supplied by PQ corporation. Zeolite Beta samples (Beta(F)-15, Beta(F)-30, Beta(F)-50, Beta(F)-100) were synthesized in our laboratory according to previous procedures [14], and their characteristics are given in Table S1. Acidity measurements were taken by adsorption–desorption of pyridine by IR spectroscopy. The infrared spectra were recorded in a Nicolet 710 FTIR using self-supported wafers of 10 mg cm^{-2}. The calcined samples were outgassed overnight at 673 K and 10^{-3} Pa dynamic vacuum. Then, pyridine was admitted into the cell at room temperature, and after saturation, the samples were outgassed at 523 K for 1 h under vacuum, cooled to room temperature, and the spectra recorded.

The $AuPPh_3NTf_2$ complex was obtained from Aldrich as a dimer-toluene adduct [15]. $AuCl_3$, $NaAuCl_4$, trioxane, formalin, glycerol, dioxane, and toluene (purity >99%) were purchased from Aldrich and were used without further purification.

5.2. Reaction procedure for acetalization of formaldehyde and glycerol with solid catalysts

Activation of the solid catalysts was performed *in situ* in closed conic glass batch reactors by heating the solid under vacuum (1 Torr) at 523 K (at 373 K in the case of Amberlyst-36) for 2 h. After this time, the system was left at room temperature and then, glycerol (625 mg, 6.6 mmol) and the formaldehyde source (200 mg, 6.6 mmol) were added at atmospheric pressure. The system was closed and heated up at the desired temperature with a silicone oil bath equipped with an automated temperature control system. After reaction, the system was cooled at room temperature, filtered under vacuum, and the catalyst was washed with methanol. For kinetics, individual reactions were run for each time, filtering the mixture after cooling at 0 °C and washing the catalyst with methanol. Nitrobenzene was added to the combined filtrates as external standard, and the solution was then analyzed. For reusing, the catalyst was reactivated by calcination as indicated earlier. Reaction products were analyzed by gas chromatography (GC) (Varian 3900 equipped with an split–splitless injector, flame ionization detector, and a 30 m × 0.25 mm × 0.25 μm fused silica capillary column (SUPELCO Equity 5)), GC–MS, and ^1H NMR (300 MHz Bruker). In all experiments, the recovered material was superior to 95 wt.%.

5.3. General procedure for acetalization reactions with Lewis acid catalysts

Catalytic reactions were carried out in a closed glass reactor (2.5 mL) equipped with a micro-syringe to extract samples for analysis. To an appropriate catalytic amount of catalyst, a mixture of the aldehyde (1 mmol) and glycerol (1 mmol) in 1 mL of dioxane was added. The reaction mixture was stirred at 80–100 °C and monitored by gas chromatography. Nitrobenzene and *n*-dodecane were used as internal standard for reactions with formaldehyde and *n*-heptanal, respectively. When the reaction was completed, the solvent was evaporated under vacuum.

For the reaction performed with the recoverable $AuPPh_3NTf_2$ catalyst, the following procedure was applied: 78.4 mg (0.1 mmol) of $AuPPh_3NTf_2$ and 184 mg (2 mmol) of glycerol were placed in an, oven-dried, 10-mL round-bottomed flask. Air evacuation-nitrogen pumping cycles were carried out, and a rubber septum was rapidly fitted after the last nitrogen refilling. The system was kept under N_2 atmosphere. Then, *n*-heptanal (228 mg, 2 mmol) and anhydrous

CH_3CN (1.5 mL) were sequentially added, and the mixture was magnetically stirred at 22 °C for 24 h. Once the reaction was finished, *n*-hexane (10 mL) was added and the mixture stirred for 15 min. After stopping, the top layer (hexane) was separated, fresh *n*-hexane (10 mL) was added, and the mixture stirred again for 15 min. This process was repeated five times. The catalyst was dried under vacuum for 1 h, and fresh reactants and solvent were added to perform a new cycle. An aliquot of the reaction mixture was taken from the combined hexane extracts and analyzed by GC. Then, volatiles were removed under vacuum to give an acetal mixture of heptanal glyceryl acetal (HGA) (344 mg, 1.74 mmol, 91.5%) with a ratio of 44:56 (dioxane:dioxolane).

The $Au(PPh_3)_2NTf_2$ species was prepared as follows: PPh_3 (16.8 mg, 0.06 mmol) was added to a solution of $Au(PPh_3)NTf_2$ (50 mg, 0.06 mmol) in acetonitrile (1 mL), and the mixture was magnetically stirred at room temperature under N_2 for 2 h, and the solvent was removed under vacuum. The solid was dissolved in $CDCl_3$ and analyzed by ^{31}P NMR to give a single signal at 45.1 ppm. Then, the formed $Au(PPh_3)_2NTf_2$ (12.7 mg, 0.012 mmol) was placed in a dried vial, and *n*-heptanal (28.5 mg, 0.25 mmol), glycerol (23 mg, 0.25 mmol), and anhydrous acetonitrile (0.3 mL) were sequentially added. The vial was rapidly sealed, and the mixture was magnetically stirred at room temperature and analyzed by GC.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.02.023.

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