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Gold and gold–platinum as active and selective catalyst for biomass conversion: Synthesis of γ-butyrolactone and one-pot synthesis of pyrrolidone

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ABSTRACT

It has been found that gold is highly active and selective catalyst for the hydrogenation of succinic anhydride (SAN) to γ-butyrolactone (GBL). Using TiO_2 as support and performing the reaction in presence of molecular sieves, it was possible to obtain the highest reaction rate ever obtained with 97% selectivity to GBL at 97% conversion. The process appears to be controlled by H_2 dissociation on gold and the catalytic activity can be further improved, without loss of selectivity, by adding a very small amount of Pt (100 ppm) to increase the rate of H_2 dissociation. We also found that gold is an efficient catalyst for the one-pot conversion of SAN into pyrrolidone and pyrrolidone derivates.

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1. Introduction

The interest for gold as catalyst has suddenly changed when gold nanoparticles were found active for low temperature CO oxidation [1,2]. Today gold as supported catalyst is known to be active for a variety of reactions such as oxidation of alcohols [3] and aldehydes [4], hydrochlorination of ethyne [5], carbon–carbon bond formation [6,7], carbon–silicon bond formation [8], and epoxidation of propene [9,10]. Bond [11] first showed that gold was active for the hydrogenation of olefins and dienes. Later gold based catalysts were used for selective hydrogenation of the carbonyl group in α–β-unsatured aldehydes [12–15], and more recently for the chemo selective hydrogenation of nitro groups in presence of other reducible functions [16,17]. While the hydrogenation activity of more classic metal catalysts such as Ni, Pd and Pt remains generally higher than gold due to the higher efficiency for H_2 dissociation, the latter may be more suitable when selectivity is important, or partially hydrogenated compounds are the desired products. With this in mind we are investigating new application of gold as hydrogenation catalysts in process of fundamental and industrial relevance.

Hydrogenation of succinic and maleic esters, anhydrides and acids, lead to the formation of γ-butyrolactone (GBL), 1,4-butanediol (BD), and tetrahydrofuran (THF). They are valuable products that find a wide market as solvents or as starting material for polymers like polyuretanes. GBL, in particular, is an excellent alternative to many chloride solvents such as trichloroethane and is a starting material for the synthesis of pyrrolidone and pyrrolidone-derivates which are used as industrial solvents, building blocks for polymers and intermediated for pharmaceuticals.

Today there are four main processes [18] for the production of GBL, BD and THF: (a) Reppe process [19,20] based on acetylene–formaldehyde condensation; (b) Arco process [21] based on isomerization of propylene oxide to allyl alcohol and subsequent hydro-formilation; (c) Mitsubishi Kasei process [22] based on the hydrogenation of maleic anhydride on Ru complexes; (d) and Davy McKee process [23] based on hydrogenation of maleic anhydride and dialkyl maleates over Cu based catalysts. Among the various available process the direct hydrogenation of maleic anhydride on copper chromite is the most economical and environmental benign [24] for the preparation of GBL [25,26]. However an alternative to this catalyst is required because of the toxicity of Cr. Maleic anhydride is a convenient feedstock because of its availability and low price due to the large scale production based on butane oxidation [27]. However an alternative feedstock material could be succinic acid (SA) [28] which is currently produced by hydrogenation of maleic anhydride but it can also be prepared by fermentation of glucose. From an economical point of view, advances in fermentation and separation technologies have reduced the production cost to 1000$/Tm, while the current competing

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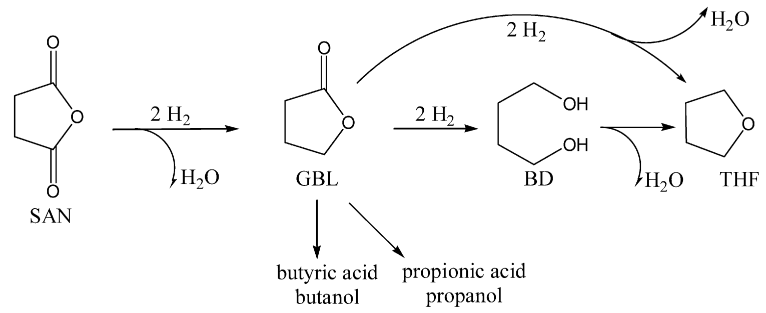


Scheme 1. Successive hydrogenation and dehydration of SAN.

butane-derived maleic anhydride price is 800$/Tm, which is already not too far [28]. Biomass derived products are today of high economical, social and political interest because they could be the key for a large scale, green and sustainable chemistry. Succinic acid, in particular, is considered among the 30 most interesting biomass derived products [29]. Its price is still higher than maleic anhydride [28], but this situation may be reversed thanks to the important investments on the development of more efficient enzymatic and chemical processes for the preparation of "building blocks" from biomass [29]. If this is so, then efficient hydrogenation processes need to be developed simultaneously in order to exploit this renewable source in an economically advantageous and environmentally friendly way. Moreover if we succeed in substituting a multi step process used today to produce N-pyrrolidones from GBL by one pot process that uses succinic acid or succinic anhydride (SAN) as a starting reactant, this may help the viability and economics of the process.

Most of the reports on the production of GBL, BD and THF using C_4 starting material are found in patent literature and refer to gas and liquid phase hydrogenation of maleic anhydride [30–35], for which Cu-based catalysts are the most used [23,36–41]. As an alternative to copper–cromite, catalysts containing Al or Ru have also been proposed [42–44]. In the open literature the liquid phase hydrogenation of maleic and succinic anhydride to GBL, DB, or THF has been studied using Cu modified by different metals [45–48], as well as noble metal catalysts like Pd and Ru [18,49–53]. Pd is the most active metal with high selectivity to GBL but problems related with catalytic deactivation due to coke deposition have still to be solved.

Since gold can be a selective hydrogenation catalyst [15], we have studied here the selective hydrogenation of SAN on this metal and its catalytic behavior is compared with that of the previously used Cu and noble metal catalysts. We will show that gold is very active for the hydrogenation of SAN giving 97% selectivity at 97% conversion, and higher reaction rates than previously reported catalysts. Owing to the high selectivity of gold for GBL and the fact that GBL is the main precursor for the production of pyrrolidone and pyrrolidone derivates, we have also carried out the catalytic synthesis of pyrrolidone and pyrrolidone derivates in a "one-pot" reaction system starting from SAN and NH_4OH or phenyl-amine.

2. Experimental

2.1. Preparation of the catalysts

Au–TiO_2 (Au 1.5 wt%) was purchased from the World Gold Council. PtAu–TiO_2 was prepared by wetness impregnation of Au–TiO_2 with a solution of H_2PtCl_6 dried overnight at 60 °C and reduced at 450 °C in H_2 flow for 3 h. Pt–TiO_2 was prepared in a similar way by wetness impregnation using TiO_2 (P-25) from Degussa. Metal loading were measured with an ICP Varian 715-ES.

2.2. Reaction conditions

The reactions were performed in a 125 ml autoclave "Autoclave Engineers." In a typical hydrogenation reaction the autoclave was loaded with 12 mmol of SAN, 0.6 ml of dodecane (internal standard), 50 ml of dioxane, 200–220 mg of catalyst and, when specified, 0.8 g of molecular sieves. The reaction mixture was purged three times with N_2 and two times with H_2 to remove air. Then the autoclave was pressurized with H_2 at 10 bar and heated at 15 °C min^{-1} under stirring (1500–2750 rpm) up to 240 or 250 °C. When the final temperature was reached, the autoclave was pressurized at the desired pressure with H_2. The one-pot reactions were performed using a similar procedure. For the synthesis of pyrrolidone the autoclave was loaded with 20 mmol of SAN, 22 mmol of NH_4OH (25% in water), 1.3 g of Au–TiO_2, 2 ml of dioxane (internal standard) and 50 ml of water and the reaction was performed at 120 bar and 250 °C. In the case of the synthesis of phenyl–pyrrolidone the autoclave was loaded with 12 mmol of SAN, 14 mmol of phenylamina, 0.8 g of Au–TiO_2, 0.6 ml of dodecane (internal standard) and 50 ml of dioxane and the reaction was performed at 250 °C and 110 bar. The samples were collected through a teflon septum after purging the sampling line and analyzed by GC and GC-MS. The quantification of the acids was performed after sylilation with an en excess of N,O-bis (trimethylsilyl)-trifluoroacetamide.

3. Results and discussion

The hydrogenation of SAN is a complex process where different hydrogenation reactions occur in a series of consecutive steps (see Scheme 1) [18]. GBL is formed when a single carbonyl group is hydrogenated while further addition of hydrogen can lead to BD or THF. These three products are commercially valuable and it would be of much interest to find catalysts selective to one of them, especially if one takes into account that hydrogenation can proceed further giving products such as butyric acid, propionic acid, butanol, propanol and products of esterification between alcohols and acids.

When hydrogenation of SAN is carried out at 60 bar, 250 °C with Au–TiO_2 as catalyst, it can be observed (Fig. 1b) the formation of GBL. SA is formed by hydration of the anhydride, while at larger reaction times butyric acid is also observed. When the yield to GBL, SA and BA are plotted versus total conversion of SAN (Fig. 2) one can deduce from the shape of the curves that SA is a primary unstable product, GBL is a primary plus secondary unstable product, and butyric acid is a secondary stable product. This selectivity behavior could be easily explained through a reaction scheme as that given in Scheme 2 where the SAN reacts through two parallel reactions to give SA (hydration) and GBL (hydrogenation). The accumulated yield to SA decreases with conversion while GBL still increasing owing to the conversion of SA into GBL by hydrogenation, being this slower than the hydrogenation of SAN.

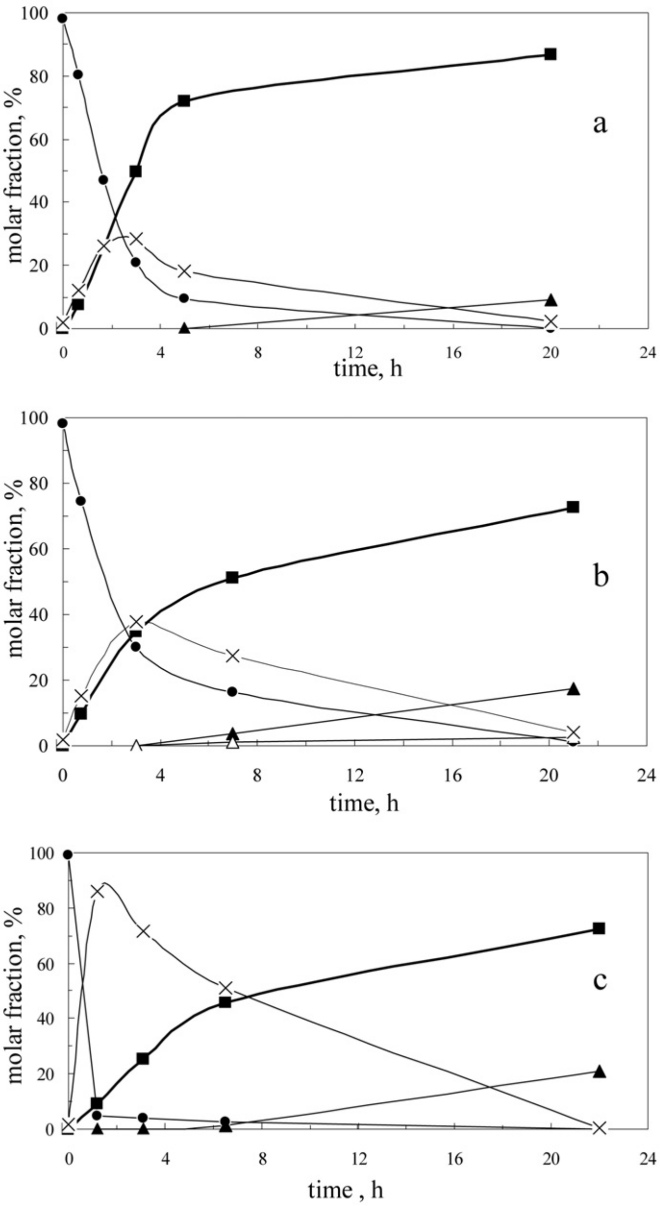


Fig. 1. Hydrogenation of SAN to GBL as a function of time. Reaction conditions: (a) SAN 12 mmol, 250 °C, 60 bar H_2 + 800 mg of molecular sieves; (b) SAN 12 mmol, 250 °C, 60 bar H_2; (c) SAN 12 mmol, 250 °C, 60 bar H_2 + 50 mmol of H_2O. The catalyst is $Au–TiO_2$ (200 mg). (●) SAN, (×) SA, (■) GBL, (△) butyric acid and (▲) THF.

Finally, at longer reaction times (high conversion levels) GBL is converted into butyric acid.

The validity of the reaction network presented in Scheme 2, has been proven by changing the concentration of water in the reaction media (Fig. 1) and observing that with larger amounts of water the yield of SA increases, while the rate of formation of GBL decreases (Fig. 1c). Then, taking into account the lower rate of hydrogenation of SA into GBL with respect to SAN, it is important to minimize the presence of free water in the reaction media for improving the rate of formation of GBL. Following this, when 4 Å molecular sieve has been introduced into the system as drying agent, the rate of the reaction was strongly increased (see Fig. 1a).

It can be seen there that in this case and if one considers the sum of SAN and SA as substrate to be hydrogenated, 72% conversion with 99% selectivity to GBL is reached in 5 h reaction time. It is interesting to observe that after 20 h the yield of GBL remains still high (87%), being butyric acid the main byproduct. Using a larger amount of catalyst (0.6% instead 0.14%) the selectivity to GBL reaches a maximum at about 6 h reaction time and then decreases owing to the hydrogenation of GBL to give THF as main product.

3.1. *Optimization of reaction conditions*

We have found that the stirring speed has a positive influence on reaction rates indicating that the reaction was affected by external diffusion. Thus, increasing the stirring speed from 1500 to 2750 rpm a yield of 80% instead of 72% was obtained after 5 h. Further increase of the stirring rate did not enhance conversion. At this point we set the reaction conditions at 240 °C, 50 bar and 2750 rpm (instead of 250 °C, 60 bar and 1500 rpm) and, under these milder reaction conditions, a selectivity of 97% to GBL at 97.5% conversion was obtained (Fig. 3).

3.2. *Comparing the activity of Au with other metal catalysts*

The results obtained with gold have been compared with those reported in the literature using Cu and Pd catalysts. Table 1 indicates that, per atom of metal, $Au–TiO_2$ is, at least, one order of magnitude more active than any Cu catalysts reported. Taking as reference the work of Emig [46] (who tested various commercial catalysts at 240 °C and 75 bar), we observe that the most active Cu catalyst giving high selectivity to GBL is $Cu–Mg_2SiO_4$. It shows a specific activity of 1.5 $mol_{GBL}\,h^{-1}\,mol_{Me}^{-1}$, which is largely 104 $mol_{GBL}\,h^{-1}\,mol_{Me}^{-1}$ surpassed with $Au–TiO_2$. The hydrogenation of GBL over $Cu–Mg_2SiO_4$ gives mainly THF (about 4% at 100% conversion) rather than BD as in the case of CuZn mixed oxide. Another important Cu catalyst selective to GBL is copper–chromite (currently used in the industrial process) for which 100% selectivity at 75% conversion is reported with a TOF of 1.3 $mol_{GBL}\,h^{-1}\,mol_{Me}^{-1}$.

Pd, like copper–chromite, is highly selective to GBL but with much higher specific activity. Comparing the specific rates of Pd–C [46] and $Au–TiO_2$ reported in Table 1, $Au–TiO_2$ is still more active than Pd–C.

There is an interesting report on the hydrogenation of maleic anhydride with the multi-component Pd–Ni–Mo supported on SiO_2. This catalyst is very active with 84.6% conversion to GBL after 4 h reaction time, without formation of byproducts [18] (Table 1). Nevertheless the highest reaction rates for the hydrogenation of SAN were reported by Jung et al. [49]. They used Pd–C and $Pd–SiO_2$ modified with Sn. The authors presented that Sn not only increases activity but also reduces the deactivation of the catalyst due to the formation of coke. $Au–TiO_2$ catalyst shows higher activity compared with $Pd–SiO_2$ and similar activity compared with the activated $PdSn–SiO_2$ (Table 1). In other words gold, by it self, is a very active and selective catalyst to produce GBL, avoiding consecutive hydrogenations to take place.

To evaluate the stability of gold catalyst upon reuses, $Au–TiO_2$ was tested in five consecutive runs at 240 °C, 50 bar and 2750 rpm. After each test the catalyst was filtered, washed with acetone and milli-Q water and finally dried overnight at 175 °C. Fig. 4 shows a deactivation of the catalyst of about 6% after the first run while the activity remains practically stable in the subsequent four runs with a loss of activity of only 2.5%. This result compares favorably with those reported for the hydrogenation of maleic anhydride on Pd-based catalyst by Jung et al. [49] that observed a deactivation of about 60% after 4 uses for $Pd–SiO_2$ and a deactivation of about 10% after 4 uses for Sn-modified $Pd–SiO_2$. Therefore gold catalyst has the advantage to be more active and also more stable under reuses without the need of a modifier.

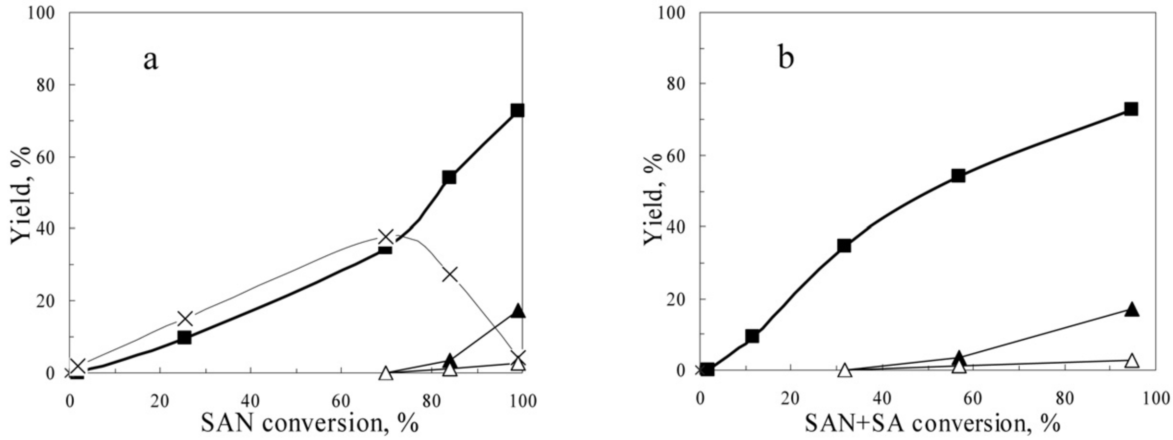
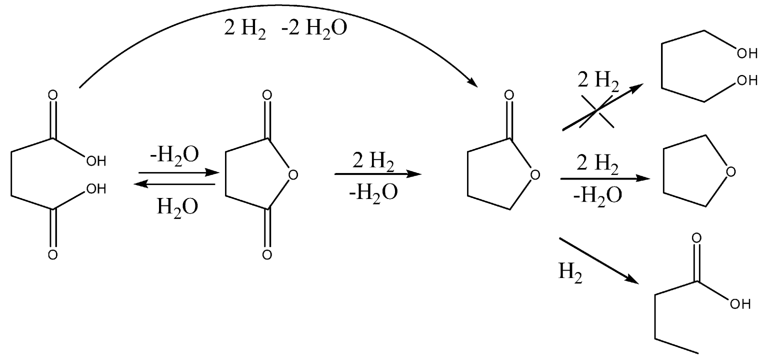


Fig. 2. (a) Yield of GBL (■), succinic acid (×), butyric acid (△) and THF (▲) plotted versus conversion of SAN. (b) Yield of GBL (■), butyric acid (△) and THF (▲) plotted versus conversion of SAN plus SA.



Scheme 2. Suggested scheme for the hydrogenation of SAN on Au–TiO_2.

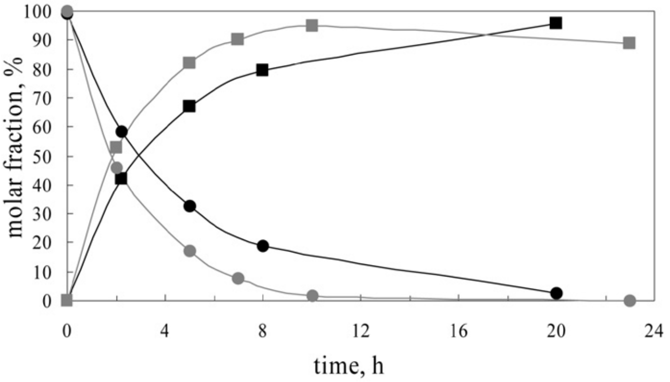


Fig. 3. Hydrogenation of SAN to GBL over Au–TiO_2 (black line) and $Pt_{0.01}$Au–TiO_2 (gray line). Reaction conditions: SAN 12 mmol, 240 °C, 50 bar H_2 + 800 mg of molecular sieves, stirring 2750 rpm. (●) SAN + SA and (■) GBL.

3.3. *Bimetallic gold base catalysts*

It has been presented [15] that gold, by being oxophilic, can adsorb and activate oxygenated products, but it is much less efficient than other noble metals for dissociating H_2. If this is also the case in our reaction, it may very well occur that, as discussed above, the dissociation of H_2 [54,55] will be the rate limiting for the hydrogenation of SAN. Following this hypothesis we thought that an improved catalyst could be prepared by adding a very small amount of a second metal (Pt) that can readily activate hydrogen. We were hoping that with the low Pt content and the more favorable adsorption properties of gold for the oxygenated products, activity should increase without paying a penalty on se-

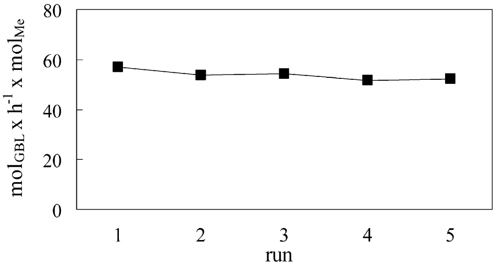


Fig. 4. Turnover frequency observed at 5 h reaction time for the selective hydrogenation of SAN to GBL over Au–TiO_2 used in five consecutive runs. The experiment was performed in absence of molecular sieves in order to allow a clean recovery of the catalyst.

Table 1
Specific rate of reaction for the selective hydrogenation of SAN to GBL over Au–TiO_2 compared with other catalysts

Catalyst	Reaction conditions	Reaction time	TOF $mol_{GBL}\ h^{-1}\ mol_{Me}^{-1}$	Ref.
Au–TiO_2	250 °C 60 bar	5 h	128	[a]
Au–TiO_2	240 °C 50 bar	5 h	104	[a]
Cu–Mg_2SiO_4	240 °C 75 bar	5 h	1.5	[46]
Pd–C	240 °C 75 bar	5 h	53[b]	[46]
PdMoNi–SiO_2[c]	240 °C 70 bar	4 h	62[d]	[18]
Au–TiO_2	240 °C 50 bar	2 h	158	[a]
Pd–SiO_2	240 °C 50 bar	2 h	137	[49]
PdSn–SiO_2	240 °C 50 bar	2 h	153[d]	[49]

[a] This work.
[b] TOF ∼120 at 2 h reaction time.
[c] The data refers to the conversion of maleic anhydride to GBL.
[d] TOF calculated per mol of Pd.

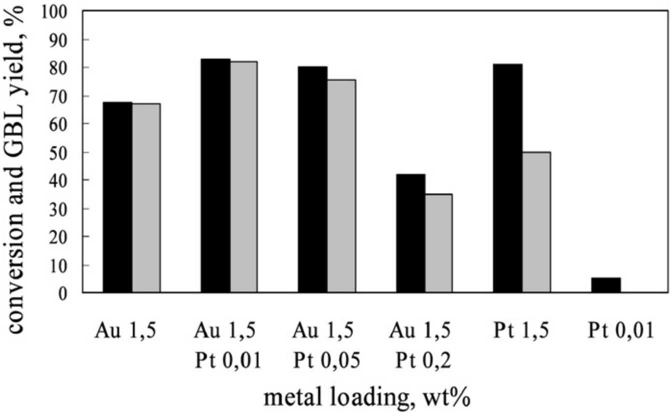


Fig. 5. Conversion (black) and GBL yield (gray) at 5 h reaction time with Pt–TiO_2 and Au–TiO_2 loaded with different amounts of Pt.

lectivity. Indeed, the addition of 100 ppm of Pt to Au–TiO_2 by wetness impregnation with H_2PtCl_6 enhanced the catalytic activity. After 10 h reaction, 97% conversion with 97% selectivity was observed with small amounts of butyric acid and traces of 1,4-butanediol being formed as byproducts. The promoting effect of Pt is evident in Fig. 3 where the conversion to GBL obtained with Au–TiO_2 and PtAu–TiO_2 are compared. Remarkably such small amount of Pt does not influence negatively the selectivity since Au–TiO_2 showed also 97% selectivity at 97.5% conversion. A series of PtAu–TiO_2 and Pt–TiO_2 samples containing different amounts of Pt were also tested and the results, reported in Fig. 5, show that larger amounts of Pt do not produce further increase in activity, but, on the contrary, it makes the activity to decreases. 1.5% platinum 1.5% on titania was more active but much less selective to GBL then gold giving butyric acid and over hydrogenated alcohols that react with SA to form esters. Using a lower loading of platinum ($Pt_{0.01}$–TiO_2) a conversion of about 5% at 5 h was observed but GBL was not formed, being the main product 1,6-dixaspiro[4.4]nonane-2,7-dione. Thus, the increase of activity observed for PtAu–TiO_2 cannot be attributed to a direct hydrogenation of SAN over Pt but, instead, the data support a mechanism where the platinum should mainly be responsible for activating the hydrogen.

In conclusions our results have confirmed that the performance of Au, as hydrogenation catalysts, can be improved with a small amount of Pt that enhances the rate of hydrogen dissociation. If this is so, then the PtAu–TiO_2 will work as a bi-functional catalytic system where SAN will be activated on gold, and H_2 will be activated on gold but also, and more efficiently, on platinum from where can be transported to the adsorbed SAN to perform the hydrogenation.

3.4. *From SAN to pyrrolidone and phenylpyrrolidone in one-pot reaction*

GBL is the best starting material for the production of pyrrolidone and its derivates as reported in numerous patents [56–58]. Since we have found that gold is highly selective for the hydrogenation of SAN to GBL, it was considered the possibility to obtain pyrrolidone and pyrrolidone derivates directly from SAN by a one-pot reaction. In the patent literature it is reported that Pd–Al_2O_{30} [59] and Rh–C [60] can produce pyrrolidone reacting SAN and ammonia at pressures above 120 bar with yields between 60 and 95%. It is also reported that pyrrolidone derivates, like methylpyrrolidone, can be obtained in the liquid phase from maleic anhydride using Cu–Al_2O_3 [61] and PdRe–Al_2O_3 [62] giving respectively 53 and 67% yield. We have performed the one-pot reaction in water at 120 bar and 250 °C using 20 mmol of SAN and 22 mmol of NH_4OH with Au–TiO_2 (Fig. 6). Under these reaction conditions 80% yield of pyrrolidone with no over-hydrogenated products (indicative of an excellent selectivity) was obtained after 10 h.

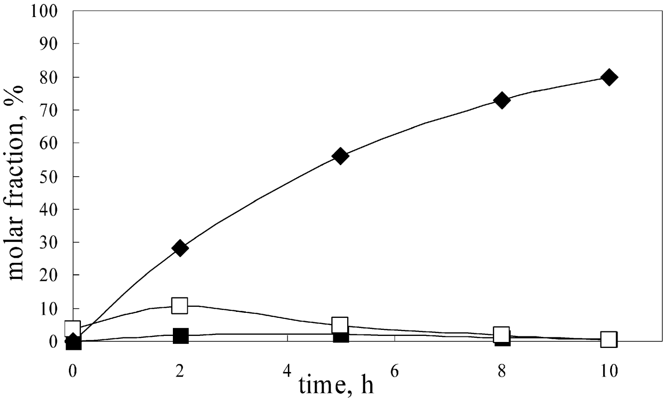


Fig. 6. Hydrogenation of SAN in presence of ammoniac, Au–TiO_2 and performed at 250 °C and 120 bar. (◆) pyrrolidone, (□) succinimmide and (■) GBL.

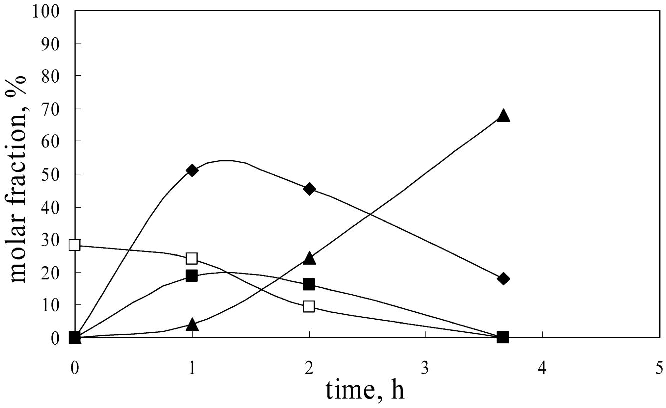


Fig. 7. Hydrogenation of SAN in presence of phenyl-amine, Au–TiO_2 and performed at 250 °C and 110 bar. (◆) phenylpyrrolidone, (□) N-phenylsuccinimmide, (■) GBL and (▲) phenylpyrrolidine.

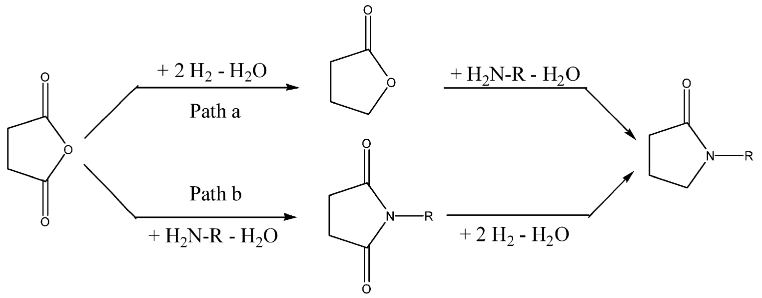
The one-pot synthesis of pyrrolidones has also been performed in dioxane at 110 bar and 250 °C with 12 mmol of SAN and 13 mmol of phenylamine in order to obtain phenylpyrrolidone as main product (Fig. 7). The reaction proceeds faster than before and 52% yield is observed after only one hour. However, at longer reaction times phenylpyrrolidone is hydrogenated to phenylpyrrolidine.

The one-pot reaction above described could proceed through two different reaction pathways: (a) the hydrogenation of the anhydride followed by the ammination of GBL to pyrrolidone; (b) ammination of the anhydride to form succinimide followed by hydrogenation of the intermediate takes place (Scheme 3).

In our case, we could conclude that both paths are possible since GBL and succinimmide were observed as products. However, it is important to note that the latter is already formed at room temperature before reaction conditions are reached and it is always present in larger amounts compared to GBL. It is therefore likely that the reaction proceeds mainly through the formation of succinimide that is subsequently catalytically hydrogenated to pyrrolidone.

4. Conclusions

In the present work we have shown that gold supported catalyst is highly active for the selective hydrogenation of SAN, a reaction relevant for exploiting biomass derivates. Contrary to other noble metals that give more hydrogenated products or require selective poisoning or alloying with other metals to produce higher



Scheme 3. Two possible reaction pathways for the preparation of pyrrolidone and pyrrolidone derivate from SAN.

yields of GBL, an Au/TiO_2 catalyst is able to achieve a selectivity to GBL >99% for 80% conversion and 97% for conversion >97%. A small amount of Pt further improves the activity of Au–TiO_2 with no sensitive lost of selectivity. Finally, we have shown that gold is able to catalyze the one-pot reaction for the direct production of pyrrolidone and pyrrolidone derivates with conversion higher than 80%.

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