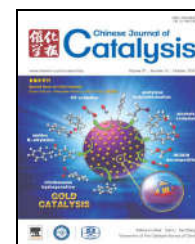


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Article (Special Issue on Gold Catalysis)

Highly selective supported gold catalyst for CO-driven reduction of furfural in aqueous media



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ABSTRACT

The reductive transformation of furfural (FAL) into furfuryl alcohol (FOL) is an attractive route for the use of renewable bio-sources but it suffers from the heavy use of H₂. We describe here a highly efficient reduction protocol for converting aqueous FAL to FOL. A single phase rutile TiO₂ support with a gold catalyst (Au/TiO₂-R) that used CO/H₂O as the hydrogen source catalyze this reduction efficiently under mild conditions. By eliminating the consumption of fossil fuel-derived H₂, our process has the benefit afforded by using CO as a convenient and cost competitive reducing reagent.

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1. Introduction

The search for chemical processes to convert biogenic feedstocks to renewable chemicals and fuels has driven efforts to discover and develop new effective reactions that enable the selective refunctionalization of these polyoxygenate materials [1–5]. In this context, furfural (FAL) represents a promising biogenic building block and the direct conversion of FAL into furfuryl alcohol (FOL) by catalytic reduction has been identified as a reliable feedstock source to open new scenarios for sustainable chemical production [6–10]. Historically, the reduction of furfural under an aggressive hydrogen atmosphere has been the focus of extensive efforts. Recent progress has demon-

strated the potential of this approach in setting up a biobased economy [11–17]. However, H₂ is mainly produced from fossil fuels, which in turn make the process dependent on fossil carbon. Moreover, the necessity of special handling for the highly flammable H₂ gas and the requirement of an organic solvent to achieve a high selectivity have diminished the appeal of these procedures [12–15]. Any strategy and conditions that can address these issues will be advantageous not only for FAL reduction but also for the reduction of biomass intermediates such as 5-hydroxymethylfurfural (HMF).

Due to the potential for the use of CO as a key intermediate in the chemical industry, mainly as a C₁ building block, there is continuous interest in the development of transformations for

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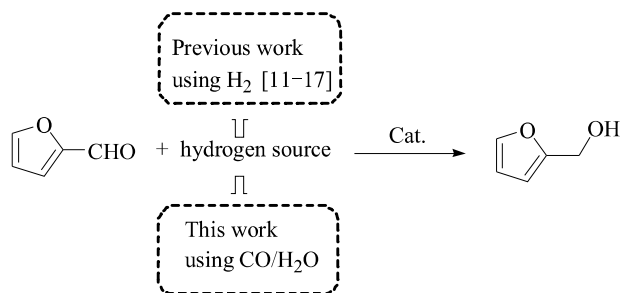
CO valorization. The use of CO instead of hydrogen or other hydrogen donor agents is particularly interesting since CO is currently produced in multi-ton quantities as a byproduct of the steel industry [18] and thus represents an abundant source for chemical reduction [19,20]. One conceptually straightforward way is to use a CO/H₂O couple as a source of hydrogen, although the most ideal scenario would be CO as sole reductant without an external hydrogen source [19]. We have contributed to this field by discovering an excellent Au-catalyzed CO/H₂O-driven strategy that allowed rapid and chemoselective reduction of substituted nitro and carbonyl groups under very mild conditions [20,21]. Our subsequent studies revealed that the Au-CO-assisted reduction strategy could be used for reductive imination and carbonylative alkyne semireduction [22,23].

Our continuing interest in the development of innovative CO-based catalytic reduction technologies led us to investigate the reduction efficiency of the Au-CO/H₂O protocol for the transformation of biogenic platform chemicals [24]. We disclose here the versatile catalytic behavior of supported Au nanoparticles (NPs) in the reductive transformation of FAL to FOL without the use of H₂. We demonstrate that adopting a suitable inorganic support such as single phase rutile TiO₂ to anchor finely dispersed Au NPs enabled a highly selective and efficient transformation of FAL to FOL in water under a mild CO atmosphere (Scheme 1). As opposed to previous procedures, this Au-CO/H₂O-mediated reduction system can deliver high selectivity in the reduction of aqueous FAL, affording exclusively the corresponding FOL in a mild, economical and green manner. This reduction using a simple and robust gold catalyst coupled with CO/H₂O as the hydrogen source under mild conditions can make a significant contribution to the catalytic potential of supported Au NPs and to establish an approach for more efficient FAL reduction.

2. Experimental

2.1. Preparation

Anatase (TiO₂-A, surface area of 154 m²/g), rutile (TiO₂-R, surface area of 65 m²/g), Au/ZrO₂ (ZrO₂, surface area of 115 m²/g), Au/TiO₂ (P25, surface area of 45 m²/g; P90, surface area of 95 m²/g), Au/CeO₂ (CeO₂, surface area of 139 m²/g) and Au/HT (HT, surface area of 118 m²/g). All the supports and catalysts were prepared by using previously described methods [23–30].



Scheme 1. Reductive transformation of FAL to FOL with various hydrogen sources.

The 0.6 wt% Au/TiO₂-R sample was prepared by a routine deposition-precipitation (DP) method [30,31]. In brief, an aqueous solution of HAuCl₄ was added to 100 mL of deionized water at 80 °C under vigorous stirring. The pH was adjusted to 7.0 and 1.0 g TiO₂-R was dispersed in the solution with the pH kept constant at 6.5–7.0. The mixture was stirred for 2 h at 80 °C. After that, the suspension was cooled to 25 °C. After thorough washing with deionised water, the samples were dried under vacuum at 25 °C for 12 h and then calcined in a muffle oven at 350 °C for 2 h. 0.6 wt% Au/TiO₂-A, 0.6 wt% Au/TiO₂-P25, and 0.6 wt% Au/TiO₂-P90 were prepared by the same method.

0.6 wt% Ir/TiO₂-R, 0.6 wt% Pd/TiO₂-R, 0.6 wt% Pt/TiO₂-R, 0.6 wt% Ru/TiO₂-R catalysts were prepared by incipient wetness impregnation (IWI) of the support with aqueous solutions of H₂IrCl₆·6H₂O, PdCl₂, H₂PtCl₆·6H₂O or RuCl₃ precursors, respectively [31]. After mixing the corresponding slurries, the mixture was vigorously stirred at 80 °C for 4 h. Then samples were dried under vacuum at 25 °C for 12 h and then reduced in 5 vol% H₂/Ar (80 mL/min) at 400 °C for 2 h.

2.2. Characterization

X-ray diffraction (XRD) analysis was carried out on a German Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation with a scanning angle (2θ) of 10°–80°, a scanning speed of 2°/min, and a voltage and current of 40 kV and 20 mA. Transmission electron microscope (TEM) images were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples were dispersed in ethanol and deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal particles was determined by measuring about 200 random particles in the images. CO temperature programmed reduction (CO-TPR) experiments were carried out on a homemade apparatus described elsewhere [32]. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg K α ($h\nu = 1253.6$ eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C 1s peak at 284.6 eV. The solution after reaction was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

2.3. Reduction of FAL to FOL

A 25-mL Hastelloy-C high pressure Parr reactor was used to carry out the liquid phase reduction reaction. A mixture of FAL (2.6 mmol, fresh distilled), supported metal catalysts, water (20 mL) were loaded into the reactor. The reactor was stirred at a rate of 800 r/min under 4 MPa CO (syngas, or H₂) for a specific reaction time at a given temperature. After reaction, the CO atmosphere was removed and the resultant product mixture was transferred with 5 mL of ethanol. An amount of *N,N*-dimethylformamide (DMF) was then added as an internal

standard substance. The samples were analyzed on a Agilent GC-6820 gas chromatograph equipped with a capillary column DB-Wax (30 m × 0.25 mm) and FID detector. The identification of the products was performed by using a GC-MS spectrometer.

3. Results and discussion

At first, the reaction was evaluated using a diluted aqueous solution of freshly distilled FAL (0.13 mol/L) and Au NPs (average diameter of ca. 2.2 nm) deposited on some common inorganic oxides with a substrate-to-gold ($n_{\text{FAL}}/n_{\text{Au}}$) ratio of 200:1 under mild conditions (4 MPa of CO pressure in neat water at 90 °C). We initially focused our attention on Au/CeO₂ because of the successful application of this Au-based catalyst for the chemoselective reduction of a range of α , β -unsaturated aldehydes, e.g., crotonaldehyde and cinnamaldehyde, to their allyl alcohols in the presence of CO and H₂O [21]. However, this material afforded only modest activity for the CO/H₂O-mediated FAL to FOL reduction under the screening conditions employed (Table 1, entry 1). We then turned our attention to the selection of other commonly used Au-support combinations that have proven effective in the Au-CO/H₂O-mediated reductive transformation, including Au/TiO₂-P25, Au/Al₂O₃, Au/ZrO₂ and Au/Mg-Al hydrotalcite (Table 1, entries 2–5). While none were found to be particularly active for FAL reduction, the modest success achieved with Au/TiO₂-P25 prompted a more detailed survey of structurally related Au-TiO₂-based systems.

We subsequently optimized the Au-TiO₂ catalysts by alter-

Table 1
FAL conversion and FOL selectivity with different catalysts.

Entry	Catalyst	p (MPa)	T (°C)	t (h)	Conversion ^a (%)	Selectivity ^a (%)
1	Au/CeO ₂	4	90	2	21	100
2	Au/TiO ₂ -P25	4	90	2	53	100
3	Au/ZrO ₂	4	90	2	15	100
4	Au/Al ₂ O ₃	4	90	2	1	100
5	Au/HT	4	90	2	18	100
6	Au/TiO ₂ -P90	4	90	2	52	100
7	Au/TiO ₂ -R	4	90	2	67	100
8	Au/TiO ₂ -A	4	90	2	48	100
9	Au/TiO ₂ -R	4	90	4	100	100
10	Au/TiO ₂ -R	2	90	7	100	100
11	Au/TiO ₂ -R	6	90	2.5	100	100
12	Au/TiO ₂ -R	4	120	2	100	100
13	Au/TiO ₂ -R	4	30	4	19	100
14 ^b	Au/TiO ₂ -R	4	90	23	100	100
15 ^c	Au/TiO ₂ -R	4	90	61	99	100
16 ^d	Au/TiO ₂ -R	4	90	4.5	100	100
17	Ir/TiO ₂ -R	4	90	4	8	100
18	Pd/TiO ₂ -R	4	90	4	1	100
19	Pt/TiO ₂ -R	4	90	4	1	100
20	Ru/TiO ₂ -R	4	90	4	1	100
21 ^e	Au/TiO ₂ -R	4	90	4	100	100

Reaction conditions: FAL 2.6 mmol, water 20 mL, $n_{\text{FAL}}/n_{\text{Au}} = 200$, 90 °C, $p(\text{CO}) = 4$ MPa, 2 h.

^a Conversion and selectivity were determined by GC and GC-MS with *N,N*-dimethylformamide as the internal standard.

^b $n_{\text{FAL}}/n_{\text{Au}} = 2000$.

^c $n_{\text{FAL}}/n_{\text{Au}} = 5000$.

^d The 5th reuse of the catalyst recovered from entry 10.

^e Using aged distillates of FAL as feedstock.

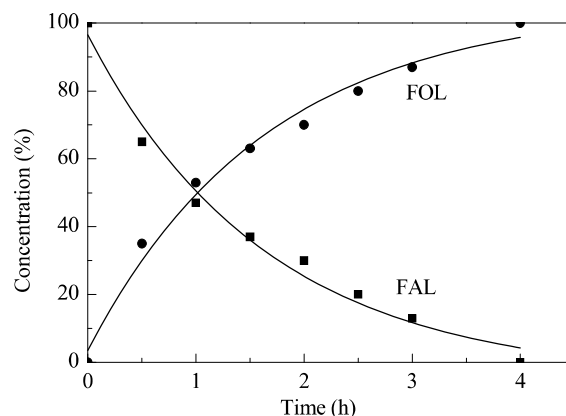


Fig. 1. Time profiles of FAL reduction over Au/TiO₂-R. Reaction conditions: FAL 2.6 mmol, water 20 mL, $n_{\text{FAL}}/n_{\text{Au}} = 200$, 90 °C, $p(\text{CO}) = 4$ MPa.

ing the TiO₂ phase during the preparation (Table 1, entry 1, 6–8). Eventually, the optimized Au/TiO₂-R comprising gold deposited on single phase rutile TiO₂ (Au/TiO₂-R) was the most efficient, which accomplished quantitative FAL-to-FOL conversion within only 4 h at 90 °C (Table 1, entry 9). A plot of the time dependent conversion of FAL (Fig. 1) revealed that the reaction proceeded smoothly and FOL was the only product, that is, we did not detect any other product during the whole reaction. Furthermore, in a series of studies examining the effect of pressure, the reaction time was shortened from 4 to 2.5 h as the p_{CO} was raised from 4 to 6 MPa (Table 1, entries 9 and 11). Further experiments on the effect of temperature indicated that the Au/TiO₂-R catalyst exhibited rather low activity at 30 °C (Table 1, entry 13). At 120 °C, quantitative formation of FOL was attained at 4 MPa within 2 h (Table 1, entry 12).

In line with several other CO/H₂O-mediated reduction [20–23], we found that Au was as active for the reduction of FAL with CO/H₂O as traditional noble metals (Table 1, entries 17–20). These results confirmed that the combination of Au NPs with a suitable TiO₂ phase could achieve a high catalytic activity for the selective reduction of FAL into FOL. After the

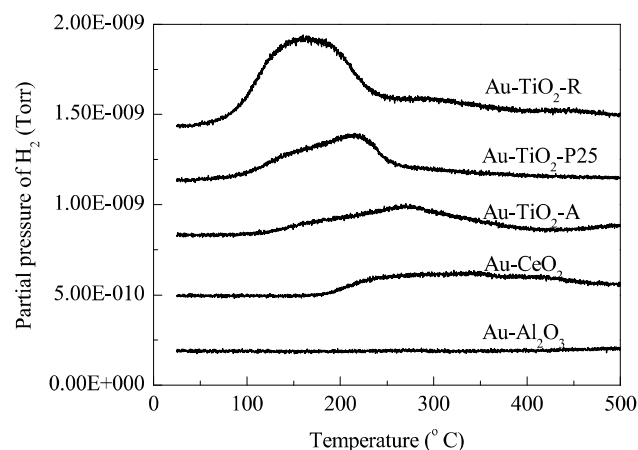
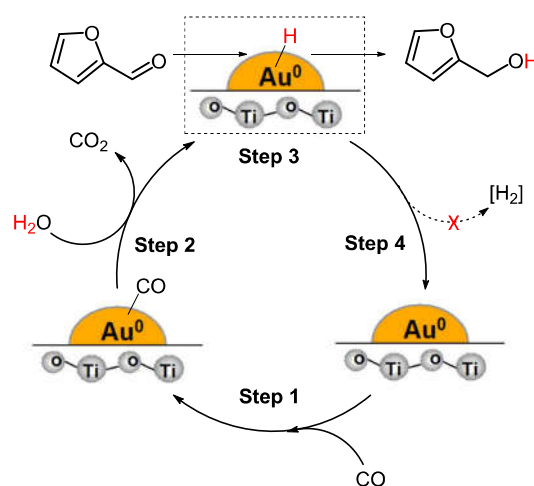


Fig. 2. CO TPR profiles (1% CO in He, 20 mL/min; heating rate: 5 °C/min; 100 mg sample) for different Au catalysts. Each sample was purged with 20 mL/min He at 100 °C for 30 min and then cooled to 30 °C in He. Before being heated from 30 to 550 °C, the sample was stabilized in 1% CO in He for 30 min.

reduction of FAL, Au/TiO₂-R can be separated from the reaction mixture and reused without loss of catalytic efficiency (Table 1, entries 16). To gain insight into the origin of the enhanced CO/H₂O-mediated reduction activity achieved by using rutile TiO₂ as the support, CO-TPR was performed for Au deposited on different supports (Fig. 2). This revealed that the lower performance observed with Au/TiO₂-A, Au/Al₂O₃ and Au/CeO₂ were due to that the H₂ formation rates catalyzed by these catalysts were significantly lower than that over the Au/TiO₂-R sample. This was reinforced by the observation that the low temperature H₂ production rate over Au/TiO₂-R also occurred at a much higher rate than that over TiO₂-P25 supported Au. Taken together, these results demonstrated that the Au-catalyzed CO/H₂O-mediated FAL reduction proceeded by a sequential water-gas-shift/FAL-reduction pathway (Scheme 2), in which the generation of a transient Au⁰-H species formed by CO-induced H₂O activation was the main step.

These results showed that the Au/rutile-based catalyst facilitated efficient FAL-to-FOL conversion without an external H₂ supply. By investigating the physicochemical properties of the Au/TiO₂-R catalyst, the following information was collected. From the XPS results, it was seen that there was only metallic Au on the Au/rutile sample (Fig. 3(a)). ICP-AES data revealed that there was no Au species in the solution after the reaction, which indicated the absence of Au leaching during the reaction. XRD analysis displayed that both the fresh and used Au/TiO₂-R catalysts showed the same crystal phase, with no obvious Au feature being identified in these two samples, which suggested that the particle sizes of Au were quite small (Fig. 3(b)). TEM



Scheme 2. Mechanism for the Au/TiO₂-R-catalyzed reduction of HMF by CO/H₂O.

confirmed that the average diameter of the Au particles was 2.2 nm in the fresh and used Au/TiO₂-R catalysts, verifying there was no Au NPs aggregation during the reaction (Fig. 3(c) and (d)). These results accounted for the remarkable stability of Au/TiO₂-R in the recycling tests.

As a further illustration of the effectiveness of the above reduction, full conversion of FAL was readily obtained at a $n_{\text{FAL}}/n_{\text{Au}}$ ratio of 2000 (Table 1, entry 14). This Au-CO/H₂O-mediated reduction still occurred with only 0.02 mol% of the Au/TiO₂-R, albeit an extended reaction time of 61

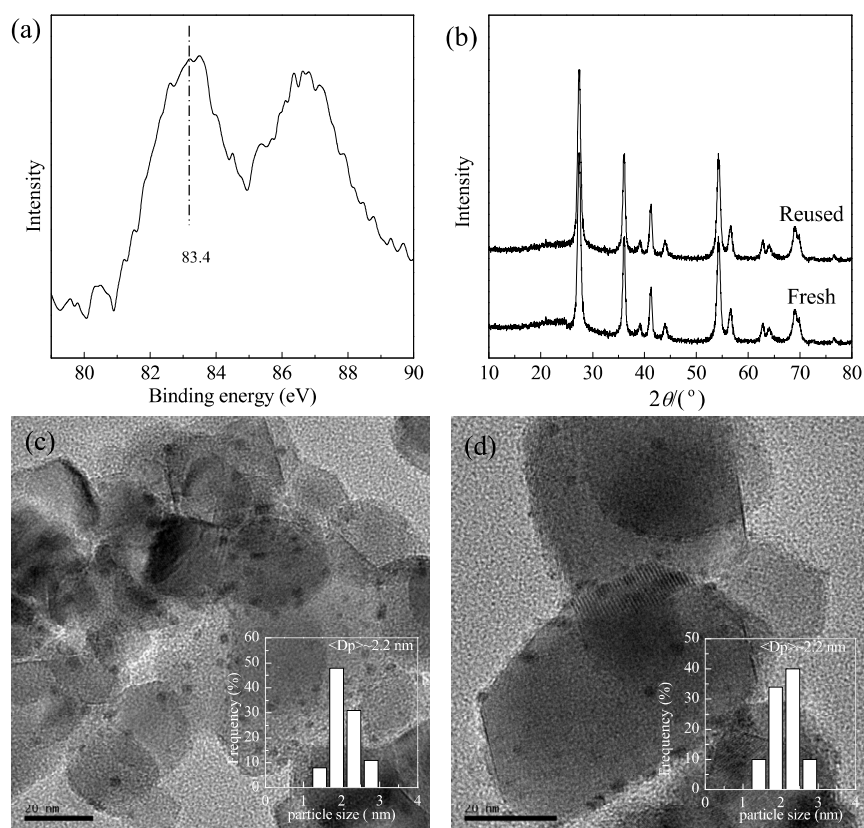
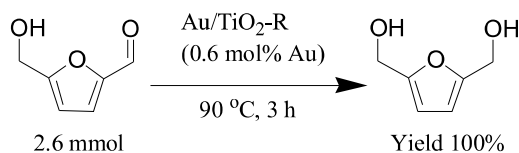


Fig. 3. (a) XPS spectrum of Au/TiO₂-R; (b) XRD patterns of fresh and used Au/TiO₂-R; TEM images of fresh (c) and used (d) Au/TiO₂-R.



Scheme 3. Reduction of HMF by CO/H₂O.

h was required (Table 1, entry 15). Under these conditions, remarkable values of the turnover number (TON = 5000) and average turnover frequency (TOF = 91 h⁻¹) were calculated (Table 1, entry 15). Perhaps the most notable finding was the ability of the Au-CO/H₂O-based protocol to convert aged distillates of FAL to value added material. Along these lines, we demonstrated that the present Au-based technology could be used to convert FAL that was set aside for more than a month into FOL with high efficiency (Table 1, entry 21). These results were extremely encouraging because they showed that crude FOL could be used directly as a feedstock for industrially relevant transformations [33,34]. Furthermore, this Au-CO/H₂O-mediated reduction process was not limited to FAL. When HMF, another key intermediate in biomass conversion, was subjected to the reduction in the presence of the Au/TiO₂-R sample, the reaction also proceeded efficiently. In this case, 2,5-bis-(hydroxymethyl) furan (BHMF), an important monomer for industrial processes, was exclusively obtained under the standard reaction conditions (Scheme 3).

Given the fact that producing CO and H₂ (syngas) from biomass is a crucial step in the production of most second generation biofuels, we explored the possibility to produce FOL by aqueous FAL reduction using simulated syngas with a varying H₂/CO feed ratio. Three different volumetric compositions of syngas were examined. As shown in Table 2, in all cases, FAL was quantitatively converted into FOL but different reaction times were required. The reaction involving the H₂-rich syngas proceeded much more rapidly than the reaction with the CO-rich syngas. This was in agreement with that the reaction proceeded at a much faster rate with H₂ as the sole reductant. More important, this revealed that cheap, renewable and easily accessible CO₂-rich bio-syngas could be successfully used for FAL reduction. These results are particularly relevant since flexible and versatile syngas can be used as a direct hydrogen source for selective biomass conversion. This would open the possibility to develop cost effective technologies for the production of bio-renewable chemicals based on CO-driven reduction.

Table 2

FAL reduction using syngas with varying H₂/CO feed ratio as hydrogen source.

H ₂ /CO	Time (h)	Conversion (%)	Selectivity (%)
1:1	2.5	100	100
2:1	1.8	100	100
bio-syngas *	2	100	100
pure H ₂	1	100	100

Reaction condition: FAL 2.6 mmol, water 20 mL, Au/TiO₂-R, $n_{FAL}/n_{Au} = 200$, 90 °C, $p(\text{CO}) = 4$ MPa.

* H₂:CO:CO₂ = 10:5:1.

4. Conclusions

TiO₂ supported Au catalysts, in particular the Au/TiO₂-R system, were very promising for the selective reduction of bio-derived furfural using CO as a convenient and cost competitive hydrogen source. This Au-based catalytic protocol constitutes the first furfural reduction system that directly used syngas as a hydrogen source and would furnish a new application of syngas. As controlled hydrogenation and reductive transformation is a very general issue in the conversion of bio-derived feedstocks, the procedure here is expected to be of broad applicability in the utilization of biomass.

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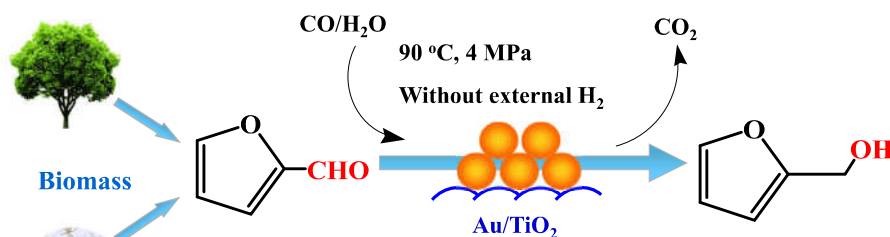
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Graphical Abstract

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Highly selective supported gold catalyst for CO-driven reduction of furfural in aqueous media

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By using a single phase rutile titania support and gold as the catalyst (Au/TiO₂-R), CO was used as hydrogen source to get furfuryl alcohol as the only product from furfural in aqueous media.

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