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Aerobic Oxidation of Benzyl Alcohol on a Strontium-Based Gold Material: Remarkable Intrinsic Basicity and Reusable Catalyst

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Abstract: The development of stable and active gold catalysts has arisen as a significant strategy for oxidation of alcohols. Nano-size PVA-stabilized gold nanoparticles immobilized on Sr(OH)₂ by colloidal deposition presented high catalytic activity for benzyl alcohol oxidation. In 2.5 h, 2 bar of O₂ and without extra-base addition, the calcined support reached 54.6% (100 °C) and 67.4% (140 °C) of conversion, presenting the remarkable and unexplored intrinsic basicity that strontium-based materials retain. With sub-stoichiometric K₂CO₃ adding, under the same catalytic conditions, the catalyst conducted the reaction with similar activity, but with excellent reusability in the process, without any gold leaching. We investigated the influence that the support synthesis method and the solvent used for the NPs stabilization have on the oxidation activity. The produced materials were fully characterized by XPS, Rietveld refinement, and TEM.

Keywords: alcohol oxidation; gold catalyst; strontium hydroxide

1. Introduction

Heterogeneous catalysts play an important role globally, not only with respect to an economic perspective, but they also are paramount to ensuring structure for the prosperity of society as a whole. Materials, foodstuffs, and pharmaceuticals, which are essential for the wellbeing worldwide, have intermediates that are heterogeneously catalyzed products. Catalysis by gold-based materials has become one of the most studied topics in chemistry for a wide range of reactions. Studies performed by Prati, Rossi, and partners demonstrated [1–3] for the first time that supported gold nanoparticles (NPs) can be used to oxidase alcohols, diols, and polyols in presence of a base, as it was originally considered to be essential for the substrate hydrogen abstraction [4]. However, the requirement of base addition to achieve satisfactory rates may be in some cases considered a restriction to the use of Au NPs catalysts, since side reactions or catalyst damage may occur [5]. In order to avoid any drawbacks, the combination of Au NPs with a second metal from the platinum group has received attention as an alternative to monometallic gold-based catalysts, for which base employment is typically required [5–7]. Although this strategy is actually interesting, one may notice that the synthesis of a catalyst using two noble metals may cause a price augmentation or the necessity of more steps for its final production. Thus, some work has been done to understand and use highly available basic supports, such as alkaline earth metal oxides and hydroxides, not just for its intrinsic basicity, but also due to the interaction of

Au NPs with the solid [8]. Charge-density models [9] that predict the strength of oxygen Lewis basic sites in such oxide catalysts decrease in the order of $O^{2-} > OH^- > H_2O > H_3O^+$; nevertheless, the most explored materials as support for Au NPs for alcohol oxidation are MgO and $Mg(OH)_2$, without the addition of extra base in the reaction medium [10,11]. While these materials may be used with excellent activity and selectivity, and there is a large body of literature dealing with magnesium compounds as support (or as base additives in some catalytic systems) [12–19], the use of strontium-based materials is somehow neglected. To the best of our knowledge, $Sr(OH)_2$ was not used as a support for Au NPs oxidation reactions, or its hydroxide phase was not considered in such experiments. Few examples showing SrO applications as a support presented no further discussion on its real function [20,21]. Studying aldol addition of acetone, Zhang et al. performed TPD measurements of alkaline earth metal oxides under the same reactive conditions. Data suggested that the strength of the basic sites of SrO are higher than the observed for MgO [22], the same conclusion achieved by Kabashima et al. when studying double bond isomerization of 5-vinylbicyclo[2.2.1]hept-2-ene [23]. In open air, strontium oxide reacts with water vapor, converting to strontium hydroxide, making it difficult to retain this compound in its oxide form. However, although metal hydroxides are weaker bases than the oxides, the strength order suggested $Sr(OH)_2 \cdot 8H_2O$ is stronger than $Mg(OH)_2$ [24], opening up the possibility of using it as a suitable support for oxidation reactions of alcohols. Therefore, data compilation suggests that materials based on strontium supports are not scrutinized in literature for gold-based catalysts.

Herein, we propose the effect of $Sr(OH)_2$ supports on the oxidation of benzyl alcohol as a model reaction. The supports were prepared with simple methodologies, and Au NPs were synthesized using a PVA-stabilized approach with $NaBH_4$ reduction. The reactions were carried out in solvent-free conditions without any addition of extra base at the beginning to demonstrate the catalyst basicity and pertinence to the reaction. Then, reactions with sub-stoichiometry K_2CO_3 were performed to improve the catalyst reusability [25]. The oxidation of benzyl alcohol by molecular oxygen in low pressure (2 bar) and in 2.5 h revealed that the catalysts have a very good activity and high selectivity, with a remarkable performance achieved with the calcined support. Studies of XPS, TEM, and recyclability were important to correlate the activity to the material obtained.

2. Results and Discussion

Gold NPs were prepared using the well-known sol-stabilization method with PVA [26]. This method was chosen due to its reproducibility, robustness, and good sol stability, although PVA may have some effect on the activity of gold catalysts [27]. Strontium-based supports were used in an attempt to enhance the basicity of the catalysts to further boost its properties. Since differences between oxide and hydroxide have been demonstrated to affect the activity of gold catalysts in magnesium-based supports [12], we decided to explore the influence of strontium-base materials on oxidation of benzyl alcohol, since studies suggested its superior activity when compared to $Mg(OH)_2$ [24], a very common material used for gold catalysts synthesis. Previous studies express by titration the strength of basic sites on a scale given by the H_- function, defined by the equation:

$$H_- = pK_a + \log \frac{[B^-]}{[BH]}$$

in which the pK_a value is for a chosen Hammett indicator and $[BH]$ and $[B^-]$ are the concentration of the indicator and its conjugated base, respectively. MgO has basic sites estimated in $H_- = 26$, and SrO presents $H_- < 18$. However, $Sr(OH)_2$ calcined at 1123 K presents basic sites with $H_- \leq 26.5$ [9]. Based on such antecedent findings, we decided to explore strontium-based materials. According to the experimental section, the material synthesized with the calcined support was assigned as Au/calc-Sr_{sup} and the one without calcination was assigned as Au/Sr_{sup}. For both materials, the base strength measured by the Hammett indicator method was found to be $13.7 < H_- < 18.4$. Such catalysts are considered to be strongly basic, and any difference from the literature may be due to the synthesis process that the supports underwent for the Au NPs impregnation and washing.

To shed some light on the chemical state of the gold species immobilized, since the NPs syntheses were performed in different solvents, Au/Sr_{sup} and Au/calc-Sr_{sup} samples were analyzed by XPS (Company, City, Country). As portrayed in Figure 1, both catalysts presented the characteristic Au 4f_{5/2} and Au 4f_{7/5} XPS bands. The two XPS components observed for the samples are indicated in Figure 1a,b and are basically the same (83.4 eV and 87.2 eV for Au/calc-Sr_{sup} and 83.5 eV and 87.3 eV for Au/Sr_{sup}). The bands are assigned to the spin-orbit components of the Au-4f level, which could be attributed to metallic gold species [28]. The acetone-stabilized Au NPs were prepared in an attempt to maintain the oxide phase of the calcined support (calc-Sr_{sup}). The XPS data for this Au NPs preparation approach presented no significant difference between the water-stabilized gold NPs. Therefore, Rietveld refinement was performed to determine the main phases obtained after the catalyst synthesis via Au NPs immobilization for both catalysts (Figure 2).

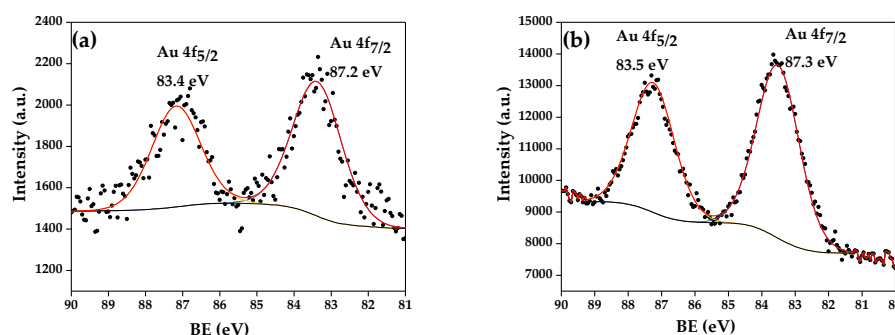


Figure 1. XPs spectra of Au 4f level of (a) Au/calc-Sr_{sup} and (b) Au/Sr_{sup} catalysts. The red line represents the fitted spectrum and the black one is the background.

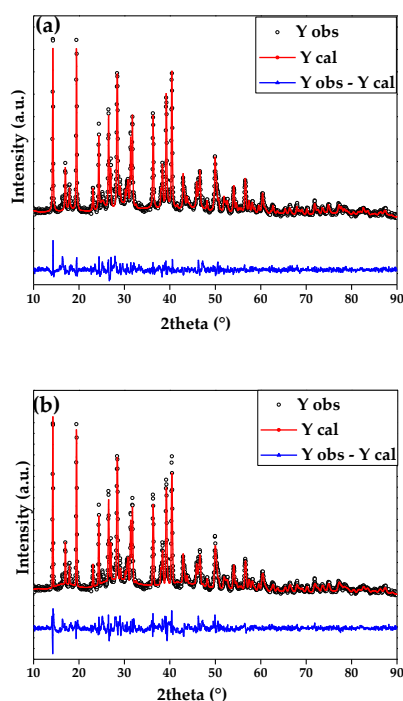


Figure 2. Rietveld refinement plot for (a) Au/calc-Sr_{sup} and (b) Au/Sr_{sup} catalysts, showing the observed, calculated, and difference pattern.

The diffraction pattern used in the refinement were indexed to SrO (ICSD 20960), SrCO₃ (ICSD 207393), Sr(OH)₂·H₂O (ICSD 60661), and Sr(OH)₂ (ICSD 15167) crystalline phases. The Rietveld refinement results for the Au/calc-Sr_{sup} catalyst indicated that the majority phases are comprised

of $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (25.5%) and $\text{Sr}(\text{OH})_2$ (59.2%); 15.3% remained as SrCO_3 . For the $\text{Au}/\text{Sr}_{\text{sup}}$ catalyst, the phase composition was 24.5% for $\text{Sr}(\text{OH})_2$ and 75.5% for $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$. The results specifically show that the acetone-stabilized Au NPs were not able to maintain the SrO phase. Hence, strontium oxide was not considered in the studies performed here due to its easy transformation to $\text{Sr}(\text{OH})_2$ via interaction with water, as attested by the refinements carried out.

The low concentration and small size of the Au NPs in both catalysts hampered the observation of Au diffraction peaks on the materials; the metal NPs characteristics were analyzed by TEM, as shown in Figure 3.

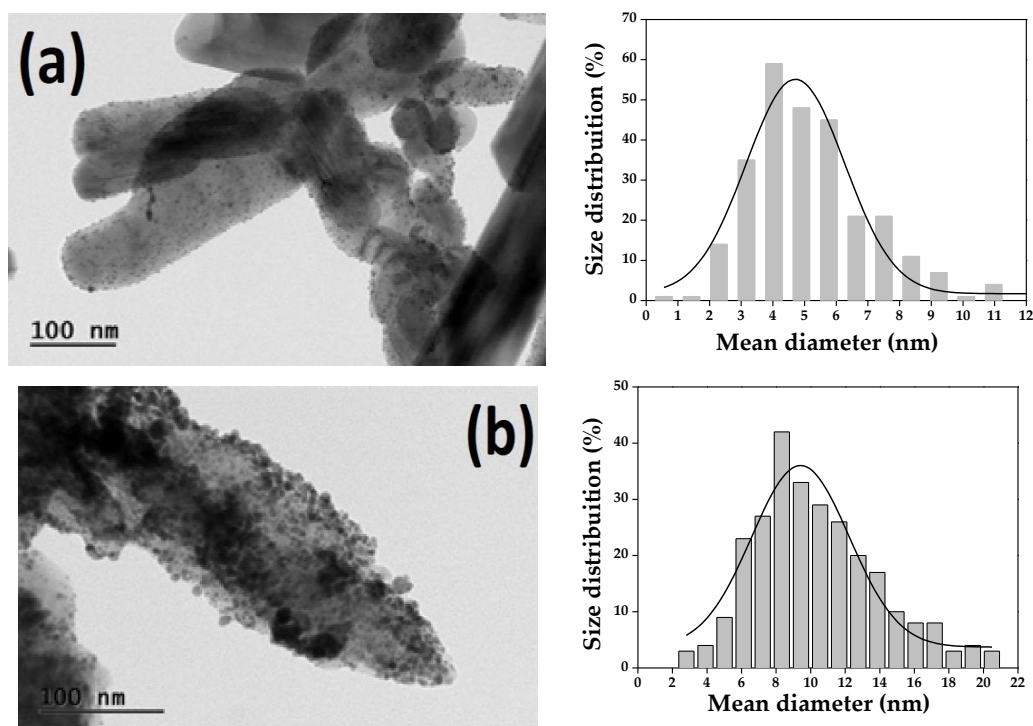


Figure 3. TEM image of (a) $\text{Au}/\text{calc-Sr}_{\text{sup}}$ and (b) $\text{Au}/\text{Sr}_{\text{sup}}$. The NPs size distributions are also provided for both materials.

TEM image for $\text{Au}/\text{calc-Sr}_{\text{sup}}$ catalyst (Figure 3a) revealed well-dispersed Au NPs with a mean diameter of 5.2 ± 1.9 nm. For $\text{Au}/\text{Sr}_{\text{sup}}$ catalyst, the size distribution was 10.3 ± 3.6 nm (Figure 3b), with a poor dispersion. One may notice that the NPs obtained for the catalyst prepared in water presented a narrow size distribution, although they were slightly broader when compared to NPs synthesized in acetone, as occasionally much larger particles are observed in the sample. This leads to larger surface-average size for the catalyst and may be associated with the solvent used for the synthesis.

The catalytic activity of the $\text{Au}/\text{calc-Sr}_{\text{sup}}$ and $\text{Au}/\text{Sr}_{\text{sup}}$ catalysts was tested in the solvent-free oxidation of benzyl alcohol (Figure 4) under the standard reaction conditions outlined in the experimental Section, without co-catalysts or additives. The metal uptake for $\text{Au}/\text{calc-Sr}_{\text{sup}}$ catalyst was 1.5 wt % and for $\text{Au}/\text{Sr}_{\text{sup}}$ was 2.0 wt %, according to FAAS data. To establish if there was any conversion of the benzyl alcohol in the absence of the catalysts, a blank reaction was performed under the same reaction conditions. Without catalyst in the reaction medium, the conversion of the reagent was 0.1%, which is within experimental error. Two other separate blank tests were carried out with the as-synthesized calcined and not-calcined supports. For both, the conversions were negligible as well. The oxidation of benzyl alcohol was carried out with $\text{Au}/\text{calc-Sr}_{\text{sup}}$ and $\text{Au}/\text{Sr}_{\text{sup}}$ without base addition at 100 °C, 120 °C, and 140 °C. The results are displayed in Table 1. The influence of the temperature reaction for both catalysts did not lead to any significant conversion increasing in a

range of 100–140 °C, although some influence on the selectivity was observed. For the Au/calc-Sr_{sup} catalyst, very remarkable conversions were obtained in just 2.5 h of reaction and 2 bar of O₂, taking into consideration that no base was used (entries 1–3). Yields of 54.6%, 62.7%, and 67.4% were achieved at 100 °C, 120 °C, and 140 °C, respectively. Increasing the temperature, a slight conversion augmentation was observed, and the selectivity to benzaldehyde was also improved. For the Au/Sr_{sup} catalyst, the temperature effect on the conversion was more noticeable, with benzoic acid enhancement (entries 4–6). Choudhary and co-workers presented a gold-magnesium catalyst for the solvent-free oxidation of benzyl alcohol. In 5 h, under 1.5 bar, 130 °C, and substrate/metal molar ratio of 725, the authors obtained 51% of conversion. The proposed Au/Sr_{sup} catalyst presented in 2.5 h, 2 bar, 140 °C, and substrate/metal molar ratio of 2180 a conversion of 67.4%, which shows the applicability of the material [29]. Other examples using MgO and Mg(OH)₂ are also available in the literature; however, with the solvent addition [11,12]. Comparisons with such studies and the Au/calc-Sr_{sup} catalyst present the superior activity of the proposed system. Albeit the temperature to some extent influenced the selectivity, the conversions are not modified, with 100 °C being the temperature that was set for other experiments that were further performed. Our studies were based on the substrate/metal ratios calculated by bearing in mind the total amount of gold, which was determined by FAAS. Such information is considered correct by many researchers, as presented before; however, one may notice that the number of surface atoms is much lower than that obtained for bulky NPs. Composition results from XPS analysis (Supplementary Information, Figures S1 and S2) of the Au/calc-Sr_{sup} catalyst showed the presence of O, Sr, Au, Cl, and Na. The Au atomic concentration was 0.13%. When removing the contributions from Na and Cl, the renormalized data presents at % for Au of 0.22. Such data may be relevant to evaluate the performance per active site.

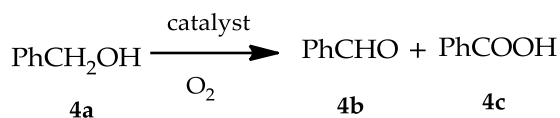


Figure 4. Oxidation of benzyl alcohol (4a) into benzaldehyde (4b) and benzoic acid (4c).

Table 1. Oxidation of benzyl alcohol (4a) with molecular oxygen using Au/calc-Sr_{sup} and Au/Sr_{sup} catalysts ¹.

Entry	Temperature (°C)	Catalyst	Conversion (%)	Selectivity (%)	
				4b	4c
1	100	Au/calc-Sr _{sup}	54.6	59.5	40.5
2	120	Au/calc-Sr _{sup}	62.7	60.6	39.4
3	140	Au/calc-Sr _{sup}	67.4	78.7	21.3
4	100	Au/Sr _{sup}	7.3	80.8	19.2
5	120	Au/Sr _{sup}	16.2	73.1	26.9
6	140	Au/Sr _{sup}	24.74	68.2	31.8

¹ Reaction conditions (solventless): benzyl alcohol (9.6 mmol), catalyst (4.4 μmol of Au), 2 bar of O₂, 2.5 h.

The NPs size differences may explain the lower activity in the Au/Sr_{sup}, whereas the sample presents larger NPs (10.3 ± 3.6 nm); however, that is not the only aspect to be considered. Significant differences were found concerning the dispersion and aggregation of the nanoparticles, which leads to a decrease in catalytic activity of the Au/Sr_{sup} catalyst by lowering its surface area. As the syntheses of the supports were found to be essentially strontium hydroxide, the size and dispersibility differences of the NPs are considered to be responsible for the effects observed. However, the support-NPs interactions may not be disregarded, as well as the support synthesis processes. Lopez-Sanchez et al. have concluded PVA-stabilized gold NPs may have its activity affected by the stabilizer for CO oxidation reactions. They proposed an efficient water extraction method that is able to clean the NPs surface, maintaining their size and morphology [30]. The Au/calc-Sr_{sup} catalyst is very active considering that no base was added to the reaction medium; therefore, we performed an extraction with acetone, and it was applied to this material with some modifications. The catalyst was refluxed

for 12 h in a Soxhlet apparatus and washed with acetone and dried. After the procedure, the catalyst was used under the same reaction conditions for benzyl alcohol oxidation. No significant activity improvement was observed, although a slight benzaldehyde selectivity enhancement was detected. Nevertheless, the PVA has no effect drawbacks on the system proposed.

One of our main interests was to determine the catalytic activity and reusability of the proposed system. For this proposal, the Au/calc-Sr_{sup} was the chosen one, since its activity is significantly higher than that observed for Au/Sr_{sup} catalyst. The stability of the catalyst was evaluated by recycling experiments (Figure 5) without base addition and with K₂CO₃ as an additional base. The base addition was decided based on previous studies [25]. In the recycling experiments without base addition, the catalyst was washed three times with acetone; nevertheless, the experiments carried out with K₂CO₃ were washed with water to remove the base from the previous cycle and, then, three times with acetone. Figure 5a clearly shows that the Au/calc-Sr_{sup} catalyst, without extra-base addition, presents considerable deactivation in successive runs. The same catalyst, in presence of the base, presented a similar conversion for the first run; however, it remained stable with similar conversion and selectivity in the recycling tests. Some of us have studied base-free promoted benzyl alcohol oxidation with comparable results [18]. It is quite unexpected that the catalyst with additional base presents similar performance as the observed for the base-free counterpart. FAAS analyses of the spent catalyst after the fifth run showed no leaching in the catalyst with K₂CO₃, but ca. of 70% of Au leaching was detected in the material used without the additional base. These results suggest that the synthesized catalyst is active without the base; however, it loses its activity due to the pronounced leaching. The base addition works on the catalyst stabilization. The catalyst used in presence of base did not show any sign of deactivation and may be used in further cycles. Data obtained open up the possibility of application of this catalyst with other pH environments in water conditions [25], improving the selectivity.

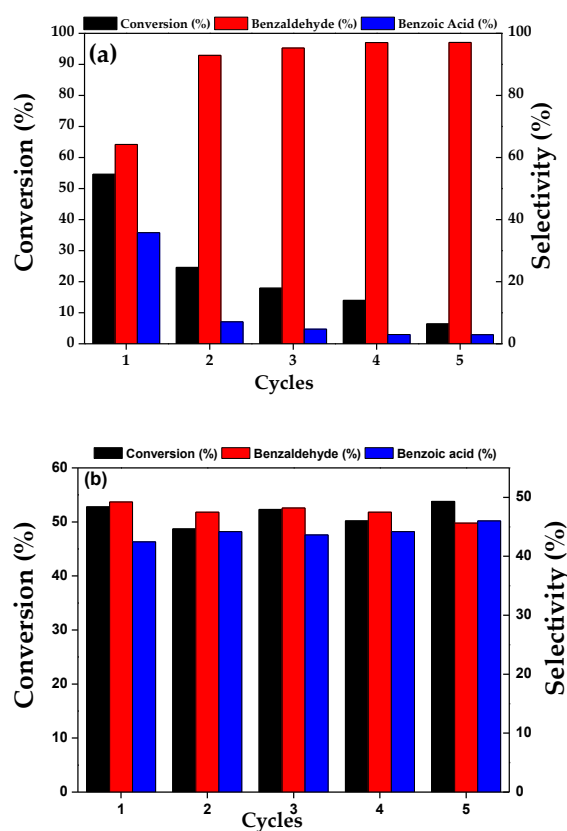


Figure 5. Recycling tests for the Au/calc-Sr_{sup} catalyst in benzyl alcohol oxidation under (a) base-free conditions and (b) K₂CO₃ extra-base addition.

3. Materials and Methods

3.1. Materials

All chemicals used in the experiments were of analytical grade and used without further purification.

3.2. Catalytic Supports Preparation

The supports were prepared according to literature with modifications [30]. For one of them, 50 mL of strontium nitrate (1 mol L^{-1}) and 50 mL of sodium hydroxide (2 mol L^{-1}) were mixed and constantly stirred for 1 h. The mixture was centrifuged for 5 min at 2400 rpm and a white precipitate was obtained by pouring the supernatant off. The solid was calcined in a muffle furnace for 4 h at 1100°C and labelled as $\text{cal-Sr}_{\text{sup}}$. The second support was prepared by a similar procedure, without calcination. After the precipitate obtaining, the solid was washed with distilled water (3 times, 20 mL each) and acetone (once, 20 mL) and dried in an oven at 70°C . This support was labelled just as Sr_{sup} .

3.3. Au NPs Synthesis

Au NPs were prepared by a method described elsewhere with modifications [26]. The Au NPs were prepared in water or in acetone, depending on the support chosen for the impregnation; the selected procedure will be highlighted when necessary. In a typical procedure, 1.80 mL of a freshly prepared 2.0 wt % aqueous solution of polyvinyl alcohol (PVA 80%, 36 mg) was added to a solution of HAuCl_4 (172.5 mg, 300 mL), in water or acetone, under magnetic stirring (800 rpm). After this step, an ice-cold freshly prepared NaBH_4 aqueous solution (7.65 mL, 0.1 mol L^{-1}) was added drop-by-drop to reduce the metal, under the same magnetic stirring. The solution turned immediately to a dark purple color and was further stirred for 30 additional minutes.

3.4. Synthesis of the Catalysts

After the sol synthesis, the colloids were immobilized on the supports. The colloidal solutions were simply added to the solids; however, the NPs prepared in water were used to the Sr_{sup} , while the prepared NPs in the acetone medium were used with the $\text{calc-Sr}_{\text{sup}}$. After the addition of the pre-formed NPs to the supports, the mixture was vigorously stirred for 2 h at room temperature. The amount of NPs was considered to provide 2.0 wt % of metal on the support. After this step, the slurry was centrifuged and further washed with acetone (3 times, 20 mL each) and dried in an oven at 70°C for 1 h. At the ending of the procedure, the catalysts were stored in amber bottles and placed in the desiccator. The catalysts were named as follows: $\text{Au/Sr}_{\text{sup}}$ (Au NPs stabilized in water) and $\text{Au/calc-Sr}_{\text{sup}}$ (Au NPs stabilized in acetone). The metal content in the catalysts was determined by FAAS.

3.5. Characterization of Catalysts

Transmission electron microscopy (TEM) images were obtained using JEM-2100 microscope (operating at 110 kV, JEOL, Peabody, MA, USA). Samples were prepared by drop casting an isopropanol suspension of the samples over a carbon-coated copper grid, followed by drying under room temperature. Furnace Atomic Absorption Spectroscopy (FAAS) was performed using AA-6300 spectrophotometer (Shimadzu, Kyoto, Japan). The X-ray diffractograms (XRD) were obtained using D8 Advance equipment (Bruker, Billerica, MA, USA) with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) and a graphite monochromator. The voltage of the copper emission tube was 40 kV and the filament current was 40 mA, at a 2θ range from 10° to 90° with a 0.02° step size and measuring the time of 5 s per step. The X-ray photoemission spectra were obtained with a ESCA + spectrometer system equipped with an EA 125 hemispherical analyzer and a XM 1000 monochromated X-ray source (Scientia Omicron, Uppsala, Sweden) in $\text{Al K}\alpha$ (1486.7 eV). The X-ray source was used with a power of 280 W, as the

spectrometer worked in a constant pass energy mode of 50 eV. The phase composition identifications were performed by Rietveld refinement using GSAS EXPGUI 2012 software [26].

3.6. Catalytic Reactions

The oxidation reactions were carried out using a 100 mL Fischer-Porter glass reactor (EMPER, Porto Alegre, Brazil) in solvent-free conditions. The reactor was loaded with the catalysts (4.4 μmol de Au), benzyl alcohol (9.6 mmol), and 2 bar of O_2 . Using a ceramic heating plate with temperature digital controller, the reactions were performed at 100 °C (except when specified) for 2.5 h under magnetic stirring. The products were separated from the catalyst by centrifugation. Then, 5 μL were collected and added to 1 mL of CH_2Cl_2 and 1 μL of the solution was injected into a CG-2010 Plus chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector and a Carbowax capillary column. For the recycling tests, two processes were performed: for base-free reactions, the catalyst was washed once with acetone; for the reactions with K_2CO_3 , the catalyst was washed 3 times with water and once with acetone.

3.7. NPs Surface Cleaning

The NPs surface cleaning was performed based on Lopez-Sanchez et al., with modifications [31]. About 1 g of catalyst was placed in a Soxhlet apparatus with 50 mL of acetone; the system was refluxed in a heating bath set to 90 °C. The process took 12 h. The mixture was centrifuged, washed 3 times with acetone, and dried overnight at 70 °C.

3.8. Basic Strength of the Catalysts

The basic strength of the catalysts (H_-) was determined by using various Hammett indicators [32]. About 100 mg of the materials were shaken with 5 mL of methanolic solutions of the indicators. The solutions were left to stand for 2 h until no color changes were observed. The basic strength is reported as being stronger than the weakest indicator, when a color change is observed, and weaker than the strongest indicator, when there is no color change. The Hammett indicators used were: neutral red ($H_- = 6.8$), bromothymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.3$), 2,4-dinitroaniline ($H_- = 15.0$), and 4-nitroaniline ($H_- = 18.4$).

4. Conclusions

PVA-stabilized gold NPs impregnated on strontium-based supports were amply considered on the studies presented herein. Seemingly, the potential of these materials is not fully explored in the literature. By using Rietveld refinements, we proposed the phase composition of the supports used in our studies, which is highly important to granting the correct characterization of the materials synthesized. The Au/calc- Sr_{sup} catalyst, prepared by support calcination prior to the Au NPs immobilization, presented the best performance. XPS analyses were used and attested metallic gold NPs obtaining, no matter which solvent (water or acetone) was used for the NPs stabilization. Also, such analyses were important, in order to specify the Au atomic concentration that was available for the catalysis. Catalytic tests evidenced that the calcination step was important in the performance, although the NPs size and dispersity may have a decisive effect on the catalytic activity. Correlations between Au/calc- Sr_{sup} and Au/ Sr_{sup} showed that the former presented a narrower size distribution after immobilization, as well as better distribution on the support. The Au/calc- Sr_{sup} catalyst was efficiently used for benzyl alcohol oxidation without base addition. Titration measurements confirmed the intrinsic basicity of the support, a feature that may explain the activity of the catalysts without extra base. However, sub-stoichiometric K_2CO_3 adding was essential for the recyclability of the material. Although the activities are similar with or without the extra base, the stability of the catalyst was only observed when K_2CO_3 was applied in the oxidation system.

Supplementary Materials: The following are available online at <http://www.mdpi.com/xxx/s1>, Figure S1: XPS pattern of the Au/Sr_{sup} catalyst considering the presence of O, Sr, Au, Cl and Na for the at.% calculation, Figure S2: XPS pattern of the Au/Sr_{sup} catalyst disregarding the presence of Cl and Na for the at.% calculation.

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Author Contributions: Edmilson M. de Moura and Marco Aurélio S. Garcia conceived the study; Karla Patrícia R. Castro, Wiury C. de Abreu, and Samuel Anderson A. de Sousa performed the experiments; Carla Verônica R. de Moura contributed with reagents/materials; Jean Cláudio S. Costa contributed with TEM analyses. All the authors contributed to the writing of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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