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Direct Formation of H_2O_2 from H_2 and O_2

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The direct combination of hydrogen and oxygen to form hydrogen peroxide in liquid media with prepared catalysts was carried out in a slurry reactor at atmospheric pressure and room temperature. An O_2/H_2 ratio of 2:1 with a 50 mL/min flow rate was used in these experiments. Catalyst activity measurements were tested by the iodometric titration method using $KMnO_4$. The results are discussed based on the effects of support material, catalyst preparation method, reaction time, and medium (type of halide and acid) on hydrogen peroxide yield in direct oxidation of hydrogen to produce hydrogen peroxide. Our results showed that the catalytic performance of a gold-based catalyst was greatly dependent upon the kind of support material, precipitation conditions, and liquid media used in the reaction. The highest yield in the study was obtained with a co-precipitated 10.7 wt% Au/CeO_2 catalyst in a reaction mixture of 0.25 N H_3PO_4, 0.1 M NaBr, and absolute ethanol.

Key Words: Direct oxidation, hydrogen peroxide, gold catalysts.

Introduction

Hydrogen peroxide is an important oxidizing agent that plays an important role in green chemistry, with water being the only byproduct. H_2O_2 has an increasing utilization as pulp bleach in the pulp and paper industry, as an oxidant in wastewater treatment, and as a source of oxygen for epoxidation reactions.[1,2] H_2O_2 is also an effective reagent in the removal of residual aromatic sulfur compounds from fuels. Currently, the commercial production of H_2O_2 is a circuitous process that involves the catalytic hydrogenation of an anthroquinone and by treatment of hydroquinone with O_2 to produce H_2O_2.[3,4] Despite its production on a multi-million-tonne scale, there are drawbacks to the commercial process, such as the cost of the quinone component and loss of this compound by oxidation.[5] This process, based on the anthraquinone/anthrahydroquinone redox pair, produces significant amounts of organic waste due to the overreduction of anthraquinone, requires several separation and concentration steps, and is economically feasible only in large-scale plants.[6]

As a potentially less expensive and environmentally friendly route to H_2O_2, its direct formation from H_2 and O_2 has been actively investigated over the past 2 decades.[7] The direct oxidation of hydrogen normally is carried out in a 3-phase system that includes a solid catalyst, a liquid phase, and reagent gases. Studies have focused on the catalyst type and the role of the liquid, which may include a solvent, an acid, and a halide.[3]

In the present study direct oxidation of hydrogen with Au-based catalysts for H_2O_2 production was studied. The effects of support material, catalyst preparation method, and quantity of Au on the activity of the catalyst were investigated. In addition to the catalyst properties, the reaction medium, such as acids and halides used, were investigated. It was observed that both catalyst properties and reaction medium have significant effects on H_2O_2 production.

Experimental

Catalyst preparation

Using the co-precipitation method, 5 wt% Au/Al_2O_3 and Au/CuO_x catalysts were prepared. Co-precipitation reactions were performed in a semi-batch system and NaOH was used as the precipitation reagent. The final value of the precipitation pH was kept constant at around 10. For preparing the Al_2O_3-supported catalyst, the precipitate was washed, vacuum dried at 105 °C for 48 h, and calcined in air at 400 °C for 2 h. For preparing the CuO_x-supported catalyst, the precipitate was washed, dried at 110 °C for 24 h, and calcined in air at 800 °C for 3 h.

With an incipient wetness method, 5 wt% Au/SiO_2 catalysts were impregnated using aqueous solutions of precursors. They were dried at 90 °C for 14 h and calcined at 800 °C for 4 h.

The effects of preparation methods were investigated with 5 wt% Au/CeO_2 catalysts prepared by co-precipitation, impregnation + precipitation, impregnation + thermal decomposition, and deposition precipitation methods. All catalysts were dried at 110 °C for 24 h and calcined in air at 650 °C for 5 h. The thermal decomposition method for the preparation of CeO_2 support was performed by the thermal treatment of $Ce(NO_3)_3.6H_2O$ at 650 °C for 4 h.

For preparing the 5 wt% Au/CeO_2 catalyst by the deposition precipitation method, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ was added to a mixture of CeO_2 particles in water. This solution was stirred at room temperature for 10 min and then a solution of NaOH in water (1 M) was added drop-wise until the pH of the solution reached 10. The solution was stirred and maintained at pH 10 for 60 min. The catalyst was then filtered, washed, and dried at 110 °C for 24 h.

All catalysts prepared were reduced under a 100 mL/min hydrogen stream at 400 °C for 6 h before being used in reaction experiments and characterization tests.

Catalyst Characterization

X-ray diffraction (XRD): X-ray powder diffraction patterns were obtained from reduced catalyst samples with a Rigaku D/MAX-Ultima+/PC X-ray diffractor.

Atomic absorption spectroscopy (AAS): The metal loadings of co-precipitated samples were determined using a Varian 250+ atomic absorption spectrometer.

Catalyst Testing

The direct oxidation of hydrogen to hydrogen peroxide reaction over the reduced catalysts was carried out in a mechanically stirred glass reactor (capacity: 500 cm^3) containing 0.5 g of catalyst, 150 cm^3 of ethanol, 30 cm^3 of (0.25 N) acid, and 10 cm^3 of (0.1 M) halide to give 190 cm^3 of reaction medium. The experiments were conducted using a 2:1 O_2/H_2 gas mixture by continuously feeding a hydrogen-oxygen-nitrogen mixture

(20 vol% H_2) at a flow rate of 50 $cm^3.min^{-1}$ through the liquid reaction medium under vigorous stirring at room temperature and atmospheric pressure for a period of 3 h. All extra pure reactants (i.e. O_2 and H_2), inert diluent (N_2), reducing gas (H_2), and purge gas (He) were fed from pressurized gas cylinders. The gas flow rates were controlled by Aalborg DFC digital mass flow controllers.

After the reaction, the catalyst from the reaction mixture was removed by filtration and the filtered reaction mixture was analyzed for the hydrogen peroxide formed in the reaction by iodometric titration using $KMnO_4$.[8]

Results and Discussion

Catalyst Characterization

Freshly reduced co-precipitated Au-based catalyst samples were characterized by XRD to identify metallic Au and support phases. XRD images of co-precipitated Au/CeO_2, Au/CuO_x, and Au/Al_2O_3 catalysts are given in Figure 1a-c.

XRD patterns of reduced 5 wt% Au/CeO_2 and Au/CuO_x catalysts show the presence of metallic Au, while no Au peak was observed for the 5 wt% Au/Al_2O_3 catalyst. The disappearance of Au peaks for the Al_2O_3-supported catalyst may have been the result of a small quantity of Au (as shown in Table 1) and/or small Au particles (< 10 nm) strongly attached to metal oxide supports.[9] Moreover, as shown in Figure 1b, the Cu_2O structure was not observed in the Cu oxides-based catalyst; therefore, the Au/CuO_x catalyst was denoted as Au/CuO in the next sections.

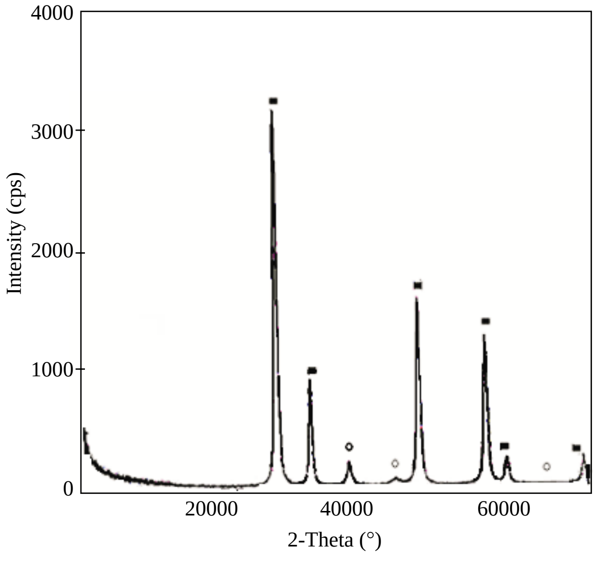

Figure 1a. XRD pattern of the 5 wt % Au/CeO_2 catalyst prepared by co-precipitation method (■ CeO_2, ○ Au).

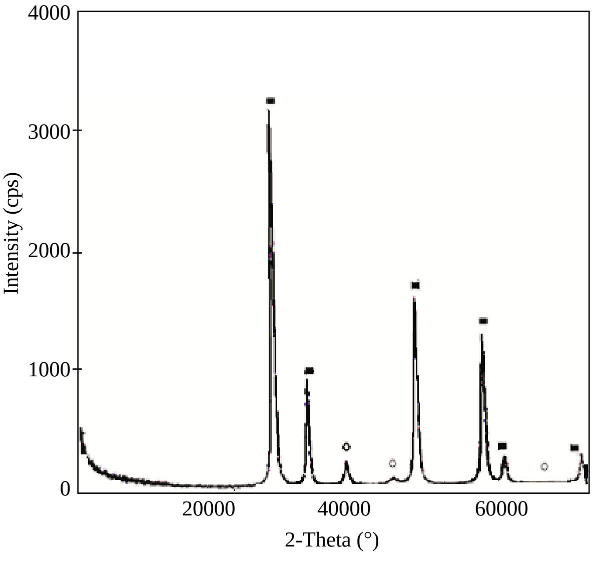

Figure 1b. XRD pattern of the 5 wt % Au/CuOx catalyst prepared by co-precipitation method.

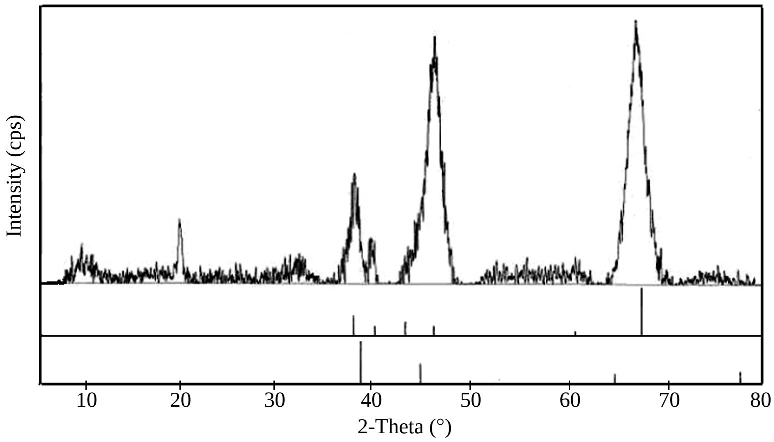

Figure 1c. XRD pattern of the 5 wt % Au/Al_2O_3 catalyst prepared by co-precipitation method.

These catalysts were tested using AAS to obtain information on their metal loading properties. Table 1 presents the aimed and measured Au loadings. Although starting with the same amount of Au precursor, aiming 5 wt% Au in the final catalyst, different Au loadings on the co-precipitated catalysts were observed. The reason for this result was the different yields of the co-precipitation reactions, which were mostly related to precipitation pH and temperature affecting the precipitation rates, and the relative amounts of the hydroxides.

Table 1. The metal loadings of co-precipitated Au-based catalysts.

Catalyst	Aimed Au wt %	Measured Au wt %
Au/Al_2O_3	5	0.2
Au/CeO_2	5	10.7
Au/CuO	5	1.9

Effect of Support Materials

To obtain 5 wt% Au-containing catalysts, 4 types of supports, Al_2O_3, CeO_2, CuO, and SiO_2, were used. Table 2 shows the effect of support materials on H_2O_2 concentration of the product solution after 3-h reaction periods of direct oxidation of hydrogen. Since all reaction conditions were the same for all experiments, H_2O_2 wt% of the product solution was directly related to the H_2O_2 yield. The results showed that the CeO_2-supported Au catalyst prepared by the co-precipitation method had the highest yield for the synthesis of hydrogen peroxide. Since the total metal loading of the co-precipitated ceria-based catalyst was higher than the others, another 5% Au/CeO_2 catalyst was prepared by impregnation and tested in the synthesis reaction. As shown in Table 2, similarly, the highest result was obtained compared to the co-precipitated catalyst. Therefore, it was concluded that ceria is an encouraging support for the rest of the study.

In order to investigate the effect of the reduction treatment of the catalysts prepared, the 5 wt% Au/CeO_2 catalyst prepared by impregnation was used in a direct oxidation reaction without a reduction in the hydrogen atmosphere. The reduced catalyst showed enhanced hydrogen peroxide production when compared to its unreduced counterpart.

Table 2. Performance of catalysts prepared using different support materials (reaction medium: absolute ethanol, 0.25 N H_2SO_4, and 0.1 M NaBr).

Catalyst	Preparation Method	H_2O_2 (wt%)
5% (0.2%)*Au/Al_2O_3	Co-precipitation	0.1
5% (1.9%)*Au/CuO	Co-precipitation	0.1
5% Au/SiO_2	Impregnation	0.2
5% Au/CeO_2	Impregnation	0.6
5% (10.7%)*Au/CeO_2	Co-precipitation	1.2
5% Au/CeO_2^{**}	Impregnation	0.1

*measured loadings; **unreduced catalyst

Effect of Catalyst Preparation Methods

The preparation method is a very important factor related to obtaining high-performance Au catalysts. Previous studies by Haruta et al. revealed that co-precipitation and deposition-precipitation can lead to a high-dispersion of Au over metal oxide supports, compared to impregnation.[10,11] In order to investigate the effect of preparation method on the performance of 5 wt% Au/CeO_2 catalysts in the direct synthesis of H_2O_2, catalysts were prepared by co-precipitation, deposition precipitation, and incipient wetness impregnation methods. Moreover, 2 different ceria supports were prepared by precipitation and thermal decomposition methods for the impregnation procedure.

Table 3. Performance of catalysts prepared using different preparation methods (reaction medium: absolute ethanol, 0.25 N H_3PO_4, and 0.1 M NaBr).

Catalyst (5 wt%)	Preparation Method	H_2O_2(wt%)
Au/CeO_2	Co-precipitation	1.2
Au/CeO_2	Impregnation + precipitation	0.1
Au/CeO_2	Impregnation + thermal decomposition	0.5
Au/CeO_2	Deposition precipitation	0.7

The highest hydrogen peroxide formation was observed with the catalyst prepared by co-precipitation. Catalysts prepared by impregnation showed a lower performance than expected, although the catalyst prepared using ceria support and the thermal decomposition method gave slightly closer values to the one prepared by deposition precipitation.

Effect of the Amount of Au

We also investigated the effect of the quantity of Au on ceria- and silica-supported catalysts in the production of hydrogen peroxide. As shown in Figure 2, CeO_2 support alone is active in the oxidation of H_2 to H_2O_2, and the addition of Au to the monometallic catalyst decreased H_2O_2 production. Observing higher H_2O_2 production with ceria was mainly related to its changes in its oxidation state with the formation/annihilation of surface defects (oxygen vacancies). These redox properties can be substantially modified by incorporation of metals on the ceria surface, as well as by the presence of counter-anions of the precursor metal salts, which are incompletely decomposed by the procedures typically used for the preparation of the catalysts.[12]

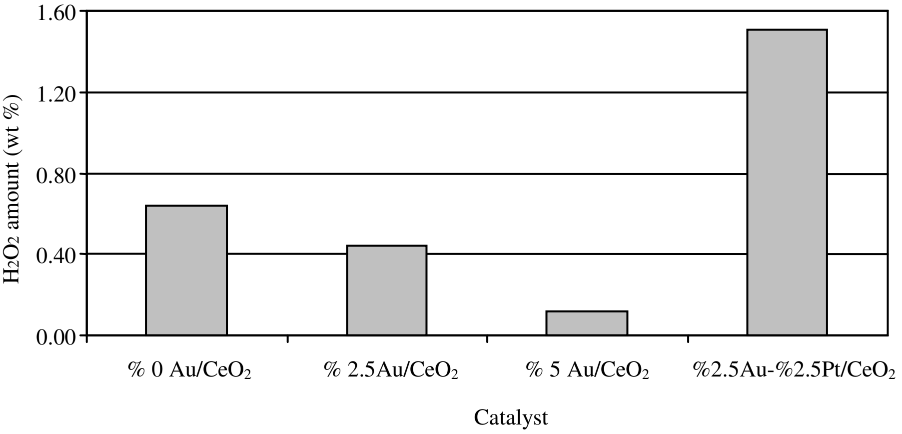

Figure 2. Performance of catalysts prepared using different quantities of Au with CeO_2 support (reaction medium: absolute ethanol, 0.25 N H_3PO_4, and 0.1 M NaBr).

Addition of Pt to Au catalysts, as shown in Figures 2 and 3, considerably improved hydrogen peroxide formation, meaning that Pt is more active than Au for this reaction. However, comparing the activity of the 2.5% Au-2.5% Pt/SiO_2 catalyst to the 5% Pt/SiO_2 catalyst, it can be concluded that the addition of Au to Pt catalysts may improve the performance of Pt catalysts in the direct production of hydrogen peroxide. Furthermore, it may be speculated that Pt and Au remain intimately mixed in the form of Pt-Au bimetallic particles and that the presence of Au in these particles modifies the behavior of Pt.[13]

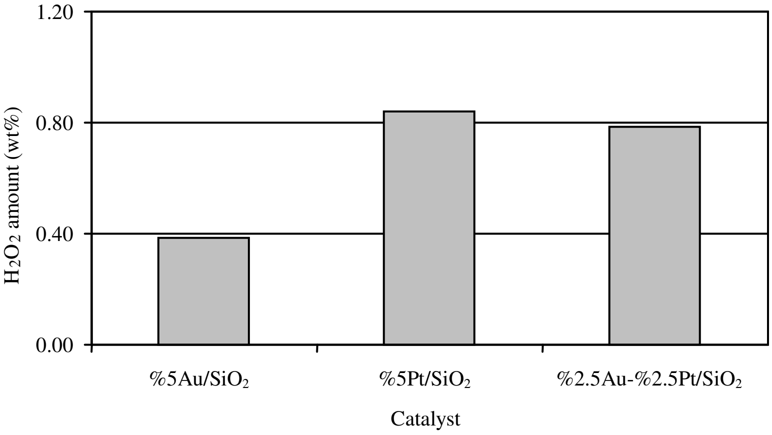

Figure 3. Performance of catalysts prepared using different quantities of Au with SiO_2 support (reaction medium: absolute ethanol, 0.25 N H_3PO_4, and 0.1 M NaBr).

Influence of Acids and Halides Added to the Reaction Medium

For the promotional effect, the presence of acid (protons) in the reaction medium is crucial for the direct oxidation of hydrogen to produce hydrogen peroxide.[14] The presence of acid in the reaction medium significantly reduces the H_2O_2 decomposition activity of the catalyst and acts as a stabilizer for the H_2O_2 formed in the reaction.

The effects of acids and halides on hydrogen peroxide formation were investigated for 5 wt% Au/SiO_2 and 5 wt% Au/CeO_2 catalysts, using 3 different acids and halides with the same reaction conditions. Results showing the effect of acids on the performance of the SiO_2- and CeO_2-supported Au-based catalysts are presented in Figures 4 and 5. An interesting situation was observed in that H_3PO_4 was the most favorable acid for silica-based catalysts, while H_2SO_4 was the most favorable for ceria-based catalysts. The presence of an acid in the reaction medium is essential for obtaining high H_2O_2 selectivity or yield, since the role of the acid is to prevent the base-catalyzed decomposition of H_2O_2.[15] However, there is no direct correlation found in the literature between the catalyst components and acid type. It is known that the sulfate and chloride ions poison the catalyst when ethanol is used in liquid phase for silica-supported catalysts.[15] Yet, it seems that 2 ionizable hydrogens in sulfuric acid prevented H_2O_2 decomposition for the ceria-supported catalyst compared to phosphoric acid, which has less acid strength.

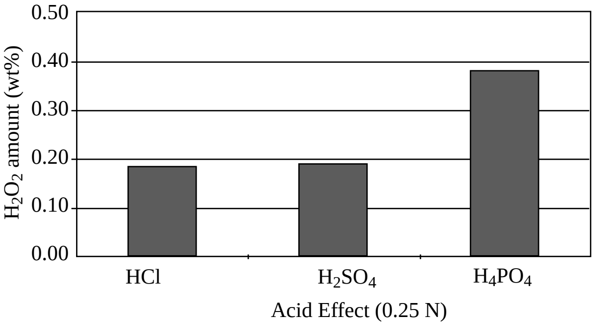

Figure 4. Effect of acids on performance of 5%Au/SiO_2.

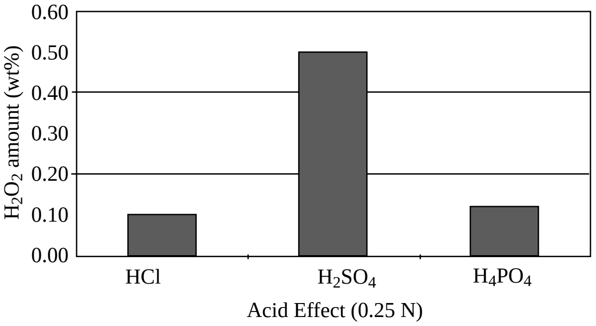

Figure 5. Effect of acids on performance of 5%Au/CeO_2.

In order to observe the effects of Br^- ions in the reaction medium for 5 wt% Au/SiO_2 and 5 wt% Au/CeO_2 catalysts, reactions were performed with liquid mixtures containing KBr, NaBr, and non-halide solutions. From Figures 6 and 7 it can be seen that the addition of Br^- ions, especially NaBr, to the reaction medium significantly enhanced H_2O_2 formation, compared to both silica- and ceria-supported Au-based catalysts.

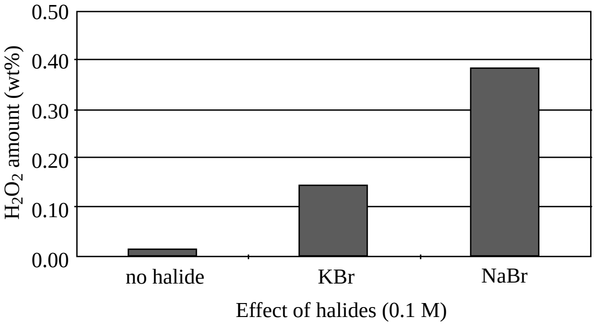

Figure 6. Effect of halides on performance of 5%Au/SiO_2(ethanol+0.25 N H_3PO_4 and 0.1 M halide).

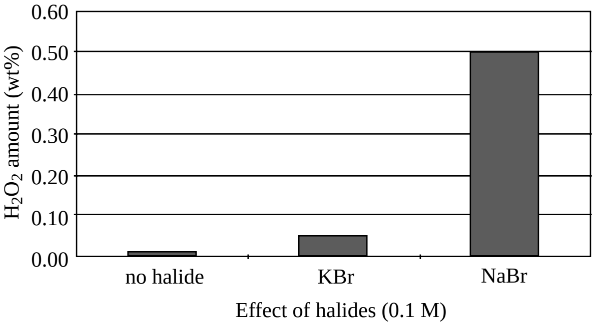

Figure 7. Effect of halides on performance of 5%Au/CeO_2 (ethanol+0.25 H_2SO_4 and 0.1 M halide).

Conclusions

Au catalysts were effective for the direct oxidation of hydrogen to form hydrogen peroxide. Nonetheless, it was found that their activities were greatly dependent on the type of support material, catalyst preparation conditions, and liquid media used in the reaction. The highest yield for the catalysts studied was obtained with the co-precipitated 5 wt% Au/CeO_2 catalyst in a reaction mixture of 0.25 N H_2SO_4, 0.1 M NaBr, and absolute ethanol. Additionally, it was concluded that adding Pt to Au-based catalysts had a great influence on H_2O_2 formation.

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