Direct Synthesis of H_2O_2 from H_2 and O_2 over Carbon Supported Au, Pd and Au-Pd/C Bimetallic Catalysts

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The direct synthesis of hydrogen peroxide from hydrogen and oxygen using Pd/C, Au/C and bimetallic Au-Pd/C in a batch reactor was investigated and the kinetic curves have been obtained. Mesoporous carbon (Sibunit) was used as a support in the forms of oxidized and non-oxidized states. The presence of two metals (Pd, Au) on the carbon support enhances the catalytic performance compared to both Pd/C and Au/C catalysts in the case of non-oxidized and oxidized Sibunit. The enhancements become more apparent as the reaction time increases. Pre-oxidizing of the catalytic support also affects the catalytic performance of both the bimetallic Au-Pd/C and monometallic Pd/C catalysts for the direct synthesis of hydrogen peroxide. In the case of the monometallic Pd/C catalyst, when a pre-oxidized support, was used, the catalytic activities of the production of hydrogen peroxide and water increase in the same order of magnitude. Additionally, the pre-oxidized sibunit enhances the yield considerably. Nonetheless, the selectivity changes were found to be minimal. For the bimetallic Au-Pd/C catalysts, the behaviour was the opposite: the use of a pre-oxidized support increases the selectivity and consequently the catalytic performance for the synthesis of hydrogen peroxide, by reducing the production of water.

1. Introduction

Hydrogen peroxide (H_2O_2) is one of the most powerful and environmentally friendly known oxidizers with a wide range of applications in pulp bleaching, waste water treatment, cosmetic and pharmaceutical industries. The main commercial method to produce hydrogen peroxide is the athraquinone auto-oxidation method. This method is economically viable only for large-scale production and high concentrations of hydrogen peroxide (Edwards and Hutchings, 2008). Because of high investment and operating costs, it is not economically rational to produce hydrogen peroxide on-site at the end users sites. The simplest method to produce hydrogen peroxide and main competitor for the anthraquinone method is the direct catalytic synthesis of hydrogen peroxide from elemental hydrogen and oxygen. The direct method suffers from two

serious technical challenges. Firstly, the safety problem: mixtures of hydrogen and oxygen are explosive over a wide range of concentrations (4-94 % H_2 in O_2) (Edwards and Hutchings, 2008). Secondly, the selectivity problem: supported Pd catalyst is the main catalyst for this reaction but it is also active for the other undesired reactions (see Scheme 1) - Samanta, 2008. Therefore, water is also produced in addition of hydrogen peroxide. Because of these two reasons, the direct method has not been commercialized yet even though it has been widely studied (Edwards and Hutchings, 2008).

$$H_2 \xrightarrow{+ O_2} H_2O_2 \xrightarrow{+ H_2} 2\ H_2O$$
$$H_2O_2 \longrightarrow H_2O + 0.5\ O_2$$
$$H_2 \xrightarrow{+ 0.5\ O_2} H_2O$$
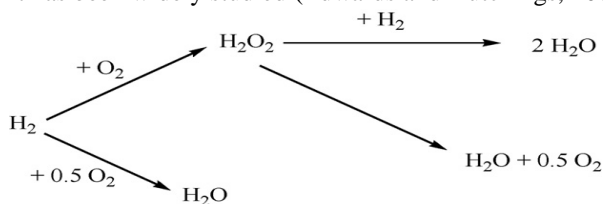
Scheme 1: Reactions involved in the direct synthesis of H_2O_2 [2]

The first problem may be avoided by working below the explosion limit or by using catalytic membranes to separate the gases. Microreactors might offer another way to eliminate the safety problem. The selectivity could be increased by using bimetallic catalysts or proper promoters, e.g. acidic solution and halide ions. Adding halide ions to an acidic reaction medium or directly to the catalyst has been shown to enhance H_2O_2 selectivity and yield over supported Pd catalysts (Samanta, 2008; Samanta and Choudhary, 2007a; Samanta and Choudhary, 2007b) and less active supported Au-Pd catalysts (Ntainjua et al, 2009). It has been reported that supported Au-Pd bimetallic catalysts are more active than Pd and Au monometallic catalysts for direct synthesis of hydrogen peroxide from H_2 and O_2 (Edwards and Hutchings, 2008).

Direct synthesis of hydrogen peroxide using gold and gold –palladium on a carbon support (Sibunit) is studied in this paper. The results are also compared with carbon supported palladium catalyst.

2. Experimental

2.1 Materials and Catalyst Preparation

Sibunit was used as the catalyst support in this study. It is a new class of porous carbon-carbon composite materials combining advantages of graphite (chemical stability and electric conductivity) and active carbons (high specific surface area and adsorption capacity) - Simakova et al, 2008. These composites are characterized by high mesopore volume and specific surface area ($S_{BET} = 450$ m^2/g). Catalysts on both non-oxidized and pre-oxidized carbon were prepared almost with the same procedure. The only difference was that when pre-oxidized Sibunit was used, the support was inmersed in 5 wt.% nitric acid at room temperature and let to stay overnight.

Preparation of Au on carbon was started by dissolving $HAuCl_4$ (ABCR, Darmstad, 49% Au) in deionized water, then polyvinylalcohol was added to form gold sol (Prati and Porta, 2005). After a few minutes of mixing, gold sols were reduced by freshly prepared 0.1 M $NaBH_4$ solution. The ruby red Au(0) sols were immobilized immediately by

adding the carbon support (Sibunit) under vigorous stirring in the amount corresponding to 2.5 wt.% Au/C. After 2 h the slurry was filtered and washed with deionized water. The catalyst was dried overnight at 60 °C.

Preparation of Pd on carbon was started by mixing with alkali solution of Na_2CO_3 at pH 8 (Simakova et al., 2008) After that aqueous solution of H_2PdCl_4 was added in the amount corresponding to 2.5 wt.% Pd/C. The slurry was mixed overnight at room temperature, then filtered and washed with deionized water. The catalyst was reduced in hydrogen flow at 150°C.

Au-Pd-catalyst on carbon was prepared by a two-steps procedure (Prati et al, 2007). First, $HAuCl_4$ (ABCR, Darmstad, 49% Au) was dissolved in deionized water was mixed with polyvinylalcohol to form a gold sol, then after a few minutes of mixing, the sol was reduced by freshly prepared 0.1 M $NaBH_4$ solution and immobilized immediately by adding carbon support under vigorous stirring in the amount corresponding to 2.5 wt. % Au/C. After 2 h of mixing at room temperature the slurry was filtered and washed with deionized water. The obtained slurry was mixed with a palladium sol, formed by mixing aqueous solution of H_2PdCl_4 with polyvinylalcohol and hydrogen bubbled at room temperature (50 mL/min) for 2 h. Then the slurry was mixed in air atmosphere overnight, filtered and washed with water. The catalyst was dried at 60°C. The catalysts were after each step of deposition (Au, Pd) by $NaBH_4$ and by bubbling H_2.

2.2 Experimental set-up

The direct synthesis of hydrogen peroxide was carried out in a stainless steel autoclave (Parr Instruments Ltd) with a nominal volume of 600 ml and a maximum working pressure of 140 bar. The autoclave was equipped with an overhead stirrer (0–2000 rpm) and facilities to measure the temperature and pressure. Hydrogen was fed into the main reactor through a pre-reactor with a volume of 35 ml and by means of a mass flow controller. The pre-reactor was used to measure the precise amount of hydrogen fed to the system. A recirculation line containing a six-way valve was used for sampling. Typically, the reactor was charged with 31-32 mg of catalyst and successively with carbon dioxide up to 15.2 bars. The pressure was thereafter elevated to 20.2 bar with oxygen and further to 35.2 bar with carbon dioxide again. 175 g of methanol were pumped in and the reactor was cooled down to -1 °C. Stirring (1250 rpm) began after 2/3 of the methanol was fed. When the desired temperature was reached, hydrogen was charged and the reaction time was started.

3. Results and Discussion

In order to evaluate the activity of the catalysts, the following two parameters were calculated:

$$Yield\,(\%) = \frac{Moles\,of\,produced\,H_2O_2}{Moles\,of\,H_2\,\,fed} \times 100$$

$$Selectivity(\%) = \frac{Moles\,of\,produced\,H_2O_2}{Moles\,of\,produced\,H_2O_2 + Moles\,of\,produced\,H_2O} \times 100$$

3.1 The effect of adding Pd to carbon supported Au catalyst:

Fig.1 shows the selectivity and yield of the catalysts versus reaction time when non-oxidized Sibunit is used as a support. Selectivity of the bimetallic Au-Pd/C catalyst is higher than the pure Pd/C catalyst, especially when the reaction time is between 15 to 90 min. Au/C catalyst is much more selective than the bimetallic Au-Pd/C and Pd/C catalysts as it produces less water. On the basis of the yield, the catalysts perform differently. The yield for the bimetallic Au-Pd/C catalyst is much higher than for both monometallic catalysts, especially at higher reaction times.

Fig.2 displays the selectivity and yield when pre-oxidized Sibunit is used as a support. Adding Pd to the Au/C catalyst increases selectivity and yield significantly. The enhancements in selectivity and yield for bimetallic Au-Pd/C compared to Pd/C were higher than when non-oxidized carbon was used. In the other words, in the case of the oxidized carbon, the bimetallic Au-Pd/C catalyst is much more selective than monometallic Pd/C catalyst.
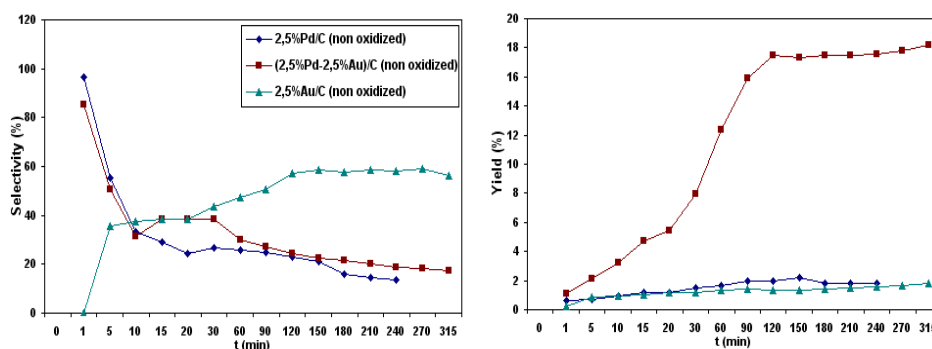

Figure 1. The selectivity and the yield of 2.5 % Au/C, 2.5% Pd/C and 2.5 %Au-2.5 % Pd/C (non-oxidized state of Sibunit was used as the support) for the direct synthesis of H_2O_2
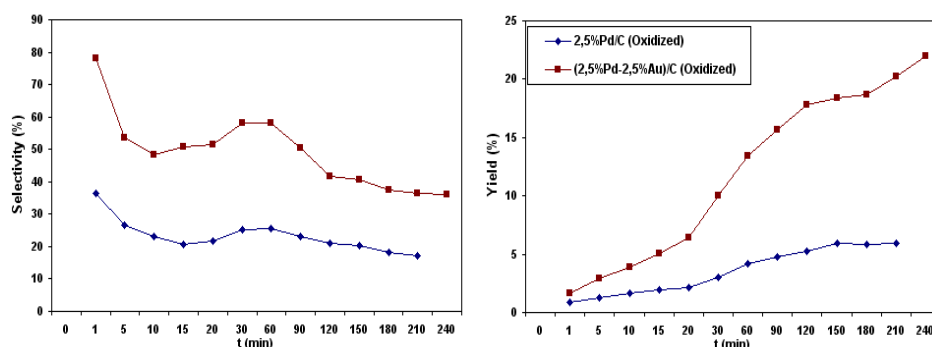

Figure 2.The selectivity and the yield of 2.5 % Pd/C and 2.5 % Au-2.5 % Pd/C (oxidized state of Sibunit was used as the support) for the direct synthesis of H_2O_2

3.2 The effect of support oxidation:

Pre-oxidizing Sibunit enhances the yield for Pd/C catalyst in the direct synthesis of hydrogen peroxide considerably (especially at higher reaction times), slightly diminishing the selectivity at lower reaction times (Fig. 3). This is because pre oxidizing the support increases the catalytic activity of pure Pd/C in the production of both hydrogen peroxide and water by almost the same order of magnitude. Therefore, the yield increases dramatically but the selectivity does not change that much.

Pre-oxidizing of the support for bimetallic Au-Pd/C catalyst made the catalyst more selective decreasing the production of water. It did not have any effect on the activity of the catalyst in the generation of hydrogen peroxide. Therefore, selectivity is increased considerably, especially at the higher reaction times and slightly the yield (Fig. 4)
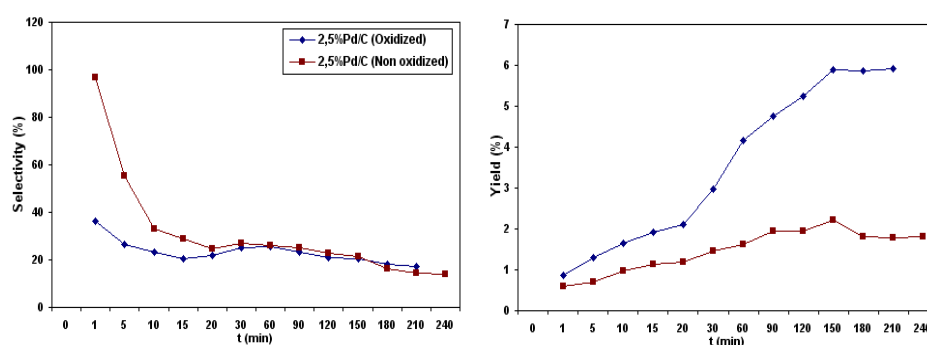

Figure 3.The effect of oxidizing state of the support on the selectivity and the yield of the 2.5%Pd/c for the direct synthesis of H_2O_2
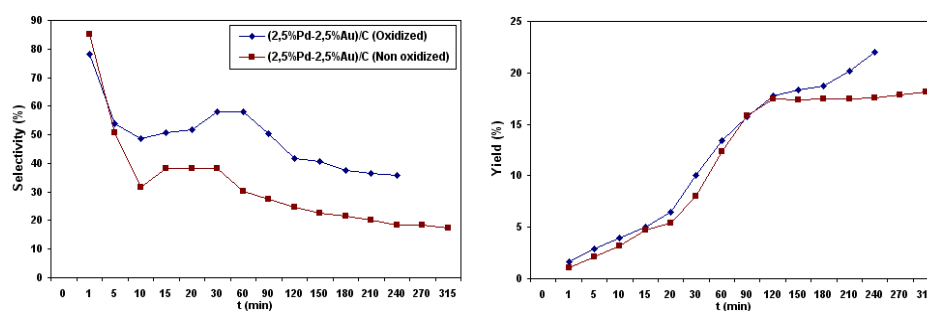

Figure 4. The effect of support oxidation on the selectivity and the yield of 2.5 % Au-2.5 % Pd/C for the direct synthesis of H_2O_2

The better results obtained with the bimetallic catalyst, (Au-Pd)/C, compared to the monometallic Pd/C and Au/C could be related with the properties of the different metals for oxidized supports. Moreover, the higher nominal metal loading (5 wt.% for the bimetallic catalyst vs. 2.5 wt.% for the monometallic ones) certainly has an effect on the catalytic activity. In addition, when oxidizing the support, different functional groups on

the external and porous surface of the Sibunit could be formed. These groups are likely to be surface oxygenated groups that have an acidic character which can influence the activity and selectivity in the hydrogen peroxide direct synthesis. It is expected that the different metals behave differently depending on the type of the support as well. Nonetheless, a more detailed characterization study is needed in order to reveal the structural differences between the oxidized and non-oxidized supports as well as the behaviours of the metals on them.

4. Conclusion

This study shows that bimetallic Au-Pd/C is more active in the direct synthesis of H_2O_2 than monometallic Pd/C and Au/C catalysts especially at higher reaction times. Pre-oxidizing of mesoporous carbon support (Sibunit) also enhances the catalytic performance of both Pd/C and bimetallic Au-Pd/C catalysts in the direct H_2O_2 synthesis considerably. Pre-oxidizing the support in the case of Pd/C increases the production of both hydrogen peroxide and water by almost the same order of magnitude, while for bimetallic Au-Pd/C catalyst on this support the water production is diminished without any considerable effect on the production of hydrogen peroxide.

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