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Direct synthesis of hydrogen peroxide from H₂ and O₂ using zeolite-supported Au-Pd catalysts

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Abstract

The direct synthesis of hydrogen peroxide from H_2 and O_2 using zeolite-supported Au-Pd catalysts is described using two zeolites, ZSM-5 and zeolite Y, using an impregnation method of preparation. The addition of Pd to Au for these catalysts significantly enhances the productivity for hydrogen peroxide. The use of zeolites as a support for Au-Pd gives higher rates of hydrogen peroxide formation when compared with aluminasupported Au catalysts prepared using a similar method. The addition of metals other than Pd is also investigated, but generally Au-Pd catalysts give the highest activity for the synthesis of hydrogen peroxide. The addition of Ru and Rh have no significant effect, but the addition of Pt does enhance the activity for the selective formation of hydrogen peroxide.

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1. Introduction

In recent years the direct oxidation of hydrogen with dioxygen has started to receive renewed attention since the observation that supported Au-Pd alloys can act as effective catalysts for this reaction [1]. Indeed, this direct oxidation reaction has fascinated scientists and engineers for almost a century. It represents a major challenge in the control of reaction selectivity, perhaps representing one of the most significant challenges, since the direct oxidation to form water, as well as the subsequent loss of hydrogen peroxide through hydrogenation or decomposition are thermodynamically favoured and are often kinetically favoured as well when contrasted with hydrogen peroxide synthesis. Against this background it is not surprising that there is as yet no commercial process for this reaction, and industrial synthesis of hydrogen peroxide uses the sequential hydrogenation and oxidation using anthraquinone as the hydrogen carrier [2]. The direct reaction has been studied for many years and until recently the catalysts used in these investigations have been based on Pd [3-13]. However, there has been renewed interest in the direct synthesis and very recently we have shown that alumina-supported Au and Au-Pd alloy catalysts are effective for this reaction when supported on Al₂O₃, TiO₂ and Fe₂O₃ [1,13–15]. Haruta and co-workers have also shown that supported Au catalysts are active for this reaction and, in particular, Au/SiO₂ has been found to be the most active catalyst for the direct synthesis reaction compared with other supports in their studies [16]. This study was recently extended by Ishihara et al. [17] and it is considered that the high rate of hydrogen peroxide synthesis observed with Au/SiO₂ is due to the decomposition reactions being minimised with this support. Zeolites and microporous materials have been extensively studied as supports for Pd and Pt catalysts for the direct synthesis of hydrogen peroxide [10,18–26]. Most recently we have shown that using zeolite H-Y and H-ZSM-5 as supports for Au only catalysts leads to an enhancement in the activity when contrasted with Al_2O_3 and SiO_2 as supports [27]. In this paper we extend our earlier studies concerning the mono-metallic Au/ zeolite catalysts using zeolites H-ZSM-5 and H-Y as supports and now we demonstrate the effect of the addition of Pd and other metals to the Au-supported catalysts.

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2. Experimental

2.1. Catalyst preparation

Supported Au, Pd and Au-Pd catalysts were prepared using impregnation via an incipient wetness method using an aqueous solutions of HAuCl₄·3H₂O (Johnson Matthey) and PdCl₂ (Johnson Matthey). This method of preparation was selected to ensure that a comparison could be made with the data obtained in our previous studies [13–15]. In the previous studies this preparation methodology has been found to lead to relatively large particle sizes (>20 nm) and we anticipate that when using zeolites as supports the Au-Pd nanoparticles that are formed will not be present within the pore structure of the support. For example, the preparation of a catalyst with a nominal concentration of 2.5 wt.% Au was as follows, and for other concentration appropriate amounts of the metal salts were used. An aqueous solution of HAuCl₄·3H₂O (10 ml, 5 g dissolved in water (250 ml) was added to the support (3.8 g). Three supports were used namely, y-alumina (Condea SCF-140), zeolite HZSM-5 (Grace ZL5201, $SiO_2/Al_2O_3 = 45$, total BET surface area 424 m²/g) and zeolite USY (Grace ZL5100, SiO₂/ $Al_2O_3 = 6$, total BET surface area 760 m²/g). The paste formed was ground and dried at 95 °C for 16 h and some samples were also calcined (400 °C) in static air for 3 h.

2.2. Catalyst testing

Hydrogen peroxide synthesis was performed using a Parr Instruments stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 14 MPa. The autoclave was equipped with an overhead stirrer (0-2000 rpm) and provision for measurement of temperature and pressure. Typically, the autoclave was charged with catalyst (0.01 g unless otherwise stated), solvent (5.6 g MeOH and 2.9 g H_2O) purged three times with CO_2 (3 MPa) and then filled with 5% H_2/CO_2 and 25% O_2/CO_2 to give a hydrogen to oxygen ratio of 1:2, at a total pressure of 3.7 MPa at 20 °C. Stirring (1200 rpm) was started on reaching the desired temperature, and experiments were run for 30 min. Gas analysis for H₂ and O₂, was performed by gas chromatography using a thermal conductivity detector and a CP-Carboplot P7 column (25 m, 0.53 mm i.d.). Conversion of H₂ was calculated by gas analysis before and after reaction. H₂O₂ yield was determined by titration of aliquots of the final filtered solution with acidified $Ce(SO_4)_2$ (7 × 10⁻³ mol/l). $Ce(SO_4)_2$ solutions were standardised against (NH₄)₂Fe(SO₄)₂·6H₂O using ferroin as indicator.

3. Results and discussion

Au-Pd catalysts supported on the zeolites were prepared using impregnation and these were evaluated for the synthesis of H_2O_2 after the catalysts had been dried or calcined at 400 °C. We selected H-ZSM-5 and zeolite H-Y as standard examples of zeolites with different Si:Al ratios and pore sizes. We selected the impregnation method so that our preparation methodology was consistent with our earlier studies with alumina, titania and

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The effect of the addition of Pd to replace gold on the performance of the supported catalysts in the synthesis of H_2O_2

Catalyst	Preparation method	H ₂ O ₂ productivity (mol/kg(cat)/h)
4.3 wt.% Au/HZSM-5	Dried	4.73
2.5 wt.% Au + 1.8 wt.% Pd/HZSM-5	Dried	138.3
2.5% Au/HZSM-5	Dried	0.5
4.3 wt.% Au/HZSM-5	400 °C, 3 h	1.75
2.5 wt.% Au + 1.8 wt.% Pd/HZSM-5	400 °C, 3 h	101.6
2.5% Au/HZSM-5	400 °C, 3 h	0.69
4.3 wt.% Au/Y	Dried	3.61
2.5 wt.% Au + 1.8 wt.% Pd/Y	Dried	131.1
2.5% Au/Y	Dried	0.95
4.3 wt.% Au/Y	400 °C, 3 h	2.99
2.5 wt.% Au + 1.8 wt.% Pd/Y	400 °C, 3 h	78.2
2.5% Au/Y	400 °C, 3 h	1.02

iron oxides as supports [13-15]. The results are shown in Table 1. Rates of hydrogen peroxide formation are determined after the reaction has been carried out in the autoclave for 30 min. These rates are a composite of the synthesis of hydrogen peroxide and its decomposition. In a previous study [13], we have shown that the reaction data can be compared at 30 min reaction time as the effects of decomposition are minimal in this time period. The reaction conditions we have selected have been found to be optimal in our previous studies [1,13–15], as the use of dilute reactants at 2 °C has been observed to give the smallest loss of hydrogen peroxide through sequential hydrogenation. Data have been published previously using alumina as support under comparable conditions [1,13]. It is apparent that the zeolite-supported catalysts give high rates of hydrogen peroxide synthesis and when compared with the alumina-supported catalysts they give higher rates since our previous studies the productivities for hydrogen peroxide synthesis are typically ca. 20 mol H₂O₂/kg(cat)/h, whereas with the zeolite-supported catalysts are about a factor of 5 higher for the calcined catalysts. Higher yields for hydrogen peroxide are found with the catalysts prepared by impregnation but with only a drying step, i.e. no calcination step is included. However, these catalysts are found to leach significant amounts of Au from the catalyst and cannot be reused successfully. This has been observed with other supports and is described more fully in our previous studies using TiO₂ and Fe₂O₃ as supports [14,15]. Catalysts calcined at 400 °C are stable and can be reused effectively.

With the zeolite-supported catalysts the addition of Pd to Au, or the replacement of some of the Au with Pd leads to a major enhancement in the yield of hydrogen peroxide. Indeed the effect is much more marked than that observed with Al_2O_3 , TiO_2 or Fe_2O_3 as supports [1,13–15] and for the data presented in Table 1 an enhancement by a factor of ca. 50 is observed. We considered that the effect may have been related to decreased decomposition of the hydrogen peroxide produced over the zeolite-supported catalysts. However, in tests using Au-Pd catalysts supported on zeolites we found that the zeolite-supported catalysts had an enhanced activity for hydrogen peroxide decomposition under

Table 2Hydrogen peroxide decomposition data

Catalyst	Reaction temperature (°C)	Hydrogen peroxide decomposition (%)
2.5 wt.% Au/Y	2	6.7
2.5% Au-2.5% Pd/Y	2	12.7
2.5% Au-2.5% Pd/Y	20	48.6
2.5% Au-2.5% Pd/HZSM-5	2	47.3
2.5% Au-2.5% Pd/HZSM-5	20	57.8

Reaction conditions: methanol 5.6 g, water 2.9 g, 0.5 wt.% H_2O_2 , catalyst 10 mg, 5% H_2/CO_2 420 psi, time 0.5 h.

Table 3

The effect of reaction temperature on the synthesis of hydrogen peroxide

Catalyst ^a	Reaction temperature (°C) ^b	Productivity (mol-H ₂ O ₂ /g(cat)/h)
2.5% Au/Y	2	0.81
2.5% Au/Y	20	0.75
2.5% Au-2.5% Pd/Y	2	88.9
2.5% Au-2.5% Pd/Y	20	35.0
2.5% Au-2.5% Pd/Y	40	4.2
2.5% Pd/Y	2	83.9
2.5% Pd/Y	20	38.3
2.5% Pd/Y	40	5.8
2.5% Au-2.5% Pd/HZSM-5	2	52.3
2.5% Au-2.5% Pd/HZSM-5	20	71.7
2.5% Au-2.5% Pd/HZSM-5	40	23.7

^a Catalysts were calcined at 400 °C for 3 h before being used in the reaction. ^b *Reaction conditions*: methanol 5.6 g, water 2.9 g, catalyst 10 mg, 5% $H_2/$

 $\rm CO_2$ 420 psi, 25% $\rm O_2/\rm CO_2$ 150 psi, time 0.5 h.

reaction conditions. Hence the enhancement in yield must be due to an increase in the activity of the zeolite-supported catalysts.

The effect of the addition of Pd to Au in enhancing the yield of hydrogen peroxide is sensitive to the amount of Pd and slightly lower yields are obtained when 2.5% Au-2.5% Pd catalysts are used in comparison with 2.5% Au-1.8% Pd catalysts (Tables 1 and 3). We have investigated the use of higher reaction temperatures with the zeolite-supported catalysts but in general lower yields of hydrogen peroxide are obtained at 20 °C (Table 3). However, an enhancement in the yield of hydrogen peroxide is observed for the Au-Pd/ZSM-5 catalyst at 20 °C. We have also investigated the use of

Table 4 Effect of reaction solvent on the synthesis of hydrogen peroxide

Catalyst	Solvents	Productivity (mol-H ₂ O ₂ /h/kg(cat))
2.5% Au/Y	Methanol + water	0.75
2.5% Au/Y	Acetone + water	0.38
2.5% Au/Y	Water	0.29
2.5% Au-2.5% Pd/Y	Methanol + water	35.0
2.5% Au-2.5% Pd/Y	Acetone + water	50.8
2.5% Au-2.5% Pd/Y	Water	11.9

Catalysts were calcined at 400 °C for 3 h before being used in the reaction. Reaction conditions: catalyst 10 mg, 5% H_2/CO_2 420 psi, 25% O_2/CO_2 150 psi, time 0.5 h, temperature 20 °C.



Fig. 1. Performance of 2.5 wt.% metal/Y for the synthesis of H_2O_2 , the 2.5 wt.% Au and Pd catalysts are also shown. Reaction condition: Methanol 5.6 g, water 2.9 g, catalyst 10 mg, 5% H_2/CO_2 420 psi, 25% O_2/CO_2 150 psi, temperature 2 °C, reaction time 0.5 h.

acetone as a solvent in place of methanol (Table 4). Acetone/ water mixtures can give higher yields, and it is important to note that no products of the oxidation of acetone or methanol are observed under these low reaction temperature conditions.

In a final set of experiments the replacement of Pd with other metals has been investigated. The results (Fig. 1) show that addition of Ru or Rh has no marked effect within experimental error. However, the addition of Pt has a marked enhancement in the yield of hydrogen peroxide which is consistent with earlier studies [24].

4. Conclusions

Zeolite-supported Au-Pd catalysts are effective for the direct oxidation of hydrogen to form hydrogen peroxide and give results that are significantly enhanced when compared with alumina-supported catalysts prepared in the same manner using impregnation [1,13]. This method of preparation is known [1] to lead to the formation of Au particles with mean sizes >5 nm and consequently we consider the zeolite-supported catalysts comprise Au nanoparticles decorating the surface of the zeolite crystals. The addition of Pd, although the addition of Pt does lead to an enhancement in the activity for hydrogen peroxide synthesis and this is considered to merit further investigation.

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