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Catalysis Communications 8 (2007) 247–250

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Direct synthesis of hydrogen peroxide from H_2 and O_2 and *in situ* oxidation using zeolite-supported catalysts

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Received 21 January 2006; received in revised form 13 June 2006; accepted 14 June 2006
Available online 27 June 2006

Abstract

Four microporous materials, zeolites HZSM-5, Y, Beta and TS-1, were used as the supports to prepare supported gold catalysts using impregnation or deposition precipitation. The gold catalysts were tested in the direct synthesis of hydrogen peroxide from H_2 and O_2 and for CO oxidation. The effect on the catalytic activity of different metal (e.g., Pd, Pt, Cu, Ag, Rh or Ru) on the synthesis of hydrogen peroxide was also tested. Organic substrates, such as cyclohexane or cyclooctene, were introduced to investigate the possibility of *in situ* H_2O_2 oxidation with these catalysts.

Keywords: Gold catalysis; Hydrogen peroxide; *In situ* oxidation

1. Introduction

Hydrogen peroxide is an environmentally friendly oxidant that plays an important role in "green chemistry". The commercial production of H_2O_2 is a circuitous process that involves the catalytic hydrogenation of an alkylanthroquinone to the corresponding hydroquinone, followed by its treatment with O_2 to produce H_2O_2 and the original anthroquinone. However, there are problems associated with the anthraquinone route, including the cost of the quinone solvent system and the requirement for periodic replacement of anthraquinone due to hydrogenation. In addition, the process is economically viable only on a relatively large scale ($4–6 \times 10^4$ tonne/annum). This necessitates the transportation and storage of concentrated solutions of hydrogen peroxide when required for use in the fine chemicals industry, because only relatively small amounts are required at any one time. Hence, the development of a new, highly efficient, and smaller-scale manufacturing process for H_2O_2 is of significant commercial interest. The direct synthesis of hydrogen peroxide from the oxidation of H_2 with O_2 has been studied for many years and until recently the catalysts used in these investigations have been based on Pd [1–6]. However, it has been shown recently that Au–Pd alloys supported on alumina can give significant improvements in the rate of hydrogen peroxide formation when compared with the Pd only catalyst [7,8]. Subsequently, Okumura et al. [9] reported that the Au/AC, Au/MCM-41, and Au/SiO_2 catalysts prepared by gas-phase grafting (GG) methods can be very active for the direct production of H_2O_2 from H_2 and O_2. The rate of H_2O_2 formation over Au/SiO_2 is 1.601 mmol/h/g-cat when the reaction is carried out at 288 K and 1.0 MPa. Ishihara et al. [10] studied the effects of additives on Au/SiO_2 catalyst and found that the addition of a small amount of Pd is effective for increasing the H_2O_2 formation rate. Edwards

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doi:10.1016/j.catcom.2006.06.021

et al. [11] reported that the H_2O_2 productivity of 5% Au/α-Fe_2O_3 and 2.5% Au–2.5% Pd/α-Fe_2O_3 prepared by impregnation is 0.54 and 16 mol/h/kg-cat, respectively. Subsequently, TiO_2 supported Au–Pd catalysts were reported to be more active and the Au–Pd particles were found with a core–shell structure, with Pd concentrated on the surface [12]. Zeolite HZSM-5 and zeolite Y were also used as the supports for Au and the catalysts can give comparable rates of hydrogen peroxide formation to alumina-supported Au catalysts prepared using a similar impregnation method although they are not as stable [13]. In this paper, the work on the use of zeolites as supports has been extended and four microporous materials, zeolites HZSM-5, Y, Beta and TS-1, have been used as supports to prepare catalysts using impregnation or deposition precipitation. The catalysts were tested in the direct synthesis of hydrogen peroxide from H_2 and O_2 and *in situ* oxidation of hydrocarbons using the H_2O_2 generated in this system was also investigated.

2. Experimental

2.1. Catalyst preparation

Supported catalysts were prepared using impregnation method using an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (Johnson Matthey). For the 2.5 wt% Au-supported catalyst the detailed procedure was as follows. Aqueous solution (5 ml) of $HAuCl_4 \cdot 3H_2O$ (2 g dissolved in 100 ml water) was added to the support (1.9 g) and stirred at room temperature. Four zeolite supports were used namely, zeolite HZSM-5 (Grace ZL5201, $SiO_2/Al_2O_3 = 45$, total BET surface area 424 m^2/g), zeolite Y (Grace ZL5100, $SiO_2/Al_2O_3 = 6$, total BET surface area 760 m^2/g), zeolite Beta ($SiO_2/Al_2O_3 = 166$, Cardiff University) and zeolite TS-1 (Cardiff University). The paste formed was dried at 90 °C for 16 h and some samples were also calcined at 400 °C in static air for 3 h. Further catalysts containing different amounts of Au or other metal were also prepared using a similar procedure.

Supported catalysts were also prepared using deposition precipitation method. For the 4.3 wt% Au-supported catalyst the detailed procedure was as follows. Aqueous solution (7 ml) of $HAuCl_4 \cdot 3H_2O$ (2 g dissolved in 100 ml water) was added into 75.9 ml distilled water, then 2.1 g urea and 1.53 g zeolite supports were added. The mixture was heated to 80 °C and kept at that temperature for 4 h with stirring. Then the solid was filtered and washed using distilled water. The paste formed was dried at 90 °C for 16 h and some samples were also calcined at 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. H_2O_2 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 $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ using ferroin as indicator.

The *in situ* H_2O_2 oxidation was carried out in the same autoclave using a similar procedure, but organic substrate (cyclohexane or cyclohexene) was added at the start of the reaction. The products of the reaction were analysed using a gas chromatograph (Varian Star 3400 CX) fitted with a DB-5 column and a flame ionization detector (FID).

The catalytic activity for CO oxidation was determined in a fixed bed quartz micro-reactor, operated at atmospheric pressure. The feed consisted of 1% CO in N_2, CO_2 and H_2 and 5% O_2 in N_2. The typical reaction condition is catalyst 50 mg, 1% CO mixed gas 10 ml/min, 5% O_2/N_2 1 ml/min and temperature 80 °C. Catalysts were tested for a minimum of 300 min and analysis of the reaction product was carried out using on-line gas chromatography. Conversion was calculated on the basis of CO_2 concentration in the effluent and carbon balances were 100 ± 2%.

3. Results and discussion

3.1. Effect of preparation method

The gold catalysts supported on zeolite HZSM-5 or Y were prepared using impregnation (IM) or deposition precipitation (DP). The catalysts were tested in the synthesis of hydrogen peroxide and CO selective oxidation (Table 1).

Table 1
Performance of catalysts prepared using impregnation (IM) or deposition precipitation (DP)

Catalyst	Preparation	Productivity[a] (mol-H_2O_2/h/Kg_{cat})	CO Conv.[b] (%)
4.3% Au/HZSM-5	IM, dried	4.73	1.7
4.3% Au/HZSM-5	IM, calcined 400 °C	1.75	<1.0
4.3% Au/Y	IM, dried	3.61	<1.0
4.3% Au/Y	IM, calcined 400 °C	2.99	<1.0
4.3% Au/HZSM-5	DP, dried	3.72	2.4
4.3% Au/HZSM-5	DP, calcined 400 °C	3.38	5.1
4.3% Au/Y	DP, dried	6.60	5.1
4.3% Au/Y	DP, calcined 400 °C	5.78	4.7

[a] Reaction conditions: 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 0–2 °C, time 0.5 h.

[b] Reaction conditions: catalyst 50 mg, 1% CO mixed gas 10 ml/min, 5% O_2/N_2 1 ml/min, temperature 80 °C.