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Journal of Catalysis 238 (2006) 28–38

JOURNAL OF CATALYSIS

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Role of chloride or bromide anions and protons for promoting the selective oxidation of H_2 by O_2 to H_2O_2 over supported Pd catalysts in an aqueous medium

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Received 14 September 2005; revised 12 November 2005; accepted 21 November 2005

Abstract

The influence of protons (mineral acid) and different halide anions (F^-, Cl^-, Br^-, or I^-) in the aqueous reaction medium on H_2O_2 formation in the direct oxidation of H_2 to H_2O_2 (at 27 °C) over different supported Pd catalysts (i.e., Pd supported on carbon, alumina, gallia, silica, zirconia, or ceria) in their reduced form, and also on the activity of the catalysts for the destruction of H_2O_2 by its decomposition and/or hydrogenation reactions at the conditions close to those used in H_2 to H_2O_2 oxidation, was thoroughly investigated to gain insight into the roles of protons and halide promoters. Among the halide anions, only the chloride and bromide anions (particularly for the Pd/C and metal oxide-supported Pd, respectively), when added to acidic reaction medium, act as a catalyst promoter to drastically enhance H_2O_2 formation selectivity or H_2O_2 yield. But the presence of protons is crucial to this promoting action. The promoting action of the halides is attributed mainly to the large decrease in the H_2O_2 decomposition and hydrogenation activities of the catalyst resulting from its poisoning of the two consecutive H_2O_2 destruction reactions. It also may be due to the inhibition caused by the halide promoters for water formation directly from H_2 oxidation. The cations associated with the halide anions play only a minor role or no role in controlling the conversion or selectivity in H_2 to H_2O_2 oxidation and H_2O_2 conversion reactions. A plausible mechanism for H_2 to H_2O_2 oxidation in the presence of chloride or bromide anions in acidic aqueous medium, explaining the beneficial roles of the halide anions and protons for promoting the selective oxidation reaction, is proposed.

Keywords: Direct oxidation of H_2 to H_2O_2; Supported Pd catalysts; H_2O_2 decomposition; H_2O_2 hydrogenation; Promoting action of chloride or bromide anions

1. Introduction

Direct catalytic liquid-phase oxidation of H_2 by O_2 to H_2O_2 (a versatile, environmentally clean oxidizing agent) is a process of great practical importance. It has a great potential to replace the presently practiced hydroquinone autoxidation process, which involves indirect oxidation of H_2 to H_2O_2 and has several drawbacks, including the use of a complex solvent system, loss of anthraquinone by nonselective hydrogenation, deactivation of hydrogenation catalyst, difficult product separation and waste treatment, and high capital costs. Hence, the production cost is too high to use the H_2O_2 produced by this process in wastewater treatment and production of bulk organic chemicals [1]. To meet the increasing demand for low-cost H_2O_2, particularly for use in wastewater treatment and environmentally friendly organic oxidation processes in the production of fine/specialty and bulk chemicals, much effort has been made to develop a more economical and environmentally friendly process for H_2O_2 production involving the direct catalytic H_2 oxidation in a liquid medium using different Pd catalysts.

This process is covered in a number of patents throughout the world but to date is not yet commercialized; it is considered a “dream process.” Apart from its hazardous nature, the main problem associated with the process is the low H_2O_2 selectivity (or high selectivity for water formation). This results from the undesirable highly thermodynamically favored nonselective water-forming reactions, such as the parallel H_2 to water oxidation and consecutive H_2O_2 decomposition and/or

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0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.11.024

hydrogenation, occurring simultaneously with the desirable H_2 to H_2O_2 oxidation over the same catalyst (Pd catalyst) as follows:

$$H_2 + O_2 \rightarrow H_2O_2 + 136\ \text{kJ/mol} \quad (\Delta G^0 = -120\ \text{kJ/mol}), \tag{1}$$

$$H_2 + 0.5O_2 \rightarrow H_2O + 242\ \text{kJ/mol} \quad (\Delta G^0 = -237\ \text{kJ/mol}), \tag{2}$$

$$H_2O_2 \rightarrow H_2O + 0.5O_2 + 106\ \text{kJ/mol} \quad (\Delta G^0 = -117\ \text{kJ/mol}), \tag{3}$$

$$H_2O_2 + H_2 \rightarrow 2H_2O + 212\ \text{kJ/mol} \quad (\Delta G^0 = -354.0\ \text{kJ/mol}). \tag{4}$$

Thermodynamic data are for the reactions at 27 °C.

An improvement in the H_2O_2 selectivity/yield in the H_2 to H_2O_2 oxidation over Pd catalysts due to the addition of chloride or bromide anions in the aqueous medium has been disclosed in several patents [2–6]. Recent studies [7–10] have also shown an increase in H_2O_2 selectivity when HCl was used as the reaction medium [7–9] or when HBr was added to the reaction medium [8,10]. Very recently, we observed a drastic increase in H_2O_2 selectivity/yield due to the bromination of various supported Pd catalysts [11]. Our earlier studies [9,12] also revealed the beneficial effect of the mineral acid (protons) present in the aqueous reaction medium in making the H_2 to H_2O_2 oxidation more selective. Therefore, it is of both practical and scientific interest to know and understand the role of different halide anions and protons (mineral acid) or other cations for their promoting and/or inhibiting actions in the H_2 to H_2O_2 oxidation in an aqueous reaction medium; this would help develop a better H_2 to H_2O_2 oxidation process. The present investigation was undertaken for this purpose.

In the present investigation we studied the promoting or inhibiting action of different halides (F^-, Cl^-, Br^-, and I^-) added to the aqueous reaction medium on the H_2 to H_2O_2 oxidation and H_2O_2 decomposition/hydrogenation reactions over different reduced Pd catalysts (Pd supported on carbon, Al_2O_3, Ga_2O_3, SiO_2, ZrO_2, and CeO_2) in the presence or absence of protons in the reaction medium. We also evaluated the relative importance of the H_2O_2 decomposition and hydrogenation reactions in controlling H_2O_2 formation in H_2 to H_2O_2 oxidation in the presence of halide promoters.

2. Experimental

The Pd (5 wt%)/Al_2O_3 and Pd (5 wt%)/C catalysts in their reduced form were obtained from Lancaster (UK). The ZrO_2-, Ga_2O_3-, CeO_2-, and SiO_2-supported Pd (2.5 wt%) catalysts were prepared by impregnating the respective support with palladium acetate from its acetonitrile solution, drying and calcining at 500 °C in a static air for 3 h, and then reducing by ammoniacal hydrazine. All the catalysts were in fine-powder form. The presence of metallic Pd (Pd^0) phase in all of the Pd catalysts was confirmed by XRD; the Pd/Al_2O_3 and Pd/C catalysts were also characterized by XPS. Pd leaching (if any) from the Pd catalyst in the reaction medium was detected by adding an aqueous ethanolic dimethyl glyoxime (1%) solution to a 5-ml filtered reaction mixture. The resulting yellow orange precipitate indicated the presence of palladium (in trace amounts) in the reaction mixture.

The direct H_2 to H_2O_2 oxidation over the Pd catalysts was carried out in a magnetically stirred glass reactor (250 cm^3 capacity) by passing a mixture of H_2 and O_2 (4.6 mol% H_2) continuously through an aqueous acidic reaction medium with or without halide anions as described previously [9,12] at the following reaction conditions: volume of reaction medium = 150 cm^3, amount of catalyst = 0.5 g, gas flow rate = 15.5 cm^3/min, temperature = 27 °C, pressure = atmospheric, and reaction period = 3 h.

H_2O_2 decomposition (in the presence of air) over the catalyst was carried out using the same reactor containing 0.2 g of catalyst in 150 cm^3 of aqueous acidic reaction medium with or without halide anions in the presence of air by injecting 1.0 ml of 30% aqueous H_2O_2 solution into the reactor under vigorous stirring in the presence of air and measuring the gas (O_2) evolved in the H_2O_2 decomposition at 27 °C and atmospheric pressure as a function of time, using a constant pressure gas collector, for 1 h.

H_2O_2 conversion in the presence of H_2 (static) by H_2O_2 decomposition and/or hydrogenation over the catalysts was carried out in the same reactor containing 0.1 g of catalyst and 150 cm^3 of the acidic reaction medium with or without halide anions at 27 °C and atmospheric pressure as follows. First, the air in the reactor, containing the reaction medium (with or without promoters), and catalyst was completely flushed by H_2 by passing a stream pure H_2 (30 cm^3/min) through the reactor for a 1 h. Then the reactor was connected to a gas burette filled with pure H_2 over water, and 1.0 ml of 30% aqueous H_2O_2 solution was injected by a glass syringe into the reactor under vigorous stirring. The gas (H_2) consumed in the H_2O_2 hydrogenation or the gas (O_2) evolved due to the H_2O_2 decomposition was measured quantitatively at a constant (atmospheric) pressure, using the gas burette, as a function of time. In the case of a sudden gas evolution instead of gas consumption, the progress of the reaction was also followed by measuring quantitatively the unconverted H_2O_2 by iodometric titration.

H_2O_2 conversion under flowing H_2, N_2, or O_2 through the reaction medium was carried out in the same reactor containing 0.1 g of catalyst and 150 cm^3 of an aqueous acidic solution with or without halide anions, as follows. First, the air from the reactor, containing the reaction medium (with or without promoter) and catalyst was completely flushed by passing the gas under consideration; then, while passing the gas through the reaction medium at a flow rate of 30 cm^3/min, 3.0 ml of 30% aqueous H_2O_2 solution was injected into the reactor under vigorous stirring at 27 °C. The progress of the H_2O_2 conversion reaction was followed by removing the liquid reaction mixture as a function of time and analyzing the unconverted H_2O_2 by iodometric titration.

After the reaction, the catalyst was separated from the reaction mixture by filtration, washed with deionized water, and