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Influence of nature/concentration of halide promoters and oxidation state on the direct oxidation of H_2 to H_2O_2 over Pd/ZrO_2 catalysts in aqueous acidic medium

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Abstract

The nature/concentration of halide promoters and influence of the Pd oxidation state on the promoted reaction system has been investigated on the direct H_2O_2 process over a 2.5 wt.% Pd/ZrO_2 catalyst in an aqueous acidic reaction medium. The oxidation state of Pd had a profound influence on the H_2O_2 synthesis process. Interestingly, the nature of the halide determined the magnitude/type of influence the Pd oxidation state exerted on the overall process. While the effect of the oxidation state on the H_2O_2 yields was large for the reaction systems containing F^- or no halide, the effect was significantly smaller for the reaction systems containing Br^- and Cl^-. The nature of the halide also strongly influenced the H_2O_2 synthesis process. Br^- strongly enhanced the H_2O_2 yields, while F^- had a negative influence on the H_2O_2 yields. The ability of the halides to enhance the H_2O_2 process was found to strongly depend on its propensity to suppress the secondary H_2O_2 decomposition reaction. The influence of Br^- and Cl^-concentration studies revealed that the optimum halide concentration for the direct H_2O_2 synthesis process was dependent on the nature of the halide. While the maximum in H_2O_2 yields for the Br^- containing reaction medium corresponded to a concentration of $\sim$0.9 mmol/dm^3 (KBr) the maximum for the Cl^- containing solution was obtained at $\sim$1.5 mmol/dm^3 (KCl). Such knowledge is crucial from the viewpoint of optimization (catalyst/reaction system screening studies) of the direct H_2O_2 process. The qualitative trends (H_2O_2 selectivity/yield) observed in case of the incorporated halide catalysts were similar to those observed with halides in reaction medium over the Pd/ZrO_2 catalyst.

Keywords: Direct H_2O_2 synthesis; Halides; Promoter; Decomposition

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1. Introduction

H_2O_2, on account of its high oxygen content and environmentally benign oxidation co-product, is being increasingly recognized as an ideal oxidizing agent for synthesizing fine chemicals. H_2O_2 is also used in other applications such as bleach in the textile and pulp/paper industry and in the treatment of waste water [1]. Currently, H_2O_2 is produced via a circuitous process which involves indirect oxidation of H_2 (anthraquinone process). Because of the complexity of the above process, there is a significant interest in developing a direct H_2 oxidation process [2]. The direct synthesis of H_2O_2 over noble metal-based catalysts has received considerable attention [3–16] in recent years. In the H_2-to-H_2O_2 oxidation, the selective H_2O_2 ($H_2 + O_2 \rightarrow H_2O_2$) and non-selective water ($H_2 + 0.5O_2 \rightarrow H_2O$) forming reactions occur simultaneously. Furthermore, the product H_2O_2 is unstable and has a proclivity to form water via secondary reactions in presence of the Pd catalyst. It is, therefore, extremely difficult to achieve high H_2O_2 selectivity/yields. The challenges posed by the direct H_2O_2 process make it

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very interesting from a scientific as well as a commercial viewpoint.

Previous studies have revealed that the H_2O_2 selectivity can be considerably improved by using promoters to suppress the undesirable non-selective reactions [14–18]. Halide promoters are considered important to the direct H_2O_2 synthesis process as they have the ability to increase the H_2O_2 yields by drastically minimizing H_2O production. Our earlier study involving several Pd-based catalysts (Pd/ZrO_2, Pd/Ga_2O_3, Pd/CeO_2, Pd/SiO_2 and Pd/H-β, Pd/ThO_2, Pd/ CeO_2–ZrO_2, Pd/BPO_4 and Pd/ Al_2O_3) had shown Pd/ZrO_2 to be a superior catalyst (in terms of H_2 conversion and H_2O_2 selectivity) for the direct H_2O_2 process [6]. Herein, we have investigated the effect of the nature and concentration of halide promoters on the direct H_2O_2 process over the promising Pd/ZrO_2 catalyst system in an aqueous acidic reaction medium. The halide promoters have been investigated in the following manner: (a) via introduction in the reaction medium and (b) via incorporation in the Pd/ZrO_2 catalyst prior to the reaction. There has been a significant discussion in literature about the influence of oxidation state on the direct H_2O_2 process [6,8,11,19]. Since the effect of the oxidation state of Pd might depend on the nature of the halide promoter in the direct H_2 oxidation to H_2O_2 process, herein this effect has been investigated for the different halide promoted reaction systems. H_2O_2 decomposition studies have also been undertaken on these catalysts (Pd in reduced and unreduced state) to gain further insights into the process.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Oxidized and reduced Pd/ZrO$_2$ catalysts

The 2.5 wt.% Pd/ZrO_2, catalyst was prepared by impregnating the ZrO_2 support with palladium acetate from its acetonitrile solution by the incipient wet impregnation technique. The ZrO_2 support was prepared from zirconyl nitrate by its hydrolysis to zirconium hydroxide by ammonium hydroxide and calcining at 500 °C for 2 h. After impregnation, the wet catalyst mass was dried at 100 °C for 2 h and then calcined under static air in a muffle furnace at 500 °C for 3 h. The supported reduced Pd catalyst was prepared from the oxidized Pd catalyst by reducing it with an ammoniacal hydrazine solution at room temperature (27 °C) for 2 h followed by washing, filtration and drying at 100 °C in an air oven.

2.1.2. Halide-modified Pd/ZrO$_2$ catalysts

The halide-modified catalysts 2.5 wt.% Pd/ZrO_2 catalysts were prepared by impregnating the 2.5 wt.% Pd/ ZrO_2 catalyst (in its reduced form) with the corresponding ammonium halide from its aqueous solution by the incipient wetness technique, drying at 100 °C for 2 h and then calcining under flowing N_2 at 400 °C for 1 h. The halide incorporated Pd/ZrO_2 catalysts calcined at 400 °C in N_2 atmosphere were found to retain the metallic Pd phase. All the catalysts were in fine powder form. The oxidation state of Pd for the catalysts was confirmed by X-ray powder diffraction method using a Holland Phillips, PW/1730 X-ray generator with Cu Kα radiation ($\lambda = 1.5406$ Å; 40 kV, 25 Ma).

2.2. Reaction procedure

2.2.1. H$_2$O$_2$ synthesis

The direct oxidation of H_2 by O_2 to H_2O_2 over the 2.5 wt.% Pd/ZrO_2 (oxidized and reduced) catalysts was carried out at atmospheric pressure (95 kPa) in a magnetically stirred glass reactor (capacity 250 cm^3) containing 0.5 g catalyst in a fine power form and an aqueous acidic solution (150 cm^3) as a reaction medium containing KBr, KI, KF and KCl. The direct oxidation and H_2O_2 destruction processes were also studied over reduced (a) 2.5 wt.% Pd/ ZrO_2 catalysts with different concentrations of KBr and KCl in an aqueous acid (0.03 M H_3PO_4) solution and (b) 2.5 wt.% Pd/ZrO_2 catalysts preloaded with different concentrations of bromide (0–1 mmol/g) in an aqueous acid (0.03 M H_3PO_4) solution at 27 °C and atmospheric pressure. A H_2/O_2 (4.6 mol% H_2) gas mixture was bubbled (using a fine glass tip) continuously through the reaction medium containing the catalyst under vigorous stirring at a constant temperature. The concentration of unreacted hydrogen present in the effluent gases, after removing the water vapors from them by condensation at 0 °C, was measured by an online hydrogen analyzer (Kathorometer, Nucon, New Delhi) based on a thermal conductivity detector. After the reaction, the solid catalyst from the reaction mixture was separated by filtration and the filtrate was analyzed for the H_2O_2 formed in the reaction by iodometric titration. The conversion of H_2, H_2O_2 yield and selectivity were obtained as follows:

$$\begin{aligned}
H_2\ \text{conversion}\ (\%) &= \{[(\text{moles of } H_2 \text{ in the feed}) \\
&\quad - (\text{moles of } H_2 \text{ in the effluent gases})] \\
&\quad \div (\text{moles of } H_2 \text{ in the feed})\} \times 100 \\
H_2O_2\ \text{selectivity}\ (\%) &= [(\text{moles of } H_2O_2 \text{ formed}) \\
&\quad \div (\text{moles of } H_2 \text{ consumed})] \times 100 \\
H_2O_2\ \text{yield}\ (\%) &= [(\text{moles of } H_2O_2 \text{ formed}) \\
&\quad \div (\text{moles of } H_2 \text{ in the feed})] \times 100
\end{aligned}$$

Unless mentioned otherwise, the conversion/selectivity/yield data reported in this paper has been taken after a reaction time of 3 h. Some of the experiments were repeated and an excellent reproducibility was observed. The reproducibility errors for the measurements (H_2O_2 selectivity and H_2O_2 yields) in this study are within 5%. The flammability and detonation limits for H_2 in O_2 (at 25 °C and 1 atm pressure) are 4.0% H_2 (lower) to 94% H_2 (upper) and 15% H_2 (lower) to 90% H_2 (upper), respectively. The process could be hazardous when operated within the flammability limits,