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Effects of varying amounts of Na on Pd/TiO_2 for the direct synthesis of H_2O_2: Identification of the Pd dispersion and catalytic activity enhancement by changing the surface electronic states

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ABSTRACT

Alkali elements have been applied as promoters of noble metals (*e.g.,* Pd or Pt) to enhance their catalytic activities by changing the surface electronic states of the noble metals. In particular, the role of alkali elements is to improve the dispersion properties of the active metal. In this study, various amounts of the alkali element sodium (Na) were used as a promoter for a Pd/TiO_2 catalyst. Importantly, the catalysts were synthesized to improve the selectivity and production rate of the direct synthesis of hydrogen peroxide (DSHP) by increasing the Pd dispersion and surface area by changing the surface electronic properties. After the addition of Na onto Pd/TiO_2, the H_2O_2 production rates were generally higher than those for pure Pd/TiO_2 due to the synergistic effects between the Pd and Na on the TiO_2 support. Particularly, among the tested catalysts, the 0.5 wt.% Na-promoted Pd/TiO_2 (PdNa(0.6)/TiO_2) catalyst exhibited the highest H_2 conversion rate (22 %) in the iso-Pd weight and the highest H_2O_2 selectivity (95.4 %) and production rate (785.9 mmol/g_{Pd}h) for the iso-H_2 conversion test. Na provides electrons to the Pd species, leading to a change in the Pd dispersion. Furthermore, the surface electronic state of Pd changed with increasing amounts of Na, and thus, heavily influenced the H_2O_2 selectivity. Ultimately, PdNa(0.6)/TiO_2 achieved the best selectivity as a H_2O_2 producing catalyst in this study.

1. Introduction

Hydrogen peroxide (H_2O_2) is used in various fields, including as a bleaching agent for pulp or paper, as a detergent, and in pharmaceutical and wastewater treatment [1–11]. A commercial process, known as anthraquinone oxidation (AO), is the most widely used H_2O_2 manufacturing process; however, there are drawbacks regarding the environmental hazards and economic costs of this process [1,12–15]. Therefore, a process for the direct synthesis of hydrogen peroxide (DSHP) is needed to solve the limiting drawbacks of the AO process [12]. The DSHP produces only water as a byproduct; thus, it has emerged as an ecofriendly alternative method [16]. However, selective H_2O_2 production is not an easy process because of spontaneous side reactions, such as water formation [17,18] (Scheme 1). Therefore, it is essential to develop catalysts to increase H_2O_2 selectivity.

Pd is an attractive metal for DSHP reactions. In various DSHP studies, Pd-based catalysts have been applied, such as Pd-Au [19–22], Pd-Pt [16,23], Pd-Ni [24], Pd-Sn [25,26], Pd-Te [27], Pd-Zn [28] and Pd-Ag [29], to enhance the DSHP reaction activity. These secondary elements play a critical role in increasing the H_2O_2 selectivity. Most secondary elements change the surface properties of Pd; thus, the H_2O_2 selectivity and production rate are generally improved. Moreover, the role of the support is another important factor for the catalytic activity of the DSHP. In our previous study, a sonochemical method was utilized to prepare Pd nanoparticles supported on SiO_2 and TiO_2 substrates [30]. We discovered that the dispersion of the metal on the support depended on the combined effects of the sonochemical method and the nature of the metal-support interactions (Pd and SiO_2 or Pd and TiO_2). Conclusively, sonochemically prepared Pd on TiO_2 showed the highest degree of metal dispersion due to its strong metal support interaction effect (SMSI effect). Therefore, we demonstrated that TiO_2 supports play a critical role in enhancing the Pd dispersion.

In this study, we applied the alkali metal Na as a secondary element to control the various electronic states of Pd; in particular, we focused on the Pd dispersion and its surface electronic states on the TiO_2 support. We prepared various Na-promoted Pd/TiO_2 catalysts, with

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