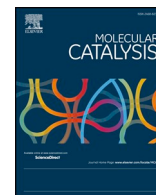




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Effects of varying amounts of Na on Pd/TiO₂ for the direct synthesis of H₂O₂: Identification of the Pd dispersion and catalytic activity enhancement by changing the surface electronic states

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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/TiO₂ 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/TiO₂, the H₂O₂ production rates were generally higher than those for pure Pd/TiO₂ due to the synergistic effects between the Pd and Na on the TiO₂ support. Particularly, among the tested catalysts, the 0.5 wt.% Na-promoted Pd/TiO₂ (PdNa(0.6)/TiO₂) catalyst exhibited the highest H₂ conversion rate (22 %) in the iso-Pd weight and the highest H₂O₂ selectivity (95.4 %) and production rate (785.9 mmol/g_{Pd}h) for the iso-H₂ 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 H₂O₂ selectivity. Ultimately, PdNa(0.6)/TiO₂ achieved the best selectivity as a H₂O₂ producing catalyst in this study.

1. Introduction

Hydrogen peroxide (H₂O₂) 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ selectivity. Most secondary elements change the surface properties of Pd; thus, the H₂O₂ 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 SiO₂ and TiO₂ 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 SiO₂ or Pd and TiO₂). Conclusively, sonochemically prepared Pd on TiO₂ showed the highest degree of metal dispersion due to its strong metal support interaction effect (SMSI effect). Therefore, we demonstrated that TiO₂ 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 TiO₂ support. We prepared various Na-promoted Pd/TiO₂ catalysts, with

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