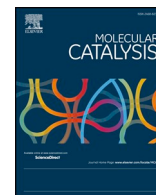




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# Effects of varying amounts of Na on Pd/TiO<sub>2</sub> for the direct synthesis of H<sub>2</sub>O<sub>2</sub>: Identification of the Pd dispersion and catalytic activity enhancement by changing the surface electronic states

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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<sub>2</sub> 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<sub>2</sub>, the H<sub>2</sub>O<sub>2</sub> production rates were generally higher than those for pure Pd/TiO<sub>2</sub> due to the synergistic effects between the Pd and Na on the TiO<sub>2</sub> support. Particularly, among the tested catalysts, the 0.5 wt.% Na-promoted Pd/TiO<sub>2</sub> (PdNa(0.6)/TiO<sub>2</sub>) catalyst exhibited the highest H<sub>2</sub> conversion rate (22 %) in the iso-Pd weight and the highest H<sub>2</sub>O<sub>2</sub> selectivity (95.4 %) and production rate (785.9 mmol/g<sub>Pd</sub>h) for the iso-H<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> selectivity. Ultimately, PdNa(0.6)/TiO<sub>2</sub> achieved the best selectivity as a H<sub>2</sub>O<sub>2</sub> producing catalyst in this study.

## 1. Introduction

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> selectivity. Most secondary elements change the surface properties of Pd; thus, the H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> and TiO<sub>2</sub> 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<sub>2</sub> or Pd and TiO<sub>2</sub>). Conclusively, sonochemically prepared Pd on TiO<sub>2</sub> showed the highest degree of metal dispersion due to its strong metal support interaction effect (SMSI effect). Therefore, we demonstrated that TiO<sub>2</sub> 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<sub>2</sub> support. We prepared various Na-promoted Pd/TiO<sub>2</sub> catalysts, with

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