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ARTICLE TYPE

Room-temperature selective oxidation of 2-naphthol to BINOL by a Au/SrTiO₃-H₂O₂ catalytic system

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Gold nanoparticle-loaded SrTiO₃ (Au/SrTiO₃) effectively catalyzes the selective C-C bond formation between 2-naphthol molecules to yield BINOL in the presence of H₂O₂, and the catalytic activity increases with decreasing Au particle size (*d*) at 2.6 ≤ *d* ≤ 8.9 nm.

2,2'-dihydroxy-1,1'-binaphthyl (BINOL) is widely used for the asymmetric organic synthesis of the pharmaceutical and agricultural chemicals. Substituted BINOL derivatives are also important as the DNA alkylating agents.^{1,2} BINOL can be synthesized by the oxidative coupling of 2-naphthol. The process usually requires the stoichiometric amount of FeCl₃ or the Cu-catalyst in chlorine-contained organic solvent (Scheme S1 in ESI).³⁻⁵ Thus, the development of the "green" oxidation process for the BINOL synthesis is highly desirable.^{6,7} On the other hand, hydrogen peroxide (H₂O₂) has recently attracted much attention as a "green" oxidizing agent,⁸⁻¹¹ while a great deal of effort has been devoted to develop the environmental friendly processes for the production of H₂O₂.¹²⁻¹⁵ However, the chemical transformations using H₂O₂ as an oxidant reported so far have been limited to adipic acid synthesis from cyclohexene,¹⁰ the oxidation of alkanes to alcohols or ketones,^{16,17} the epoxidation of alkenes,¹⁸ and the oxidations of alcohols,¹⁹⁻²² sulfides,²³ and anilines.²⁴ In this case, the key is the development of the catalyst for the H₂O₂ activation leading to the effective reaction. By using a Fe-porphyrine catalyst, the oxidation of 2-naphthol by H₂O₂ has been studied, but this system affords a mixture of BINOL, 1,2-dihydroxynaphthalene, and 1,2-naphthoquinone (1,2-NAPQ) (Scheme S1 in ESI).²⁵ We have recently reported that Au nanoparticle (NP)-loaded metal oxides (Au/MOs) exhibits catalytic activities for the H₂O₂ decomposition,²⁶ and among Au/MOs, Au/SrTiO₃ possesses a particularly high activity.²⁷

Here we report the selective oxidative coupling of 2-naphthol to BINOL catalyzed by the Au/SrTiO₃-H₂O₂ system.

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The influence of the metal oxide supports and Au particle size on the activity are also studied. To our knowledge, this is the first report on the selective C-C bond formation by using H₂O₂ as an oxidizing agent with heterogeneous catalyst.

The catalytic activity of Au/MOs depends on the loading amount as well as its particle size.^{28,29} To study the effect of Au particle size (*d*/nm) on the activity, the loading amount should be constant. We prepared the Au/SrTiO₃ samples by the heating temperature-varied deposition-precipitation method. In this method, the *d* value can be controlled by the post-heating temperature (*T_c*) and time (*t_c*) and the samples were designated as Au(*d*)/SrTiO₃. Fig. S1 in ESI shows transmission electron microscope (TEM) images of Au/SrTiO₃ samples prepared at different *T_c* and *t_c*. In every sample, Au NPs are highly dispersed on the SrTiO₃ surface. Also, the *d* value increases with increasing *T_c* and *t_c*, while the loading amount is comparable.²⁹

The oxidation of 2-naphthol by the Au/SrTiO₃-H₂O₂ system was carried out at 298K in the dark. Fig. 1A shows time courses for the oxidation of 2-naphthol at the initial concentration ([2-NAP]₀) of 10 μmol dm⁻³ in the Au(*d* = 2.9 nm)/SrTiO₃ system. The initial decrease in the concentration of 2-naphthol is mainly caused by the adsorption on Au/SrTiO₃. The addition of H₂O₂ initiates the rapid oxidation of 2-naphthol to BINOL. With prolonging reaction time, the 2-naphthol concentration decreases, while the concentration of BINOL ([BINOL]) increases. The sum of [2-NAP] and 2 × [BINOL] is almost constant, and no other by-products such as 1,2-di-OH-NAP or 1,2-NAPQ was observed. But BINOL can be adsorbed on the surfaces of both Au NPs and SrTiO₃ (Fig. S2 in ESI). Thus, the slight reduction of the sum would result from the adsorption of BINOL on the Au/SrTiO₃. Several control experiments were carried out. As shown in Fig. 1B, no reaction proceeds with only H₂O₂ or SrTiO₃. Interestingly loading Au NPs on SrTiO₃ and TiO₂ causes the oxidation of 2-naphthol, and the addition of H₂O₂ remarkably promotes the reaction in the Au/SrTiO₃ system. Also, in the presence of H₂O₂, the activity of Au/SrTiO₃ is much higher than that of Au/TiO₂. Further, 2-naphthol is hardly adsorbed on unmodified SrTiO₃, which indicates the selective adsorption of 2-naphthol on the Au NP surface of Au/SrTiO₃. The reaction was also carried out at [2-NAP]₀ = 1 mmol dm⁻³. As shown in Fig. 1C, the oxidation of 2-naphthol proceeds in the two-order higher concentration reaction system, and the

amount of BINOL increases linearly with increasing reaction time. Clearly, the Au/SrTiO₃-H₂O₂ catalytic system exhibits a high activity for the selective oxidation of 2-naphthol to BINAP at room temperature.

It is well known that the catalytic activity of Au NPs is sensitive to its particle size d . The d -dependence of the catalytic activity of Au/SrTiO₃ for the 2-naphthol oxidation was examined. The reaction was carried out in the presence of

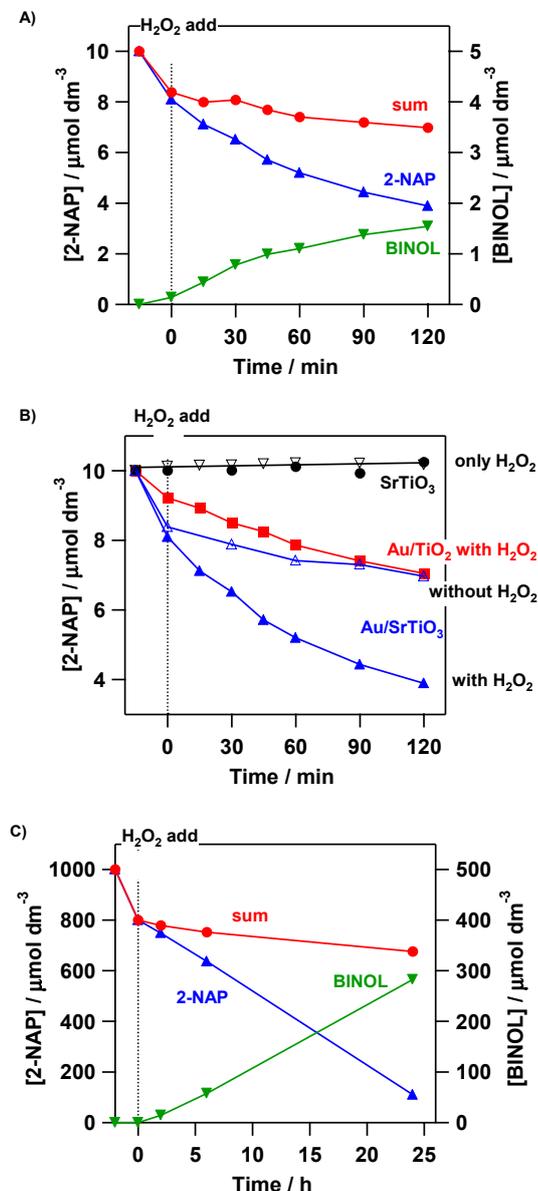


Fig. 1. A) Time courses for the 2-naphthol oxidation ($[2\text{-NAP}]_0 = 10 \mu\text{mol dm}^{-3}$) on Au($d = 2.9 \text{ nm}$)/SrTiO₃ with H₂O₂: sum denotes the value $[2\text{-naphthol}] + 2 \times [\text{BINOL}]$. B) Time courses for the 2-naphthol oxidation on Au($d = 2.9 \text{ nm}$)/SrTiO₃ or SrTiO₃ or Au($d = 3.0 \text{ nm}$)/TiO₂ with or without H₂O₂. C) Time courses for the 2-naphthol oxidation ($[2\text{-NAP}]_0 = 1 \text{ mmol dm}^{-3}$) on Au($d = 2.9 \text{ nm}$)/SrTiO₃ with H₂O₂.

H₂O₂ and Au(d)/SrTiO₃ with varying d . Figs. 2A and B show time courses for the consumption of 2-naphthol and the generation of BINOL, respectively. In the Au($d = 8.9$)/SrTiO₃ system, the reaction is sluggish. Downsizing Au NP drastically enhances the catalytic activity, and Au($d =$

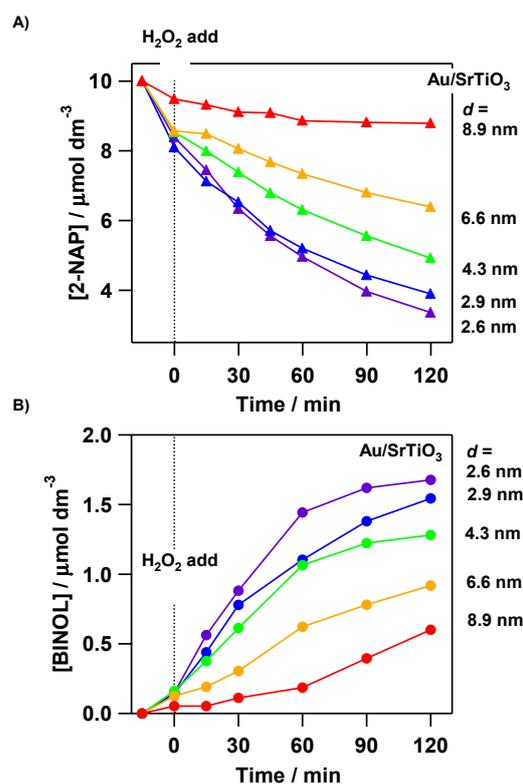


Fig. 2. A) Time courses for the 2-naphthol oxidation on Au/SrTiO₃ with varying d . B) Time courses for the BINOL generation on Au/SrTiO₃ with varying d .

2.6)/SrTiO₃ shows the highest activity at $2.6 \leq d \leq 8.9$. This reaction apparently follows the first-order kinetics. Fig. 3 shows plots of the rate constant k as a function of d . When the Au loading amount is constant, the Au surface area of Au/SrTiO₃ increases inversely as d . The k values are significantly larger than those expected only from the increase in the Au surface area. A similar trend was observed also in the Au/SrTiO₃-catalyzed H₂O₂ decomposition.²⁷ Density functional calculations and experiments have indicated that the periphery of the Au-MO support interfaces and/or low-coordinated Au atoms can be active sites in the Au/MOS-catalyzed oxidation of carbon monoxide.^{29,31} The number of the active sites increases inversely as d^2 . The k values are near

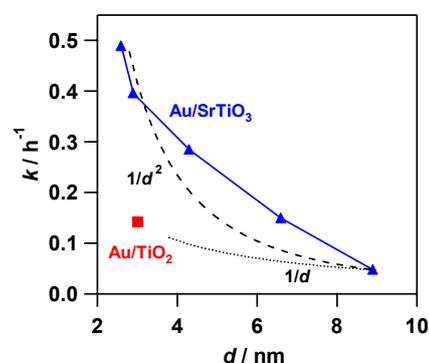
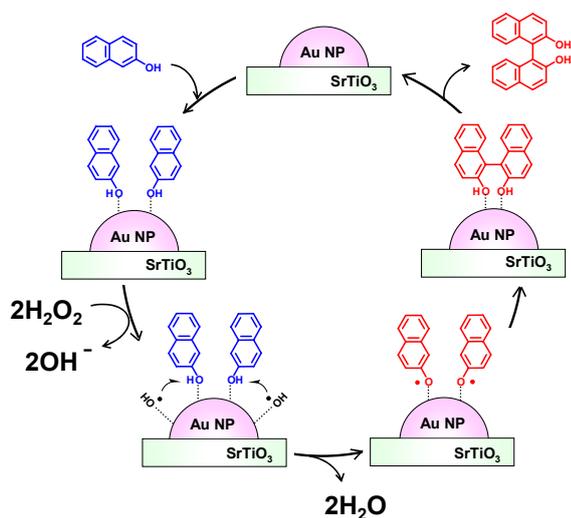


Fig. 3. Plots of rate constant k as a function of Au particle size d .

to the values on the $1/d^2$ curve as Fig. 3. Thus, the increase in k with decreasing d would mainly result from the increase in the number of such catalytic active sites on the Au NP surface.

On the basis of these results, we can summarize the basic reaction mechanism as shown in Scheme 1. A large amount of 2-naphthol is selectively adsorbed on the Au NP surface of Au/SrTiO₃. H₂O₂ is reductively decomposed to an \bullet OH radical and OH⁻ ion by the catalytic action of Au NPs.²⁶ The 2-naphthol adsorbed on Au NP is oxidized by the \bullet OH radicals to yield 2-naphthylxyl radical. The large amount of 2-naphthylxyl radicals generated on the Au NP surface leads to



Scheme 1. Proposed mechanism for oxidation of 2-naphthol to BINOL.

the preferential dimerization to produce the BINOL. A previous literature reported that anodic oxidation of 2-naphthol shows two oxidation peaks at +1.12 V and +2.0 V vs. standard hydrogen electrode (SHE), and the over oxidation at +2.0 V affords naphthylxyl cation to yield 1,2-NAPQ as the by-product.³² The oxidation ability of \bullet OH radical ($E^0(\bullet$ OH/OH⁻) = +1.9 V vs SHE)³³ is insufficient for the oxidation of 2-naphthol to 1,2-NAPQ, and actually, it was not detected in this reaction system. In the present system, there is a possibility that the oxidizing ability of the \bullet OH radical is somewhat reduced by the adsorption on Au NP, which could also contribute to the high selectivity of the reaction.²⁶ Further, the much higher activities of Au/SrTiO₃ for the 2-naphthol oxidation and the H₂O₂ decomposition²⁷ as compared to those of Au/TiO₂ strongly suggest that the rate-determining step in this reaction is the reductive decomposition of H₂O₂.

In summary, this study has shown that the selective oxidative coupling of 2-naphthol to BINOL is effectively catalyzed by the Au/SrTiO₃-H₂O₂ system at room temperature. We anticipate that this catalytic system can be useful for the development of various “green” oxidation processes.

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