Catalysis

Palladium-tin catalysts for the direct synthesis of \( \text{H}_2\text{O}_2 \) with high selectivity

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The direct synthesis of hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) from \( \text{H}_2 \) and \( \text{O}_2 \) represents a potentially atom-efficient alternative to the current industrial indirect process. We show that the addition of tin to palladium catalysts coupled with an appropriate heat treatment cycle switches off the sequential hydrogenation and decomposition reactions, enabling selectivities of >95% toward \( \text{H}_2\text{O}_2 \). This effect arises from a tin oxide surface layer that encapsulates small Pd-rich particles while leaving larger Pd-Sn alloy particles exposed. We show that this effect is a general feature for oxide-supported Pd catalysts containing an appropriate second metal oxide component, and we set out the design principles for producing high-selectivity Pd-based catalysts for direct \( \text{H}_2\text{O}_2 \) production that do not contain gold.

Currently, the demand for \( \text{H}_2\text{O}_2 \) is met by an indirect process, which produces \( \text{H}_2\text{O}_2 \) through the sequential hydrogenation and oxidation of a substituted anthraquinone (7). For economic reasons, the process is operated at large scale and produces concentrated \( \text{H}_2\text{O}_2 \). In reality, many applications, such as disinfection and water purification, require the purification of the \( \text{H}_2\text{O}_2 \) before use. We report the development of Sn-containing Pd catalysts on commercially available TiO2 and SiO2 supports that can achieve >95% selectivity to \( \text{H}_2\text{O}_2 \). Because \( \text{O}_2 \) dissociation is undesirable in the direct synthesis of \( \text{H}_2\text{O}_2 \), the reaction can be treated as a selective hydrogenation of \( \text{O}_2 \). We explored other Pd-metal combinations that are used for selective hydrogenation reactions as potential catalysts for \( \text{H}_2\text{O}_2 \) synthesis, focusing on nonprecious metals to lower costs. Tin (Sn) has been used to modify hydrogenation catalysts in reactions such as the selective hydrogenation of 1,3-butadiene (11). Further examples have been reported for the liquid-phase hydrogenation of hexa-1,3-diene and hexa-1,5-diene (12) as well as the hydrogenation of unsaturated alcohols (13). The addition of Sn to Pd or Pt can alter the behavior of the catalyst during hydrogenation reactions and, in particular, may have an effect on subsequent reactions of the products with the catalyst.

We report the development of Sn-containing Pd catalysts on commercially available TiO2 and SiO2 supports that can achieve >95% selectivity toward direct \( \text{H}_2\text{O}_2 \) synthesis. These catalysts, after being subjected to an appropriate heat treatment regimen, obviate the need for pre-treating the support with acids and contain far less precious metal than Au-Pd catalysts. We also present the general principles whereby high-selectivity catalysts can be obtained with other Pd-metal combinations.

Simple impregnation of Au and Pd metal salts onto many catalyst supports has been shown to generate highly active catalysts for direct \( \text{H}_2\text{O}_2 \) synthesis. In addition, high-temperature calcination or reduction treatments are known to be crucial to improve the stability of the catalyst. As a starting point, we used this simple catalyst preparation methodology to prepare a 2.5 weight percent (wt%) Pd–2.5 wt% Sn/TiO2 catalyst as well as its monometallic analogs (8, 10). A synergistic effect toward higher \( \text{H}_2\text{O}_2 \) productivity was observed when both metals were present

Although this approach was very successful on an activated carbon support material, the same blocking effect could not be fully achieved on other commercial support materials such as SiO2 and TiO2. Because \( \text{O}_2 \) dissociation is undesirable in the direct synthesis of \( \text{H}_2\text{O}_2 \), the reaction can be treated as a selective hydrogenation of \( \text{O}_2 \). We explored other Pd-metal combinations that are used for selective hydrogenation reactions as potential catalysts for \( \text{H}_2\text{O}_2 \) synthesis, focusing on nonprecious metals to lower costs. Tin (Sn) has been used to modify hydrogenation catalysts in reactions such as the selective hydrogenation of 1,3-butadiene (11). Further examples have been reported for the liquid-phase hydrogenation of hexa-1,3-diene and hexa-1,5-diene (12) as well as the hydrogenation of unsaturated alcohols (13). The addition of Sn to Pd or Pt can alter the behavior of the catalyst during hydrogenation reactions and, in particular, may have an effect on subsequent reactions of the products with the catalyst.

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after calcination in static air at 500°C for 3 hours (Table S1). The measured activity of this 2.5 wt % Pd–2.5 wt % Sn/TiO2 catalyst (62 mol kg\(^{-1}\) hour\(^{-1}\)) is similar to that of a 2.5 wt % Pd–2.5 wt % Au/TiO2 catalyst (8) (i.e., 64 mol kg\(^{-1}\) hour\(^{-1}\)). We then optimized the Sn/Pd ratio while maintaining a total metal content of 5 wt% (Table S2) and found an optimum nominal composition, 3 wt % Pd–2 wt % Sn/TiO2, that exhibited an \(\text{H}_2\text{O}_2\) productivity of 68 mol kg\(^{-1}\) hour\(^{-1}\) (Table 1, entry 1). By comparison, the \(\text{H}_2\text{O}_2\) degradation activity of the optimized Sn-Pd catalyst was very low relative to that reported for Au-Pd systems (65 mol kg\(^{-1}\) hour\(^{-1}\) for 3 wt % Pd–2 wt % Sn/TiO2 versus 235 mol kg\(^{-1}\) hour\(^{-1}\) for 2.5 wt % Pd–2.5 wt % Au/TiO2); this result indicates that Sn is also playing a beneficial role in preventing the overhydrogenation and decomposition of \(\text{H}_2\text{O}_2\). However, the Sn-Pd catalysts calcined at 500°C for 3 hours under static air were unstable to multiple reaction cycles (Table 1, entry 1).

The nature of the catalyst surface, in particular the oxidation state of the active metal, is crucial to obtaining high selectivity. Therefore, we characterized this 3 wt % Pd–2 wt % Sn/TiO2 catalyst after calcination by x-ray photoelectron spectroscopy (XPS). This showed that the majority of the surface Pd was present as Pd\(^{2+}\), whereas the Sn Auger parameter showed that SnO\(_2\) was present in the calcined catalyst (fig. S1 and table S3). Analysis of the nanostructure of this catalyst using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and electron energy loss spectroscopy (EELS) revealed that the SnO\(_2\) was present as a thin amorphous film (thickness <2 nm) coating the TiO\(_2\) support particles (Fig. 1, A to D, and fig. S2). A population of 5- to 10-nm NPs was also present in the sample that contained a homogeneous mixture of both Pd and Sn (Fig. 1, A to D, and fig. S3). Lattice fringe fitting of these particles strongly suggests a metallic Pd-Sn alloy structure rather than segregated metal/metal oxides or mixed oxides, which would mean that only the surface of the particles is oxidized. Many sub–2-nm Pd-rich NPs were also observed and were often associated with the SnO\(_2\) thin films, and because these species were much less numerous in a 5 wt% Sn-only/TiO\(_2\) sample (fig. S4), they were primarily associated with the PdO\(_2\) component in the bimetallic catalyst.

A limiting factor in achieving high selectivity toward \(\text{H}_2\text{O}_2\) with Au-Pd/TiO\(_2\) catalysts prepared...
by the wet impregnation method is that the catalyst nanoparticles exhibit a variation in composition with particle size, with the smallest particles being Pd-rich (9). These small Pd-rich NPs are likely to be highly active for H$_2$O$_2$ synthesis and also for its subsequent hydrogenation and decomposition, as has been shown when Au-Pd catalysts are prepared by colloidal techniques with particle sizes typically 2 to 4 nm (14). In the case of the Sn-Pd system, the small Pd-rich NPs are often associated with the amorphous SnO$_2$ films. We postulated that it might be possible to further decrease the H$_2$O$_2$ degradation activity of the catalyst by inducing encapsulation of the ultrasmall Pd-rich NPs by this SnO$_2$ film. We therefore used subsequent thermal treatments in an attempt to induce a strong metal-support interaction (SMSI) between the Pd and SnO$_2$ layer (15–20). We first added a low-temperature reduction step (200°C, 2 hours, 5% H$_2$ in Ar), which made the catalysts stable to multiple reaction cycles (Table 1, entry 2). However, the H$_2$O$_2$ degradation activity increased markedly, from 65 mol kg$^{-1}$ h$^{-1}$ to 300 mol kg$^{-1}$ h$^{-1}$; this rate increase was associated with the reduction of Pd$^{2+}$ to metallic Pd, as shown by XPS (table S3 and fig. S1). Metallic Pd is known to be a more effective H$_2$O$_2$ hydrogenation catalyst (7).

Detailed STEM analysis of this reduced sample was carried out to investigate any structural changes in the sample on reduction (figs. S5 and S6). Analysis identified the presence of thin SnO$_2$ films, sub-2-nm Pd NPs, and 5- to 10-nm NPs whose lattice fringe spacings and angles were consistent with Pd-Sn metallic alloy phases. We then reoxidized this reduced catalyst to restore Pd$^{2+}$ as the predominant surface species (as confirmed by XPS; fig. S1 and table S3), thereby completing an oxidation-reduction-oxidation (O-R-O) cycle, with the aim of encapsulating the small Pd species and regenerating the oxidized Pd-Sn surface on the larger NPs. Reoxidizing the reduced catalyst for various time periods at 400°C under static air had little effect on the H$_2$O$_2$ synthesis productivity but markedly decreased the H$_2$O$_2$ degradation activity (Fig. 2A). After 4 hours of reoxidation treatment, the catalyst showed no activity toward H$_2$O$_2$ degradation and could produce H$_2$O$_2$ with a H$_2$ selectivity of >95% (Table 1, entry 3). This catalyst was stable to multiple reaction cycles and showed negligible leaching of Sn (0 ppb) or Pd (2 ppb) during a 30-min reaction, as measured by inductively coupled plasma mass spectrometry. This reoxidized 3 wt % Pd–2 wt % Sn/TiO$_2$ catalyst was subjected to further H$_2$O$_2$ testing, including multiple sequential H$_2$O$_2$ synthesis tests (Fig. 2B). After running the reaction five times consecutively, the H$_2$O$_2$ concentration increased linearly to 0.53 wt %, retaining both the high H$_2$O$_2$ synthesis and zero H$_2$O$_2$ degradation rates. This result implies that no subsequent decomposition or hydrogenation reactions of H$_2$O$_2$ took place with this catalyst. The reoxidized 3 wt % Pd–2 wt % Sn/TiO$_2$ catalyst was also tested for H$_2$O$_2$ degradation with varying concentrations of H$_2$O$_2$ under a pressure of 5% H$_2$/CO$_2$ (Fig. 2C) and showed no degradation of H$_2$O$_2$ in solutions of up to 8 wt%, whereas the corresponding Au-Pd/TiO$_2$ catalyst showed substantially higher H$_2$O$_2$ degradation activity at all concentrations studied.

The nanostructure of the catalyst after the O-R-O treatment was characterized to identify any structural changes that could be responsible for the observed high selectivity. Three structures were again revealed to be present in the catalyst: amorphous SnO$_2$ films on the TiO$_2$ particles, small Pd species associated with these films, and larger Pd–Sn NPs (Fig. 1, E to H, and figs. S7 and S8).

Detailed EELS analysis of the thin film regions (fig. S9) after various heat treatments indicated the presence of SnO$_2$ films, which can be either reduced or oxidized depending on the final heat treatment stage, as indicated by the absence or presence of the O K edge in the EELS spectrum. In contrast to the thin films, EELS analysis of Sn-Pd nanoparticles (fig. S10) at different stages of the heat treatment cycle showed no clear O K edge. This confirms these nanoparticles to be metallic Pd-Sn alloys, at least in the bulk, which
is also consistent with the lattice fringe fitting. Some slight oxidation of the surface of these particles is possible, as detected by our XPS measurements, but at such a level that it is below the detectability limit of the EELS measurements. The 3 wt % Pd–2 wt % Sn/TiO2 catalyst after the O-R-O cycle shows evidence that the small Pd-rich NPs responsible for high hydrogenation activity of the catalyst is limited (Fig. 3A). The larger uncovered Pd-Sn alloy NPs are then mainly responsible for the H2O2 degradation (Fig. 3B and figs. S12 and S13), whereas after the O-R-O treatment, the Pd particles showed clear evidence of an SnO2 overlayer (Fig. 3C and figs. S14 and S15).

Further evidence that the suppression of the H2O2 degradation does not originate from encapsulation of small Pd particles by TiO2 but is an SMSI effect arising from the secondary Sn component was obtained by using a nonreducible SiO2 support in place of the TiO2. When the Sn/Pd ratio on SiO2 was optimized (table S5) and the same O-R-O heat treatment regimen was applied (Table 1, entries 7 to 9), the resulting 1 wt % Pd–4 wt % Sn/SiO2 catalyst produced H2O2 at a rate of 50 mol kg−1 hour−1 (Table 1, entry 9) and showed no activity toward subsequent H2O2 degradation. This 1 wt % Pd–4 wt % Sn/SiO2 catalyst showed no propensity to decompose or hydrogenate H2O2 even in solutions containing up to 12 wt % H2O2 (fig. S16). Furthermore, the catalytic performance of the 1 wt % Pd–4 wt % Sn/SiO2 material was stable through multiple uses (table S5). XPS analysis (fig. S1 and table S4) and electron microscopy characterization (figs. S17 and S18) of the 1 wt % Pd–4 wt % Sn/SiO2 catalyst showed compositional and structural features (i.e., amorphous SnO2 films and associated ultra-small Pd-rich NPs, as well as larger Pd-Sn alloy particles) analogous to its 3 wt % Pd–2 wt % Sn/TiO2 counterpart. Our approach of encapsulating small Pd-rich species generated by wet impregnation preparations with secondary oxides can be generalized if the second metal oxide added to the Pd/primary oxide (e.g., TiO2/SiO2) support system (i) shows no decomposition activity toward H2O2 when in oxide form, (ii) forms an alloy or mixed oxide phase with Pd, and (iii) can encapsulate small Pd-rich particles by SMSI. Following these design rules with the use of a nominal composition of 0.5 wt % Pd–5 wt % M/TiO2 that had been subjected to the optimized O-R-O treatment, we synthesized a series of metal catalysts where M = Ni, Zn, Ga, In, and Co. All of these catalysts showed activity for H2O2 synthesis (30 to 64% of that displayed by the Sn-Pd catalyst) and no activity for H2O2 degradation (table S6). Thus, our approach opens up the possibility of designing reusable catalysts with greatly reduced precious metal content while still retaining high selectivity to H2O2.

Fig. 3. Evolution of catalyst through oxidation-reduction-oxidation cycle. (A) Proposed mechanism for switching off H2O2 hydrogenation by small Pd-rich NPs through a strong metal-support interaction (SMSI). The secondary metal must both form an alloy with Pd and oxidize to form a secondary support (i.e., SnO2) that can encapsulate the relatively small, poorly alloyed, Pd-rich NPs after an O-R-O cycle. This step prevents these NPs from decomposing and hydrogenating the H2O2 product. (B and C) STEM-EELS mapping of a 5 wt % Pd/SnO2 model catalyst at the oxidized (B) and O-R-O (C) stages, showing partial encapsulation of the Pd NP (red) by SnO2 (green) after the O-R-O heat treatment cycle. The Sn intensities in the SnO2 support area were deliberately saturated to reveal any relatively weak signals in the particle region. Scale bars, 1 nm.

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS
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Palladium-tin catalysts for the direct synthesis of H₂O₂ with high selectivity

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Direct hydrogen peroxide synthesis

Hydrogen peroxide is synthesized industrially without direct contact of hydrogen and oxygen in order to achieve high concentrations. For many applications, only dilute aqueous solutions are needed. Freakley et al. report an improvement in the direct synthesis of hydrogen peroxide over using palladium-tin alloys. This catalyst still achieves selectivities of >95%, like palladium-gold alloys, but is cheaper and can suppress reactions that decompose the product. Science, this issue p. 965