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Controlling Mechanism of the Water–Gas Shift Reaction Activity Catalyzed by Au Single Atoms Supported on Multicomponent Oxides

Jungwoo Choi,^{||} Hyuk Choi,^{||} Ju Hyeok Lee, Eunji Kang, Kihyun Shin, Hyuck Mo Lee,* and Hyun You Kim*



better performing catalysts. Here, we use density functional theory to study the mechanism of WGSR catalyzed by Au single atoms stabilized at the CeO_x-TiO_2 interfaces on TiO_2 particles (ACT catalyst). We constructed two energetic landscapes of the WGSR (redox and associative mechanisms), concurrently presenting the H₂ formation as a rate-determining step. Electronic analysis data showed that the charge state of the oxygen ions participating in WGSR strongly correlates with the oxygen vacancy formation energy (OVF) and hydrogen binding energy (ΔE_H), directly scaling the CO oxidation power and the H₂ production ability. Further expansion toward various Au on oxide—oxide combinations confirmed that the delicate control of metal-oxide-oxide interfaces with optimized local electronic structures expresses the rational design of a WGSR catalyst.

1. INTRODUCTION

The water-gas shift reaction (WGSR, CO + $H_2O \leftrightarrow CO_2$ + H_2) is essential in generating high-purity hydrogen fuel for fuel-cell applications, ammonia synthesis, and selective hydro-⁷ The syngas (CO + H₂) produced by methane genation. steam reforming $(CH_4 + H_2O \rightarrow 3H_2 + CO)$ can be posttreated by the WGSR to remove CO and thus increase the purity of hydrogen fuel.^{8,9} Since the WGSR is exothermic by 41.1 kJ/mol, a lower reaction temperature is thermodynamically beneficial to promote the forward reaction (prevent the backward reaction), even though it penalizes the reaction kinetics.¹⁰ In this manner, improving the low-temperature performance of the catalyst is critical for facile WGSR. Gold nanoparticles (NPs) have shown noticeable catalytic properties compared to other catalysts toward the low-temperature WGSR (LT-WGSR).^{2–4,11–20}

The practical value of a catalyst is an ensemble of performance and cost-effectiveness. Single-atom (SA) catalysts with atomically distributed reactive species have suggested a new strategy for maximizing the specific mass activity (MA) of precious metal catalysts.^{21–24} The optimal MA of precious metal catalysts can be achieved if each metal atom becomes an active site. However, SA catalysts always accompany inherent stability issues because thermodynamics propels the agglomeration of SAs into larger clusters or NPs.^{25–28} Therefore, SA catalysts with ultralow concentrations of precious metals are usually used to study the inherent catalytic nature of SAs, even though the low concentration worsens the overall conversion performance.

To resolve the stability issue and increase the loading of SAs, several atomic precision tuning of the chemical potential of SAs, for example, strengthening the SA-support interactions or driving the decomposition of NPs into SAs, is suggested.^{21,22,29,30} Several studies have reported that the electronic metal–support interaction (EMSI) improves catalytic activity and stabilizes and prevents agglomeration of metallic species.^{29,31} For example, the Senftle group revealed that the reducibility of the support material and the oxophilicity of SAs concurrently affect the stability of SAs.²⁹ Wei and coworkers confirmed that the increased EMSI between Au NPs and TiO₂ improves the catalytic performance of Au/TiO₂ for LT-WGSR.³¹ Understanding the inherent roles of EMSI on the catalytic functionality of supported SAs and their stability under the reaction conditions will resolve the issues for practical applications of SA-based catalysts.

Cluster oxide

high reducible

Sinale

atom

Support oxide

low reducible

To enhance the properties of SAs through EMSI, we have previously suggested a hybrid oxide of CeO₂ and TiO₂ as optimal supporting materials for Au-SAs and Pt-SAs.^{22,30,32} The Pt-SAs stabilized at the CeO_x-TiO₂ interfaces activate CO oxidation with high specific MA.³⁰ The interfacial oxygen

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at the $Pt-CeO_x$ -TiO₂ interface facilitates CO oxidation by the Mars-van Krevelen mechanism. This implies that the catalytic activity of the metal-hybrid oxide interface in oxidation reactions can be optimized by carefully selecting the appropriate metal-oxide combinations.

Based on our previous findings, we initially model Au-SAs supported on CeO_r -TiO₂ particles (ACT) and theoretically analyze the catalytic activity of ACT toward LT-WGSR. Because the chemical nature of the bridging oxygen ion at the Au-CeO_x-TiO₂ interface determines the catalytic activity of CO oxidation and H₂ production, we focused on clarifying whether our hybrid oxide structure could be used as a general catalytic support for LT-WGSR. The overall pathway and energetics of LT-WGSR explored by density functional theory (DFT) calculations predict the two critical reaction descriptors, oxygen vacancy formation energy (OVF), and hydrogen adsorption energy ($\Delta E_{\rm H}$), both closely linked with the electronic state of oxygen. We further analyzed the electronic state variation of Au-oxide interfaces resulting from modifying the oxide-oxide combinations. We found that the Bader charge of the interfacial oxygen scales the OVF and $\Delta E_{\rm H}$, influencing the activity of Au-SAs in LT-WGSR. Eventually, we suggest a new catalyst combination, Au-SAs supported on $CeO_2 - ZrO_2$ as a better performing catalyst for LT-WGSR.

2. COMPUTATIONAL DETAILS

We used the Vienna Ab-initio Simulation Package (VASP)³³ for generalized gradient approximation (GGA) level DFT calculations. The exchange-correlation energy of the Kohn-Sham equation was estimated with the Perdew and Wang, PW91,³⁴ functional. The projector-augmented wave (PAW)³ method was used to interpret the interaction between the valence electrons and the ionic core. The kinetic energy limit of the plane wave basis was set to 400 eV. The convergence criteria were set to 10⁻⁴ eV and 0.03 eV·Å⁻¹ for electronic and geometry optimizations. The Brillouin zone was sampled at the Γ -point. The Gaussian smearing method with a finite temperature width of 0.05 eV was used to improve the convergence of states near the Fermi level. We used the DFT +U approach³⁶ to treat the Ti $(U_{\rm eff} = 4.5 \text{ eV})^{37}$ and Zr $(U_{\rm eff} =$ 4.0 eV)³⁸ d-orbitals and Ce f-orbitals ($U_{eff} = 4.5 \text{ eV}$).³⁷ The location and energy of transition states (TSs) were calculated using the climbing image nudged elastic band method.^{39,40}

We modeled a TiO₂(101) surface with a diagonal (surface vectors of [1-1-1] and $[0\ 1\ 0]$) 3×4 slab with three triple layers. A 15 Å of vacuum was introduced to separate the adjacent slabs along the z-axis. To construct a cluster-on-TiO₂ model, we first found the most stable location of a metal cation on TiO₂ and sequentially optimized the oxide clusters with additional oxygen ions.⁴¹ The final form of an oxide-TiO₂ model was confirmed if the additional oxygen increases the total energy of the system. The details of the atom-by-atom formation sequence of CeO_x clusters and CeO_x architectures on TiO₂ can be found elsewhere.⁴¹ The Au/oxide-TiO₂ model was constructed by finding the stable location of an Au atom over the oxide-TiO₂ model.²² Details of the structural models and how the DFT-calculated energies can be used to find the stable structure of metal-on-multicomponent oxides are elsewhere.^{22,30,32,41}

To maximize the areal fraction of the CT interfaces and stabilize Au as SAs at the CT interfaces, we use a CeO_x clusteron-TiO₂ model here.^{30,32,41} The model structure for DFT calculations (Figure 1a) was accordingly constructed.²² We have confirmed experimentally that the uniformly distributed CT interfaces on TiO_2 stabilize Au-SAs.²²



Figure 1. Formation of energetically stable Au single atom at the CeO_2-TiO_2 interface. (a) DFT-calculated binding trend of Au on $TiO_2(101)$ and CeO_2-TiO_2 . E_{bind} of *n*Au represents the calculated average binding energy of *n* Au atoms. (b) DFT-calculated Bader charge of Au-TiO_2(101), $CeO_2-TiO_2(101)$, and $Au/CeO_2-TiO_2(101)$. Black and yellow numbers represent the Bader charge of metal Au and oxygen, respectively. Original data in panel (a) were adopted from our previous report.²²

To construct additional oxide clusters on TiO_2 models, a single cation (M) was stabilized on TiO_2 by finding the most energetically stable location.⁴¹ Oxygen ions were sequentially added and optimized to find the stable morphology of MO_x . The total number of oxygen (*x*) was determined at the point at which the binding energy of oxygen becomes energetically uphill.⁴¹ The final geometries of the MO_x on TiO_2 models are presented in Figure S2. A 2 × 2 × 4 (11–1) slab of ZrO_2 was sliced and expanded from a monoclinic ZrO_2 unit cell.

3. RESULTS AND DISCUSSION

The strong electronic interaction between metal SAs and oxides stabilizes SAs at the metal-oxide interfaces. $^{42-50}$ In addition, the modified electronic ensemble at the metal-oxide interfaces alters the catalytic nature of SAs. We found that CeO_x clusters formed on TiO₂ oxide particles enhance the MA of Pt-SAs stabilized at the CT interfaces toward the interfacemediated MvK type CO oxidation.³⁰ The oxygen ions at the Pt-CT interfaces actively oxidize Pt-COs* with reduced E_{act} compared with Pt-SAs on pristine TiO₂. We found a similar function of the CT interfaces on catalytic CO oxidation by Au-SAs.²² Consistent with a consensus that Au is reactive for CO oxidation at lower temperature ranges than Pt,¹² the DFTcalculated $E_{\rm act}$ of Au-SAs at CT was about 75% of that of Pt-SAs at CT. The weaker Au-O-Ce interaction energy than that of Pt-O-Ce made the Au-SAs volatile and thus move out from the CT interfaces and diffuse along the TiO₂ surfaces, entailing the retardment in conversion. However, the light-on temperature of Au-SAs (75 °C) was lower than that of Pt-SAs (125 °C), showing that Au-SAs on CT are a suitable catalyst for low-temperature CO oxidation, a mandatory condition in LT-WGSR. The reduced Ce³⁺ ions at the Au-CT interfaces may assist water binding and utilization.

The DFT-estimated energetic trend in Au-CT or $-\text{TiO}_2$ interactions shows that the Au-SA is a stable form of Au at the CT interfaces. In contrast, Au clusters grow on TiO₂ (Figure



Figure 2. Schematic illustration of possible mechanisms of WGSR catalyzed by ACT. (a) Initial sequential binding of CO and H_2O , (b) redox mechanism, and (c) associative mechanism. In both cases, H_2O dissociation and H_2 production are highly endothermic with high E_a . An and Rn in (b) and (c) represent the *n*th stage along the associative and dissociative pathways. ΔE between the states was calculated by extracting the absolute energy of the current state from that of the previous state. To recover stage R3 to the initial/final structure, we added a H_2O molecule to heal the vacancy; however, we recolored the pink oxygen of the water to green to keep the consistency between the initial and the final structure. Each ΔE of H_2 (R1 to R2 and A3 to A4) and CO₂ (A2 to A3 and initial to R1) desorption can be reduced by -0.41 and -0.66 eV at 298.15 K due to the entropic contribution to the Gibbs free energy of desorption.

1a, data adapted from our previous publication under the permission of the Institute of Physics).²² The Bader charge analysis shows that Au and Ce ions are electronically coupled (Figure 1b). The Au-SA donated 0.42 e to the adjacent Ce ion, reducing it to Ce³⁺. More detailed experimental electronic structure analysis results on the reduction of Ce⁴⁺ to Ce³⁺ due to the Au-Ce interaction can be found in our previous report.²² The additional density of states (DOS) plots of ACT, Au/TiO_{2} , and CT (Figure S1) clearly show that the empty signature 4f states of Ce ions are filled upon interaction with Au-SAs. In addition, the consistent morphology of the Ce 4f and Au bands near the Fermi level shows that Ce and Au are electronically well-coupled. These results confirm that CeO_r clusters on TiO₂ behave as electronic anchoring sites for stabilizing Au-SAs. The DFT-calculated binding energy, $E_{\rm bind}$, values of a Au-SA at CT interface, stoichiometric CeO₂-TiO₂ (-2.33 eV), exceed the E_{bind} of Au_n (n = 1, 2, 3, 4) species on TiO₂. This means that the CT interface is the thermodynamically preferred location of an Au-SA on TiO₂.

Based on the DFT-predicted Au-SA pinned at the CT interface model (Figure 1), ACT, we explored the reaction mechanism of WGSR. In Figure 2, the Au-SA of ACT binds the first CO with $E_{\rm bind}$ of -1.60 eV (Stage A). This value is greater than the generally reported $E_{\rm bind}$ of CO of CeO₂-supported Au clusters or NPs.^{45,46,48} Previously, we found that CO interacts with a Au₁₂ nanocluster supported on CeO₂(111) with -1.28 eV of $E_{\rm bind}$.⁴⁸ The average $E_{\rm bind}$ of eight CO molecules bound on a Au₉ cluster supported on CeO₂(100) was -0.99 eV.^{45,46}

The reduced Ce³⁺ ion of ACT subsequently binds two water molecules at the bridging position between the Ce³⁺ and the oxygen ion with E_{bind} of -0.88 and -0.79 eV, respectively

(Stages B and C, Figure 2a). The water-activating role of the reduced Ce³⁺ has been reported as the origin of catalytic WGSR by CeO₂-supported catalysts. One adsorbed water molecule was dissociated into an OH at the surface oxygen of TiO₂ near Ce³⁺ and into an H at the bridging oxygen between Ce³⁺ and Ti⁴⁺ (Stage E, Figure 2a). This dissociation is thermodynamically driven with -1.12 eV of reaction energy, ΔE . After dissociation, one more water molecule was adsorbed on the Ce ion with E_{bind} of -0.79 eV (Stage F, Figure 2a).

From stage F, the reaction proceeds in two ways: associative mechanism (Figure 2c) and redox mechanism (Figure 2b). The associative mechanism includes forming the COOH* carboxyl group upon early dissociation of a water molecule (Stage A1). After filling the open space formed during water dissociation with one more water molecule (Stage A2), CO₂ desorbs from the catalyst (Stage A2 and A3). We found that H₂ can be formed and released from the residual H of carboxyl adsorbed on Au and one H on the bridging oxygen between Ce and Ti (Stages A3 and A4). The initial stage was recovered upon adsorption of CO. Although the overall process is complete, the H₂ formation and release were uphill by 1.70 eV (A3 to A4), indicating that the associative pathway contributes less to the overall LT-WGSR activity of ACT than an the Redox mechanism with ΔE of 1.39 eV. In both cases, the H₂ formation step determines the overall rate of WGSR, becoming the rate-determining step. This finding aligns with previous studies reporting slow water dissociation and H₂ formation as a challenge in WGSR.

Because 0.41 eV of additional energy can be provided by entropic contribution $(-T\Delta S = -0.41 \text{ eV})$ to the Gibbs free energy of H₂ desorption at 298.15 K, this energy requirement could be reduced below 0.98 eV in the Redox mechanism, ^{51,52}

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Figure 3. Scaling linear relationship between the (a) $\Delta E_{\rm H}$ (*x*-axes), (b) OVF, and the Bader charge of oxygen (*y*-axis). Blue dots correspond to the interfacial oxygen of Au/oxide–oxide systems. Black squares denote four representative reducible or irreducible oxides. Red stars represent the data points from the suggested Au/CeO₂–ZrO₂ catalyst. All data points clearly show the linear relationships between the OVF and $\Delta E_{\rm H}$ and the Bader charge of interfacial oxygen (surface oxygen of single component oxide).



Figure 4. Simplified WGSR mechanism over the (a) $Au/CeO_2-TiO_2(ACT)$ and (b) $Au-CeO_2-ZrO_2(ACZ)$. Elemental reaction stages A to C present CO oxidation, and the stages from C to E and A describe H₂ formation and production. Enhanced ΔE and reduced E_a of H₂O dissociation in ACZ suggest that ACZ more effectively produces H₂ than ACT. Each ΔE of H₂ (E1 to A1 and E2 to A2) and CO₂ (B1 to C1 and B2 to C2) desorption can be reduced by -0.41 and -0.66 eV at 298.15 K due to the entropic contribution to the Gibbs free energy of desorption.

meaning that H_2 production is not thermodynamically forbidden. A similar consideration applies to the desorption of CO_2 , whose entropic contribution to the Gibbs free energy of desorption at 298.15 K is -0.66 eV.^{51,52}

The oxygen vacancy formed upon CO oxidation facilitates water dissociation during the redox pathway (stages R1 and R2). The additional thermodynamic driving force of carboxyl formation activates water dissociation during the associative pathway (stage A1). However, the H_2 formation step still needs to be more activated by reducing the energy of H_2 desorption from the catalyst surface.

Based on our theoretical understanding of the WGSR mechanism by ACT, we separately studied the overall pathway of WGSR into CO oxidation and H₂ formation steps. We selected the OVF (CO oxidation) and the adsorption energy of H ($\Delta E_{\rm H}$, H₂ formation) as an energetic descriptor of each part. A lower OVF facilitates CO oxidation, and a higher $\Delta E_{\rm H}$ in negative (high absolute value) retards H₂ formation and H₂ release from the catalyst. The OVF and $\Delta E_{\rm H}$ have been used as property descriptors in various CO oxidation and hydrogen evolution reaction studies.^{46,50,53–55}

The OVF accompanies the electron transfer between the removing oxygen and the residual structural motifs. Therefore, the initial charge state of the oxygen ion may predict the OVF and influence the extent of the electron redistribution upon hydrogen binding. To confirm these hypotheses, we plotted the Bader charge values of the interfacial oxygen as a function of their OVF and $\Delta E_{\rm H}$. In addition, to generalize and acquire more analyzable data, we expanded our ACT system with different oxide clusters (VO₃, FeO₂, and FeO₃) on TiO₂ with one Au-SA (refer to Figure S2 for structural information). The data presented in Figure 3 show a clear relationship between the OVF and $\Delta E_{\rm H}$ and the Bader charge of the interfacial oxygen of Au/oxide-TiO₂ catalysts (blue dots). The less reduced oxygen species with the lower absolute Bader charge value exhibit the lower OVF and the higher (in negative) $\Delta E_{\rm H}$. A highly reduced oxygen species with high absolute Bader charge values is required to weaken the hydrogen binding (low absolute value of $\Delta E_{\rm H}$) and facilitate hydrogen formation, which is vital for LT-WGSR. However, as the absolute value of the Bader charge increases, the OVF correspondingly increases, retarding the oxidation of CO. These results present a general trade-off relationship between the CO oxidation and

 H_2 formation performance of a catalyst during WGSR. A catalyst with well-balanced OVF and ΔE_H facilitates CO oxidation and H_2 formation, achieving optimal LT-WGSR performance.

To extend the data set and gain insight into the catalyst design method, we additionally calculated and plotted the Bader charge, OVF, and $\Delta E_{\rm H}$ of MgO(100), ZrO₂(11–1), TiO₂(101), and ZnO(100) and plotted in Figure 3 (black squares). Details on the structural models are presented in Figure S3. Remarkably, the added data points strengthen the linear relation between the Bader charge, OVF, and $\Delta E_{\rm H}$. Two representative irreducible oxides (MgO(100) and ZrO₂(11–1)) have a high absolute Bader charge value and, thus, a low absolute $\Delta E_{\rm H}$. The other two reducible oxides (TiO₂(101) and ZnO(100)) show similar Bader charge values with the Auoxide-TiO₂ models with moderate $\Delta E_{\rm H}$. However, the high OVF of two irreducible oxides, ZrO₂(11–1) and MgO, presents an apparent trade-off relationship between the OVF and $\Delta E_{\rm H}$ in a single catalyst system.

Considering that a catalyst with balanced OVF and $\Delta E_{\rm H}$ will record excellent low-temperature WGSR performance, a tentative hybrid oxide system with a reducible oxide cluster (beneficial for decreasing the OVF) on an irreducible support (assists in decreasing the absolute value of $\Delta E_{\rm H}$) may meet both requirements. To confirm this hypothesis, we constructed a hybrid oxide system, CeO2-ZrO2, composed of a reducible CeO₂ cluster on an irreducible ZrO₂ support. The calculated E_{bind} of an Au single atom at the CeO₂-ZrO₂ interface (-2.26 eV) predicts that the CeO₂-ZrO₂ interface strongly binds an Au-SA (refer to Figure S4 for structural details). In addition, new data points of Au/CeO₂-ZrO₂ (ACZ) plotted in Figure 3 (red star) show that OVF and $\Delta E_{\rm H}$ move in the beneficial direction to facilitate H₂ production and CO oxidation. The energetics of the simplified WGSR steps catalyzed by ACT and ACZ demonstrate that the H₂O dissociation is thermodynamically and kinetically driven in ACZ (D2 to E2, Figure 4b) compared to ACT (Figure 4a). The ΔE of H₂O dissociation becomes highly negative in ACZ, and the corresponding E_a decreases by 0.15 eV (20%) compared to ACT. The increased activity of ACZ toward WGSR is also confirmed by the rate map (Figure S5, equivalent to the experimental light-off profile) based on microkinetic modeling.

The overall trends in Figure 3 predict that using ZrO_2 or MgO as a supporting oxide accelerates H_2 production, which is thermodynamically and kinetically difficult in ACT. Although ZrO_2 and MgO slightly retard CO oxidation, the entropic contribution to the Gibbs free energy of CO_2 release may compromise the adverse effect. Other combinations of Au-SAs with CeO_2 -MgO, VO_3 -ZrO₂, or FeO₃-MgO can be a candidate.

4. CONCLUSIONS

In summary, we explored the mechanism of WGSR catalyzed by ACT, a CeO₂-TiO₂ hybrid oxide-supported Au-SA catalyst, and found that both redox and associative mechanisms are operative. The DFT-based mechanism analysis confirmed that individual CO oxidation and H₂ formation reactions comprise the overall WGSR. The H₂ formation becomes the rate- determining step of the WGSR by ACT. Based on Bader charge analysis, we found an apparent correlation between the electronic state of oxygen at the Au-CT interface and the OVF and $\Delta E_{\rm H}$. We found that achieving a compromise between the low OVF and the negatively low $\Delta E_{\rm H}$ is required to accelerate both parts of WGSR and record the excellent LT WGSR performance. A direct Bader charge-OVF- $\Delta E_{\rm H}$ relationship derived from our ACT system was confirmed through various Au-oxide—oxide combinations. Based on the linear correlation between the Bader charge and OVF and $\Delta E_{\rm H}$, we found that using an irreducible oxide as a supporting material of an oxide—oxide combination is beneficial in accelerating H₂ production. Our results suggest that the delicate and atomic precision control of metal—oxide—oxide interfaces with optimized and balanced local electronic structures expresses the rational design of an LT-WGSR catalyst.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.4c01559.

Structure of various hybrid oxide interface systems, support oxides, considered oxygen sites, and methods of microkinetic modeling (PDF) Archive of CONTCAR (ZIP)

AUTHOR INFORMATION

Corresponding Authors

- Hyuck Mo Lee Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea; orcid.org/0000-0003-4556-6692; Email: hmlee@ kaist.ac.kr
- Hyun You Kim Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, Republic of Korea; orcid.org/0000-0001-8105-1640; Email: kimhy@cnu.ac.kr

Authors

- Jungwoo Choi Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea; orcid.org/0000-0003-3988-6331
- Hyuk Choi Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, Republic of Korea; orcid.org/0000-0002-7899-2631
- **Ju Hyeok Lee** Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, Republic of Korea
- Eunji Kang Department of Materials Science and Engineering, Chungnam National University, Daejeon 34134, Republic of Korea
- Kihyun Shin Department of Materials Science and Engineering, Hanbat National University, Daejeon 34158, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.4c01559

Author Contributions

^{IJ}.C. and H.C. are contributed equally to this work. **Notes**

The authors declare no competing financial interest.

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