Catalytic behavior of metal catalysts in high-temperature RWGS reaction: In-situ FT-IR experiments and first-principles calculations

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High-temperature chemical reactions are ubiquitous in (electro) chemical applications designed to meet the growing demands of environmental and energy protection. However, the fundamental understanding and optimization of such reactions are great challenges because they are hampered by the spontaneous, dynamic, and high-temperature conditions. Here, we investigated the roles of metal catalysts (Pd, Ni, Cu, and Ag) in the high-temperature reverse water-gas shift (RWGS) reaction using in-situ surface analyses and density functional theory (DFT) calculations. Catalysts were prepared by the deposition-precipitation method with urea hydrolysis and freeze-drying. Most metals show a maximum catalytic activity during the RWGS reaction (reaching the thermodynamic conversion limit) with formate groups as an intermediate adsorbed species, while Ag metal has limited activity with the carbonate species on its surface. According to DFT calculations, such carbonate groups result from the suppressed dissociation and adsorption of hydrogen on the Ag surface, which is in good agreement with the experimental RWGS results.

The demand for carbon-neutral technologies has increased over the last two decades because of the negative effects of global warming and climate change caused by excessive carbon dioxide (CO\textsubscript{2}) emissions\textsuperscript{1,2}. Various techniques\textsuperscript{3–5} have been studied to directly or indirectly reduce and/or utilize CO\textsubscript{2} in the atmosphere. Among these approaches, high-temperature chemical reactions have attracted increasing interest as next-generation fuel processing and energy conversion/storage processes\textsuperscript{6–8}. The reverse water-gas shift (RWGS) reaction is one of the most promising high-temperature chemical reactions because of its thermodynamic favourability and its direct gas-phase reaction\textsuperscript{9}, expressed as

\[ \text{CO}_2(g) + \text{H}_2(g) \leftrightarrow \text{CO}(g) + \text{H}_2\text{O}(g), \quad \Delta G_{298}^{\circ} = 0 \text{kJ mol}^{-1}, \]  

where \( G \) is the Gibbs free energy. In addition, the RWGS reaction offers further (CO-based) synthetic processes to obtain methanol through CO\textsubscript{2} hydrogenation\textsuperscript{9}, or long-chain hydrocarbons through the Fischer–Tropsch reaction\textsuperscript{10}.

To date, various catalysts, including supported noble metals (e.g., Pt/8Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} and Rh/Al\textsubscript{2}O\textsubscript{3})\textsuperscript{11,12}, supported transition metals (e.g., Ni/Na/CeO\textsubscript{2} and Cu/SiO\textsubscript{2})\textsuperscript{13–15}, and perovskite oxide catalysts (e.g., La\textsubscript{1−x}Sr\textsubscript{x}CoO\textsubscript{3} and BaCe\textsubscript{0.8}Zr\textsubscript{0.2}Y\textsubscript{0.05}Zn\textsubscript{0.06}O\textsubscript{3})\textsuperscript{16} have been used in the RWGS reaction. Despite the comprehensive studies conducted to develop high-performance catalysts for the RWGS reaction, a fundamental understanding of the roles of metal catalysts and their mechanisms during the spontaneous, dynamic, and high-temperature RWGS reaction.

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is lacking. Hence, in-situ measurements and density functional theory (DFT) predictions of the surface adsorption and intermediate functional groups are required, which will substantially contribute to the development of advanced high-temperature RWGS reactions.

In this study, we investigated the RWGS reaction catalyzed by four different metal catalysts (Pd, Ni, Cu, and Ag) on an inert Al2O3 support as a function of temperature (T) and H2-to-CO2 ratio (Rmix), and developed a comprehensive understanding of their roles at high temperatures using in-situ Fourier-transform infrared spectroscopy (FT-IR) and DFT calculations. These advanced experimental and computational techniques allow us to directly study the adsorbed functional groups by analyzing the IR spectra of the surfaces of the metal catalysts and comparing the results with the DFT-predicted reaction energies and electronic-state changes of the intermediate functional groups.

Results and Discussion
Synthesis and characterization of metal catalysts on Al2O3 support. To analyze the roles of the metal catalysts in the high-temperature RWGS reaction, we synthesized and examined various metal nanocatalysts supported on Al2O3 spherical powder. Figure 1(a) presents a schematic illustration of catalyst synthesis by deposition-preparation with urea hydrolysis. The surface charge of the Al2O3 powder changes with solution pH, which facilitates positive metal ion adsorption above the point of zero charge (PZC; for Al2O3, PZC = pH 8.5–9.017). At 90 °C, urea can decompose in water to form hydroxide anions (OH−), thereby increasing the pH. We also applied freeze dehydration to avoid the agglomeration and coalescence of nanocatalysts during the drying and calcination step. Finally, various metal nanocatalysts (well-dispersed on an Al2O3 support) were successfully obtained for application in high-temperature RWGS reactions. Transmission electron microscopy (TEM) images of the reduced metal/Al2O3 catalysts powder are shown in Fig. 1(b–e). The reduced metal catalysts have an average particle diameter of ~10 nm with standard error of ~0.4, while the spherical Al2O3 support has a diameter of ~40 nm (see Table S1 in Supplementary Information). Note that the average particle size and its standard error were determined using TEM image processing over 50 randomly selected particles on Al2O3. We also verified the surface area of the as-prepared metal/Al2O3 samples using the Brunauer–Emmett–Teller surface area (SBET). All samples exhibited similar surface areas (SBET values) in the range of 29.0–34.2 m2 g−1 (see Table S1 in Supplementary Information). The reducibility of the as-synthesized metal catalysts was examined by temperature-programmed reduction (TPR). The profiles in Fig. S1 (Supplementary Information) noticeably show their inherent reducing features [for Pd, decomposition of palladium hydrides at ~80 °C18; for Ni, strong interaction of Ni(O)-Al2O3 and its reduction at ~500 °C19; for Cu, the reduction of surface and bulk CuO at ~200 °C20; for Ag, no oxidation under this calcination condition]. The X-ray diffraction (XRD) patterns shown in Fig. 2 confirmed the crystalline structures of the metal nanocatalysts. Ignoring the complex XRD spectra of the Al2O3 support, we identified the metallic state of each catalyst. Using such fully-reduced metal catalysts (Pd, Ni, Cu, and Ag), we investigated the RWGS performance as a function of reactant mixing ratio and temperature using a gas chromatograph (GC) and in-situ FT-IR experiments.

RWGS performance of various metal catalysts. Figures 3 and 4 present the RWGS catalytic performance, CO2 conversion (Xco2), and CO selectivity (Sco) [see Eqs (2) and (3) in Methods] achieved by various metal catalysts on the Al2O3 support. In general, the RWGS reaction is considered an equilibrium gas-phase process without any dynamic or transient conditions1. By formulating thermodynamic models for the RWGS reaction11, the equilibrium compositions of product gases can be predicted for various temperatures and reactant gas ratios at a specific pressure. The thermodynamic equilibrium performance of Xco2 under our experimental conditions is presented as a dashed line in Fig. 3. In addition, the preliminary experiments using the Al2O3 support alone and a blank reactor were summarized in Fig. S2 (Supplementary Information). These preliminary results—associated with the possible catalytic effects of the Al2O3 support (at 800 °C, Xco2 ≈ 15.9 and 27.9% for
$R_{\text{mix}} = 1$ and 3) and blank system (at $800 \, ^\circ\text{C}, X_{\text{CO}_2} \approx 0.0$ and 0.0% for $R_{\text{mix}} = 1$ and 3)—also serve as a reference for measuring the RWGS performance of the metal catalysts. These results are in general agreement with the

Figure 2. XRD patterns of the catalysts reduced at $600 \, ^\circ\text{C}$ for 2h. The red, yellow, green, and blue lines and symbols correspond to the supported Pd, Ni, Cu, and Ag catalysts, respectively. The black line represents the XRD pattern of the $\text{Al}_2\text{O}_3$ support.

Figure 3. CO$_2$ conversion of each catalyst with respect to temperature and $R_{\text{mix}}$. The red, yellow, green, and blue lines correspond to temperatures of 900, 800, 700, and 600 $^\circ\text{C}$, respectively. For reference, all X$_{\text{CO}_2}$ profiles of the empty tube and $\text{Al}_2\text{O}_3$ support are presented in Fig. S2 (Supplementary Information).
literature\textsuperscript{12}, the $\text{X}_{\text{CO}_2}$ of Al$_2$O$_3$ $\approx$ 40% at 800 °C for $R_{\text{mix}}$ = 4. We expect such conversion results of the Al$_2$O$_3$ support are caused by the inherent features of the RWGS reaction (gas-phase equilibrium limited and favoured at high temperature)\textsuperscript{12}. Interestingly, we observed limited (or suppressed) RWGS reaction in our fixed-bed column reactor system. These results raise questions about the roles of the metal catalysts during the spontaneous, dynamic, and high-temperature RWGS reaction.

As shown in Fig. 3, all metal catalysts except Ag exhibited similar behaviours and maximum conversion activities (reaching the thermodynamic equilibrium limit): at 800 °C, $\text{X}_{\text{CO}_2}$ $\approx$ 49.5 and 71.5% for $R_{\text{mix}}$ = 1 and 3, respectively. In contrast, Ag metal has a significantly lower catalytic activity under all conditions of temperature and $R_{\text{mix}}$: at 800 °C, $\text{X}_{\text{CO}_2}$ $\approx$ 21.3 and 46.7% for $R_{\text{mix}}$ = 1 and 3, respectively. Surprisingly, these values obtained for Ag metal are approximately 50% lower than those for other metals and the thermodynamic equilibrium conversion. These catalytic RWGS performances of the metal/Al$_2$O$_3$ catalyst are competitive with Fe$_2$O$_3$ powder, one of the widely used industrial catalysts for WGS (at $T$ = 350 to 450 °C)\textsuperscript{22}. As shown in Fig. S3 (Supplementary Information), the overall $\text{X}_{\text{CO}_2}$ and $\text{S}_{\text{CO}}$ of Fe$_2$O$_3$ generally increase with temperature, but the measured $\text{X}_{\text{CO}_2}$ results are slightly scattered and suppressed (at 800 °C, $\text{X}_{\text{CO}_2}$ $\approx$ 23.4 and 40.4% for $R_{\text{mix}}$ = 1 and 3) due to its significant sintering behaviour in a highly reducing atmosphere at high temperature.

Figure 4 presents the $\text{S}_{\text{CO}}$ values measured for various metal catalysts at different temperatures and $R_{\text{mix}}$ values. From the theoretical thermodynamic models\textsuperscript{21} and previous experimental results\textsuperscript{23} for the RWGS reaction, CH$_4$ formation is generally observed in the intermediate temperature range ($T$ $\leq$ 700 °C) and/or high $R_{\text{mix}}$ condition, not above 800 °C. Thus, we found that the $\text{S}_{\text{CO}}$ of all catalysts for $T$ $\geq$ 800 °C is 100%. For $T$ $\leq$ 700 °C, however, the catalytic behaviour of CO$_2$ conversion was noticeably changed. The $\text{S}_{\text{CO}}$ values of the Pd and Ni catalysts decreased with increasing $R_{\text{mix}}$ due to the formation of CH$_4$ at 600–700 °C. In contrast, the Cu and Ag catalysts achieved $\text{S}_{\text{CO}}$ values of 100% under all experimental conditions, and no CH$_4$ production was observed. Cu and Ag favoured CO production, while Pd and Ni were partially active toward CH$_4$ formation. Such a difference was mainly caused by the opposed ability toward H$_2$ dissociation of each metal catalyst. The Pd and Ni catalysts including general noble metals (e.g., Pt, Rh, Ru) have higher activity toward H$_2$ dissociation than the others, and provide an interesting result of CH$_4$ formation at $T$ $\leq$ 700 °C\textsuperscript{23}. The details regarding the different abilities of H$_2$ dissociation will be discussed later.

Based on the $\text{X}_{\text{CO}_2}$ and $\text{S}_{\text{CO}}$ results in Figs 3 and 4, we found that temperature and the amount of hydrogen (or H$_2$ dissociation process) are the dominant factors in high-temperature RWGS reactions, as the Gibbs free energy is negative above 827 °C and CO$_2$ gas was stable even at high temperatures in the absence of a reducing atmosphere or reduction process. Additionally, we concluded that the catalytic effects of most metal catalysts (Pd, Ni, and Cu) are rather high, whereas that of Ag metal is generally negligible.

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**Figure 4.** CO selectivity of each catalyst with respect to temperature and $R_{\text{mix}}$. The red, yellow, green, and blue lines correspond to temperatures of 900, 800, 700, and 600 °C, respectively. For reference, the $\text{S}_{\text{CO}}$ of the Al$_2$O$_3$ support in all cases is 100% in spite of its limited $\text{X}_{\text{CO}_2}$ performance.
In-situ characterization of surface transient species. To clarify the roles of metal catalysts in the high-temperature RWGS reaction, we conducted in-situ diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) characterization to identify the intermediate species adsorbed on the metal surface. Figure 5 depicts the DRIFTS spectra of various metal catalysts during the RWGS reaction at 600 and 800 °C. As reported, three different formate bands can be assigned based on several vibrational modes. The first bands, ν(O-C-O)as and ν(C-H), are calculated to be in the regions of 1590 and 2855–2850 cm⁻¹, respectively. A second combination band, ν(O-C-O)as and δ(C-H), is found from 2905 to 2900 cm⁻¹. The third formate band, δ(C-H) and ν(O-C-O)s, is located from 1395 to 1375 cm⁻¹. For the highly active metal catalysts (e.g., Pd, Ni, and Cu), formate (HCOO⁻) groups were clearly detected as a major adsorbed species in the RWGS reaction. Additionally, methane (CH₄), adsorbed methyl (CH₃), and carbonate (CO₃²⁻) groups were observed in small quantities on the catalyst surface. Gaseous CH₄ and adsorbed CH₃ were only found on the Pd and Ni/Al₂O₃ catalysts at 600 °C, as indicated by the peaks at 3000 and 2890 cm⁻¹, respectively. This result is in agreement with the suppressed CO selectivity observed at 600 °C due to CH₄ formation. In contrast, the Ag/Al₂O₃ catalyst had two distinct bands not observed in the other highly active metal catalysts: one indicating monodentate carbonate, ν(O-C-O)as, at 1465 cm⁻¹ and one indicating a chelating bidentate carbonate, ν(C=O), at 1575 cm⁻¹. We conclude that the presence of these carbonate species is closely related to the lower catalytic activity of the Ag metal catalyst, as formate species are generally formed by the interaction between the spillover of a H atom to an adsorbed CO₂. Based on literature reports, the catalytic RWGS reaction mostly occurs at the interfacial area between the metal and the support. Considering the limited H₂ dissociative adsorption from the Al₂O₃ support, we cannot expect a sufficient combination of CO₂ adsorption on the metal and H₂ dissociative adsorption on the support, especially in the case of Ag, which has a limited capability for H₂ dissociative adsorption. Therefore, we attribute the superior (or suppressed) CO₂ conversion with the existence (or absence) of carbonate species resulting from the abundance (or lack) of activated H atoms, as supported by the DFT calculations described in the following section.

DFT prediction of surface reactions on various metal catalysts. To predict the reaction mechanisms on the metal surfaces, we considered the overall reaction pathway and observed their behaviours with relative energies using the DFT formalism. Here, we adopted the slab model (first three layers free to relax) to simulate the metal catalysts, considering the computational convenience and cost for metal nanocatalysts (~10 nm diameter and highly-crystalline structure). Note that some reaction energies such as H₂ dissociative chemisorption may lead to small uncertainties due to the structural limits and coverage effects of the slab model. First, the surface energy results of various metals were investigated and are summarized in Table 1. Among the four metals, Ag has the lowest surface energy and Ni the highest. The (111) surface has the lowest energy among the three surfaces in the studied metals, followed by the (100) surface and then the (110) surface, except in the case of Ag. We then calculated the reaction energy diagram on various metal (111) surfaces to simulate the overall RWGS pathway including a formate intermediate and a dissociative H adsorbent, which are experimentally observed in above in-situ characterization. Figure 6(a) presents the overall energetics of different metal catalysts.
These findings agree well with the above-mentioned GC experimental results and reaction steps, (i) H$_2$ related to the local reactivity of the surfaces (Pd, Ni, Cu, and Ag) and the density difference surfaces at an iso-value of 0.0067 of H atoms onto a metal surface. Figure 7(a) shows the charge density difference for H adsorbed on various metal surfaces. As shown in Fig. 7(b), the anti-bonding resonances between 1 $d$-bands after adsorption. Similar to the literature$^{37}$, the $E_d$-band centre (i.e., higher $E_{d\text{-band centre}}$) of Ag metal results in the weakest bonding and the lowest reactivity. We conclude that the metal surfaces studied, except Ag, encourage H dissociation and a significant charge polarization of adsorbed H atoms, facilitating the formation of specific intermediate formate functional groups (e.g., HCOO$^-$) that promote the RWGS reaction. These findings agree well with the above-mentioned GC experimental results and in-situ FT-IR data.

**Conclusion**

In summary, the catalytic activity and adsorption properties of various metals (Pd, Ni, Cu, and Ag) on an Al$_2$O$_3$ support for the high-temperature RWGS reaction were investigated by in-situ FT-IR experiments and DFT calculations. The CO$_2$ conversion shows the maximum activity on the Pd, Ni, and Cu catalysts, reaching the thermodynamic limit, while that of Ag metal is suppressed. According to our in-situ high-temperature FT-IR measurements
and comprehensive DFT calculations, we directly observed that the formate group is an intermediate adsorbed species on all highly activated catalysts during the high-temperature RWGS reaction. In addition, this formation of a formate group is noticeably determined by the H$_2$ dissociation and H adsorption capabilities of the metal surface. Interestingly, the suppressed catalytic activity of Ag is clearly verified by the reaction energy diagram and d-band analysis. Such an understanding of the roles of metal catalysts and their mechanisms during the high-temperature RWGS reaction allows for technological advances for superior high-temperature RWGS catalysts.

**Methods**

**Catalyst preparation and characterization.** Ag(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich), Cu(NO$_3$)$_2$·2.5H$_2$O (Sigma-Aldrich), Pd(NO$_3$)$_2$·2H$_2$O (Sigma-Aldrich), and Ni(NO$_3$)$_2$·6H$_2$O (Sigma-Aldrich) were used as the metal precursors. To suppress any catalytic or size effects originating from the support material, spherical Al$_2$O$_3$ powder (Alfa Aesar, specific surface area = 28 m$^2$ g$^{-1}$) was chosen as the support. To prepare the catalyst, Al$_2$O$_3$ was dispersed in water with vigorous stirring. An appropriate amount of the metal precursor (5 wt%) was dissolved in water. Next, urea (Yakuri Pure Chemical) and the metal precursor were poured into the Al$_2$O$_3$ slurry, and this mixed solution was heated to 90 °C with vigorous stirring. After 4 h of reaction, the mixed solution was rapidly frozen using liquid nitrogen and dried in a freeze-dryer (FD 5512, Ilshin) overnight. The dried powder was then calcined in an electric box furnace for 3 h at 400 °C.

The $S_\text{BET}$ of the reduced catalysts were determined using the multipoint BET measurement (Quadsorbor SI, Quantachrome) with N$_2$ adsorption, as summarized in Table S1 (Supplementary Information). Prior to BET measurement, the catalyst samples were degassed in vacuum at 130 °C for 12 h. The TPR spectra (AutoChem II 2920, Micromeritics) of the as-prepared powders were obtained by using 10 mol% H$_2$ balanced in Ar with a flow rate of 50 mL min$^{-1}$ ($T$ = 50 to 900 °C, ramp rate = 10 °C min$^{-1}$). All powders were pre-oxidized at 400 °C for 1 h before the TPR measurement.

The crystalline phases of the reduced catalysts were examined using XRD (D/Max-2500, Rigaku) with Cu-K$_\alpha$ radiation. All XRD patterns were obtained in the 2θ range of 20 to 80° with a step size of 0.01°. The size and morphology of the metal catalysts on the Al$_2$O$_3$ powder were observed by TEM (Talos F200X, FEI) operated at 200kV. TEM specimens were prepared by dispersing the catalyst powder in ethanol and then placing the sample onto a porous carbon film supported on a Cu grid (or a nickel grid in the case of Cu metal).
Gas chromatography and IR measurements. The RWGS reaction was conducted in a fixed-bed tubular quartz reactor operated at atmospheric pressure. The synthesized catalyst powder (0.3 g) was placed in the middle of the reactor, on a porous quartz bed fixed by blowtorching. The reactor was placed inside a tube furnace to control the reaction temperature using a proportional-integral-derivative temperature controller. The reactant gas, which contained H2 and CO2 with a balance of Ar (total feed flow rate = 100 mL min⁻¹), was pre-mixed and fed at $R_{\text{max}}$ varying from 0.5 to 3. To prevent surface oxidation of the metallic catalysts, all catalysts were reduced under 10 mol% H2 gas balanced in Ar at 600 °C for 2 h before the RWGS reaction. The catalytic activity tests were performed in the temperature range 600 to 900 °C using a GC (7890B, Agilent) with a cold trap to separate steam from the product gas. Two columns with different reference flows (Ar and He) were used to maximize the thermal conductivity signals of the product gases. The catalytic activity was evaluated by the CO2 conversion and CO selectivity, as given by

$$X_{\text{CO}_2} = \frac{[\text{moles of CO}_2 \text{ converted}]}{[\text{moles of CO}_2 \text{ fed}]} \times 100,$$

(2)

$$S_{\text{CO}} = \frac{[\text{moles of CO produced}]}{[\text{moles of CO}_2 \text{ converted}]} \times 100.$$

(3)

We used in-situ DRIFTS to investigate the materials adsorbed on the catalysts during the RWGS reaction. The DRIFTS system was composed of an FT-IR spectrometer (Nicolet 6700, Thermo Scientific) and a high-temperature reaction chamber (DiffusIR, PIKE Technologies). All IR spectra were recorded using a HgCdTe detector over the wavenumber range 4000 to 650 cm⁻¹ at a 4 cm⁻¹ resolution, and 128 scans were collected at each wavenumber step. All metal catalysts were reduced at 600 °C prior to use in the in-situ IR experiments, and ~7 mg catalyst powder was loaded in a porous Al2O3 crucible serving as a reactor in a high-temperature gas flow system. The sample was then cleaned with high-purity He gas (to remove residual air) for 5 min, and the pre-mixed reactant gas with $R_{\text{max}} = 1$ was introduced into the chamber with increasing temperature.

First-principles calculations. All calculated energies in this work were obtained using the plane-wave DFT calculations as implemented in the Vienna ab initio simulation package. The generalized gradient approximation using Perdew-Burke-Ernzerhof parameterization was employed for the exchange-correlation energy, and the projector augmented wave method for describing ionic cores was used. The kinetic energy cutoff for the plane wave basis set was chosen as 1.3 times the energy maximum listed in the potential file of the element. Surface energy and H adsorption energy calculations were performed on slabs consisting of 6 layers of 54 atoms for the (100) and (111) surfaces and 8 layers of 72 atoms for the (110) surface. The layers in the top halves of the slabs were allowed to relax, while the rest were kept at a fixed position with a 15 Å vacuum space (in the z-direction). The $2 \times 2 \times 1 \kappa$-point grids in the Brillouin zone were sampled by a gamma-centered grid. The surface energy ($E_{\text{surf}}$) and H adsorption energy ($E_{\text{H,ads}}$) including the coverage effect were defined as

$$E_{\text{surf}} = \frac{1}{2A} \cdot \left[ E_{\text{lab}} - \left( \frac{N_{\text{surf}}}{N_{\text{bulk}}} \right) \cdot E_{\text{bulk}} \right],$$

(4)

$$E_{\text{H,ads}} = E_{\text{surf,H}} - E_{\text{surf}} - N_{\text{H}} \cdot E_{\text{H}},$$

(5)

where $E_{\text{s}}$ is the total energy of system $x$, $N_x$ is the number of atoms in system $x$, and $A$ is the area of each surface of the slab. The charge density difference ($\Delta \rho$) was also calculated to understand the adsorption behavior between the metal surface and H atom. $\Delta \rho$ was given by

$$\Delta \rho = \rho_{\text{surf,H}} - \rho_{\text{surf}} - \rho_{\text{H}},$$

(6)

where the subscripts surf, H, surf refer to the charge density of the surface with a H atom, the surface alone, and a free H atom, respectively. To calculate the H2 bond-dissociation energy, a rectangular cell with a 20 Å vacuum space in the x-, y-, and z-direction was used for the relaxation of the hydrogen atom or molecule. The calculated bond-dissociation energy for H2 is 4.51 eV, in good agreement with the experimental value of 4.48 eV at 0 K.

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Author Contributions
The project was conceived by S.C. under supervision of B.-I.S. and H.K. Sample preparation and characterization, and GC measurement were carried out by S.C., J.H., K.J.Y., J.-W.S., and H.K. The in-situ IR analysis and first-principles calculations were performed by S.C., J.-H.L., B.-K.K., and H.K. The manuscript was written by S.C., B.-I.S., and H.K. All authors have commented on the manuscript.

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Additional Information

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