High-efficiency direct methane conversion to oxygenates on a cerium dioxide nanowires supported rhodium single-atom catalyst

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Direct methane conversion (DMC) to high value-added products is of significant importance for the effective utilization of CH4 to combat the energy crisis. However, there are ongoing challenges in DMC associated with the selective C–H activation of CH4. The quest for high-efficiency catalysts for this process is limited by the current drawbacks including poor activity and low selectivity. Here we show a cerium dioxide (CeO2) nanowires supported rhodium (Rh) single-atom (SAs Rh-CeO2 NWs) that can serve as a high-efficiency catalyst for DMC to oxygenates (i.e., CH3OH and CH3OOH) under mild conditions. Compared to Rh/CeO2 nanowires (Rh clusters) prepared by a conventional wet-impregnation method, CeO2 nanowires supported Rh single-atom exhibits 6.5 times higher of the oxygenates yield (1231.7 vs. 189.4 mmol gRh−1 h−1), which largely outperforms that of the reported catalysts in the same class. This work demonstrates a highly efficient DMC process and promotes the research on Rh single-atom catalysts in heterogeneous catalysis.

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Methane (CH₄) is in fact among the most important and attractive feedstocks for producing methanol (CH₃OH) and other high value-added products in the chemical industry. In the traditional processes, CH₄ is converted into CH₂O₂H indirectly via the formation of syngas (H₂ and CO), which is an energy-hungry process that needs to be performed under high temperature. Therefore, the direct CH₄ conversion (DMC) to CH₂₃O₄H, which is regarded as a "dream reaction" in chemical industry, has been the subject of intensive study for decades. For instance, Periana et al. reported that CH₄ can be converted to CH₂₃O₄H by mercuric ions in the presence of concentrated sulfuric acid. Sushkevich et al. synthesized a copper-containing zeolite catalyst and used it for the conversion of CH₄ to CH₂₃O₄H with high selectivity (~97%) at 200°C. More recently, Agarwal et al. used colloidal gold–palladium nanoparticles (Au–Pd NPs) to catalyze the DMC to CH₂₃O₄H, methylene- hydroperoxide (CH₂O₂H), and formic acid (HCOOH) in the presence of hydrogen peroxide (H₂O₂) and oxygen (O₂). The yield of these primary oxygénates product reaches ~53.6 mol kgcat⁻¹ h⁻¹ at a selectivity of 88.0% at 50°C. Shan et al. reported that mononuclear rhodium species on ZSM-5 can catalyze DMC to CH₂₃O₄H and acetic acid (CH₃COOH) using O₂ and carbon monoxide (CO) with the total yield of oxygénates ~10 mmol gcat⁻¹ h⁻¹ and the selectivity of CO₂ ~15%. Despite the tremendous progress on the development of catalysts and technologies, DMC to oxygénates is extremely challenging because the selective activation of C–H bonds in CH₄ under mild conditions is a tough issue. It is thus highly desired to develop active and selective catalysts for the DMC to oxygénates.

Noble metals-based single-atom catalysts (SACs) have emerged as a new frontier in heterogeneous catalysis because of large ratio of surface atoms, low-coordination environment of metal centers, and strong metal–support interactions. They have been widely studied in diverse processes with superior catalytic performance, including CO oxidation, CH₄ conversion, oxygen reduction, water gas shift reaction, and so on. Recent investigations show that SACs can be used as highly active and selective catalysts for alkynes hydrogenation, in which the isolated active sites are geometrically in favor of the selective hydrogenation of alkynes. For instance, Kyrilikou et al. demonstrated that the isolated Pd atoms in a Cu surface can be used as a highly selective catalyst for the hydrogenation of styrene and acetylene as compared with pure Cu or Pd metal. Yan et al. claimed that Pd SACs can selectively catalyze butadiene to butene because of the mono–π-adsorption mode and the steric effect induced by butadiene adsorption on the isolated Pd atoms. Typical for CH₄ conversion, Tang et al. reported that the single-site RhO₃ anchored in microporous aluminosilicates (ZSM-5) can catalyze the DMC to CH₂₃O₄H and CH₂O₂H in the presence of CH₄, CO, and O₂ at ≤150°C. It is found that the single-site RhO₃ plays the role of the active site for DMC, while the rhodium oxide NPs on ZSM-5 are even not active for this transformation. Kwon et al. demonstrated that Rh SAC on ZrO₂ can be used for the DMC to CH₂₃O₄H and CH₂O₂H in H₂O₂ solution at 70°C. However, the selectivity of oxygénates from Rh SAC on ZrO₂ is ~70% due to the different decomposition rate of H₂O₂ and CH₂O₂H on ZrO₂. Inspired by these reports, we believe that SACs Rh-CeO₂ NWs can be used as a highly active and selective catalysts for the DMC to oxygénates. The total yield and selectivity of oxygénates reach ~1231.7 mmol gRh⁻¹ h⁻¹ and 93.9%, respectively. To the best of our knowledge, the current DMC performance outperforms the reported catalysts in literatures. In situ characterizations and theoretical calculations show that CeO₂ NWs play a vital role in the formation of -OH and -OH radicals. SACs Rh-CeO₂ NWs can selectively activate CH₄ to CH₃, which further combines with -OH and -OH radicals to form CH₂₃O₄H and CH₂O₂H, respectively. By contrast, the Rh/CeO₂ NWs tend to overoxidize CH₄ to CO₂ species with the assistance of -OH, leading to a low oxygénates’ yield and selectivity (189.4 mmol gRh⁻¹ h⁻¹ and 56.4%).

Results

Preparation and morphology characterization. CeO₂ NWs were prepared via a simple hydrothermal process by adding cerium chloride (CeCl₃), sodium oleate, deionized water (H₂O), and n-butylamine into a stainless reactor. The synthetic method of SACs Rh-CeO₂ NWs was the same as that of CeO₂ NWs, except for adding additional sodium hexachlororhodate (Na₃RhCl₆). Rh/ CeO₂ NWs and Rh/CeO₂-com were prepared by impregnating Na₃RhCl₆ on the as-prepared CeO₂ NWs and commercial CeO₂ via a conventional wet-impregnation method. The physicochemical properties are listed in Supplementary Table 1. Transmission electron microscopy (TEM) image shows that uniform CeO₂ NWs with a diameter and length of ~6.2 nm and ~260 nm are obtained (Supplementary Fig. 1). No Rh nanoparticles are observed in TEM image, indicating that Rh atoms are well dispersed in SACs Rh-CeO₂ NWs (Fig. 1a). The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF/STEM) image in temperature color of SACs Rh-CeO₂ NWs indicates Rh atoms are presented as SA state (Fig. 1b, c; Supplementary Fig. 2). By contrast, Rh clusters with the size of ~1.5 nm appear in the AC-HAADF/STEM image in temperature color of Rh/CeO₂ NWs (Fig. 1d, e; Supplementary Fig. 3). X-ray diffraction (XRD) pattern of SACs Rh-CeO₂ NWs, only the characteristic peaks of CeO₂ at 2θ = 28.5, 33.1, 47.5, 56.3, 69.4, 76.7, 79.1, and 88.4° (PDF No. 43-1002) are observed (Supplementary Fig. 4), indicating that Rh atoms are highly dispersed on CeO₂ NWs and commercial CeO₂ despite the full wavelength at half maximum (FWHM) of the characteristic peaks corresponding to CeO₂ NWs is much broader than that of commercial CeO₂ due to its small diameter of ~6.2 nm. It should be noted that the absence of peaks corresponding to Rh clusters in the XRD pattern of Rh/CeO₂ NWs might be attributed to the very small-sized Rh clusters and low content of Rh in the catalyst. X-ray photoelectron spectroscopy measurements were performed to characterize the chemical states of elements on the surface of CeO₂ NWs, SACs Rh-CeO₂ NWs, Rh/CeO₂ NWs, and Rh/CeO₂-com. As shown in Supplementary Fig. 5, it is found that Rh are in their oxidation state (Rh³⁺), while Ce consist of Ce⁴⁺ (881.8, 888.3, 897.6, 900.3, 907.2, and 916.0 eV) and Ce⁵⁺ (884.6 and 903.1 eV). The binding energy shifts of Rh in XPS spectra indicate that the different synergies among those catalysts. Compared with the Rh/ CeO₂-com (308.9 eV) and Rh/CeO₂ NWs (309.1 eV), Rh 3d⁵/₂ peak obviously shifts to 309.4 eV in SACs Rh-CeO₂ NWs, suggesting the existence of electron transfer from Rh to CeO₂ in SACs Rh-CeO₂ NWs (Supplementary Fig. 5a). On the other hand, detailed peak fittings demonstrate that the proportions of Ce⁵⁺ are different among these samples (Supplementary Fig. 5b). In particular, the proportion of Ce⁵⁺ in Rh/CeO₂-com is 12.4%, which is much lower than that in CeO₂ NWs (16.0%), Rh/CeO₂ NWs (16.5%), and SACs Rh-CeO₂ NWs (16.7%). XPS results imply a much stronger synergy exists in SACs Rh-CeO₂ NWs in the formation of radicals, which can further enhance the activity of DMC. The total yield and selectivity of oxygénates reach ~1231.7 mmol gRh⁻¹ h⁻¹ and 93.9%, respectively. To the best of our knowledge, the current DMC performance outperforms the reported catalysts in literatures. In situ characterizations and theoretical calculations show that CeO₂ NWs play a vital role in the formation of -OH and -OH radicals. SACs Rh-CeO₂ NWs can selectively activate CH₄ to CH₃, which further combines with -OH and -OH radicals to form CH₂₃O₄H and CH₂O₂H, respectively. By contrast, the Rh/CeO₂ NWs tend to overoxidize CH₄ to CO₂ species with the assistance of -OH, leading to a low oxygénates’ yield and selectivity (189.4 mmol gRh⁻¹ h⁻¹ and 56.4%).
Fig. 1 Structural analyses of SAs Rh-CeO2 NWs and Rh/CeO2 NWs. a TEM image of the SAs Rh-CeO2 NWs. b AC-HAADF/STEM image in temperature color of the SAs Rh-CeO2 NWs. The isolated Rh atoms are marked with black circles. c The intensity profile recorded from the line in panel (b). d AC-HAADF/STEM image in temperature color of the Rh/CeO2 NWs. The Rh cluster is marked with blue line. e The intensity profile recorded from the line in panel (d). f, g Rh K-edge XANES spectra (f) and Rh K-edge EXAFS spectra in R space (g) of the Rh foil, Na3RhCl6, Rh2O3, SAs Rh-CeO2 NWs, and Rh/CeO2 NWs. The scale bars in (a), (b), and (d) are 100, 2, and 2 nm, respectively.

comparison with Rh/CeO2 NWs and Rh/CeO2-com. No obvious peaks in Na 1s and Cl 2p XPS spectra suggest that neglect amount of Na and Cl remain on catalysts (Supplementary Fig. 5c, d).

To study the electronic structures and coordination states of Rh in the SAs Rh-CeO2 NWs and the Rh/CeO2 NWs, X-ray absorption near-edge spectroscopy (XANES) and extended X-ray fine structure (EXAFS) were measured at Rh K-edge. Rh foil, Rh2O3, and Na3RhCl6 were used as references. Comparing with the edge position in the XANES spectra of references, Rh in SAs Rh-CeO2 NWs and Rh/CeO2 NWs are presented as their oxidation states (Fig. 1f). As shown in Fig. 1g, the Rh–Rh coordination, Rh–Cl coordination, Rh–O, and the second shell of Rh–O coordination are observed at ~2.3 Å, ~1.9 Å, ~1.7 Å, and ~2.7 Å, respectively. For Rh/CeO2 NWs, Rh–O, and Rh–Rh coordination appear at ~1.6 Å and ~2.4 Å in the R-space EXAFS spectrum, indicating the presence of Rh clusters in Rh/CeO2 NWs. By contrast, only the feature of Rh–O coordination at ~1.6 Å is observed in the R-space spectrum of SAs Rh-CeO2 NWs (Fig. 1g). The disappearance of Rh–Rh coordination implies that Rh atoms in SAs Rh-CeO2 NWs are presented as isolated atoms, which is in good agreement with the observations in AC-HAADF/STEM image. It is noted that no obvious Rh–Cl coordination is observed in the EXAFS spectrum of SAs Rh-CeO2 NWs, indicating that the Rh atoms are anchored by O atoms in CeO2 NWs via Rh–O coordination. In addition, the structures of SAs Rh-CeO2 NWs and Rh/CeO2 NWs were verified by the diffuse reflectance-infrared Fourier transform spectroscopy (DRIFTS) measurement using CO as a probe. As shown in Supplementary Fig. 6a, different from the previous reports that Rh SA gives geminal peaks in 2000–2100 cm$^{-1}$, only one broad and weak peak is observed at 2000–2150 cm$^{-1}$ in the CO-DRIFTS spectrum of SAs Rh-CeO2 NWs, which may be attributed to the low CO coverage on SAs Rh-CeO2 NWs$^{24}$. The presence of oxidation species at 1250–1700 cm$^{-1}$ indicates that the adsorbed CO molecules are oxidized, further confirming the low CO coverage on the surface of SAs Rh-CeO2 NWs. When SAs Rh-CeO2 NWs was pretreated in CO at 50 °C for 0.5 h, the intensity of peak at 2000–2150 cm$^{-1}$ obviously increases, despite the appearance of oxidation species. Further increasing the pre-treatment temperature to 150 °C, two intense peaks appear at 2101 and 2030 cm$^{-1}$ in CO-DRIFTS spectrum of SAs Rh-CeO2 NWs, which correspond to the symmetric and asymmetric vibration of gem-dicarbonyl doublet CO (i.e., Rh(CO)$_2$) (Supplementary Fig. 6a, red curve)$^{25}$. For Rh/CeO2 NWs, in addition to the peaks of oxidation species, multiple peaks corresponding to the symmetric (2101 cm$^{-1}$) and asymmetric vibration (2030 cm$^{-1}$) of Rh(CO)$_2$ and CO linear adsorption on Rh$^{5+}$ (2133 cm$^{-1}$) are observed in CO-DRIFTS spectrum (Supplementary Fig. 6b). When Rh/CeO2 NWs was pretreated at 50 °C and then 150 °C for 0.5 h, two peaks appear at 1860 and 2060 cm$^{-1}$ in CO-DRIFTS spectrum, which correspond to the CO bridge adsorption on Rh, respectively (Supplementary Fig. 6b, red curve)$^{24,25}$. The absence of CO bridge adsorption in the CO-DRIFTS spectrum further confirms the structures of Rh SA in SAs

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Rh-CeO₂ NWs, which is in good agreement with the result of AC-HAADF/STEM and X-ray absorption spectroscopy.

DMC performance of SAs Rh-CeO₂ NWs and Rh/CeO₂ NWs.

All the catalysts of Rh/CeO₂-com, Rh/CeO₂ NWs, and SAs Rh-CeO₂ NWs were used for DMC in a pressurized reactor. Products were analyzed by gas chromatography and ¹H nuclear magnetic resonance spectroscopy (¹H-NMR). As shown in Fig. 2a, Rh/CeO₂-com gives the CH₃OH, CH₃OOH, and CO₂ yield of 17.6, 15.6, and 137.4 mmol g⁻¹ h⁻¹, respectively. When Rh/CeO₂ NWs are used as a catalyst, the yield of CH₃OH and CH₃OOH increase to 170.4 mmol g⁻¹ h⁻¹ and 19.0 mmol g⁻¹ h⁻¹, respectively, while the total yield of CO₂ is 146.3 mmol g⁻¹ h⁻¹. The low selectivities of oxygenate on Rh/CeO₂-com (19.5%) and Rh/CeO₂ NWs (56.4%) indicate that CH₄ tends to be over-oxidized into CO₂ on Rh/CeO₂-com and Rh/CeO₂ NWs. By contrast, when SAs Rh-CeO₂ NWs are used as a catalyst, the selectivity of CO₂ significantly decreases to 6.1%, indicating that the overoxidation of CH₄ is strongly suppressed on SAs Rh-CeO₂ NWs. Correspondingly, the yield of CH₃OH and CH₃OOH significantly increase to 940.3 and 291.4 mmol g⁻¹ h⁻¹, respectively. Moreover, SAs Rh-CeO₂ NWs were tested for DMC under different conditions (i.e., temperature, H₂O₂ concentration, CH₄ pressure, and catalyst amount). As depicted in Fig. 2b, it is found that the increase of temperature leads to a volcano-shape selectivity and yield of oxygenates. Typically, the selectivity and yield of oxygenates are 91.4% and 786.3 mmol g⁻¹ h⁻¹ at 30 °C, which further increases to 93.9% and 1231.7 mmol g⁻¹ h⁻¹ at 50 °C. Further increase in temperature will lead to a decrease in both the selectivity and yield of oxygenates. A similar tendency is observed when the concentration of H₂O₂ is increased from 0.1 to 1.5 M (Fig. 2c). For instance, the selectivity and yield of oxygenates are 67.1% and 145.0 mmol g⁻¹ h⁻¹ at the H₂O₂ concentration of 0.1 M, which significantly increase to 93.9% and 1231.7 mmol g⁻¹ h⁻¹ at the H₂O₂ concentration of 1.0 M, indicating H₂O₂ can significantly promote the DMC activity. It is noted that a further increase of H₂O₂ concentration to 1.5 M will result in a slight decay in oxygenates selectivity and yield. Furthermore, the effects of CH₄ partial pressure on DMC performance were studied. As shown in Fig. 2d, the selectivity of CO₂ strongly increases from 6.1% to 21.1% when the CH₄ partial pressure is increased from 0.5 MPa to 3 MPa, despite the similar yield of oxygenates. We thus further tested the DMC performance by altering the weight of the catalyst, as shown in Supplementary Fig. 7. It is found that the yield of CH₃OH and CH₃OOH steadily increase as the increasing weight of catalyst, while the selectivity of CH₄ is kept at ~94%. The positive effects of H₂O₂ concentration and catalyst weight but negligible effects of CH₄ partial pressure on the oxygenates selectivity imply that Rh SA can efficiently activate C‒H bonds in CH₄ under optimized conditions, and the rate-determining steps solely involve the reaction of CH₄ activation intermediates with H₂O₂ (Fig. 2; Supplementary Fig. 7). In addition, SAs Rh-CeO₂ NWs were used in ten consecutive DMC cycles to test the stability. As shown in Supplementary Fig. 8, no obvious decays in oxygenates selectivity and yield are observed after ten consecutive DMC cycles. The structures of Rh SA are reserved in the spent SAs Rh-CeO₂ NWs, indicating that SAs Rh-CeO₂ NWs can be used as a stable catalyst for DMC (Supplementary Fig. 9). Moreover, to the best of
our knowledge, the current DMC performance has outperformed the reported catalysts (Supplementary Table 2), suggesting that SAs Rh-CeO2 NWs can be used as a highly efficient catalyst for DMC to oxygenates under mild conditions.

**Mechanistic studies on DMC.** In order to study the mechanism of CH4 selective oxidation on SAs Rh-CeO2 NWs, DMC was performed using O2 as the oxidant. As depicted in Supplementary Table 3, the selectivity of oxygenates is 5.9% when O2 is solely used as the oxidant, which significantly increases to 92.8% after the addition of 10 μmol H2O2. Correspondingly, the yield of oxygenates increases from 17.6 to 1159.4 mmol gRh−1 h−1, indicating that H2O2 can significantly promote DMC to oxygenates. Based on the previous reports,[19,20] we speculated that the DMC in the presence of H2O2 might follow radical-triggered reaction paths. Therefore, electron paramagnetic resonance (EPR) was performed to detect the radicals in the present reaction system by using 5,5’-dimethyl-1-pyrroline-N-oxide (DMPO) as the radical scavenger. In order to label the radicals, two contrast experiments were performed in the systems of DMPO + H2O2 + Fe2+ and DMPO + H2O2 + Fe2+ + CH3OH (detailed information has been given in the experimental section). As shown in Supplementary Fig. 10, a four-line EPR spectrum with a relative peak ratio of 1:2:2:1 is obtained from the DMPO + H2O2 + Fe2+ system (Supplementary Fig. 10, green curve), which can be assigned to -OH radical.[26] For the system of DMPO + H2O2 + Fe2+ + CH3OH, a six-line EPR spectrum is recorded, which can be indexed as the characteristic peaks of -CH3 radical (Supplementary Fig. 10, blue curve)[26]. When DMPO is added into the reaction system, some new peaks of -OOH appear in the EPR spectrum in addition to those peaks of -CH3 and -OH radicals (Supplementary Fig. 10, red curve).[27] The presence of -CH3, -OOH, and -OH radicals in the reaction system further confirms that the DMC on the SAs Rh-CeO2 NWs in H2O2 solution is triggered by radicals.

To further study the working mechanism of the radical-triggered DMC on SAs Rh-CeO2 NWs, in situ DRIFTS measurements were performed to analyze the surface species on SAs Rh-CeO2 NWs and Rh/CeO2 NWs. As shown in Supplementary Fig. 11, three intense peaks are observed at 3401, 3214, and 1654 cm−1 in the spectra of SAs Rh-CeO2 NWs and Rh/CeO2 NWs, which can be assigned to -OH, -OOH, and -OH2, respectively.[28] Based on the observations in EPR spectra (Supplementary Fig. 10) and previous reports, we conclude that H2O2 can decompose into active radicals on CeO2 NWs[29,30]. When the SAs Rh-CeO2 NWs are exposed to CH4, the characteristic bands of -CH3 appear at 1412 and 1304 cm−1 (see ref. [31]), indicating that SAs Rh-CeO2 NWs can selectively activate CH4 into -CH3 (Fig. 3a, black curve). Moreover, two additional bands are observed at 1635 and 3401 cm−1, which can be ascribed to -OH2 and -OH, respectively, suggesting that -OH may combine with H from CH4 decomposition to form -OH2. When SAs Rh-CeO2 NWs are exposed to the mixture of CH4 and H2O2 (Fig. 3a, red curve), new peaks appear at 2935, 2837, 1438, 1353, 1220, and 1148 cm−1 in the spectrum, which can be assigned to the C−H asymmetric stretching vibration, C−H symmetric stretching vibration, CH3 scissoring vibration, CH3 asymmetric rocking vibration, C−O stretching vibration and CH3 symmetric rocking vibration of -OCH3, respectively.[32,33] The appearance of -OCH3, -OH, and -OOH demonstrates the formation of CH3OH and CH3OOH. By contrast, when Rh/CeO2 NWs are exposed to CH4, only two strong bands of CO2 and CO2 are observed at 1589 and 1293 cm−1 (Fig. 3b, black spectrum).[34] The absence of -CH4, 'OH, and 'OOH suggests that CH4 is overoxidized into COx species. When Rh/CeO2 NWs are exposed to the mixture of CH4 and H2O2, the intense band of CO2 is in the spectrum implies that CO2 are the dominate products despite the appearance of -OCH3 and -OH bands (Fig. 3b, blue curve)[35], which is consistent with our experimental results (Fig. 2a).

To further confirm the activation of CH4 on Rh, CH4 temperature programmed surface reaction (TPSR) was performed to investigate the CH4 conversion on CeO2 NWs, SAs Rh-CeO2 NWs, and Rh/CeO2 NWs. No obvious peaks are observed in the TPSR pattern of CeO2 NWs, suggesting that CeO2 NWs are inactive for CH4 activation under the indicated conditions (Supplementary Fig. 12). When CH4–TPSR measurements were performed on SAs Rh-CeO2 NWs and Rh/CeO2 NWs, the peaks of CH4, CO, CO2, and H2O appear in TPSR patterns, suggesting that Rh atoms play as the active sites for CH4 activation (Fig. 3c, d), which is in good agreement with results from the in situ DRIFTS measurement (Fig. 3a, b). Despite the appearance of peaks in TPSR patterns, the different onset temperatures (Tonset) suggest that the reaction paths are different on SAs Rh-CeO2 NWs and Rh/CeO2 NWs (Fig. 3c, d). For SAs Rh-CeO2 NWs, the Tonset of CH4 (~82 °C, formed via -CH3 hydrogenation) is closed to that of CO (~82 °C) and CO2 (~82 °C), indicating that -CH3 hydrogenation (to form CH2) and overdehydrogenation (to form CO2) competitively occur on the SAs Rh-CeO2 NWs. By contrast, the Tonset of CO (~67 °C) and CO (~61 °C) is significantly lower than that of CH4 (~74 °C) in TPSR patterns of Rh/CeO2 NWs, indicating that overoxidation for the formation of CO and CO2 is preferential[36].

**DFT calculations.** Finally, DFT calculations were performed to reveal the reaction paths of CH4 oxidation on SAs Rh-CeO2 NWs and Rh/CeO2 NWs. The real spatial orbital distribution apparently shows the concentrated electron-rich feature on SAs Rh, which indicates the Rh site possesses a superior reaction priority among the available sites on the surface. Meanwhile, Rh cluster on CeO2 shows widely separated electronic distribution over the surface, which shows the disperse electroactive region (Fig. 4a). The projected density of states (PDOS) support that the highly concentrated electronic activity of SAs Rh on the surfaces is attributed to the sharp Rh-4d occupation near the Fermi level (EF). The Ce-4f bands mainly locate above EF, while O-2p bands concentrate on EF − 4.5 eV. The evident coupling between Rh-4d and Ce-4d confirms the stabilization of SAs Rh by the protection of bottom Ce (Fig. 4b). In comparison, the Rh-4d bands become much broad in Rh/CeO2, covering from EF − 5.0 eV to 2.0 eV. The evident match among Rh-4d bands and O-2p bands and Ce-4f bands indicates a strong coupling between the surface Rh cluster and bottom CeO2 (Fig. 4c). The electronic structures of CH4 adsorption are further presented to illustrate the different activity toward the DMC process. It is noted the dominant peak of Rh-4d in SAs Rh-CeO2 upshifts from EF − 2.0 eV toward EF − 1.0 eV due to the electron transfer with CH4 (Fig. 4d). Meanwhile, the close distance between Rh-4d bands and O-2p bands on Rh/CeO2 NWs demonstrates the strong couplings between CH4 and local O atoms, which lead to the over-binding effect with increased energy barriers for the consecutive dehydrogenation of CH4 (Fig. 4e).

Since EPR and in situ DRIFTS results show that lattice O atoms of CeO2 are feasibly bonded with H in H2O2. From the energetic view, DFT also proves the superior flexibility of O in SAs Rh-CeO2 NWs with only 0.16 eV energy barrier. Due to the steric hindrance from the surface coverage of Rh cluster, the energy barrier of the detachment of O in Rh/CeO2 NWs increases to 4.06 eV, demonstrating a slow efficiency of generating -OOH...
radicals (Fig. 4f). The further reaction energies also support that the generations of both \( \cdot \text{OH} \) and \( \cdot \text{OOH} \) radicals are much more preferred in SAs Rh-CeO\(_2\) NWs, satisfying the prerequisite of radical-mediated DMC process (Fig. 4g). The SAs Rh-CeO\(_2\) NWs deliver an overall downhill trend to the formation final product CH\(_3\)OH and CH\(_3\)OOH, representing a high electronic activity. The spontaneous adsorption of CH\(_4\) and facile C–H bond cleavage indicates the fast activation of C–H bond, which leads to the efficient DMC process. Particularly, the further reaction of CH\(_3\)OOH toward HCOOH has been suppressed by the high energetic barrier of 1 eV, guaranteeing the reaction locking for desired products. The formation of CH\(_3\)OH releases 2.87 eV, which is slightly larger energy than that of CH\(_3\)OOH (2.53 eV), explaining the higher yield of oxygenates in our experiments. Meanwhile, the high energy cost (2.01 eV) to achieve further C–H bond cleavage of CH\(_3\) facilitates the high selectivity of DMC on the SAs Rh-CeO\(_2\) NWs (Fig. 4h). In contrast, the activation of C–H bond in CH\(_4\) faces stepped energy barriers toward \( \cdot \text{CH}_2 \) on Rh/CeO\(_2\) NWs, indicating a much lower selectivity of oxygenates. The formation of CH\(_3\)OOH induced by the \( \cdot \text{OH} \) radical requires an energy cost of 0.47 eV, while the generation of CH\(_3\)OH is energetically favorable. Notably, both \( \cdot \text{CH}_2 \) and CH\(_3\)OOH exhibit an evident energy drop toward the formation of HCOOH, indicating that the overoxidation of CH\(_3\) is preferred. However, the further oxidation of HCOOH to CO shows an energy barrier of 2.08 eV, which further lowers the DMC efficiency. The overall energy release is 1.92 eV, which is much smaller than that of SAs Rh-CeO\(_2\) NWs, supporting the stronger reaction activity of SAs Rh-CeO\(_2\) NWs toward the DMC conversion (Fig. 4i).

**Reaction pathways.** Combining the results from EPR, in situ DRIFTS and DFT calculations, we thus summarized the reaction paths of DMC on the SAs Rh-CeO\(_2\) NWs and Rh/CeO\(_2\) NWs (Supplementary Figs. 13 and 14). As displayed in Supplementary Fig. 13, for the SAs Rh-CeO\(_2\) NWs, H\(_2\)O\(_2\) can decompose into \( \cdot \text{OH} \) on two neighboring Ce (III) atoms (step 1). On the other hand, H\(_2\)O\(_2\) can decompose into \( \cdot \text{OOH} \) on Ce (IV), and the remaining \( \cdot \text{H} \) will combine with [O] (lattice O of CeO\(_2\) connected with the Ce (IV) in CeO\(_2\) NWs to form \( \cdot \text{OH} \) (step 2). The adsorbed CH\(_4\) on Rh SA can be oxidized into \( \cdot \text{CH}_3 \) and H\(_2\)O with the assistance of \( \cdot \text{OH} \) (step 3). As a result, the formed \( \cdot \text{CH}_3 \) will react with the \( \cdot \text{OH} \) to CH\(_3\)OOH (step 4), or (ii) combine with \( \cdot \text{OH} \) to produce CH\(_3\)OOH (step 5), or (iii) be further oxidized into \( \cdot \text{CH}_2 \) by \( \cdot \text{OH} \) (step 6). Both the CH\(_3\)OOH and \( \cdot \text{CH}_2 \) will be converted into CH\(_3\)O (steps 7 and 8) and then to HCOOH on the Rh/CeO\(_2\)
of CH4 adsorption on SAs Rh-CeO2 NWs surface. CeO2 on SAs Rh-CeO2 NWs and Rh/CeO2 NWs.

*CH4 via different reaction paths. To be more specific, SAs Rh-CeO2 NWs can selectively activate CH4 to *CH3, leading to the formation of oxygenate in the presence of H2O2, while Rh/CeO2 NWs favor the overoxidation of CH4 to form COx, leading to a low selectivity and yield of oxygenates. DFT calculations reveal the facile C–H bond activation and reaction locking on SAs Rh-CeO2 NWs guarantees the high selectivity and yield of DMC, supplying solid evidence for experimental results. This work may not only provide a highly active and selective catalyst for DMC to oxygenates but also promote the researches of SACs in heterogeneous catalysis.

**Methods**

**Preparation of CeO2 nanowires (NWs) and SAs Rh-CeO2 NWs.** In a typical preparation of CeO2 NWs, 12 mL CeCl3 (0.5 mmol, Alfa Aesar) and sodium oleate (0.75 mmol, Tokyo Chemical Industry) aqueous solution were added into a 20-mL Teflon-lined stainless-steel autoclave. The mixture was magnetically stirred at 800 rpm (round per minute) for 0.5 h. To this solution, n-butylamine (1 mL, Sino-pharm) was slowly added into the solution under stirring for another 0.5 h.
Afterward, the autoclave was heated at 160 °C for 10 h before it was cooled to room temperature. The resulting products were collected by centrifugation and washed three times with DI water. The wet mixture was then dried at room temperature overnight. The powder products were subjected to thermal annealing in an air atmosphere at 400 °C for 10 min at a heating rate of 10 °C min−1. For SAs Rh/ CeO2 NWs, all the parameters were the same with CeO2 NWs, except for adding extra Na2RhCl6 (5 μmol, Aldrich).

Preparation of Rh/ CeO2 NWs and Rh/ CeO2-com. The Rh/ CeO2 NWs and Rh/ CeO2-com were prepared via a conventional wet-impregnation method. Typically, a certain amount of Na2RhCl6 solution was dropwise added into the as-prepared CeO2 NWs and commercial CeO2 (99.9%, Inoke) under moderate stirring. The resultant slurry was mixed evenly and then dried in an oven at 80 °C overnight, and then subjected to thermal annealing in air at 400 °C for 10 min at a heating rate of 10 °C min−1. Finally, the calcinated samples were re-washed water for three times via centrifugation, and then dried at 100 °C overnight.

Characterization. The morphologies and sizes of the NWs were determined by TEM (Hitachi, HT7700) at 120 kV. Atomic emission spectroscopy (ICP-AES) (710-ES, Varian) was used to determine the Rh loading amounts in Rh/ CeO2 NWs and Rh/ CeO2-com. XRD patterns were collected on X’Pert-Pro MPD diffractometer (Netherlands PANAnalytical) with a Cu Ka X-ray source (λ = 1.540598 Å). XPS was done with an SSI S-Probe XPS Spectrometer. The carbon peak at 284.6 eV was used as a reference to correct for charging effects. The X-ray absorption data at the Rh K-edge of the samples were recorded at room temperature in transmission mode using ion chambers at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (311) double-crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5 eV and a current between 150 and 210 mA. The photon energy was calibrated with the first inflection point of Rh K-edge in Rh metal foil.

Typical process for selective oxidation of CH4. The selective oxidation of CH4 was performed in a 60 mL stainless-steel autoclave. Typically, 20 mL H2O2 solution (1 M) and 10 mg of catalyst were added into a Teflon input. Afterward, the autoclave was pressurized with CH4 (0.5 MPa). The reaction was performed at 50 °C with stirring at 800 rpm for 1 h. In our work, we used a commercial Agilent GC integrator equipped with a flame ionization detector (FID) for the detection of gaseous products. This system contains three columns (two hayesep Q columns and one 5 A mol sieve column) for the separation of gaseous products. Both CO and CO2 were converted into CH4 via a methanator to analyze by FID. All the gaseous products were introduced into two tandem hayesep Q columns for pre-separation. 1H nuclear magnetic resonance spectroscopy (1H-NMR, Bruker 600 MHz) was employed for structural analysis of liquid products, in which dimethylsulfoxide (DMSO, 1%) and deuterioxide were used as the internal standard and solvent, respectively. The liquid products were analyzed by a gas chromatograph (Persee G5) with a FID using a KB-5 column. In total, 10 μL of isopropanol/H2O (1%) was used as the internal standard adding into 1 mL reaction mixture for analyzing CH3OH and CH2O. The amount of CH2O was calculated using the standard curve method. Afterward, CH2O was converted to CH3OH using hydrazine hydrate (0.1 M). The total amount of CH3OH and CH2OOH was analyzed by gas chromatograph, and the amount of CH2OOH was obtained by minus. For each catalytic test, error bar was obtained by repeating three times. The yields of products and the selectivity were calculated using Eqs. (1) and (2).

\[
\text{Yields of products (mmol g}^{-1}\text{ h}^{-1}) = \frac{\text{mmol of products/g of Rh/h of reaction time}}{100/\text{mmol of all products}}
\]

\[
\text{Oxgenates selectivity (\%)} = \frac{\text{mmol of (CH}_3\text{OOH + CH}_2\text{O})}{\text{CH}_3\text{OH}} \times 100/\text{ mmol of all products}
\]

EPR measurement. The detection of free radicals in the reaction process of DMC was performed at a JEOL IES-FA200 electron paramagnetic resonance spectroscopy (EPR, 9.062 GHz), using DMPO as the scavenger. Typically, 1 mL DMPO-H2O (100 mmol L−1) was added into 1 mL of reaction mixture. The mixed solution was immediately transferred to a capillary tube (diameter: 0.1 mm; filling liquid height: ~5 cm), which was then fixed in the resonant cavity of the spectrometer. EPR measurements were detected at room temperature and recorded by three scans. The contrast experiments were performed to determine the type of radicals by characteristic peaks. Contrast experiment 1 (labeled as DMPO + H2O2 + Fe2+) was mixed with 1 mL ferrous (II) sulfate (FeSO4, 50 mmol L−1) and nitric acid solution (pH = 4) were mixed with 1 mL DMPO-H2O (100 mmol L−1) under moderate stirring for 2 min, followed by adding 50 μL of H2O2 (30 wt.%). Contrast experiment 2 (labeled as DMPO + H2O2 + Fe2+ + CH3OH): all the processes were the same with contrast experiment 1, except for the addition of 1 mL of CH3OH (100 mmol L−1) into the solution.

CO-DRIFTS measurement. In all, 20 mg sample was packed into a Harrick Praying Mantis high-temperature reaction chamber (CaF2 windows) mounted inside of a Thermo Scientific Praying Mantis diffuse reflectance adapter, set inside of a Thermo Scientific Nicolet 6700 Fourier transform infrared (FT-IR) spectrometer using liquid nitrogen cooled mercury–cadmium–telluride detector (MCT). Gases were flowed to the reaction chamber using Alicat mass flow controllers. Prior to CO-DRIFTS measurement, the sample was pretreated by heating in CO/Ar (10 vol.%) flow (50 mmol min−1) at different temperatures (e.g., −30 °C, 50 °C, and 150 °C), followed by flushing with Ar flow (50 mmol min−1) for 1 h. After cooling to −30 °C in the same Ar flow, CO/Ar (10 vol.%, 50 mmol min−1) was flowed through the sample at −30 °C for 0.5 h. Finally, the sample was flushed with Ar flow (50 mmol min−1) at −30 °C for 0.5 h to remove the physically adsorbed CO on the surface sample. The CO-DRIFTS spectra were obtained by averaging 16 sequentially collected scans at a resolution of 4 cm−1.

In situ CH4-DRIFTS measurement. For in situ CH4-DRIFTS, 20 mg sample was packed into a Harrick Praying Mantis high-temperature reaction chamber (CaF2 windows) mounted inside of a Thermo Scientific Praying Mantis diffuse reflectance adapter, set inside of a Thermo Scientific Nicolet 6700 FT-IR spectrometer using liquid nitrogen cooled MCT detector. The sample was pretreated by heating in Ar flow (50 mmol min−1) at 400 °C for 1 h and cooled down to 50 °C in the same Ar flow. Gases (5 vol.% CH4/Ar or Ar) were flowed using Alicat mass flow controllers. The hydrogen peroxide is brought into the chamber by a carrier gas (5 vol.% CH4/Ar) with a positive pressure (0.15 MPa). Afterward, 5 vol.% CH4/Ar with the hydrogen peroxide was flowed through the catalytic bed at 50 °C for 0.5 h, followed by flushing with Ar flow (50 mmol min−1) for 0.5 h at the same temperature. The in situ CH4-DRIFTS spectra were obtained by averaging 16 sequentially collected scans at a resolution of 4 cm−1. For CH4-DRIFTS measurement, all the parameters are the same with in situ CH4-DRIFTS measurement, except for the absence of H2O2.

DFT calculations. All calculations were carried out using DFT implemented in the CASTEP. The electron exchange and correlation interaction were calculated with the generalized gradient approximation (GGA) in the parameterization of Perdew–Burke–Ernzerhof (PBE) pseudopotentials. To minimize the computational cost for the surface modeling, ultrasoft pseudopotential scheme has been chosen with the cutoff energy of 40 eV.40,41 For both SAs Rh-CeO2 and Rh/CeO2-com, the CeO2 crystal has been cleaved along the (111) plane with three-layer thickness. For SAs Rh-CeO2 model, only one Rh atom is deposited onto the CeO2 surface within the unit cell to demonstrate the single-atom catalyst. For Rh/CeO2-com, the Rh cluster consists of eight atoms, which is cleaved from the bulk Rh crystal along the (111) plane. We imposed a 15 Å vacuum space along z-direction to supply sufficient space for the adsorption behaviors without interactions between lattice. For all the geometry optimizations, the Hellmann–Feynman forces will be converged to <0.001 eV/Å, while the total energy has been converged to 5 × 10−3 eV per atom. The coarse k-point has been applied for the energy minimization based on the Broyden–Fletcher–Goldfarb–Shannon (BFGS) algorithm41,42.

Data availability. The data supporting this study are available in the paper and Supplementary Information. All other relevant source data are available from the corresponding authors upon reasonable request.

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Author contributions

X.H. and X.Y. conceived and supervised the research. X.H., S.B., and Y.X. designed the experiments. X.H., S.B., and X.Y. performed most of the experiments and data analysis. J.W. and Fan Li performed and analyzed the STEM characterization. X.H., S.B., Y.X., Q.S., Fangfang Liu, and H.L. participated in various aspects of the experiments and discussions. Fangfang Liu, B.H., H.L., T.W., and M.S. performed the DFT simulations. X.H., S.B., and Y.X. wrote the paper. All authors discussed the results and commented on the paper.

Competing interests

The authors declare no competing interests.

Additional information

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