Selective oxidation of methane to methanol over Au/H-MOR

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Abstract

Selective oxidation of methane to methanol by molecular oxygen is a fascinating route for upgrading abundant methane resource and represents one of the most challenging reactions in chemistry due to the overwhelmingly higher reactivity of the product versus the reactant. Here, we report that monometallic gold nanoparticles loaded on mordenite zeolite efficiently catalyze the selective oxidation of methane to methanol by molecular oxygen in the presence of carbon monoxide in aqueous medium. The methanol productivity reaches 1300 μmol g\textsubscript{cat}^{-1} h^{-1} or 280 mmol g\textsubscript{Au}^{-1} h^{-1} with 75% selectivity at 150 °C, outperforming most of those reported under comparable conditions. Both hydroxyl radicals and hydroperoxide species participate in the activation and conversion of methane; the lower affinity of methanol on gold mainly accounts for higher methanol selectivity.
Methane, which is the main component of natural/shale gas and an inexpensive resource with very large reserves, can be a key feedstock in the transition of energy supplies from fossil fuels to cleaner and renewable energy, contributing to establishing a carbon-neutral society. The catalytic transformation of CH$_4$ into value-added liquid chemicals that are favorable for transportation and storage has attracted an increasing attention.$^1$ Methanol is one of the most attractive target products because of its versatility as an energy carrier or a platform molecule for the synthesis of important bulk chemicals like olefins and aromatics.$^2,^3$ In the current chemical industry, the conversion of CH$_4$ to CH$_3$OH relies on an energy-intensive two-step process, involving the high-temperature reforming of methane to syngas (a mixture of CO and H$_2$) and the high-pressure methanol synthesis. The direct conversion of CH$_4$ to CH$_3$OH, usually viewed as a “holy grail” in chemistry, would play a game-changing role in chemical utilization of CH$_4$. The challenge arises not only from the activation of CH$_4$ molecule with only inert C-H bonds but also from the selectivity control due to the overwhelmingly higher reactivity of CH$_3$OH compared to CH$_4$.

In spite of advances in CH$_4$ selective oxidation using a special oxidant such as oleum in homogeneous catalysis,$^4$ heterogeneous catalysis using molecular oxygen as an oxidant is more practically attractive but is also more challenging.$^5^-^7$ The Cu- or Fe-containing zeolite catalyst in combination with a gaseous oxidant (O$_2$ or N$_2$O) or the chemical looping approach with Cu-zeolite as a mediator has been demonstrated to be effective for gas-phase CH$_4$ selective oxidation, but the CH$_3$OH productivity is low.$^8^-^{11}$ The exploitation of H$_2$O$_2$ as an oxidant could enhance CH$_3$OH formation over several types of heterogeneous catalysts in the liquid phase,$^{12^-^{17}}$ but the reaction still suffers from limited CH$_3$OH productivity and CH$_3$OH selectivity in most cases due to the formation of other C$_1$ oxygenates, e.g., methyl hydroperoxide (CH$_3$OOH) and formic acid (HCOOH), or even CO$_2$. Further, the rapid decomposition of H$_2$O$_2$ leads to low efficiency of H$_2$O$_2$ usage in CH$_4$ selective oxidation, and the consumption of expensive H$_2$O$_2$ would hinder the practical application of the H$_2$O$_2$-based CH$_4$ to CH$_3$OH process.

The reductive activation of O$_2$ in the presence of a biological reductant, typically dihydronicotinamide adenine dinucleotide (NADH), is a general strategy for selective oxidation in enzymatic systems such as methane monooxygenase.$^{18}$ The exploitation of a simple
reductant such as H\textsubscript{2} instead of NADH for O\textsubscript{2} activation over a suitable catalyst could generate active species such as H\textsubscript{2}O\textsubscript{2} \textit{in situ}, accomplishing the selective oxidation of CH\textsubscript{4} to CH\textsubscript{3}OH in aqueous medium.\textsuperscript{19-21} A CH\textsubscript{3}OH formation rate of 92 mmol g\textsubscript{Au-Pd}\textsuperscript{-1} h\textsuperscript{-1} was recently achieved over a zeolite-embedded Au-Pd alloy catalyst.\textsuperscript{20} The wasteful over-oxidation of H\textsubscript{2}, a strong reductant, to H\textsubscript{2}O and the risk of explosion associated with the H\textsubscript{2}/O\textsubscript{2} mixture, however, need to be addressed. The use of a milder reductant carbon monoxide to activate O\textsubscript{2} represents an attractive alternative for the selective oxidation of CH\textsubscript{4} with Rh-based catalysts most commonly investigated for this reaction.\textsuperscript{22-25} Besides CH\textsubscript{3}OH, acetic acid could also be formed in some cases owing to the catalytic role of Rh in carbonylation in the presence of CO.\textsuperscript{22-25} Recent studies disclosed that promoters, such as Cu\textsuperscript{2+} added into the aqueous solution, were required to suppress the over-oxidation of CH\textsubscript{3}OH,\textsuperscript{25, 26} making the system quite complicated and hard to control. The design of new types of heterogeneous catalysts and the elucidation of active species formed during the activation of O\textsubscript{2} by CO are needed to increase the potential of this reaction.

Here, we report our discovery that monometallic Au nanoparticles loaded on mordenite zeolite (H-MOR) with strong Brønsted acidity efficiently catalyze the direct oxidation of CH\textsubscript{4} to CH\textsubscript{3}OH in aqueous medium by O\textsubscript{2} in the presence of CO. The CH\textsubscript{3}OH selectivity and productivity reach 75\% and 280 mmol g\textsuperscript{-1} Au\textsuperscript{-1} h\textsuperscript{-1}, respectively, without any promoters. Nuclear magnetic resonance (NMR) spectroscopy and density functional theory (DFT) calculations suggest that the weak affinity of CH\textsubscript{3}OH on the catalyst surface is crucial to maintaining high CH\textsubscript{3}OH selectivity.

H-MOR-supported monometallic noble metal (including Au, Rh, Pd, and Ir) catalysts with a typical nominal metal content of 0.50 wt\% were prepared by an incipient wetness impregnation method, followed by H\textsubscript{2} reduction at 400 °C. The transmission electron microscopy (TEM) images showed that the average sizes of metal particles ranged from 3.6 to 6.5 nm (Figure S1 and S2). We observed a 2.35 Å lattice spacing for Au nanoparticles by high-resolution TEM (HRTEM), corresponding to the Au (111) facet (Figure S1B). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and the energy dispersive X-ray (EDX) mapping revealed that the Au nanoparticles were dispersed on
the external surface of H-MOR (Figure S3). Only X-ray diffraction lines ascribed to H-MOR were observed and no diffraction lines of loaded metals appeared (Figure S4), in agreement with the high dispersion of metal nanoparticles.

The catalytic oxidation of CH$_4$ was performed in a batch reactor typically at 150 °C with gaseous reactants of CH$_4$, O$_2$, and CO in a molar ratio of 4/1/1 and a total pressure of 30 bar. The parent H-MOR was inactive for the conversion of CH$_4$, and the loading of Au, Rh, Pd, and Ir nanoparticles all catalyzed the formation of organic oxygenates from CH$_4$ (Table S1). The product distribution strongly depended on the identity of the noble metals (Figure 1A). The Au/H-MOR catalyst demonstrated both highest CH$_3$OH and lowest CO$_2$ selectivities; the CH$_3$OH selectivity reached 75% in total carbon-containing products and 94% in all organic oxygenates. Small amounts of CH$_2$OOH and CH$_3$COOH as well as trace HCOOH were detected with Au/H-MOR. In contrast, the selectivities of CH$_3$OH over Rh/H-MOR, Pd/H-MOR, and Ir/H-MOR were only 35%, 8.8%, and 0.9%, respectively with HCOOH formed as the major oxygenated product together with significantly more CO$_2$ over these catalysts. The higher selectivity of HCOOH versus CH$_3$OH was also observed for the supported Pd, Rh, and Ir catalysts reported previously.$^{14, 23, 26}$ To the best of our knowledge, this is the first report to demonstrate the high efficiency of the supported monometallic Au catalyst for the selective oxidation of CH$_4$ to CH$_3$OH by O$_2$.

We investigated the effect of Au loadings over the Au/H-MOR catalyst. The increase in Au loadings from 0.07 to 0.87 wt% gradually increased the average size of Au nanoparticles from 2.0 to 9.7 nm (Figure S5). The CH$_3$OH productivity increased significantly with the Au loading from 0.07 to 0.46 wt% and reached the maximum of about 1300 μmol g$_{\text{cat}}$⁻¹ h⁻¹ at an Au loading of 0.46 wt% (Figure 1B). CH$_3$OH was the major product and the selectivity of CH$_3$OH in organic oxygenates was maintained at ≥ 93% for all investigated Au loadings (Table S2). The CH$_3$OH productivity per gram of Au decreased significantly with an increase in the Au loading and the 0.07 wt% Au/H-MOR catalyst displayed the highest CH$_3$OH productivity per gram of Au (370 mmol g$_{\text{Au}}$⁻¹ h⁻¹) (Figure S6). The estimated turnover frequency (TOF) of CH$_3$OH, i.e., the moles of CH$_3$OH formed per mole of surface Au sites per second, displayed a volcanic relationship with the Au particle size (Figure S7), and the Au/H-MOR with an Au particle size
of 5.9 nm showed the highest TOF, indicating that the oxidation of CH$_4$ to CH$_3$OH is a structure-sensitive reaction. The combination of CH$_3$OH selectivity and productivity demonstrates that the present Au/H-MOR system outperforms most of the reported catalytic systems for CH$_3$OH formation using O$_2$ in combination with CO or H$_2$ (Table S3). We further examined the stability of the Au/H-MOR catalyst, and no significant changes in catalytic performances were observed during the catalyst repeated uses (Figure S8). The characterizations for the used catalyst revealed no change in the crystalline structure of H-MOR and no leaching of Au to the liquid solution (Figure S9). The metallic state and the average size of Au nanoparticles were sustained after the reaction (Figure S10).

The effect of support on catalytic behaviors of the supported Au catalyst was also investigated. An Au/SiO$_2$ catalyst with an average Au particle size of 6.4 nm (Figure S11A) could catalyze the selective oxidation of CH$_4$ to CH$_3$OH by O$_2$ in the presence of CO, but the CH$_3$OH productivity was only 273 μmol g$_{cat}^{-1}$ h$^{-1}$, about 20% of that for the Au/H-MOR catalyst (Figure 1C). Thus, the Brønsted acidity of zeolite may play a key role in the present system. Au nanoparticles with similar average particle sizes were loaded on several other typical zeolites (Figure S11B-D), and the catalytic studies revealed that all Au/zeolite catalysts showed higher CH$_3$OH productivity than the Au/SiO$_2$ catalyst. Among the supported Au catalysts investigated, the Au/H-MOR catalyst demonstrated the highest CH$_3$OH productivity (Figure S12 and Table S4). Previous studies revealed that H-MOR possesses the strongest Brønsted acidity and the weakest O–H bond among a series of zeolites. The high activity of Au/H-MOR possibly arises from the uniquely strong Brønsted acidity of H-MOR zeolite (Figure S13). We further investigated the effect of density of Brønsted acid sites by varying the Si/Al ratio of H-MOR. The increase in the Si/Al ratio from 12.5, the typical value adopted in our work, to 20 decreased the density of Brønsted acid sites while keeping its crystalline structure (Figure S14). The average sizes of Au nanoparticle over these H-MOR samples were kept at 5.4–6.4 nm (Figure S1 and S15). The CH$_3$OH productivity increased significantly with the density of Brønsted acid sites in spite of slight decreases in the selectivity of CH$_3$OH due to the enhanced formation of CH$_3$OOH, CH$_3$COOH and CO$_2$ (Figure 1C and Table S5). Therefore, the Brønsted
The acidity of H-MOR zeolite plays a pivotal role in the oxidation of CH$_4$ to CH$_3$OH by O$_2$ in the presence of CO. The Au/H-MOR catalyst initiated CH$_4$ oxidation at approximately 80 °C, and CH$_3$OH and CH$_3$OOH were observed products (Figure 1D and Table S6). The formation of CH$_3$OH was significantly accelerated upon increasing the reaction temperature and its productivity reached as high as 1920 μmol g$_{cat}^{-1}$ h$^{-1}$ at 180 °C. It is noteworthy that CH$_3$COOH was formed considerably at 180 °C, and its selectivity and productivity increased to ~7% and ~200 μmol g$_{cat}^{-1}$ h$^{-1}$. CH$_3$COOH is usually formed over Rh-based catalysts owing to the catalytic function of Rh site in CH$_3$OH carbonylation.$^{24, 25}$ thus the present result indicates that the carbonylation of the formed CH$_3$OH with CO could also proceed significantly at a high reaction temperature even over the supported monometallic Au catalyst. In the absence of CH$_4$, no oxygenated products are formed (Table 1, Entry 1). CH$_3$OH was formed as the major product upon introducing CH$_4$ and the CH$_3$OH productivity increased with the CH$_4$ pressure (Figure S16 and Table S7). These observations clearly indicate that the organic oxygenates are formed from the conversion of CH$_4$. The O$_2$ pressure was found to affect the conversion of CH$_4$ (Figure S17 and Table S8). At fixed CH$_4$ and CO pressures, a higher O$_2$ pressure favored the formation of CH$_3$OH. The CH$_3$OH selectivity only changed slightly at O$_2$ pressures ≤ 5 bar.

No products were observed in the absence of CO (Table 1, Entry 2), indicating that O$_2$ alone could not oxidize CH$_4$ at 150 °C over the Au/H-MOR catalyst. The introduction of CO induced the formation of oxygenated products as well as CO$_2$ (Table 1, Entry 3). The formation rates of products increased monotonically with the CO pressure, while the CH$_3$OH selectivity remained almost unchanged (Figure S18 and Table S9). We investigated the role of CO by performing CH$_4$ oxidation by O$_2$ in the presence of $^{13}$CO instead of CO. The mass spectrum of CH$_3$OH formed under $^{13}$CO was very close to that under normal CO (Figure S19), clearly revealing that the carbon in CH$_3$OH originated from CH$_4$ and not from CO. Further, the $^{13}$C nuclear magnetic resonance (NMR) spectroscopic study for the reaction using $^{13}$CO indicates that the carbon in carboxyl group of CH$_3$COOH originated from CO (Figure S20), confirming that the present Au/H-MOR could catalyze the carbonylation by CO to form CH$_3$COOH. Regarding the nature of the role of CO in accelerating CH$_4$ conversion, it was once proposed...
that CO can assist the generation of \( \text{H}_2\text{O}_2 \) over a supported Rh catalyst by the reaction of \( \text{O}_2 \) with \( \text{H}_2 \) formed via water-gas shift reaction (WGS, \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)) (25), whereas two other studies using Ir catalysts suggested that CO enhanced the selective oxidation of \( \text{CH}_4 \) or \( \text{C}_2\text{H}_6 \) with \( \text{O}_2 \) by maintaining the metallic state of Ir during the reaction.\(^{26,28}\) It is noteworthy that \( \text{H}_2\text{O}_2 \) was observed during the reaction of \( \text{O}_2 \), \( \text{CO} \) and \( \text{H}_2\text{O} \) over the Au/H-MOR catalyst (Table 1, Entry 1). We found that the Brønsted acidity of H-MOR favored \( \text{H}_2\text{O}_2 \) formation (Figure S21). \( \text{H}_2\text{O}_2 \) could even be detected in the presence of \( \text{CH}_4 \) and the amount of \( \text{H}_2\text{O}_2 \) showed a maximum at 120 °C (Figure S22). The decreased amount of \( \text{H}_2\text{O}_2 \) at higher temperatures might arise from the increased reactivity of \( \text{CH}_4 \). We further performed the oxidation of \( \text{CH}_4 \) using \( \text{H}_2\text{O}_2 \) as an oxidant, and the conversion of \( \text{CH}_4 \) could occur even at 50 °C, a lower temperature as compared to that for the oxidation by \( \text{O}_2 \) in the presence of CO. Similarly, \( \text{CH}_3\text{OH} \) was formed as a major product together with \( \text{CH}_3\text{OOH} \) and \( \text{CO}_2 \) but without \( \text{CH}_3\text{COOH} \). This further supports that \( \text{CH}_3\text{COOH} \) results from carbonylation of \( \text{CH}_3\text{OH} \) with CO. The \( \text{CH}_3\text{OH} \) productivity was comparable by using (\( \text{O}_2 + \text{CO} \)) or \( \text{H}_2\text{O}_2 \) for \( \text{CH}_4 \) oxidation at the same temperature (Table 1, Entries 3 and 4, Figure 1D and Figure S23). These results suggest that the active oxygen species formed during the activation of \( \text{O}_2 \) by CO is similar to that derived by \( \text{H}_2\text{O}_2 \) over our Au/H-MOR catalyst.

Hydroxyl radicals (•OH) were assumed to be active species responsible for the oxidation of \( \text{CH}_4 \) to \( \text{CH}_3\text{OH} \) by \( \text{H}_2\text{O}_2 \) in several systems.\(^{13,19,26}\) By using terephthalic acid as a probe molecule, which can readily react with •OH to form a product (2-hydroxyterephthalic acid) with significant fluorescence at around 420 nm,\(^{29}\) we confirmed the generation of •OH radicals in the Au/H-MOR-catalyzed oxidation of \( \text{CH}_4 \) either using \( \text{H}_2\text{O}_2 \) or using \( \text{O}_2 \) in the presence of CO (Figure 2A). The electron paramagnetic resonance (EPR) spectroscopy using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a radical trapping agent further revealed the generation of •OH radicals during the reaction (Figure 2B).\(^{30}\) We could not observe carbon-centered radicals probably because their reaction with •OH radicals was too quickly.\(^{15}\) It is noteworthy that \( \text{H}_2 \) could not be detected during the oxidation of \( \text{CH}_4 \) by \( \text{O}_2 \) in the presence of CO over the Au/H-MOR catalyst. The formation of \( \text{H}_2 \) was also quite slow in the reaction of CO and \( \text{H}_2\text{O} \), suggesting that the WGS activity of the present Au/H-MOR catalyst is negligible at 150 °C.
Thus, we speculate that H$_2$O$_2$ is not generated by the reaction between O$_2$ and the formed H$_2$ but directly from CO and O$_2$ in aqueous solution in the presence of our catalyst.$^{31}$ In short, the reaction involves *in situ* generation of H$_2$O$_2$ from CO, O$_2$, and H$_2$O, followed by its conversion to •OH and the subsequent oxidation of CH$_4$ by •OH.

The addition of an •OH scavenger, Na$_2$SO$_3$, into our system for the oxidation of CH$_4$ by O$_2$ in the presence of CO at 150 °C caused a drop in the productivity of organic oxygenates from 1380 to 507 μmol g$_{cat}$$^{-1}$ h$^{-1}$, providing further evidence for the role of •OH in the formation of CH$_3$OH (Table S10). Nevertheless, the considerable remaining activity may suggest that other active species besides •OH also participates in the reaction, considering that the added scavenger is in excess and is able to quench all the •OH radicals generated during the reaction.$^{13}$

We employed *in situ* infrared (IR) spectroscopy to monitor the surface species. Two IR bands at 918 and 854 cm$^{-1}$ were observed after the adsorption of H$_2$O$_2$ on Au/H-MOR at 50 °C (Figure S24), which could be assigned to free H$_2$O$_2$ and the O–O stretching of adsorbed peroxide species, respectively.$^{32,33}$ The introduction of O$_2$, CO and H$_2$O gas mixture instead of H$_2$O$_2$ onto Au/H-MOR at 150 °C resulted in a broad IR band centered at 850-860 cm$^{-1}$ (Figure 2C), indicating the formation of hydroperoxide species on the catalyst surface. Thus, we speculate that the surface hydroperoxide species might also participate in the oxidation of CH$_4$ to CH$_3$OH.

The reaction kinetics was analyzed to gain mechanistic insights into the formation of different products. The time course for the oxidation of CH$_4$ by O$_2$ in the presence of CO over the Au/H-MOR catalyst showed that CH$_3$OH and CH$_3$OOH were formed at the very initial stage with selectivities approaching 90% and 10%, respectively, and thus both were primary products (Figure 3A). The formations of CH$_3$OH and CH$_3$OOH were confirmed even after 1 min of reaction (Figure S25). Upon increasing the reaction time, the selectivity of CH$_3$OOH decreased and that of CH$_3$OH increased, indicating that CH$_3$OOH could be converted to CH$_3$OH (Figure 3A). We further compared the time course for Au/H-MOR with those for Rh/H-MOR, Ir/H-MOR, and Pd/H-MOR. CH$_3$OH and CH$_3$OOH were the primary products over all these catalysts, but the ratio of CH$_3$OH/CH$_3$OOH was the highest over the Au/H-MOR catalyst (Figure 3A and Figure S26). Furthermore, as compared to other catalysts, the Au/H-
MOR catalyst demonstrated a remarkably slower increase in the HCOOH selectivity over the time, suggesting its significantly lower ability of over-oxidation of CH$_3$OH. The control experiments for the oxidation of CH$_3$OH instead of CH$_4$ under equivalent conditions provided further evidence that among the catalysts investigated, the Au/H-MOR catalyst is the least active for the conversion of CH$_3$OH by O$_2$ in the presence of CO (Figure 3B).

Generally, CH$_3$OH can readily be oxidized into over-oxidized products by active species including •OH radicals, and this is the biggest challenge for selective oxidation of CH$_4$ to CH$_3$OH. To maintain the high selectivity of CH$_3$OH, a radical scavenger like Cu$^{2+}$ is usually required to be added into the system to suppress the over-oxidation.$^{12, 21, 23, 26}$ The present work discovered that the H-MOR-supported monometallic Au catalyst offers the highest CH$_3$OH selectivity among a series of supported noble metal catalysts in the absence of other metal additives. The characterization with fluorescence emission spectroscopy showed that the concentration of •OH radicals during the reaction using the Au/H-MOR catalyst was not unique and was on a similar level with those using other catalysts (Figure S27). The unique CH$_3$OH selectivity of the Au/H-MOR catalyst suggests that besides the concentration of •OH radicals, other factors may also control the CH$_3$OH selectivity. The low activity of Au/H-MOR toward CH$_3$OH oxidation (Figure 3B) enables us to speculate that the affinity of CH$_3$OH on the catalyst may determine the CH$_3$OH selectivity, because a low affinity of CH$_3$OH on catalyst surfaces would mitigate its over-oxidation due to the favored desorption and the suppressed re-adsorption of CH$_3$OH. It is known that the relaxation time of an adsorbed molecule measured by NMR spectroscopy, described by $T_1$ (longitudinal relaxation time) and $T_2$ (transverse relaxation time), can reflect the adsorption strength of a molecule, and a higher $T_1/T_2$ value corresponds to a stronger interaction with the surface.$^{34-36}$ We thus measured the relaxation time for different catalysts as shown in Figure S28-S30 and Table S11. As summarized in Figure 3C, the $T_1/T_2$ ratio is clearly correlated to the CH$_3$OH selectivity. The Au/H-MOR catalyst, which has the lowest $T_1/T_2$ ratio and thus the lowest affinity to CH$_3$OH, displays the highest CH$_3$OH selectivity, whereas the Ir/H-MOR catalyst shows the highest $T_1/T_2$ ratio and the lowest CH$_3$OH selectivity. Therefore, our work demonstrates that the $T_1/T_2$ ratio is a useful
descriptor for the affinity of CH$_3$OH onto the catalyst surface and thus the CH$_3$OH selectivity during CH$_4$ oxidation.

We also performed computational studies to evaluate the non-dissociative adsorption energy of CH$_3$OH, which is closely related to its affinity, on different metal surfaces. Using a slab model, the CH$_3$OH molecule was adsorbed on the most representative facet, i.e., (111) facet, of different metals. The non-dissociative adsorption energy values are summarized in Figure 3D and Table S12, and the related optimized models are displayed in Figure S31-S34. The non-dissociative adsorption energy of CH$_3$OH on Au (111) is −0.36 eV, and its absolute value is 0.27, 0.30, and 0.63 eV lower than those on the Rh (111), Pd (111) and Ir (111) surfaces, respectively. In agreement with the NMR results, this result offers further evidence that the affinity of CH$_3$OH onto the Au surface is the lowest among the surfaces of metal catalysts investigated.

In conclusion, we have discovered that the H-MOR zeolite-supported monometallic Au catalyst demonstrates superior activity and selectivity in the selective oxidation of CH$_4$ to CH$_3$OH by O$_2$ in aqueous medium. Au nanoparticles with medium sizes and Bronsted acidity of H-MOR both play crucial roles in the formation of CH$_3$OH. CO is proposed to accelerate the activation of O$_2$ in aqueous medium to form hydroxyl radicals and hydroperoxide species responsible for the activation and conversion of CH$_4$. The excellent CH$_3$OH selectivity can be ascribed to the low affinity of CH$_3$OH on Au surfaces. This work opens a new avenue for the selective oxidation of CH$_4$ to CH$_3$OH as well as other important reactions, where the facilitation of product desorption is a key to selectivity.
References


Acknowledgments

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Supporting Information

Details of supplementary characterization and computations have been included in the supporting information.
**Figure 1.** Catalytic performances for CH4 selective oxidation. (A) Performances of H-MOR-supported several noble metal catalysts. (B) Effect of Au loadings over the Au/H-MOR catalyst. (C) Performances of Au/SiO$_2$ and Au/H-MOR with different Si/Al ratios (the number after H-MOR denotes the Si/Al ratio). (D) Effect of reaction temperature. Reaction conditions: catalyst, 0.10 g; H$_2$O, 20 mL; total pressure, 30 bar; CH$_4$ pressure, 20 bar; CO pressure, 5 bar; O$_2$ pressure, 5 bar; reaction time, 1 h; reaction temperature, 150 °C for (A), (B), and (C).
Figure 2. Characterizations of active oxygen species. (A) *In situ* fluorescence emission spectra during CH$_4$ oxidation by O$_2$ with CO or by H$_2$O$_2$ over Au/H-MOR. (B) *In situ* EPR spectra during CH$_3$OH oxidation by O$_2$ with CO or by H$_2$O$_2$ over Au/H-MOR. Signals marked by solid diamonds are attributable to the degradation of DMPO to 5,5-dimethyl-2-oxopyrrrole-1-oxyl (31). (C) *In-situ* IR spectra of the adsorbed species on Au/H-MOR under O$_2$, CO and H$_2$O vapor.
Figure 3. Relationship between CH$_3$OH selectivity and its affinity. (A) Changes of product selectivity and organic oxygenate productivity with reaction time during CH$_4$ oxidation over Au/H-MOR. Reaction conditions: catalyst, 0.10 g; H$_2$O, 20 mL; reaction temperature, 150 °C; total pressure, 30 bar; CH$_4$ pressure, 20 bar; CO pressure, 5 bar; O$_2$ pressure, 5 bar. (B) Amounts of HCOOH and CO$_2$ during the oxidation of CH$_3$OH. Reaction condition: catalyst, 0.10 g; H$_2$O, 20 mL; CH$_3$OH, 200 μmol; reaction temperature, 150 °C; total pressure, 30 bar; N$_2$ pressure, 20 bar; CO pressure, 5 bar; O$_2$ pressure, 5 bar; reaction time, 1 h. (C) CH$_3$OH selectivity during CH$_4$ oxidation versus the T$_1$/T$_2$ ratio measured by NMR. (D) Calculated non-dissociative adsorption energy of CH$_3$OH on noble metal surfaces. The inset represents the computation model of CH$_3$OH adsorbed on the Au (111) facet.
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$^a$ Reaction conditions: catalyst, 0.10 g; H$_2$O, 20 mL; reaction temperature, 150 °C; reaction time, 1 h; total pressure, 30 bar; CH$_4$ pressure, 20 bar; CO pressure, 5 bar; O$_2$ pressure, 5 bar.

$^b$ CH$_3$OH selectivity in all organic oxygenates.

$^c$ The formation of 64 μmol H$_2$O$_2$ was detected by titration of liquid products with a standard solution of Ce(SO$_4$)$_2$. 

**Table 1.** Catalytic results for control experiments using Au/H-MOR$^a$