



A breakthrough in direct conversion of methane to oxygenates under mild conditions

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Methane is an attractive C1 resource for production of value-added chemicals. The current industrial utilization of methane involves indirect route *via* preliminary oxidation to syngas (a mixture of CO and H₂) that can be converted to desired products [1]. Such two-stage process is energy-intensive. Considerable efforts have been devoted to developing catalytic processes that can efficiently and directly transform methane through oxidative or non-oxidative pathways [2,3]. Since the pioneering work of methane dehydroaromatization under nonoxidative conditions in 1993 [4], a variety of catalysts based on metal ions (Mn, Fe, Zn, Mo, W, etc.) dispersed on zeolites have been tested to improve the efficiency and product selectivity of non-oxidative methane conversion [3]. Recently, lattice-confined single-iron catalyst embedded in a silica matrix has been developed to convert methane exclusively to ethylene and aromatics with total hydrocarbon selectivity exceeding 99% at methane conversion of 48.1% [5]. However, the catalysis requires an extremely high operating temperature of 1090°C. Oxidative conversion of methane to oxygenates over heterogeneous transition metal oxide catalysts (typically MoO₃ and V₂O₅) are also generally performed under high temperatures (>350°C) [6,7]. Although homogeneous metal (e.g., Pt, Pd, Au, etc.) catalysis opened up the possibility of oxidizing methane at low temperatures (0–220°C) with high selectivity [8], the commercial application is hampered by the need for highly corrosive or expensive chemicals and the difficulty in separation/recycling of the catalysts. The natural methane monooxygenases (MMOs) can selectively catalyze the transformation of methane to methanol at ambient conditions [9]. Attempts to artificially mimic the activity of MMOs at low temperatures have been made by encapsulating the active binuclear

centers of Cu and Fe, in a form analogous to MMOs, within the zeolite catalysts [10]. Nonetheless, those artificial catalysts are far from industrial application due to the low product yield (<200 μmol g_{cat}⁻¹).

Recently, Shan, Li, and Flytzani-Stephanopoulos at Tufts University in collaboration with their co-workers from Oak Ridge and Argonne National Laboratories reported an exciting discovery that the atomically dispersed rhodium catalysts on zeolite (ZSM-5) and titanium dioxide (titania) can catalyze the direct oxidation of methane to oxygenates (acetic acid and methanol) using oxygen and carbon monoxide at aqueous solution [11]. Furthermore, the catalysts can be operated at low temperature of 150°C. The product yields of acetic acid over 0.5 wt% Rh-ZSM-5 and methanol over 0.6 wt% Rh-TiO₂ can reach ~22,000 μmol g_{cat}⁻¹ and ~230 μmol g_{cat}⁻¹, respectively. The product selectivity ranges from 60% to 100%.

The meticulous performance test of the catalysts revealed that the product selectivity is oxygen-limited and acidity-sensitive. For Rh-ZSM-5 catalysts, the product selectivity of methanol and acetic acid increases significantly upon decreasing the partial pressure of oxygen (*p*_{O₂}, 4 bar → 2 bar). When the *p*_{O₂} is lowered down to 0.5 bar, the highest acetic acid selectivity is achieved. The presence of Brønsted acid sites in zeolite can promote the selectivity for acetic acid [12]. The authors ingeniously designed the catalyst of Rh-Na-ZSM-5 with fewer Brønsted acid sites for comparison. It was found that the primary product can be tuned toward methanol. When the Rh-TiO₂ catalyst that lacks the acid sites of H-ZSM-5 is used, the sole product of methanol is identified. The formation of acetic acid thus requires the presence of Brønsted acid sites while the acid site is not essential for

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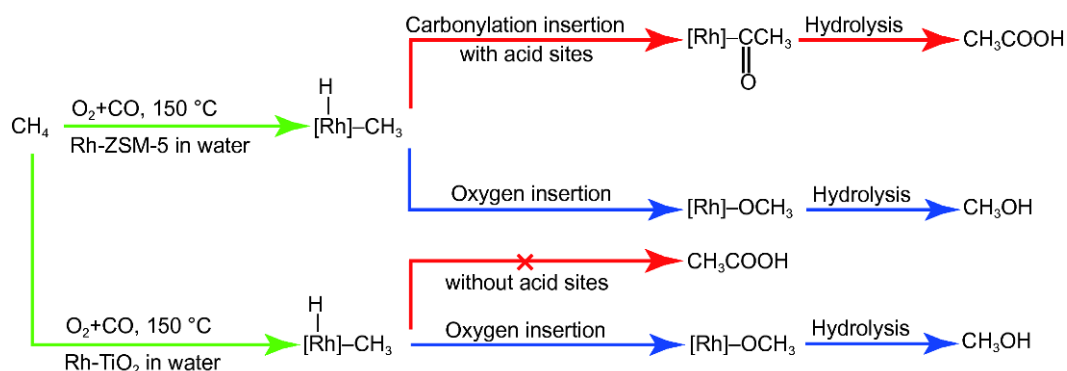


Figure 1 Proposed mechanisms for direct conversion of methane to acetic acid and methanol over supported mononuclear rhodium catalysts.

methanol production.

To uncover the superior catalytic activity of the catalysts, diverse morphological and spectroscopic characterizations have been performed for Rh-ZSM-5 to determine the dispersion state and valence state of rhodium. The authors concluded that the active sites are the isolated mononuclear rhodium cations [dominantly $\text{Rh}^{\text{I}}(\text{CO})_2$] inside the zeolite micropores. Taking into account that no oxygenates are formed when the catalysts are exposed to the atmosphere with only ($\text{CH}_4 + \text{CO}$) or only ($\text{CH}_4 + \text{O}_2$), methane activation by Rh in the presence of CO and O_2 has been proposed (Fig. 1).

The independent reaction pathways for the formation of acetic acid and methanol have been figured out relying on more experimental evidence. Isotope (^{13}C) labeling measurements suggested that CO inserts directly into the $\text{Rh}-\text{CH}_3$ bond to form $\text{Rh}-\text{COCH}_3$ in the presence of acid sites in the Rh-ZSM-5 catalysts. The CO molecule may also act as a co-catalyst in the form of Rh-bonded CO ligand to promote the insertion of an oxygen atom into the $\text{Rh}-\text{CH}_3$ bond to form $\text{Rh}-\text{OCH}_3$. The formed $\text{Rh}-\text{COCH}_3$ and $\text{Rh}-\text{OCH}_3$ can be further hydrolyzed to acetic acid and methanol, respectively (Fig. 1).

Although the exact mechanisms of methane activation and $\text{Rh}-\text{CH}_3$ functionalization remain unclear, this study has made a breakthrough in the direct oxidation of methane under mild conditions for production of value-added chemicals. The crucial roles of CO molecule to facilitate catalytic methane conversion have been emphasized. The introduction of CO can lead to effective engineering of the geometric and electronic structures of the active metal centers, as reported in coordination chemistry, organometallic chemistry, and catalytic chemistry [13–16].

In the context of methane activation, a previous study

has indicated that the dissociative CO-adsorption can tune down the spin density distribution on metal centers, which then promotes methane activation through oxidative addition [17]. The creative idea of introduction of alien molecules to promote catalytic processes can guide the design of new and more efficient catalysts for selective methane oxidation.

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