

Editorial

Advances in Catalytic Oxidation of Methane and Carbon Monoxide (2nd Edition)

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The catalytic removal of carbon monoxide and methane produced from human activities is an important method for eliminating these pollutants, and can solve their associated environmental problems. So far, heterogeneous catalysis has been considered one of the most appropriate and sustainable strategies to remove pollutants that are harmful to the atmosphere. This Special Issue within the Section “Environmental Catalysis”, “Advances in Catalytic Oxidation of Methane and Carbon Monoxide (2nd Edition)”, is a collection of seven articles, including three original papers and four review papers, which address the issues of CO oxidation, CH₄ combustion, and the partial oxidation of CH₄ to oxygenates.

The catalytic oxidation of CO at low temperatures is an important aspect of air purification. Since the discovery of CO oxidation catalyzed by TiO₂-supported nanoparticles (NPs) at a temperature far below 0 °C, reported by Haruta et al. in 1987 [1], Au NPs supported on reducible metal oxides [2–6] have gained much attention. Since the catalytic performance of Au NPs significantly depends upon the particle size and the type of support used [7], a large number of preparation methods have been developed to enable the loading of noble metal NPs onto different supports [7–9], in which Au works as the CO adsorption site, and O₂ is activated in the oxygen vacancies of the reducible metal oxide supports [9–12].

In contribution 1, Takahashi et al. investigated Au clusters supported on defect-rich Ni-Ti oxides derived from ultrafine layered double hydroxides (LDHs) for CO oxidation at an ambient temperature. The authors found that the rich hydroxyl groups at the edge sites of the LDHs could serve as the anchoring sites for the metal nanoparticles (NPs), and the transformation of the LDHs into mixed metal oxides (MMOs) gave rise to abundant oxygen vacancies favorable for O₂ activation during the CO oxidation process, thus exemplifying the high activity rate and good hydrothermal stability of the Au/Ni-Ti MMO/SiO₂ catalyst. In contribution 2, Timmer et al. presented an investigation into the active phase of RuO₂ in a catalytic CO oxidation reaction, employing operando CO diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and online mass spectrometry (MS). By utilizing the combined techniques of DRIFTS and MS, the authors clarified the active phase of RuO₂ supported on rutile TiO₂ (RuO₂@TiO₂) during a CO oxidation reaction, and concluded that the partially reduced RuO₂@TiO₂ catalyst was the most active during CO oxidation, and this was independent of the reducing or oxidizing condition and whether the starting material was the fully oxidized or partially reduced RuO₂@TiO₂ catalyst. Qin et al. (contribution 3) studied CO oxidation over Au/SBA-15 modified with TiO₂ films grown via atomic layer deposition (ALD), and found a synergy between the Au and TiO₂ phases when it related to the bonding and conversion of CO, which could be controllably tuned by varying the synthesis parameters. Simultaneously, the authors also suggested that the ALD of TiO₂ films could be an effective way to maximize the Au–TiO₂ interface sites, which would be beneficial for the activation of molecular oxygen.

As the main component of natural gas, incomplete methane combustion results in wasted resources and aggravates air pollution. Over the last twenty years, the global



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warming potential of CH₄ has been shown to be at least 72 times higher than that of CO₂, inducing a strong greenhouse effect on the atmosphere. CH₄ with a regular tetrahedral structure is the most stable hydrocarbon, meaning it is difficult to activate and oxidize under mild conditions. The conventional combustion of natural gas requires high temperatures (>1500 °C) and produces pollutants (e.g., carbon monoxide and nitrogen oxides) that must be completely eliminated. As of late, the complete catalytic oxidation of methane (i.e., catalytic methane combustion) has been one of the most promising pathways for removing emitted methane, in which the key issue is the availability of high-performance catalysts. In the past few decades, a large number of catalysts have been developed for the combustion of methane, including transition metal oxides, noble metals, mixed metal oxides (such as perovskites (ABO₃), double perovskites (A₂BBO₆), perovskite-like oxides (A₂BO₄), and pyrochlore (A₂B₂O₇)), and hexaaluminates. In recent years, several reviews on catalytic methane combustion have been reported in the literature [13–17].

Of the abovementioned catalysts, porous materials are the most promising candidates. For example, Dai and coworkers (contribution 4) summarized the recent progress made in preparation methods and applications of ordered porous oxides. They supported the use of noble metal catalysts for methane combustion, and suggested that their well-ordered and -developed three-dimensional porous structure, large surface area, ultrahigh component dispersion, fast mass transfer, low-temperature reducibility, reactant activation ability, and strong metal–support interaction were accountable for their good catalytic activity, hydrothermal stability, and moisture and sulfur resistance. Additionally, the authors envisioned a future trend in the development of oxide materials for industrial applications. In contribution 5, Wu et al. summarized the development of zeolite-based catalytic materials for the activation of the C–H bonds in CH₄ and the mechanisms of complete and selective methane oxidation. In the developed catalysts, a Pd/zeolite material was used for the complete oxidation of methane to CO₂ and H₂O, while Fe- and Cu-zeolite materials were employed for the partial oxidation of methane to methanol (MTM), formaldehyde, formic acid, etc. The authors also proposed possible perspectives and challenges for zeolite-based catalysts in future research and practical applications.

Direct MTM conversion is an ideal strategy for significantly reducing transportation and storage costs [18]. The partial oxidation of MTM as a liquid fuel and chemical feedstock has been considered one of the most desirable methane conversion pathways. In the past few years, many efforts have been made to explore new catalyst systems and design strategies for direct methanol production from methane under mild conditions with controlled oxidation processes [19–21].

Zhao and coworkers (contribution 6) presented an overview of a rational design of catalysts for the direct conversion of methane to methanol based on a descriptor approach, in which they explored the suitable energy, electronic, and structural descriptors to construct and understand the linear scaling relationships between the fundamental physicochemical properties of the catalysts and their catalytic activities in direct MTM conversion. According to the selectivity descriptor, the limitation of the inverse scaling relationship between methane conversion and methanol selectivity was discussed, and how this limitation can be exceeded to achieve the simultaneous enhancement of activity and selectivity. The authors believed that their descriptor-based review article provided theoretical insights into the understanding, optimization, and rational design of efficient catalysts for direct MTM conversion. In contribution 7, Tavani et al. explored MTM oxidation over iron and copper sites in metal–organic frameworks (MOFs). They focused on the utilization of diverse spectroscopic techniques to clarify the electronic and structural properties of iron- and copper-embedded MOF catalysts at microscopic levels and their reaction pathways and intermediates, and also discussed the catalytic efficiency and selectivity of these MOF-based materials for the MTM reaction. In the end, the authors provided a perspective on possible directions for future research on advancing the use of MOFs for the MTM reaction.

Hence, this Special Issue allows readers to gain a clear insight into the oxidation of CO and the complete or partial oxidation of methane over the supported transition metal or noble metal catalysts.

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List of Contributions

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