

Decorating Single-Atom Catalysts with CO for Efficient Methane Conversion

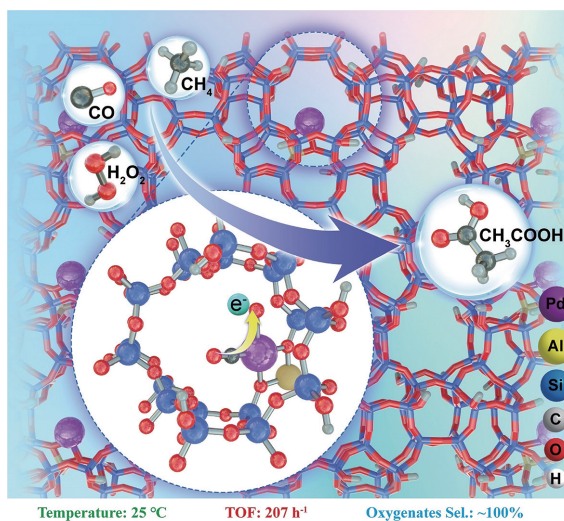
Direct methane conversion has advantages such as low energy consumption, less processes, and being more economical. However, it is difficult to activate methane at room temperature due to the high dissociation energy of C-H bonds of methane. Additionally, the target products, such as methanol, acetic acid, and other oxygenates, are prone to over-oxidation, resulting in the generation of CO₂. Therefore, the design of catalysts with high activity and selectivity is important.

Recently, a group led by Prof. ZHANG Tao, Prof. WANG Xiaodong, and Asso. Prof. HUANG Chuande from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences (CAS), in collaboration with Prof. CHANG Chunran's group from Xi'an Jiaotong University, have realized the efficient direct conversion of methane through single-atom catalysis at room temperature.

This study was published in *Angewandte Chemie International Edition* on February 29, 2024.

The researchers proposed a strategy involving CO molecule modification to regulate the electronic structure of single-atom catalyst M₁-ZSM-5 (M = Rh, Ru, Fe), which enhances the efficiency of direct methane conversion. They realized catalyzing methane conversion with H₂O₂ as an oxidant at room temperature (25°C), the turnover frequency (TOF) of Pd₁-ZSM-5 reached 207 h⁻¹ with nearly 100% selectivity towards oxygenates.

Combining experimental characterization with density functional theory (DFT) calculations, the researchers discovered that the C atom in the CO molecule tends to coordinate with the Pd₁ single atom, transferring electrons from CO to the active oxygen center L-Pd₁-O (L = CO), resulting in the reduce of the dissociation barrier of C-H bonds of methane, from 1.27



Direct methane conversion to acetic acid over CO-promoted Pd₁-ZSM-5 single-atom catalyst (Image by XU Weibin)

eV to 0.48 eV.

Moreover, this strategy exhibited good universality as TOF of the M₁-ZSM-5 (M = Rh, Ru, Fe) series catalysts could be increased by 3.2 to 11.3 times through CO molecule modification.

“We have developed the electronically tunable molecular sieve-supported M₁-O isolated active centers, providing a new method to achieve selective methane conversion to chemicals under mild conditions,” said Prof. WANG.

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(Source: DICP)

Reference

Xu, W., Liu, H. X., Hu, Y., Wang, Z., Huang, Z. Q., Huang, C., . . . Zhang, T. (2024). Metal-Oxo Electronic Tuning via *In Situ* CO Decoration for Promoting Methane Conversion to Oxygenates over Single-Atom Catalysts. *Angew Chem Int Ed Engl*, e202315343. doi:10.1002/anie.202315343