



# Editorial: Heterogeneous Catalysis for Methane Activation

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## Editorial on the Research Topic

### Heterogeneous Catalysis for Methane Activation

Directly converting methane into value-added chemicals and fuels is a “dream reaction” in heterogeneous catalysis because it allows abundant natural gas and shale gas to be used as C1 building block for producing chemicals (Zou et al., 2021). The high molecular stability, however, makes it difficult to directly convert methane into desired chemicals in an economically attractive way. Despite the challenges, significant progress has been made recently in the selective activation of methane into methanol (Agarwal et al., 2017; Sushkevich et al., 2017; Jin et al., 2020), acetic acid (Shan et al., 2017; Tang et al., 2018), ethylene (Wang et al., 2017; Dong et al., 2022), and aromatics (Guo et al., 2014). With the ever increasing of oil-to-gas price ratio, some methane-based chemical production (e.g., ethylene production) is even expected to compete with oil-based technologies in around 20 years (Cruellas et al., 2019). For a better understanding of direct methane conversion through heterogeneous catalysis, we proposed this Research Topic and invited researches worldwide to contribute original research and review articles.

Direct methane conversion reactions can operate at both high temperature and low temperature. Thermocatalytic direct non-oxidative methane conversion (DNMC) and oxidative coupling of methane (OCM) are usually conducted at high temperatures (>900 K) as they require high temperature to activate methane on the catalyst surface and desorb methyl radicals into gas phase for following transformation (Zou et al., 2021). With the development in precision synthesis, advanced *in-situ* characterization, and comprehensive theoretical modelling, the knowledge on OCM and DNMC has advanced considerably. Guo et al. (2014) reported that single iron sites embedded in a silica matrix enable DNMC exclusively to ethylene and aromatics. Unprecedented methane conversion at 48.1%, ethylene selectivity at 48.4%, and total hydrocarbon selectivity exceeded 99% was achieved at 1363 K. Cheng et al. achieved stable and high methane conversion and low coke selectivity in Fe/SiO<sub>2</sub> catalyzed DNMC by using SrCe<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>3-δ</sub> (SCZO) as “hydrogen transformer” to lower its local concentration, favor “soft coke” formation and mitigate the reverse reaction of DNMC. Zhou et al. investigated the activation processes of lanthanum-containing OCM catalysts by *in situ* X-ray photoelectron spectroscopy, X-ray diffraction, and online mass spectroscopy. They found that the activation of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> involved a migration to the surface followed by surface desorption while the activation of La(OH)<sub>3</sub> showed three major phase change steps of the catalyst structure. Thum et al. synthesized phase-pure precursor materials for transition-metal-doped CaO and systematically investigated their performances in OCM. The results indicate that transition metal (i.e., Mn, Ni, and Zn) doping in low quantities can be applied to improve the catalytic performance of CaO, but the overall effect is limited. Combining *in situ*

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characterizations with theoretical studies, Qian et al. (2020) suggested single  $\text{Mg}_{4c}^{2+}$  site as the most active sites for Li/MgO while Kiani et al. (2021) identified isolated, pseudotetrahedral, Na-coordinated  $\text{WO}_4$  surface sites as the active sites for Mn- $\text{Na}_2\text{WO}_4/\text{SiO}_2$  catalyzed OCM reaction. In contrast to the considerable progresses in mechanism studies, no breakthrough in OCM performance was obtained. The uncontrollable homogeneous transformation of  $\cdot\text{CH}_3$  in the presence of  $\text{O}_2$  thermodynamically favors the production of  $\text{CO}_x$  and sets a theoretical upper bound on  $\text{C}_2$  yield ( $\sim 28\%$ ). Theoretic studies suggest that the limit can be broken only if catalysts play significant role in both heterogeneous generation of  $\cdot\text{CH}_3$  and their subsequent transformations (Arutyunov and Strekova, 2017). The latter is viewed as a “miracle” and has not been achieved till recently. Zou et al. (2021) demonstrated that 5 wt%  $\text{Na}_2\text{WO}_4/\text{SiO}_2$  (5NaWSi) can capture  $\text{CH}_3\cdot$  radicals desorbed from  $\text{La}_2\text{O}_3$  and selectively convert them into  $\text{C}_2$  species on the catalyst surface. A bifunctional OCM catalyst system, which use  $\text{La}_2\text{O}_3$  as the methane activation center and 5NaWSi as  $\text{CH}_3\cdot$  coupling center, exhibits much improved  $\text{C}_2$  selectivity and achieves a  $\text{C}_2$  yield up to 10.9% at 570°C. This study confirms the feasibility of surface coupling of  $\text{CH}_3\cdot$  and point in an exciting new direction for OCM studies.

Inputting external electric potentials or light irradiation as driving forces can break the thermodynamic barrier of C-H activation and facilitate direct methane conversion at low temperature. In this Research Topic, Januario et al. reviewed recent advances on heterogeneous photocatalysis for methane conversion under mild conditions into valuable products. The combination of metal and semiconductor is suggested to be a good strategy to develop more active photocatalysts. For example, Yu et al. (2020) developed an inspiring

photochemical looping process for conversion of  $\text{CH}_4$  to  $\text{C}_2\text{H}_6$  over  $\text{Ag}/\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ , achieving a methane coupling selectivity of over 90%, a quantitative yield of ethane of over 9%, high quantum efficiency (3.5% at 362 nm) and excellent stability. Recently, an ethane production rate of over 5,000  $\mu\text{mol g}^{-1}\text{h}^{-1}$  with 90% selectivity is achieved in a flow reactor using Au nanoparticle decorated  $\text{ZnO}/\text{TiO}_2$  hybrid as photocatalysts for oxidative coupling of methane (Song et al., 2021). In addition to low-temperature OCM and DNMC, considerable progresses have also been achieved in the selective oxidation of methane into oxygenated products at low temperature. Typical heterogeneous catalysts including AuPd nanoparticles (Agarwal et al., 2017; Jin et al., 2020), Rh single-atom catalysts (Shan et al., 2017; Tang et al., 2018), graphene-confined single Fe atoms (Cui et al., 2018), and metallocavities (Shteinman).

At last, our guest editor team would like to acknowledge the valuable contribution of all the authors and referees. We hope the readers enjoy the research of direct methane conversion and pursue their efforts in this important area.

## AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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