Establishing Novel Types of Metal Oxide Compounds for Oxidative Coupling of Methane (OCM)

Xiang Wang*, Junwei Xu, Rong Xi, Yan Zhang, Yameng Liu, Xianglan Xu, Xiuzhong Fang

Key Lab of Jiangxi Province for Environment and Energy Catalysis, College of Chemistry, Nanchang University, Nanchang, Jiangxi, 330031, China
E-mail of corresponding author: xwang23@ncu.edu.cn

Abstract: OCM reaction is one of the important routes for value-added transformation of methane, which has aroused much interest over past decades. At present, the large scale industrialization of this important reaction is still restricted by lacking catalysts having enough one-way C_2 product yield. Therefore, with open thoughts to design novel kinds of efficient catalysts that can be operated at relatively lower temperature region, or can meet the minimum industrialization requirement is of great necessity.

Over recent years, we discovered that some $A_2B_2O_7$ pyrochlore compounds, which owns bulk 8a oxygen vacancies, intrinsic alkalinity and high thermal stability, can match most of the active site requirements for a good OCM catalyst [1]. When studying $La_2B_2O_7$ (B = Ti, Zr and Ce) compounds for OCM, we found that by decreasing the r_A/r_B radius ratio from $La_2Ti_2O_7$ > $La_2Zr_2O_7$ > $La_2Ce_2O_7$, a monoclinic layered perovskite, ordered cubic pyrochlore or defective cubic fluorite phase can be formed in sequence, which induces the change of the surface alkalinity and the amount of active oxygen sites. As a consequence, the reaction performance of the catalysts follows the order of $La_2Ce_2O_7$ > $La_2Zr_2O_7$ > $La_2Ti_2O_7$, testifying that the change of the crystalline structures impacts the reactivity of the catalysts eventually. To further confirm this, two $La_2Zr_2O_7$ compounds with ordered cubic pyrochlore or defective cubic fluorite phase have also been intentionally designed and used for OCM. The catalyst with a cubic fluorite structure displays much better reaction performance than the one with a pyrochlore structure. More recently, we have constructed strontium stannate catalysts with different crystalline phases for OCM reaction. A Sr_2SnO_4 catalyst with a perovskite-like stack of mono-layered structure demonstrates the best reaction performance among all the samples.

It is concluded that that the abundance of surface alkaline sites and active electrophilic oxygen species is the major factor accounting for the OCM performance. In comparison with the State-of-the Art $Mn/NaWO_4/SiO_2$, $La_2Ce_2O_7$ and $La_2Zr_2O_7$ display much improved reaction performance below 750 ºC. In addition, these catalysts possess potent resistance to sulfur and lead poisoning. By further tuning the chemical compositions, optimizing the preparation methods and adding certain additives, catalysts with low temperature OCM performance could be achieved. The structure-reactivity relationship of these metal oxide compounds have been systematically elucidated.

Key words: OCM, Pyrochlore, Perovskite, Strontium stannate, Structure-reactivity

References

[1] J. W. Xu, Y. Zhang, X.L. Xu, X.Z. Fang, R. Xi, Y.M. Liu, R. Zheng, X. Wang. ACS. Catal., 9 (2019) 4030.