Co_2C(101)催化剂表面不同暴露端对 FTS 产物选择性的影响

梁丹丽，章日光*，王宝俊*

太原理工大学煤科学与技术教育部和山西省重点实验室，山西省太原市迎泽西大街 79 号，030024

*Email: zhangriguang@tyut.edu.cn; wangbaojun@tyut.edu.cn

长期以来合成气选择性转化到含氧化物，使用的催化剂均为贵金属，而碳化钴（Co_2C）长期以来被认为是费托反应（FTS）的非活性相。近来 FTS 实验研究表明，当 Co_2C 催化剂暴露(101)和(020)晶面时能够高选择性生成低碳烯烃 [1]，其中 Co_2C(101)表面为主要暴露面。同时 Co_2C 催化剂对 FTS 反应显示出晶面结构的敏感性 [2]。本研究通过密度泛函理论（DFT）计算方法研究了 Co_2C(101)的 C 端和 Co 端暴露表面上的 FTS 反应机理，结果表明在 C 端 Co_2C(101)表面上，CH_3 是主要的 CH_x 物种，CH_3 加氢容易生成 CH_4，不易形成 C_{2+}烃类物种；在 Co 端 Co_2C(101)表面上，CH 是主要的 CH_x 物种，CH 耦合容易生成 C_2H_2 产物，不易加氢生成甲烷。因此，Co_2C(101)催化剂的不同暴露端对 FTS 反应产物呈现出不同的选择性；同时实际的 FTS 反应体系为富氢气氛，Co_2C(101)主要暴露 Co 端表面，故主要产物为低碳烃类物种。研究结果很好地阐明了 FTS 反应中 Co_2C 催化剂暴露(101)晶面时能够高选择性生成低碳烯烃所对应的微观表面结构。

关键词：碳化钴；暴露端；选择性；密度泛函理论

参考文献

[1] Zhong, L. S.; Yu, F.; An, Y. L.; Zhao, Y. H.; Sun, Y. H.; Li, Z. J.; Lin, T. J.; Lin, Y. J.; Qi, X. Z.; Dai, Y. Y.; Gu, L.; Hu, J. S.; Jin, S. F.; Shen, Q.; Wang, H. *Nat.*, **2016**, **538**: 84.

[2] Zhang, R. G.; Wen G. X.; Adidharma, H.; Russell, A. G.; Wang, B. J.; Radosz, M.; Fan, M. H. *ACS Catal.* **2017**, **7**: 8285.

The Effect of Surface Termination on the Product Selectivity over Co_2C(101) Surface in Fischer-Tropsch Synthesis

Danli Liang, Riguang Zhang*, Baojun Wang*
Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, P.R. China

For a long time, syngas has been selectively converted to oxides on the precious metals catalysts, and Co_2C is considered to be an inactive phase of the FTS. Recently, the experimental studies have shown that Co_2C nanoprisms preferentially exposed the (101) and (020) crystal facets, which present the high selectivity toward the formation of lower olefins and inhibit the formation of CH_4, in which Co_2C(101) surface is the dominantly exposed surface. Simultaneously, Co_2C catalyst exhibits the structural sensitivity to the product distribution of FTS reaction. In this work, the effect of Co_2C(101) surface termination on the FTS reaction mechanism was studied using DFT calculation. These results show that on C-Co_2C(101) surface, CH_3 species is the dominant form of CH_x species, CH_3 hydrogenation to CH_4 is the dominant C_1 species. Whereas on Co-Co_2C(101) surface , CH species is the dominant form of CH_x species, CH self-coupling to C_2H_2 is the dominant C_2 species. Therefore, Co_2C(101) surface termination can alter the product selectivity of FTS reaction.

This work is supported by the National Natural Science Foundation of China (21476155), the Key Projects of National Natural Science Foundation of China (21736007).