New Concepts of Confined Catalysis and Catalytic Conversion of Energy Molecules

Xinhe BAO[a,b]

[a] *University of Science and technology of China(USTC), Hefei 230026, China. baoxh@ustc.edu.cn*

[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics(DICP), Chinese Academy of Sciences, Dalian 116023, China. xhbao@dicp.ac.cn*

Abstract:

Our current work has demonstrated the dynamic nature of the catalytic active center and the driving force to maintain its stability and functionality, which originates from the inherent energetic character of the nanostructure (confinement energy) that makes up the active center and resists changes in the intrinsic property of the system. The concept of "catalysis by nano-confinement" developed from the theoretical and experimental research in several catalytic systems has found generality in catalysis and is widely accepted as "new catalytic concept" . This concept provides guidance for re-directing catalysis from crafts to sciences. Thus invented lattice-confined single-site iron catalyst has enabled direct conversion of methane to high-value chemicals, reducing substantially the production cost of chemicals. Furthermore, the newly developed nano-composite catalyst achieves direct synthesis of light olefins from syngas, which can reduce water consumption showing scientific significance and potentials for application in coal chemistry.

Keywords: Nano-catalysis, Confined Catalysis, Syngas, Methane

Catalysis, as a key and enabling technology, plays an increasingly important role in fields ranging from energy, environment and agriculture to health care. Rational design and synthesis of highly efficient catalysts has become the ultimate goal of catalysis research [1,2]. Thanks to the rapid development of nanoscience and nanotechnology, and in particular a theoretical understanding of the tuning of electronic structure in nanoscale systems, this element of design is becoming possible via precise control of nanoparticles' composition, morphology, structure and electronic states [3]. In this talk, I will discuss nano-confinement effects in catalysis, a concept that we has put forward and developed over several years, and the emphasis will be laid on the development of the novel nano-materials as catalysts for energy processes. Taking the confined catalytic systems of carbon nanotubes (CNTs), metal-confined nano-oxides, two-dimensional (2D) layered nano-catalysts and nano composite as the examples, we summarize and analyze the fundamental concepts, the research methods and some of the key scientific issues involved in nanocatalysis [4-7]. The important applications of such materials in catalytic conversion of methane and syngas to valuable chemicals will be introduced, as the examples.

First, I will discuss the innovation of nano-composite catalysts for the selective conversion of coal-based syngas to lower olefins, which overcome two major drawbacks of the conventional Fischer-Tropsch synthesis (FTS)1. The technology converting CO molecules into liquid fuels via hydrogenation is known as Fischer-Tropsch synthesis (FTS). It was first developed by two German scientists, Fischer and Tropsch, in the 1920s and has now become the core technology for Gas-to-Liquid (GTL) and Coal-to-Liquid (CTL) in industry. Chemicals produced via FTS have also gone beyond liquid fuels, including other high-value hydrocarbons, such as light olefins, wax and oxygenates. Despite significant advances in both fundamental understandings and commercial applications, there are two major drawbacks in FTS technology: (1) a wide distribution of hydrocarbons with different chain lengths, i.e. a poor product selectivity; (2) the large consumption of H2, which requires the energy intensive Water-Gas-Shift (WGS) process to generate more H2 to replenish the coal-derived syngas [8,9]. Recently, we developed a technology, completely different from conventional FTS, based on a nanocomposite catalyst composed of metal oxide and zeolite (OX-ZEO). With our innovation, a partially reduced oxide surface (ZnCrOx) was used to activate CO and H2, while C−C coupling is subsequently manipulated within the confined acidic pores of zeolites. The selectivity of light hydrocarbons containing two to four C atoms (C2-C4) is over 94% and that of light olefins (C2=-C4=) reaches 80%. The CO activation and C-C coupling are separated onto two different types of active sites with complementary properties. Particularly, the selective chain growth via C-C coupling is controlled within the confined environment of zeolite pores (Fig.1) [10]. Particularly, oxygen from CO dissociation is removed by the reaction with CO to form CO2, which thus may allow the direct use of coal- and biomass-derived syngas with a low H2/CO ratio (with H2/CO ratio at ~0.5-0.8) and remove the additional process of water-gas-shift (WGS) reaction. As such, both water and energy consumption could be reduced tremendously. This OX-ZEO differs from conventional FTS in the design concept, catalyst and reaction mechanisms, and this process has been recognized as “a milestone in the direct synthesis of light olefins”.

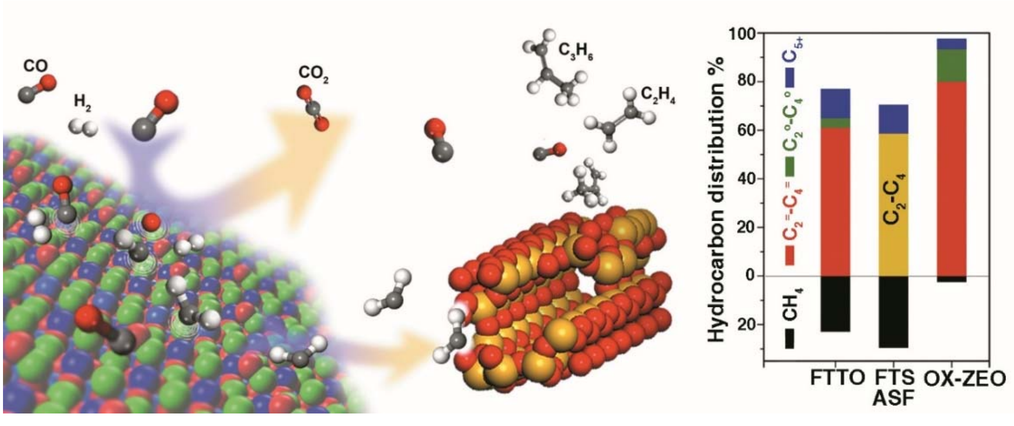

Fig.1. The schematic mechanism and the product distribution of the new process based on a nano-composite catalyst composed of metal oxide and zeolite (OX-ZEO). [10]

A latest result will be also reported in the present talk, and as you can see, the selectivity can be effectively steered toward ethylene employing the oxide-zeolite (OX-ZEO) catalyst concept with ZnCrOx-mordenite (MOR) [11]. The selectivity of ethylene alone reaches as high as 73% at 26% CO conversion, in stark contrast to a maximum 30% predicted for C2 hydrocarbons by the Anderson-Schultz-Flory (ASF) model in FTS. Ethylene selectivity is also significantly higher than those obtained in any other direct syngas conversion or the multi-step methanol-to-olefin process. Selective site blocking experiments reveal that this highly selective pathway is realized over the catalytic sites within the 8-membered ring (8MR) side pockets of MOR via ketene as an intermediate. The 12MR channels are not at all selective for ethylene. This study provides substantive evidence for a new type of syngas chemistry with ketene as the key reaction intermediate that enables extraordinary ethylene selectivity within the OX-ZEO catalyst framework.

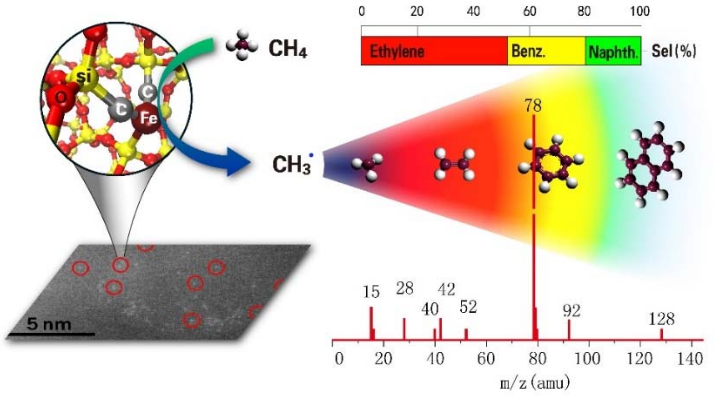

Fig.2 The schematic mechanism of the catalytic conversion of methane to valued chemicals based on a single site catalyst with confined iron in SiO2 lattice. [12]

As the second example, the current results on the direct and selective conversion of methane to valuable chemicals by the invention and development of lattice-confined single-site iron catalyst will be illustrated. As been confirmed, the C-H bond of methane could be cleaved over the single-site iron center embedded in the lattice of SiO2 and SiC, which leads to the formation of •CH3 radicals to leave the surface and couple in the gas phase (Fig.2) [12]. The controlled activation of C-H bond by the single-site catalyst prevents the complete dehydrogenation of methane to form coke on the catalyst surface. Thus, this catalyst provides a potential solution to the selective activation of methane, which has been a grand challenge in chemistry lingering around for over a century. As a result, methane conversion at 1090 ºC reaches 48% and the selectivity to ethylene and aromatics is 100% with no CO2 emission, which thus realizes the atom-economy process for the direct conversion of methane. The process enables the removal of the energy-intensive syngas production process from the conventional natural gas utilization technologies [13].

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