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Nanocatalysts for conversion of natural gas to liquid fuels and petrochemical feedstocks

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ABSTRACT

The conversion of natural gas (methane) as an alternative to petroleum into valuable chemicals and clean fuels has received much attention. However, because of high stability and symmetry of methane molecule, relatively few number of natural gas conversions, mostly indirect routes, have been commercialized and the remainders are still not competitive to petroleum-based processes and are in research and development stage. With the advent of nanocatalysts in chemical processes and energy sector, the potentials of these catalysts in natural gas conversions have been studied extensively all around the world. In indirect conversions, especially gas-to-liquid (GTL) technologies, effective nanocatalysts have been developed. However, in direct conversions, further research and development works are necessary. In this work, the advances in application of nanocatalysts in natural gas conversions are reviewed and areas for further research are addressed. Both theoretical aspects such as density functional theory (DFT) and characterizations and practical achievements in scientific and patent literature will be considered.

Contents

1. Introduction

Natural gas (methane) is considered as an alternative to petroleum for production of chemicals and clean liquid fuels. Natural gas has several advantages over petroleum as a feedstock. Its

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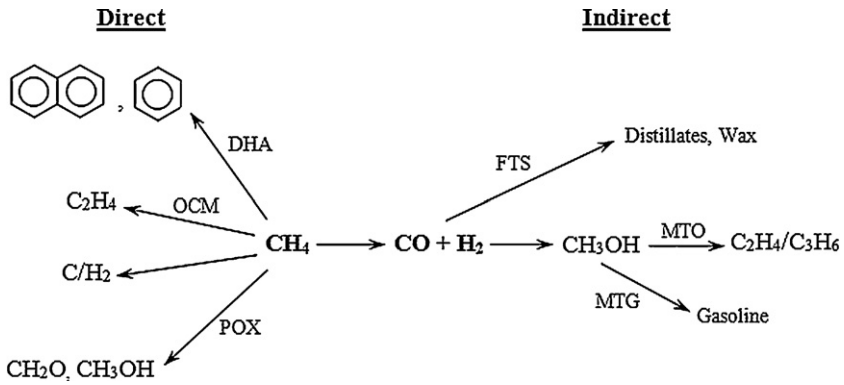

Fig. 1. Main paths from natural gas to value-added products: DHA (dehydro-aromatization), POX (partial oxidation), OCM (oxidative coupling of methane), MTG (methanol-to-gasoline), MTO (methanol to olefins), and FTS (Fischer–Tropsch synthesis).

potential reserves are much larger. It has a high hydrogen/carbon ratio and its composition is virtually source independent [1]. The incorporation of natural gas as a refining feedstock would be the result of a preference for building specific molecules instead of cracking (less selective) the large ones [2,3]. The gas-to-liquid (GTL) technology with virtually unlimited markets offers a way to utilize large gas reserves, complementary to other traditional technologies such as liquefied natural gas (LNG) and pipelines [4,5].

The conversion of natural gas to value-added chemicals can be either direct or indirect, that is, via a methane derivative such as synthesis gas (or syngas, a mixture of H_2 and CO) or methanol in the latter (Fig. 1). Although direct conversions could have definite potential economic advantage, most of the commercialized technologies are based on indirect routes which proceed catalytically.

The effective conversion of methane has been a challenge to heterogeneous catalysis. Methane activation is a crucial step in the conversion of natural gas to valuable products. The high stability and symmetric structure of methane molecule makes it efficient activation for reaction unfavorable both thermodynamically and kinetically.

Fig. 2 compares the Gibbs free energy of formation per mole of carbon of methane with that of C_2 hydrocarbons and benzene. It shows that the direct conversion of methane to higher hydrocarbons is favorable only at higher temperatures where both methane and products are susceptible to decomposition.

In heterogeneous catalysis, methane activation often leads to complete dissociation: If a catalyst can activate the first C—H bond in CH_4 to make methyl radicals, it can often break the remaining

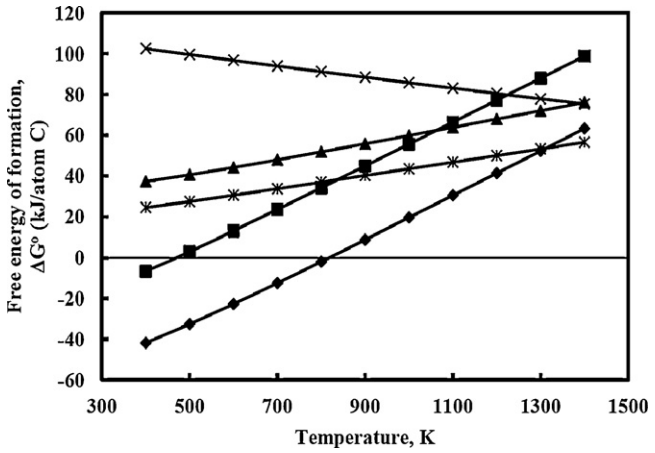

Fig. 2. Gibbs free energy of formation of methane (♦) versus higher hydrocarbons (ethane (■), ethylene (▲), acetylene (×) and benzene (*)) as a function of temperature.

C—H bonds [6]. However, density functional theory (DFT) simulation results have shown theoretically that the presence of metal adatoms on catalyst surface can enhance the first dehydrogenation of CH_4 while hindering the further decomposition of CH_3 [7,8].

Therefore, catalysis could play an important role in conversion of natural gas. Drivers for development of advanced catalysts include (i) production of high value products from inexpensive raw materials, (ii) energy-efficient and environmentally benign chemical conversion processes, (iii) increasingly stringent environmental regulations, and (iv) low-cost catalysts such as with reduction or replacement of precious metals [9]. Most of these can be achieved by using nanocatalysts.

Nanocatalysis have received much attention especially in energy sector to utilize alternatives to ever-decreasing oil reservoirs. Generally a nanocatalyst is a substance or materials with catalytic properties which have at least one nanoscale dimension, either externally or in terms of its internal structures, or have been subjected to nanoscale structural modification in order to enhance its catalytic activity [10]. Nanocatalysts could be classified into four distinct types, namely: nanoparticulate, nanoporous, nanocrystalline, and supramolecular catalysts. In fact, catalysts have been reported to represent the oldest commercial application of nanotechnology. The field of nanoparticles catalysis includes both the homogeneous or unsupported (e.g. colloids) and heterogeneous catalysis communities, and these catalysts are sometimes therefore called "semi-heterogeneous" [11–14]. This field has undergone an explosive growth during the past decade, both in homogeneous and heterogeneous catalysis, with an exponential growth. Most of the publications are for the use of the supported nanomaterials in heterogeneous catalysis. The use of colloids in homogeneous catalysis comprises 15–20% [15].

Particle size effects in catalysis are of growing interest. One goal in nanocatalyst researches is to understand how decreasing the size of catalytic particles alters the intrinsic catalytic performance beyond simply expanding surface area. Nanosized effects in catalysis by metals are known for a long time since the Boudart's classification of structural sensitive and structural insensitive reactions in a review article [16]. In the case of semiconducting metal oxides and sulfides, when the size of the nanocrystals is smaller than the Bohr excitation radius of the material, they exhibit properties which are size-dependent and distinct from the bulk [17]. For both supported and unsupported particles various examples are known where the catalytic performance was proven to be dependent on particle size and shape [18–20]. Colloidal sized metal and semiconductor particles with diameters of 1–20 nm (nanoclusters) are of current interest because they mark a material transition range between molecular and bulk properties. With decreasing particle size, bulk properties are lost as the continuum of electronic