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Journal of Energy Chemistry 22(2013)1–20

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journal-of-energy-chemistry/2095-4956
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Review

Recent progress in methane dehydroaromatization: From laboratory curiosities to promising technology

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[Manuscript received January 7, 2013; revised January 10, 2013]

Abstract

Direct conversion of methane to benzene or other valuable chemicals is a very promising process for the efficient application of natural gas. Compared with conversion processes that require oxidants, non-oxidative direct conversion is more attractive due to high selectivity to the target product. In this paper, an alternative route for methane dehydrogenation and selective conversion to benzene and hydrogen without the participation of oxygen is discussed. A brief review of the catalysts used in methane dehydroaromatization (MDA) is first given, followed by our current understanding of the location and the active phase of Mo species, the reaction mechanism, the mechanism of carbonaceous deposit and the deactivation of Mo/zeolite catalysts are systematically discussed. Ways to improve the catalytic activity and stability are described in detail based on catalyst and reaction as well as reactor design. Future prospects for methane dehydroaromatization process are also presented.

Key words

direct conversion; methane; methane dehydroaromatization; Mo-based catalyst

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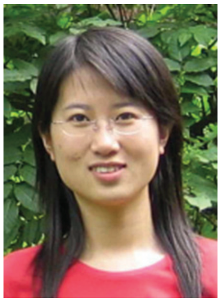

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This work was financially supported by the National Natural Science Foundation of China (No. 21103181).

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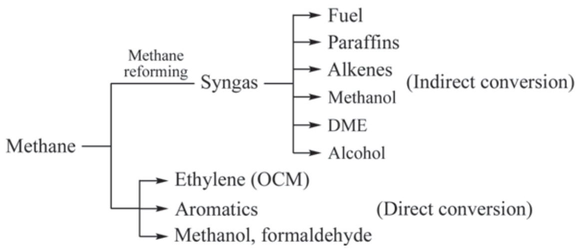
1. Introduction

The world appears to have abundant reserves of methane, especially with the recent discoveries of significant deposits of shale gas in continental North America and methane hydrate in the sediments of the ocean floors, which are conservatively estimated to represent twice the amount of carbon in all other known fossil fuel reserves [1]. Methane, the most abundant compound in natural gas, can be converted catalytically to liquid fuels or useful chemicals. As world reserves of readily accessible petroleum are progressively depleted, methods for efficient use of methane are becoming more important. The two major routes to produce valuable chemicals from methane, indirect and direct conversion, are shown in Scheme 1. Currently, the most widely used method is indirect conversion, which requires more than one chemical reaction step. Typically, methane is first converted to synthesis gas either by reforming or by partial oxidation. In the second step, products such as diesel fuel, gasoline, methanol, dimethyl ether, lower α-olefins, paraffins, and higher alcohols are made from the synthesis gas. The indirect conversion of methane to liquid fuels or valuable chemicals is economically viable, which has already been commercialized. Several large facilities, including the Sasol plants near Johannesburg, the PetroSA plant at Mossel Bay, the Shell SMDS (Shell Middle Distillate Synthesis) plant in Malaysia, the Oryx GTL (gas-to-liquid) plant in Qatar, as well as a GTL plant in Nigeria, are currently operational. In addition, many large petroleum companies, including Shell, Sasol, ExxonMobil, ConocoPhillips, and British Petroleum (BP), have plans to construct new plants. However, because methane is an extremely stable molecule, requiring severe reaction conditions to activate the C−H bond, the preparation and compression of synthesis gas typically accounts for about 60−70% of the capital cost and almost all of the energy consumption to operate the plant. Consequently, direct conversion of methane into desired chemical products is an important goal to reduce cost and energy consumption relative to conventional processing.

A number of processes have been proposed for direct conversion of methane to valuable chemicals or liquid hydrocarbon fuels, including direct partial oxidation of methane to methanol and formaldehyde, oxidative coupling of methane to ethylene, and dehydroaromatization to aromatics. The direct conversion of methane becomes thermodynamically favorable with the assistance of oxidants, and therefore it has received much attention from researchers. One widely-pursued strategy has focused on finding an effective method for direct and selective oxidation of CH_4 to methanol or/and formaldehyde. Unfortunately, it has not yet been successful in making direct conversion competitive with indirect reforming via synthesis gas. Although there are prospects for improvement, the development of such a process appears to be one of the toughest goals in C_1 catalysis and technology. In recent years, extensive studies have been carried out on the catalytic oxidative coupling of methane (OCM) to ethylene (or C_{2+} hydrocarbons). The best single-pass C_2 yield reported so far, approaching 25%, with a selectivity to C_2 approaching 80%, was deemed insufficient for commercialization of OCM process. Nevertheless, successful future development of cost-effective technology for the direct conversion of methane to ethylene and its commercialization will cause the nature of feedstocks used by the petrochemical industry to be profoundly changed. A major barrier is that, in the presence of oxygen, the hydrocarbon products are readily further oxidized to carbon dioxide and water, decreasing the selectivity at high methane conversion.



Scheme 1. Comparison of indirect and direct routes for methane conversion

Another route for efficient utilization of natural gas involves transformation of methane to aromatics, either in the presence or absence of oxygen. Similar to OCM, direct transformation of methane to aromatics with the participation of oxygen is thermodynamically favorable. Unfortunately, the reaction of methane with O_2 to form CO_2 and H_2O is again thermodynamically much more favorable. In 1993, Wang et al. [2] reported methane dehydroaromatization (MDA) for the formation of aromatics (mainly C_6H_6) and H_2 under non-oxidizing conditions in a flow reactor, using a zeolite catalyst (HZSM-5) modified with molybdenum. Compared with oxidative process, the oxygen-free conditions resulted in higher benzene selectivity. Since then, many researchers have worked on this process, and made encouraging progress.

Based on the analytical data from Web of Science, chronological distribution of published articles from 1993 to 2000 related to MDA is shown in Figure 1. It shows that amount of articles has grown fast at first eight years and then