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Methane Activation by Heterogeneous Catalysis

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Abstract Methane activation by heterogeneous catalysis will play a key role to secure the supply of energy, chemicals and fuels in the future. Methane is the main constituent of natural gas and biogas and it is also found in crystalline hydrates at the continental slopes of many oceans and in permafrost areas. In view of this vast reserves and resources, the use of methane as chemical feedstock has to be intensified. The present review presents recent results and developments in heterogeneous catalytic methane conversion to synthesis gas, hydrogen cyanide, ethylene, methanol, formaldehyde, methyl chloride, methyl bromide and aromatics. After presenting recent estimates of methane reserves and resources the physico-chemical challenges of methane activation are discussed. Subsequent to this recent results in methane conversion to synthesis gas by steam reforming, dry reforming, autothermal reforming and catalytic partial oxidation are presented. The high temperature methane conversion to hydrogen cyanide via the BMA-process and the Andrussow-process is considered as well. The second part of this review focuses on one-step conversion of methane into chemicals. This includes the oxidative coupling of methane to ethylene mediated by oxygen and sulfur, the direct oxidation of methane to formaldehyde and methanol, the halogenation and oxy-halogenation of methane to methyl chloride and methyl bromide and finally the non-oxidative methane aromatization to benzene and related aromates. Opportunities and limits of the various activation strategies are discussed.

Keywords Methane · Heterogeneous catalysis · Synthesis gas · Oxidation · Halogenation · Aromatization

1 Introduction

Methane, CH_4, the most simple hydrocarbon, exists in enormous quantity on our planet. It occurs as the principal component of natural gas with a concentration between 70 and 90 % by volume. According to the annually published BP Statistical Review of World Energy [1], proven world natural gas reserves were specified for the year 2013 to $187.3 \times 10^{12}\ m^3$. Reserves denote only all that natural gas that can be recovered from known reservoirs under existing economic, technical and operating conditions. It does not include reservoirs yet to be discovered or natural gas which is currently too expensive for exploitation. In particular this number does not include natural gas found in crystalline hydrates at the continental slopes of many oceans and in permafrost areas. Estimates of the amount of methane stored in hydrates differ widely ranging from $2{,}500 \times 10^{12}\ m^3$ [2] to $15{,}000 \times 10^{12}\ m^3$ [3]. Methane chemistry experiences a boom not only because of its enormous reserves and resources but also because of improved production technology. Natural gas extraction from shale rock in the United States by hydraulic fracturing triggered the so called 'shale gas revolution' [4]. Other countries in possession of huge shale gas resources, e.g. China, are currently following. Finally, methane is the main component of biogas formed by anaerobic digestion of energy crops,

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