



Comparison of oxidizing agents for the oxidative coupling of methane over state-of-the-art catalysts

Kirsten Langfeld^a, Benjamin Frank^b, Verena E. Strempel^a, Claudia Berger-Karin^c, Gisela Weinberg^b, Evgenii V. Kondratenko^c, Reinhard Schomäcker^{a,*}

^a Institute of Chemistry, Technical University Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany

^b Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

^c Leibniz Institute for Catalysis at the University of Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany

ARTICLE INFO

Article history:

Received 19 October 2011

Received in revised form

20 December 2011

Accepted 21 December 2011

Available online 31 December 2011

Keywords:

C–H activation

Oxygen

Nitrous oxide

Cellulose templating

Deactivation

ABSTRACT

The synthesis of selected state-of-the-art catalysts providing high performances in the oxidative coupling of methane (OCM) with O₂ was reproduced according to the respective recipes reported in literature. A reference material with identical stoichiometric composition was further synthesized by applying the cellulose templating method. This method increases the surface area and affects the phase composition and crystallite size of the catalysts as determined by N₂-physisorption, X-ray diffraction and scanning electron microscopy. This, however, is in most cases detrimental to the catalytic OCM performance due to enhanced global activity resulting in hot spots in the catalyst bed. Catalysts were tested in the OCM under variation of temperature (973–1073 K), GHSV (3600–100,000 h^{−1}) and oxidizing agent (O₂ and N₂O). In general, conversions of CH₄ when using N₂O are lower than in the presence of O₂, however, the selectivities to C₂ products ethane and ethylene are higher even at a similar level of CH₄ conversion. This confirms the presence of different oxygen species formed by activation of these oxidizing agents.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The use of methane as a chemical feedstock and its transformation into higher hydrocarbons has been the focus of a number of research efforts for several decades. With increasing oil prices especially the Fischer–Tropsch (FT) process via synthesis gas, which is obtained, e.g., by steam reforming of methane, actually retrieves a lot of attractiveness. However, one drawback with regard to process costs is the need for two individual reactors to consecutively produce synthesis gas and higher hydrocarbons or alcohols. Even more complex is the route to high-value olefins via methanol, which is synthesized from synthesis gas. A highly attractive one-step transformation is the oxidative coupling of methane (OCM) to C₂ hydrocarbons (C₂H₆ and C₂H₄) discovered in the early 1980s [1]. This reaction, even though extensively investigated and optimized for almost three decades, provides low C₂ selectivities at high industrially relevant methane conversions due to consecutive oxidation of produced hydrocarbons to CO and CO₂. A C₂-yield of 30% is regarded as the economically feasible limit for industrial realization of the process [2].

To improve the OCM selectivity a variety of less active oxidizing agents such as N₂O, CO₂, and H₂O have already been tested. This is not only for environmental reasons – N₂O and CO₂ are important greenhouse gases and their value added chemical transformation is highly desired [3] – but the major intention is the formation of more selective surface oxygen species on the catalyst. Clearly, the formation of electrophilic peroxy-species, which would favor the combustion of adsorbed hydrocarbons during OCM [4,5], is less probable when using these mild oxidizing agents because N₂O, CO₂, and H₂O, contrarily to O₂, can provide only one O atom for the catalyst reoxidation. The reaction mechanisms proposed for OCM are quite similar for each oxidizing agent and start with generation of surface active oxygen species from the oxidizing agent (Eqs. (1)–(4)). Depending on the oxidizing agent, N₂ [6–9], CO [10–12], or H₂ [13] are formed as the by-product in these reaction steps. The reaction of O₂ (Eq. (1)) is reported to pass a peroxy intermediate [5,14].



The following (selective) reaction pathway is the oxygen-assisted CH₄ activation to form a methyl radical and a surface

* Corresponding author. Tel.: +49 30 314 24973; fax: +49 30 314 79552.

E-mail addresses: evgenii.kondratenko@catalysis.de (E.V. Kondratenko), schomaecker@tu-berlin.de (R. Schomäcker).