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$Mn–Na_2WO_4/SiO_2$ as catalyst for the oxidative coupling of methane. What is really known?

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ABSTRACT

$Mn–Na_2WO_4/SiO_2$ is one of the very few catalysts for the oxidative coupling of methane, whose stability over extended times on stream has been reported by different research groups. The high stability turned $Mn–Na_2WO_4/SiO_2$ into an object of research, despite the rather complex composition and structure. The nature of the active site or the active phase is unclear, in spite of the research on this catalytic system. This manuscript tries to critically summarize the literature on this system and to discuss the available information about the relationship of structure and activity.

1. Introduction

There are large resources of natural gas, rivaling those of crude oil [1]. Currently, natural gas is underutilized, as there are no feasible ways to convert large amounts of CH_4, the main component of natural gas, into value added products [2]. The oxidative coupling of methane (OCM) to C_2H_6 or C_2H_4 is a possible reaction (see Eq. (1)), which has received a lot of attention since the fundamental works of Keller et al. [3] and Hinsen et al. [4].

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_6 \text{ or } C_2H_4 + H_2O \quad (1)$$

The reasons are, that the oxidative coupling of methane is a direct and exothermic process, therefore not limited by any thermodynamic constraints. Moreover, the products are C_2 compounds, a vital building block in the chemical industry with an expectedly increasing demand. However, until now no economically viable process has been put into practice despite all efforts [5–9]. The reasons are a lack of active, selective and in particular stable catalysts. Furthermore, the thermodynamically favored reaction is the total oxidation of CH_4, as shown in Eq. (2).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (2)$$

In the search for a suitable catalyst, hundreds of materials have been tested in the past [6,5]. The stability of possible OCM catalysts was often not reported and it is therefore doubtful in many publications. A prominent example is Li/MgO: in many publications it was either reported to be a stable catalyst or information and experiments on the stability were neglected [10,11], and references therein. Recently, it has been shown that Li/MgO suffers from an intrinsic instability, prohibiting any practical application [10,12].

The $Mn–Na_2WO_4/SiO_2$ catalyst was first reported by the group of Li [13,14], unfortunately these two publications are in Chinese. However, this catalyst has a remarkable stability under the high temperatures required for the oxidative coupling of methane. This fact has been confirmed by different research groups [15–19]. Moreover, the catalytic performance (CH_4 conversions of 20–30% at C_2 selectivities of 70–80%) is suitable for a practical application.

Since $Mn–Na_2WO_4/SiO_2$ is one of the very few suitable OCM catalysts, the existing literature is summarized in this manuscript with focus on the structure-activity relationship, completing and updating two review articles from the catalyst's inventor Prof. Li from 2001 and 2003, respectively [20,21]. The main aim of this manuscript is to critically summarize and discuss the published results, contributing to unraveling the structure-activity

Abbreviations: C_2, ethane + ethylene; C_{2+}, ethane + ethylene + higher hydrocarbons; DFT, Density Functional Theory; EDX, Energy Dispersive X-Ray Spectroscopy; EPR, Electron Paramagnetic Resonance; GHSV, gas hourly space velocity; IR, infrared; OCM, oxidative coupling of methane; TPD, Temperature Programmed Desorption; XAFS, X-ray absorption fine structure; XRD, X-Ray Diffraction; XPS, X-Ray Photoelectron Spectroscopy.

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