Journal of Catalysis 360 (2018) 102–117

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Investigation of the role of the $Na_2WO_4/Mn/SiO_2$ catalyst composition in the oxidative coupling of methane by chemical looping experiments

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ARTICLE INFO

Article history:
Received 23 April 2017
Revised 18 January 2018
Accepted 19 January 2018

Keywords:
Oxidative coupling of methane
Chemical looping
Catalyst
Characterization
Oxygen storage capacity
EPR spectroscopy
XPS analysis

ABSTRACT

A series of $Na_2WO_4/Mn/SiO_2$ catalysts supported on mesoporous silica were prepared and tested for the oxidative coupling of methane in chemical looping experiments. The parameter variations were done for specific surface area, Mn-loading and support material. Chemical looping experiments reveal that highest catalytic activity is observed at 2 wt% Mn and 5 wt% Na_2WO_4 on mesoporous silica. Repetitive methane pulse experiments allowed us to determine the oxygen uptake of the $Na_2WO_4/Mn/SiO_2$ catalyst in chemical looping experiments. We found a correlation between oxygen storage capacity and manganese loading, which is in line with the reversible change of Mn(III) concentration observed in oxidation and reduction cycles of the material. Furthermore, we observed that ethylene formation is independent of the catalyst material in chemical looping conditions. No indication for the presence of W(V) was found.

1. Introduction

The steam cracking process, using naphtha as feedstock, is most widely utilized for ethylene production. In the last decade, the shale gas production came up as an alternative process to provide natural gas. Such gas contains different amounts of methane, ethane, and propane [1–3]. However, methane is still the major compound of shale gas, bio gas, and raw gas. Currently, methane is typically used for heat generation or energy production, but processes converting methane into more valuable chemicals are highly desirable [4–6]. The oxidative coupling of methane (OCM) is one such process to convert methane into ethane and ethylene and would hence allow utilizing the mentioned resources as additional feedstock for the formation of C_2 compounds. A suitable catalyst material for this process is $Na_2WO_4/Mn/SiO_2$, which was introduced by Fang et al. [7]. This material shows stability and high-performance for several 100 h [8,9]. However, it was reported that C_2 yields of the OCM reaction in various reactor concepts never exceeded 0.25 [10–12]. To overcome this limitation, it is necessary to understand the mechanism of the OCM process and the functionality of this complex catalyst material.

For a better comprehension of this catalyst material, many groups carried out compound variations. Palermo et al. found that the phase transition of the support material from amorphous silica to α-cristobalite is a key step for a high-performance catalyst, which can be induced by sodium ions [13]. The role of sodium in the catalytic activity was studied in more detail by exchange experiments with lithium, potassium, and cesium [14]. It was found that the Na_2WO_4/Mn film on the support material offers a high structural flexibility during the OCM process. This was due to the presence of the alkali metal ions, which offers the ability to adapt the structure to the key transition state of methyl radical formation by hydrogen abstraction [15–17]. A variation of tungsten oxide on "nano-catalysts" loading was studied by Mahmoodi et al. [18]. Exchanging tungsten by molybdenum, niobium, chromium or vanadium results in a different degree of crystallinity on the catalyst surface with decreasing ion radius of the transition metal ions. The formation of microcrystals on the catalyst surface

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https://doi.org/10.1016/j.jcat.2018.01.022

was found advantageous for C_2 selectivity rendering tungstate loaded catalyst the most selective one for C_2 production in this series. The crystallinity was directly related to the catalytic activity, which is in contrast to the findings of other groups. They reported that M—O—M and terminal M═O oxygen species from the lattice contribute to methane activation. However, the crystallization of the "nano-catalyst" is strongly affected by the presence of sodium ions [16].

The group of Mortazavi performed catalytic tests by exchanging the manganese ion by other transition metal ions in the catalysts [19]. They found that this compound is responsible for the redox reactivity potential of the catalyst material. Tuning of this potential has a tremendous influence on both C_2 selectivity and methane conversion. By varying the support material, Yildiz et al. showed the silica supported catalyst to have the best long-time stability as well as the highest performance in catalytic tests. Among different silica support materials, they observed the highest performance for a mesoporous structured silica catalyst [15]. The inexpensive analogue of SBA-15, COK-12, also showed good catalytic performance, which is important for industrial application [20–22]. Sadjadi et al. found that well dispersed active compounds will agglomerate under OCM conditions [23]. They also showed the presence of sodium ions to be responsible for the formation of an amorphous phase of the active compounds on the catalyst surface, which is in good agreement with the results of the Lambert group [13].

From the mechanistic point of view, the Wang group carried out detailed XPS and Raman spectroscopy studies focusing on tungsten oxide species to understand the role of the activation process [24]. EPR studies by Jiang et al. indicate that the manganese ion changes its oxidation state from + III to + II in non-steady-state experiments [25]. The latter are generated by methane reduction but can be reoxidized easily. Jiang et al. further concluded that manganese is reduced in an electron transfer from C—H bond cleavage induced by tungsten oxide. The reduction of manganese oxide was also reported to result in the formation of $MnWO_4$ [23,26]. The $Na_2WO_4/Mn/SiO_2$ catalyst exhibits two different oxygen species responsible for methane activation during steady-state conditions as deduced by Beck et al. from temporal analysis of products (TAP) experiments [27]. While the strongly bound oxygen species are responsible for selective methane activation, the weakly bound oxygen lead to deep oxidation products.

In our previous work, we investigated the catalyst material by temperature programmed and dynamic experiments [28]. Such experiments revealed that lattice oxygen seems to be involved in the OCM process on the $Na_2WO_4/Mn/SiO_2$ material, too. In addition, our results indicated that several oxygen species are stored on the catalyst material even in dynamic experiments. In another study, we could show that the involvement of lattice oxygen can be interpreted as oxygen storage function [29]. That functionality was successfully adapted for conducting OCM in a chemical looping process [29,30]. Such reactor concept allows separating parallel reaction steps in steady state operation into consecutive steps of catalyst reduction by methane conversion and subsequent catalyst reoxidation. This has the advantage that gas phase reactions induced by gas phase oxygen are excluded. In chemical looping processes, one of the most important parameters is the oxygen storage capacity [31]. The redox system of Mn(II)/Mn(III) is already known as an attractive oxygen storage system in chemical looping combustion [32].

In this work, we want to study the oxygen storage functionality and its mechanistic aspects for COK-12 supported $Na_2WO_4/Mn/SiO_2$ catalysts in chemical looping experiments. Furthermore, a non-ordered mesoporous silica supported catalyst will be compared. It has to be noted, that the $Na_2WO_4/Mn/SiO_2$ material acts as both an oxygen storage material and a catalyst, simultaneously. An alternative mode in chemical looping experiments is the repetitive pulsing of a reactant. Such experiments will give new insights with respect to the involvement of lattice oxygen in the OCM surface reaction mechanism. For a better understanding of the pathways of stored oxygen, repetitive pulse experiments were modeled and simulated in Berkley Madonna. Furthermore, gas phase simulations were carried out in Reaction Design Chemkin.

2. Experimental

2.1. Catalyst preparation

The catalyst support, COK-12, was synthesized in an up-scaled batch synthesis as previously described by Colmenares et al. [22]. The preparation of $Na_2WO_4/Mn/SiO_2$ catalysts supported on COK-12 follows the procedure described in [20] for powder catalysts. Solutions of appropriate amount of manganese (II) nitrate tetrahydrate (Merck) and sodium tungstate dihydrate (Sigma-Aldrich) were separately coated on the COK-12 support material via incipient wetness impregnation. After each impregnation step, the catalyst was dried overnight at 100 °C. Afterwards, the catalysts were annealed in air for 8 h at 800 °C with a 10 °C/min heating ramp in a muffle furnace. The Mn amount was varied from 0 to 4 wt%. In addition, catalysts with a variation in surface area were prepared by varying the annealing temperature between 750 °C and 850 °C. The COK-12 catalysts were taken as powders and were not pelletized. The reference catalyst supported on silica gel was prepared similar to the method described by Simon et al. [33]. The final 4 wt % Na_2WO_4 and 2 wt% Mn reference catalyst had a specific surface area of 1.86 m^2/g. The particle size of the SiO_2 support material (Davisil 636, Sigma Aldrich) was 150–350 μm.

2.2. Catalyst characterization

All samples were heated up to 150 °C for 24 h before nitrogen adsorption experiments were performed. The experiment was carried out in an Autosorb (Quantachrome, FL, USA) at −196.15 °C. The range of P/P_0 was varied from 0.05 to 0.25.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out in a Horiba Scientific ICP Ultima2 (Horiba, Japan), to determine the content of Na, Mn, and W.

The X-ray powder diffraction was done with a Philips X-ray diffractometer utilizing a Bragg–Brentano geometry with a $CuK_{\alpha1}$ radiation wavelength of 0.1541 nm (Philips, Germany) and a Bruker AXS D8 ADVANCE with a Bragg–Brentano geometry and a Lynx Eye 1D detector with a $CuK_{\alpha1}$ radiation wavelength of 0.1541 nm (Bruker, Germany). Measurements were carried out in the range of 2Θ values between 10° and 90° with a step time of 1 s and a step size of 0.02° at 40 kV and 30 mA and a step time of 370 s and a step size of 0.014° at 40 kV and 40 mA respectively. The patterns were analyzed using the Diffrac-Plus/EVA software from Bruker AXS.

XPS analysis was carried out by a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al K_α source (Thermo Scientific, Germany). The spectra were processed with Avantage software from Thermo Scientific.

EPR experiments were performed with a BRUKER ElexSys E680 spectrometer, operating in conventional continuous wave (cw) or in pulsed mode with a microwave (mw) frequency of approximately 9.5 GHz (X-band). Using cw mode detection with field modulation results in field-derivative spectra emphasizing structures with significant changes in EPR absorption, originating for instance from van Hove singularities in powder samples lacking orientational order. Such spectra were recorded for defining the total spectral range. For spectral analysis and curve fitting, we used pulse mode detection with a 2-pulse Hahn echo sequence