

Silica material variation for the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ M. Yildiz^{a,**}, Y. Aksu^{b,1}, U. Simon^c, T. Otremba^{a,2}, K. Kailasam^{d,3}, C. Göbel^d, F. Girgsdies^e, O. Görke^c, F. Rosowski^f, A. Thomas^d, R. Schomäcker^a, S. Arndt^{a,*}^a Technische Universität Berlin, Institut für Chemie, Technische Chemie, Sekr. TC8, Straße des 17. Juni 124, 10623 Berlin, Germany^b Technische Universität Berlin, Institut für Chemie, Metallorganische Chemie & Anorganische Materialien, Straße des 17. Juni 115, 10623 Berlin, Germany^c Technische Universität Berlin, Institut für Werkstoffwissenschaften und -technologien, Fachgebiet Keramische Werkstoffe, Sekr. BA3, Hardenbergstraße 40, 10623 Berlin, Germany^d Technische Universität Berlin, Institut für Chemie, Funktionsmaterialien, Sekr. BA2, Hardenbergstraße 40, 10623 Berlin, Germany^e Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abteilung Anorganische Chemie, Faradayweg 4-6, 14195 Berlin, Germany^f BasCat UniCat BASF JointLab, Technische Universität Berlin, Sekretariat EW K 01, Hardenbergstraße 36, 10623 Berlin, Germany

ARTICLE INFO

Article history:

Received 11 January 2016

Received in revised form 30 May 2016

Accepted 30 June 2016

Available online 1 July 2016

Keywords:

Oxidative methane coupling

OCM

 $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$

Silica support material variation

Mesoporous silica

SBA-15

ABSTRACT

The oxidative coupling of methane (OCM) is one of the best methods for the direct conversion of methane. Among the known OCM catalysts, $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ is a promising candidate for an industrial application, showing a high methane conversion and C_2 selectivity, with a good stability during long-term catalytic activity tests. In the present study, some results have been already published and discussed briefly in our previous short communication. However, we herein investigated comprehensively the influence of various silica support materials on the performance of the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ system in the OCM by means of *ex situ* and *in situ* XRD, BET, SEM and TEM characterization methods and showed new results to reveal possible support effects on the catalyst. The catalytic performance of most $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts supported by different silica support materials did not differ substantially. However, the performance of the SBA-15 supported catalyst was outstanding and the methane conversion was nearly twofold higher in comparison to the other silica supported catalysts at similar C_2 selectivity as shown before in the communication. The reason of this substantial increase in performance could be the ordered mesoporous structure of the SBA-15 support material, homogeneous dispersion of active components and high number of active sites responsible for the OCM.

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Abbreviations: BET, Brunauer Emmett Teller; C_2 , ethane + ethylene; EDX, energy-dispersive X-ray spectroscopy; OCM, oxidative coupling of methane; S, selectivity; SEM, scanning electron microscopy; TEM, transmission electron microscopy; X, conversion; XRD, X-ray diffraction; XRF, X-ray fluorescence.

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1. Introduction

According to the statistical review on the worldwide energy resources, the proven reserves contain 187.1 trillion cubic meters natural gas by the end of 2014 [1]. Natural gas is used for home and industrial heating and the generation of electrical power, but it is still an underutilized resource for chemicals and liquid fuels. Since the reserves are far away from industrial areas and the high costs of building pipelines for transportation, on-site conversion of methane, the main constituent, to more useful chemicals (e.g. ethylene, methanol) could be of great importance for using it more effectively in industry [2–8].

Generally, there are two different ways for CH_4 utilization: the indirect and the direct way. All indirect methods for CH_4 conversion require a highly endothermic and expensive synthesis gas step. The disadvantages of indirect methods could be avoided by direct conversion of CH_4 into value added compounds. One of the most important direct reactions is the oxidative coupling of

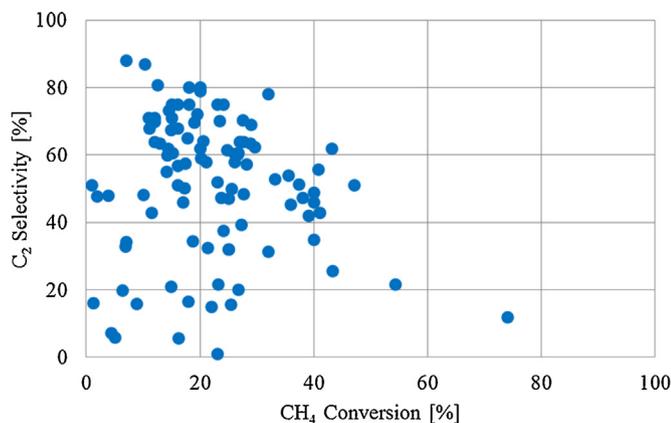


Fig. 1. A general comparison of some OCM catalysts published in literature (approximately 100 results were selected randomly from [10]).

methane (OCM) to ethane and ethylene. The targeted reaction and the desired product are shown in Eq. (1):



However, up to date, this reaction has not reached the stage of commercial application, even though a large number of catalysts [9–11] have been tested since the first attempts by Keller et al. and Hinsel et al. [12,13]. Methane is the most stable hydrocarbon, having the strongest C–H bond; therefore, the activation of this bond is most difficult [14]. Thus, the oxidative coupling of methane occurs at high temperatures, usually above 700 °C. At these high temperatures, many catalysts suffer from severe stability and selectivity problems, e.g. Li/MgO as shown by Arndt et al. [15,16].

The most vital challenge for the OCM is the stability of the catalyst. Among the known OCM catalysts, $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ is a promising one [17,18] in the literature for the commercialization of an industrial process [19–28]. Moreover, its catalytic performance (CH_4 conversions of 20–30% at C_2 selectivities of approximately 70–80%) is superior to the most OCM catalysts.

Besides that it is a very difficult issue to compare own results with reported results in literature due to the very different conditions and the very temperature-sensitive features of the OCM reaction. Therefore, as seen in Fig. 1 some selected results from literature are broadly scattered, prohibiting any conclusion.

Although the incipient wetness impregnation has been the most applied method for the catalyst preparation, different preparation procedures for the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ like solution combustion, flame spray pyrolysis and sol-gel routes have been used in recent years [29–32]. Besides that, Hiyoshi and Ikeda showed an improving effect of alkali chloride addition into $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$. However, the most important challenge was the deactivation due to the evaporation of alkali metal chlorides from the catalyst [33].

Liu et al. carried out experiments with SiC as a support material for this trimetallic system and the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiC}$ showed similar performance compared to the silica supported catalyst [34]. Yu et al. applied La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Dy_2O_3 , Yb_2O_3 and SiO_2 compounds as support material for only Na_2WO_4 as active component. However, some of the used support materials like Sm_2O_3 and Nb_2O_3 are known as active catalysts themselves for the OCM [35]. Wang et al. and Pak et al. investigated $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ and $\text{Mn-Na}_2\text{WO}_4/\text{MgO}$ systems to figure out the active sites and the elementary reactions. Na-O-Mn species as active site, sodium as suppressing component for the CH_4 total oxidation, tungstate ions as stability providing component and surface oxygens as hydrogen abstracting species from CH_4 were concluded [36,37]. Recently, Elkins and Hagelin-Weaver have compared $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$, $\text{Mn-Na}_2\text{WO}_4/\text{MgO}$,

$\text{Mn}_x\text{O}_y/\text{SiO}_2$ and $\text{Na}_2\text{WO}_4/\text{SiO}_2$ and indicated that except $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$, other compared catalyst showed lower methane conversion in the OCM. Furthermore, Na_2WO_4 and Mn_2O_3 phases were more stable in the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ in comparison to that of $\text{Mn-Na}_2\text{WO}_4/\text{MgO}$ and the reason of that was suggested the α -cristobalite phase of the SiO_2 support material [38]. Serres et al. increased the loading amount of active compounds with respect to the support material to improve the performance of the catalyst sustaining its high C_2 selectivity. After they had concluded to hinder a substantial decreasing of the surface area of the catalyst at high loadings, the SiO_2 support material of the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst was replaced with porous SiC and $\alpha\text{-Al}_2\text{O}_3$ expecting a catalyst with high surface area at high loading of the active components. Increasing the amount of the active compounds improved evidently the performance of the catalyst but it is limited to a proper loading level. While a replacement of the SiO_2 support with porous SiC providing a high surface area upgraded the activity, an application of $\alpha\text{-Al}_2\text{O}_3$ instead of SiO_2 resulted in poor performance due to a differently composed surface in the absence of silica. In spite of the improvements of catalyst activity in that study, even the performance of the optimized Mn-Na-W-/SiC do not reach to a La based catalyst, La/Sr/CaO [39].

In a previous study [40], we investigated a wide-range variety of support materials for the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst, in order to test alternative support materials to SiO_2 , which could suppress the pathway of the total oxidation of methane and found that SiO_2 , TiO_2 -rutile and SiC were the most suitable support materials. Furthermore, a $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4$ catalyst without support material showed remarkable activity, raising questions on the role of the support material. Recently, we showed the catalytic activity results of the differently performing $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts (Cat-H, Cat-M and Cat-L) prepared from three various silica materials, superiority of the SBA-15 supported $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4$ and discussed concisely some results on BET surface area, XRD phase analysis and SEM-EDX images [41]. Herein, we studied more intensively the effect of different SiO_2 materials as support for the $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4/\text{SiO}_2$ catalyst and the structural impact on the catalytic performance. Hence, we included also the previously published results of our short communication in this paper for the sake of completeness of the scientific discussion.

2. Experimental part

2.1. Support material preparation

Each silica type material has been given a code, since there were many different types of silica support materials. All of the used silica support materials, their origins, specific surface areas and the codes are shown in Table 1. The preparation method of ordered mesoporous silica material produced in the laboratory of the Functional Materials Department of the Technische Universität Berlin is explained in the supporting information.

2.2. Catalyst preparation

Eleven different silica supported $\text{Mn}_x\text{O}_y\text{-Na}_2\text{WO}_4$ catalysts were prepared by a standard two-step wet impregnation procedure and a mixed milling method as explained in the supporting information. The amounts of the active components were 5 wt% Na_2WO_4 and 2 wt% Mn_xO_y . Manganese was present in the form of manganese oxides or Mn-containing mixed oxides, however, the loading was calculated for pure Mn. For a structural analysis after the reaction, it is necessary to retrieve the catalysts. With the applied quartz sand this is not possible, because its particle size distribution is too large and overlaps with the particle size of

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