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Support material variation for the Mn_xO_y-Na_2WO_4/SiO_2 catalyst

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A B S T R A C T

Mn_xO_y-Na_2WO_4/SiO_2 is an active catalyst for the oxidative coupling of methane, with a remarkable stability and a suitable performance for an industrial application. Mn_xO_y-Na_2WO_4 was supported on different support materials and the catalytic activity was investigated with a parallel reactor system, allowing a direct comparison of all results. Considering the C_2 yield and the potential practical application, SiO_2 is indeed the best support material for this catalyst. However, the comparison in an X–S plot with a reference Mn_xO_y-Na_2WO_4/SiO_2 catalyst indicates that SiC, Fe_2O_3-based oxides and TiO_2-rutile are also promising support materials.

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1. Introduction

The oxidative coupling of methane (OCM, see Eq. (1)) is an attractive direct route for the conversion of methane into value added compounds.

$$aCH_4 + bO_2 \rightarrow cC_2H_6 + dC_2H_4 + eH_2O \tag{1}$$
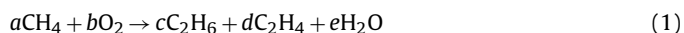
In the search for a suitable catalyst, hundreds of materials have been tested in the past [1–5]. The Mn_xO_y-Na_2WO_4/SiO_2 catalyst has attracted a lot of attention as an OCM catalyst for a practical application [6–9,14]. The literature about this material has recently been reviewed by our research group [3]. The stability of this material is remarkable and confirmed by different research groups [10–15]. Moreover, the catalytic performance (CH_4 conversions of 20–30% at C_2 selectivities of approximately 70%) makes this catalyst system a potential candidate for practical applications.

The formation of a surface cluster species of tetrahedral WO_4 species with one W=O bond and three W—O—Si bonds were suggested and presumed to be the active site by Jiang et al. [16]. Wu et al. showed that the tetrahedral WO_4 is distorted, most probably due to the presence of Na ions [17].

It was reported that at the surface of the reduced catalyst in the presence of gas phase O_2, F-centers (an oxygen ion vacancy with two trapped electrons) exist, which are able to activate molecular O_2 above 80 °C, forming lattice oxygen. A redox mechanism with W—O—Si bonds and electron transfer between a tungsten species and F-centers was suggested [18], which was later modified to a two metal site model, including an oxygen spillover from the Mn_2O_3 to the Na_2WO_4 [19]. The two site model seemed to be in accord with XAFS (X-ray Absorption Fine Structure) and XPS (X-Ray Photoelectron Spectroscopy) studies before and after the reaction [20].

The exact composition and functionality of the active centers are still not clear. Palermo et al. [21] studied the oxides of Mn, Na and W supported on SiO_2 alone and/or in combination. They reported that amorphous SiO_2 undergoes a phase transition to highly crystalline α-cristobalite during calcination at 750 °C, far below the usual transition temperature of 1500 °C. This is caused by the presence of Na [21]. A suitable catalyst requires all three metal atoms/oxides, so it was concluded that strong synergies are present between these three metal oxides and a Na-induced crystallization of the support material occurred, converting it from an active and unselective

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Table 1
The determined factors $[f_i = k_i(CD_4)/k_i(CH_4)]$ for the reaction constants obtained from CD_4 and CH_4 with 100 mg catalyst at 750 °C. Reprinted from Yildiz, M., Arndt, S., Simon, U., Otremba, Y. A. T., Berthold, A., Görke, O., Thomas, A., Schubert, H., Schomäcker, R., 2012. Mn-Na_2WO_4/SiO_2 – an industrial catalyst for methane coupling. In: Ernst, S., Balfanz, U., Buchholz, S., Lichtscheidl, J., Marchionna, M., Nees F., Santacesaria E., (Eds.), Reducing the Carbon Footprint of Fuels and Petrochemicals, Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V., pp. 125–132., with permission from DGMK.

f_i	Feed gas composition (CH_4:O_2:N_2)		
	2:1:4	4:1:4	8:1:4
f_1	0.6	0.5	0.6
f_2	0.7	0.7	0.7
f_3	0.3	0.4	0.5
f_4	0.5	0.5	0.4
f_5	0.2	0.2	0.2

material into an inert support material. However, the exact active site could not be revealed.

Wang et al. compared Mn_xO_y-Na_2WO_4/SiO_2, Mn_xO_y-Na_2WO_4/MgO and $NaMnO_4$/MgO [22]. Due to the identical catalytic performance of all three materials, it was suggested that a common active site, consisting of Na–O–Mn species exists. This is inconsistent with the suggestion of Wu et al. [17], who proposed that the W—O bonds of a distorted WO_4 tetrahedron could be the active site.

Besides determination of the active center, the production of large amounts of this catalyst is important. Therefore, Simon and co-workers developed an up-scaled preparation of this catalyst [14], which is crucial for any practical application.

A variation of the composition has been investigated, trying to find substitutes for Mn [23–26], for Na [27–30] and for W [31–33], respectively. It was found that any other elements are also active, but the combination of the oxides of Mn–Na–W was superior to all tested catalysts.

Despite the research performed till now, the role of the SiO_2 support material remains unclear. Moreover, there are only very few attempts using other support materials than SiO_2. Liu et al. reported the successful application of SiC as support material [34], giving a similar performance compared to SiO_2. Yu et al. reported a study of different support materials. The applied support materials were rare earth oxides (La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Dy_2O_3 and Yb_2O_3) and SiO_2 for Na_2WO_4 as active component [31]. CeO_2 and Pr_6O_{11} were mainly total oxidation catalysts. Covered with Na_2WO_4 they exhibited good C_2 selectivities. However, it is unclear why typical support materials such as Al_2O_3, TiO_2, etc., were not used in these experiments. Moreover, the applied rare earth oxides are active OCM catalysts themselves, Sm_2O_3 and Nd_2O_3 in particular. A blank experiment with only support material was not reported in this study. Generally, it is questionable if supporting an active OCM catalyst on a material which is an active OCM catalyst itself, leads to results, which could significantly increase the knowledge on the supported material due to expectable complex interactions.

In the previous work, we performed kinetic isotope effect experiments with CD_4 for Mn_xO_y-Na_2WO_4/SiO_2 catalyst to contribute to the understanding of the reaction pathways and the origin of CO_x products [35]. The results of these experiments in Table 1 indicate that the most influenced reactions were the consecutive reactions which convert the C_2 products towards the total oxidation products (Fig. 1). The kinetic isotope effect is as discussed in the literature [36–45] agrees with the observed results. The consecutive reactions might be suppressed by reaction engineering (e.g. applying new reactor concepts, such as membrane reactor) [46,47]. However, oxidation of CH_4 molecules towards CO_x products, because of unselective catalysts or unselective sites of the selective catalysts,
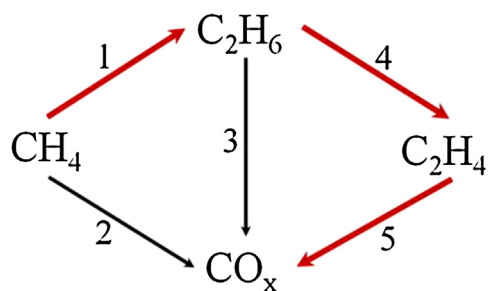
Fig. 1. Simplified reaction network [2]. Adapted from Ref. [2].

can be prevented only by a development of a new highly selective material or an improvement of a catalyst.

One issue which has not been thoroughly studied for the Mn_xO_y-$NaWO_4$ catalyst is the effect of support materials other than SiO_2. Therefore, in the present manuscript we investigated a detailed variation of different metal oxides as support material for the Mn_xO_y-Na_2WO_4 in order to study their influence on the catalytic performance. Moreover, we studied in detail how the different components of the active materials (Mn_xO_y and Na_2WO_4) act on these support materials alone. Furthermore, a test with pure Mn_xO_y-Na_2WO_4 was performed to study the catalytic activity without any support material.

All catalytic materials have been studied in a parallel reactor under identical conditions, allowing a direct comparison of the obtained results; this is important because results reported in different publications in literature are often not comparable, due to very different reaction conditions [48].

2. Experimental part

2.1. Catalyst preparation

The prepared catalysts, the loading of the active components and the abbreviations used in the figures and tables are presented in Table 2. Manganese is present in the form of manganese oxides or Mn-containing mixed oxides, however, the loading is calculated for pure Mn.

The applied support materials (some of them e.g. La_2O_3, CaO, MgO, are also known active components themselves in the OCM [49]), their origin and specific surface area are shown in Table 3.

2.1.1. WO_3/support

Supported tungsten oxide catalysts were prepared via a wet impregnation method of the different support materials (Table 3) with the appropriate aqueous solution of the $(NH_4)_{10}H_2(W_2O_7)_6 \cdot xH_2O$ (Aldrich, 99.99%, the number of hydrate was assumed four for calculations) at room temperature. Samples were dried in air overnight at 65 °C. The calcination process was performed in air, heating the samples in 4 h from room temperature to 750 °C (with a heating rate of approximately 3 K/min) and holding the temperature for 1 h at 750 °C, consecutively. The prepared catalysts were then ground into fine powder and sieved. The particle size of the catalysts used for the reaction was ≤200 μm.

Table 2
Prepared catalysts, applied loadings and used abbreviations.

Catalyst	Abbreviation
Blank	Support
5 wt% WO_3/Support	W/Support
5 wt% Na_2WO_4/Support	Na/W/Support
2 wt% Mn_xO_y/Support	Mn/Support
2 wt% Mn_xO_y–5 wt% Na_2WO_4/Support	Mn/Na/W/Support