



Investigation of the surface reaction network of the oxidative coupling of methane over $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalyst by temperature programmed and dynamic experiments



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ABSTRACT

In this work a series of temperature programmed experiments were carried out on a $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalyst. In TPR experiments we tested the reducibility of this catalyst and O_2 desorption behavior was investigated by TPD. TPSR experiments in a flow of methane, ethane or ethene gave information about the reaction network of OCM on the catalyst surface, without the presence of gas phase reactions, induced by gas phase oxygen. We found indications of involvement of two different active oxygen species on the catalyst surface. Furthermore an activation energy of 275 kJ/mole for selective methane activation was determined. Dynamic experiments were performed to determine the amount of available oxygen species for the OCM reaction. Variation of methane partial pressure and flow rate showed a linear correlation between methane partial pressure and surface oxygen conversion in dynamic experiments.

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1. Introduction

A well-established process for ethylene production is the steam cracking process, which cracks naphtha to olefins and other hydrocarbons. Shortage of crude oil reserves has attracted attention toward alternative processes, which use more available feedstocks. The high availability of methane in natural gas makes it a suitable feedstock alternative for short-chain olefins [1,2]. The oxidative coupling of methane (OCM) is a promising reaction for ethylene production. One of the most stable catalysts described for OCM in the literature is $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$, which has good performance and stability as shown in several publications [3–5].

One of the major challenges in experimental studies of OCM is the parallel reaction network of gas phase and surface reactions, which have a strong influence on each other. For gas phase reactions, Dooley and coworkers published an extended micro kinetic model [6]. This micro kinetic model considers a network of 1582 reactions and 269 species, which are mainly radical reactions. Unfortunately this complex reaction network allows only simulation of ideal reactors, because of the large set of reactions. However, the gas phase network is well described by the Dooley model, which was shown by Schwarz and Coworkers [7]. Formal kinetic models of OCM were published by several groups for

different catalysts [8–16]. All of these proposed mechanisms show similar pathways for reactants and products. All groups who carried out these experiments with extensive experimental efforts, were using similar reactors operated in the classical steady state mode.

The surface reaction network, which is not fully explored, is strongly influenced by gas phase reactions, and its kinetic parameters offer several constellations to fit experimental results. Such complexity is caused by the mentioned involvement of various radical species which are formed via gas phase reactions or during reactions on the catalyst surface [17–20]. In addition for several OCM catalysts different oxygen intermediates contribute to selective and unselective activation of methane on the catalyst surface. The presence of these different species is also influenced by gas phase oxygen [21–23].

A micro kinetic surface reaction model for the surface reactions was published by Lee and Coworkers for the $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalyst [24]. Another one is the model published by Sun and Thybaut for a MgO catalyst [25]. Both models were developed for different catalysts but have similar elementary surface reaction steps which are shown in Table 1. Their models assume dissociative adsorption of oxygen on a free site of the catalyst (*), which is in equilibrium with gas phase oxygen. Methane activation occurs by a surface reaction with dissociated oxygen (O^*) and releases methyl radicals to the gas phase. The coupling reaction of the radicals happens in gas phase close to the catalyst surface where excess heat is released, which is not shown in Table 1. The same activation

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Table 1
Comparison of micro-kinetic surface reaction models from Lee et al. and Sun et al. (x, y, z = stoichiometric factors) [24–26].

| Lee et al. [24] | Sun et al. [25] | Beck et al. [26] |
|---|---|--|
| $O_2 + 2^* \rightleftharpoons 2O^*$ | $O_2 + 2^* \rightleftharpoons 2O^*$ | $O_2 + * \rightleftharpoons O_{2,ads}$ |
| $CH_4 + O^* \rightleftharpoons CH_3 + OH^*$ | $CH_4 + O^* \rightleftharpoons CH_3 + OH^*$ | $O_{2,ads} \rightleftharpoons yO_x^*$ |
| $C_2H_4 + O^* \rightleftharpoons C_2H_3 + OH^*$ | $C_2H_4 + O^* \rightleftharpoons C_2H_3 + OH^*$ | $CH_4 + O^* \rightleftharpoons CH_3 + OH^*$ |
| $C_2H_6 + O^* \rightleftharpoons C_2H_5 + OH^*$ | $C_2H_6 + O^* \rightleftharpoons C_2H_5 + OH^*$ | $C_2H_4 + O^* \rightleftharpoons C_2H_3 + OH^*$ |
| | $2OH^* \rightleftharpoons H_2O^* + O^*$ | $C_2H_6 + O^* \rightleftharpoons C_2H_5 + OH^*$ |
| $CH_3 + 3O^* \rightleftharpoons HCO^* + 2OH^*$ | $CH_3 + O^* \rightleftharpoons CH_3O^*$ | $2OH^* \rightleftharpoons H_2O^* + O^*$ |
| | $CH_3O^* + O^* \rightleftharpoons CH_2O^* + OH^*$ | |
| $HCO^* + O^* \rightleftharpoons CO^* + OH^*$ | $CH_2O^* + O^* \rightleftharpoons HCO^* + OH^*$ | |
| $CO^* + O^* \rightleftharpoons CO_2 + *$ | $HCO^* + O^* \rightleftharpoons CO^* + OH^*$ | |
| | $CO^* + O^* \rightleftharpoons CO_2 + *$ | |
| | $CO^* \rightleftharpoons CO^*$ | |
| | $CO_2 + * \rightleftharpoons CO_2^*$ | |
| $2OH^* \rightleftharpoons H_2O + O^* + *$ | $4HO_2 \rightarrow 3O_2 + 2H_2$ | $xO_{2,ads} + CH_4 \rightleftharpoons CO_y + zH_2O^*$ |
| | | $xO_{2,ads} + C_2H_6 \rightleftharpoons 2CO_y + zH_2O^*$ |
| | | $xO_{2,ads} + C_2H_4 \rightleftharpoons 2CO_y + zH_2O^*$ |

may also happen to the formed ethane and even ethene, which leads to the formation of C_2H_5 or C_2H_3 radicals. An interesting fact is that no ethene combustion on the catalyst surface is considered in both literature models. A typical formation route for deep oxidation products is the reaction of methyl radicals and surface bound oxygen which forms a HCO^* radical which is bound on the catalyst surface, which is further oxidized to CO^* and surface bound OH groups (OH^*) in a parallel route to the coupling reaction. The origin of CO_2 on the catalyst surface (CO_2^*) is the oxidation of CO^* by O^* . A new aspect of the catalyst surface reaction network was published by Beck et al. for the $Na_2WO_4/Mn/SiO_2$ as well as for MgO . In temporal analysis of products (TAP) experiments, they could show the presence of two different oxygen species, which exist in parallel on the catalyst surface. Furthermore they could show that both species have different reaction pathways [26]. One of them is weakly bound ($O_{2,ads}$) and opens the route to deep oxidation products. The other, stronger bound oxygen species (O_x^*) is responsible for the selective methane activation. Following these results a plausible surface reaction network is also presented in Table 1.

In addition, there is also a discussion about the formal kinetic mechanistic aspects of oxygen and methane activation described by an Eley-Rideal, Mars-van-Krevelen or dual site Langmuir-Hinshelwood mechanism [12,27,28]. On the one hand, in the Eley-Rideal mechanism gas phase oxygen is required for selective activate methane in the OCM process. On the other hand, in a Mars-van-Krevelen type mechanism lattice oxygen is involved during C–H bond cleavage of methane to form a methyl radical. A possible interaction of lattice oxygen with methane offers the opportunity to avoid the presence of gas phase oxygen in temperature programmed experiments and dynamic experiments. During these unsteady state experiments the catalyst oxidation and the methane coupling reaction can be separated into two different steps. One of the first overviews about these techniques and experimental results from several groups was published by Falconer and Schwarz [29]. Another review about these techniques was presented by Niemantsverdriet [30].

One important factor in temperature programmed reduction experiments is the bond dissociation energy of the reactants. For methane (439 kJ/mole) and hydrogen (436 kJ/mole) these energies are similar, and for ethane (423 kJ/mole) it is lower than those of hydrogen and ethene (464 kJ/mole), which has the highest bond dissociation energy in this group of compounds [31]. Therefore it is possible to reduce the catalyst in the same manner as in a H_2 -temperature programmed reduction (TPR) experiments using OCM reactants to study their pathways in the reaction network in absence of gas phase oxygen. These types of experiments were

introduced as temperature programmed surface reactions (TPSR) by McCarty and Wise some decades ago [32]. Heating rate variations in TPSR experiments allow the determination of the activation energy of desorption or surface reaction steps. This is known as the Redhead method [33]. In this work we want to study the OCM surface mediated reaction network in absence of gas phase oxygen, to understand the role of surface bound oxygen on the $Na_2WO_4/Mn/SiO_2$ catalyst material. Temperature programmed reaction experiments utilizing methane, ethane and ethene as reactant give qualitative insights to their interaction with the surface bound oxygen species. In addition we performed a series of kinetic TPSR studies for the selective activation of methane. The focus of further dynamic experiments at constant temperature is to quantify the converted amount of strongly surface bound oxygen, the stability of the oxygen intermediates on the catalyst surface and the nature of active sites for that material.

2. Experimental

2.1. Catalyst preparation

The details of the preparation and the characterization of the catalyst are described elsewhere [34]. The final catalyst contains 5 wt.% Na_2WO_4 , 2 wt.% Mn(II) ions and has a specific surface area of 1.86 m²/g. The catalyst material was analyzed by nitrogen adsorption and X-ray diffraction analysis after oxidation pretreatment and after dynamic experiments. The results are presented and discussed in the supporting information.

2.2. Experimental setup and mass spectrometer

All experiments were carried out in a fixed bed reactor made of quartz. The catalyst was placed on a quartz frit (200 μ m pore size) in the isothermal zone. The isothermal zone is above the frit and has a length of 5 cm. A scheme of the reactor, a construction plan of the setup and analysis of temperature profile aspects are shown in the supporting information. The inner diameter is 9 mm. The type K thermocouple (NiCrNi) is covered by a quartz-made capillary ($d_{in} = 4$ mm), which seals the reactor on top. The reactants come through the upper inlet. The bottom part of the reactor shrinks in diameter and is connected to a mass spectrometer or thermal conductivity detector. The feed composition was controlled by mass flow controllers (MFC) and switching valves were installed, enabling the ability to interrupt reactant flow immediately. Detection was carried out with a quadrupole mass spectrom-

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