Oxidative coupling of methane—A complex surface/gas phase mechanism with strong impact on the reaction engineering

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ABSTRACT

The oxidative coupling of methane over $Mn/Na_2WO_4/SiO_2$ has been investigated at reaction conditions suitable for industrial applications up to 10 bar in a fixed bed reactor as well as by temporal analysis of products (TAP) by admitting pulses of methane, ethane and ethene oxygen mixtures. The influence of pressure on selectivity is investigated and a concept for optimizing it is derived. A maximum yield is estimated from the ratios of the involved main reactions of the reaction network assuming that the undesired parallel reactions can be suppressed.

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1. Introduction

Oxidative coupling of methane (OCM) to ethylene offers great industrial potential, because it would broaden the feedstock basis for chemical industry. Today crude oil derived olefins and aromatic hydrocarbons via steam cracking of naphtha are still the crucial raw materials for the majority of value added chains in chemical industry. The importance of alternative carbon sources for chemical processes becomes greater as oil price increases [1].

For the development of an OCM process $Mn/Na_2WO_4/SiO_2$ has been highlighted as catalyst from the rich literature on OCM [2,3], but little is known about its structure and the reaction mechanism at this catalyst. Its reported stability and high yield were the important motivations to select the catalyst for detailed studies [4–6]. However, the obtained yield still needs to be improved for industrial application.

In most reports the focus is mainly directed to the catalyst material, and reactor setups and conditions are designed and selected in a way that no reaction of methane is observed in an empty reactor. One has to mention that for industrial application high pressures are necessary to make the process economically viable, but detailed studies of empty reactors at higher pressures are missing in literature. Furthermore, the consecutive reactions of the targeted C_2 products has the strongest negative impact on the yield [7–9]. Reactivity data of ethane or ethylene at increased pressures are almost not existent in the literature. At typical OCM conditions of 800 °C virtually no material typically used for these reactors or packing is absolutely chemically inert. For the development of an industrial scale reactor one should expect that these factors contribute even more to the reaction, due to use of materials like stainless steel. The purpose of this paper is to point out important factors which have to be considered for the reaction engineering of OCM including the interaction of gas phase and surface reactions.

The design of an industrial scale reactor requires knowledge about the reaction kinetics. If a reaction network shares strong contributions of gas phase and surface reactions, it is very difficult to derive this knowledge from experimental series at typical reaction conditions with the use of a fixed bed reactor only. This is due to inseparable kinetic data of gas phase and surface contribution. OCM is known to function in a very complex reaction network containing a variety of surface and gas phase reactions, which is depicted in a simplified scheme in Fig. 1. Obviously, the yield of ethane and ethylene is strongly dependent on the parallel and consecutive reactions to carbon oxides. Obtaining more information about the surface catalyzed activation of methane, ethane and ethene requires suppression of the gas phase activation of these components, which can be attained at the very low pressure such as the condition of temporal analysis of products (TAP) reactors.
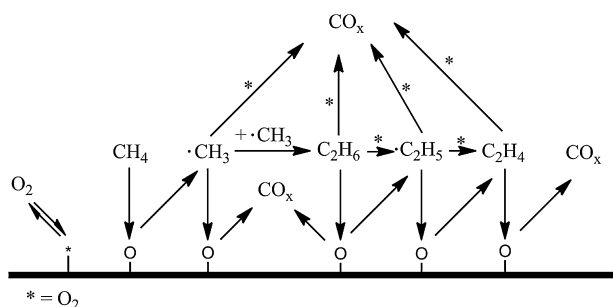

Fig. 1. Simplified reaction network of the oxidative coupling of methane at oxides.

2. Experimental

2.1. Catalyst synthesis

$Mn/Na_2WO_4/SiO_2$ catalyst material was prepared by fluidized bed processing of the constituent substances as described elsewhere [4]. The final catalyst contains 2 wt% Mn(II) and 5 wt% Na_2WO_4. A detailed characterization was also performed by Simon et al. [4].

2.2. Fixed bed reactor

OCM was investigated in a stainless steel reactor (65 cm length and 4 mm i.d.) equipped with an inlay made of corundum to minimize catalytic reactions at the reactor walls. This reactor can be operated up to 10 bars. The reaction temperature was between 700 and 800 °C. The product gases were analyzed with a gas chromatograph GC-2014 by Shimadzu, which was equipped with a methanizer and thermal conductivity and flame ionization detectors.

The reactor was filled with a fixed bed of quartz granules of 400 to 800 μm diameter up to height of 38 cm to end in the isothermal zone of the reactor. On the top of the quartz bed, a small piece of quartz wool was placed to keep the 100 mg $Mn/Na_2WO_4/SiO_2$ in position. The feeding mixture contained 95 vol% methane and 5 vol% oxygen with an overall gas flow rate between 50 to 500 N ml/min, in such a way that the residence time is kept constant with varying pressure. The shift of the explosion region to lower oxygen fractions with increasing pressure prohibits the usage of high oxygen fractions.

2.3. Temporal analysis of products

TAP experiments was conducted in a TAP-2 device, which is described in detail elsewhere [10]. In a small reactor (71 mm length and 4.6 mm i.d.) made of quartz, fixed bed 50 mg of catalyst (2–3 mm thickness) was placed, sandwiched by two layers of quartz particles. Both catalyst and quartz particles were in the 200–300 μm range. Before the TAP measurements the catalyst was pretreated for 30 min at 650 °C in oxygen flow. Measurements were performed at temperatures between 500 and 800 °C with pulse sizes large enough to be affected by intermolecular collisions (ca. 10^{17} molecules per pulse) due to the absence of desired products at small pulse sizes. Using the large pulse size, the mass transport is generally characterized as molecular diffusion regime.

Two types of experiments were conducted: simultaneous pulsing and sequential pulsing of oxygen and the specific hydrocarbon; i.e. methane, ethane or ethylene. The pulsed gas consisted of a hydrocarbon to oxygen to neon (internal standard) mixture of 2/1/4. In the case of sequential pulsing the methane to oxygen ratio cannot set accurately due the usage of two pulse valves and is adjusted individually to obtain accurate TAP responses. In the case
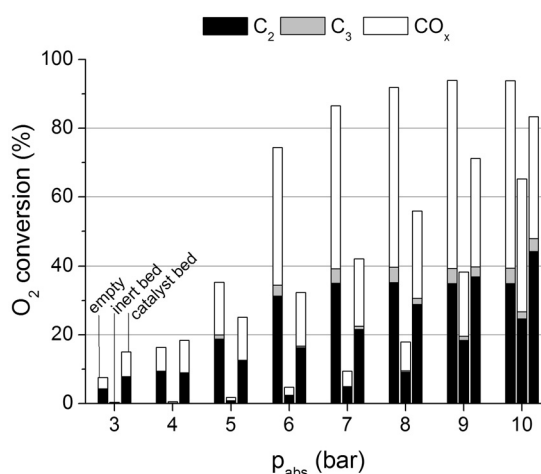

Fig. 2. Oxygen conversion with resulting product distribution at constant residence time at various pressures at 700 °C.

of MgO a methane to oxygen ratio of roughly 6 to 1 is obtained. In the case of $Mn/Na_2WO_4/SiO_2$ the methane to oxygen ratio was roughly 1 to 1. The response pulses of each component were calculated by averaging ten pulses per investigated atom mass unit (amu). Since carbon monoxide, carbon dioxide, ethene and ethane share some relevant amus, it was necessary to use the fragmentation patterns of these compounds for quantification. For the sake of comparison, we have also investigated magnesia by TAP as reference beside $Mn/Na_2WO_4/SiO_2$. It is well known that doping magnesia with lithium results in an enhanced catalytic performance, but the instability of this system prevents a closer investigation by TAP experiments.

3. Results and discussion

3.1. Catalyst characterization

A detailed characterization of the used $Mn/Na_2WO_4/SiO_2$ is given by Simon et al. [4]. The catalyst support was homogenously coated with Na/WO_4 and Mn precursors resulting in crystalline phases of Mn_2O_3 and Na_2WO_4. The support is transformed into the stable cristobalite phase with a macroporous surface morphology. The final catalyst contains 2 wt% Mn(II) and 5 wt% Na_2WO_4 and has a surface area of 1.86 m^2/g. The catalyst was chemically and mechanically stable during OCM. Magnesium oxide was purchased from Sigma-Aldrich (99.9%) and has a surface area of 78 m^2/g.

3.2. Pressure experiments

The results of the OCM reaction at up to 10 bar and 700 °C are shown in Fig. 2. Experiments were performed with an empty reactor (left), a fix bed of quartz granules (middle) and a fixed bed of quartz granules with a layer of catalyst on top of it (right). The tint inside the columns specifies the yield to carbon oxides, C_2 and C_3 components, respectively. The carbon balance for the pressure experiments did not deviate more than 0.5%. Strikingly the empty reactor results in the highest conversion of oxygen over the full range of examined pressure, reaching almost complete conversion at 8 bar. Only a small increase in C_{2+} yield is observed above 5 bar, which is caused by the increasing influence of the total oxidation of the C_{2+} components. The sigmoid characteristic of the oxygen conversion is typical for reactions with orders higher than one. In contrast, the fixed bed of quartz granules results in a reduced residence time that leads to the lowest conversion over the complete range of pressure. The behavior seems to be almost the same as