Originally published as:

Nanostructured Catalysts: Selective Oxidations

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Abstract

The catalytic conversion of methane to C_2 hydrocarbons, i.e. ethane and its consecutive product ethylene, as well as to methanol and formaldehyde is dealt with. The heterogeneous catalysts and the mechanisms of these reactions are described and discussed. For an advanced understanding of catalytic methane conversion, some emphasis is put on the similarities of enzymatic conversion of methane to methanol; this might contribute for an improved design of respective heterogeneous catalysts.

Chapter 3

Catalysis of Oxidative Methane Conversions

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3.1 Introduction

This chapter deals with the catalytic conversions of methane to C_2 hydrocarbons, i.e. ethane and its consecutive product ethylene, as well as to methanol and formaldehyde. The heterogeneous catalysts and the mechanisms of these reactions are described and discussed. For an advanced understanding of catalytic methane conversion, mechanistic aspects of enzymatic conversion of methane to methanol are also dealt with assuming that this might be a contribution for an improved design of respective heterogeneous catalysts.

3.2 Methane as a Feedstock for Oxidative Conversions

In the future, the reserves of methane being the main constituent of natural gas will exceed those of crude oil. Currently, combustion of natural gas is mainly used for heating and generating electrical power. However, such utilization of methane does not meet the future needs for efficient use of raw materials. Therefore, a strong economical interest exists in developing processes enabling methane conversion to higher-valued products. Selected research programs underline the present interest in this field: E.g., since 2007 Dow Chemicals[1] is funding a research program "Methane Challenge". This focuses on methods for methane conversion to ethylene and propylene. At Cardiff University, Graham Hutchings group is designing supported gold and bimetallic gold alloy catalytic materials for methane oxidation below 473 K. At Northwestern University K. Tobin Marks' team is aiming on achieving selective methane oxidation to olefins or other useful feedstock. According to[1] this group approaches the task by i) controlling oxidant concentrations by nano/sub-nanoscale catalyst environment engineering, ii) application of μ-oxo complexes creating centres tuned for methane partial oxidation to methanol, and iii) use of soft oxidants (presumably N_2O and SO_3) to avoid over-oxidation. From an applied point of view, strategies for the utilization of methane depend on its price, location, the demand for products, and the required effort for

separating reaction products and unconverted feed within such a process. From a chemical point of view, the methane molecule is very stable; the strength of the C-H bond amounts to 439 kJ/mol (the molecule does not have any functional groups which might facilitate chemical attacks). The situation is changed in the presence of oxidizing agents. The most attractive present technologies for utilization of methane are shown on the right-hand side of Figure 3.1.
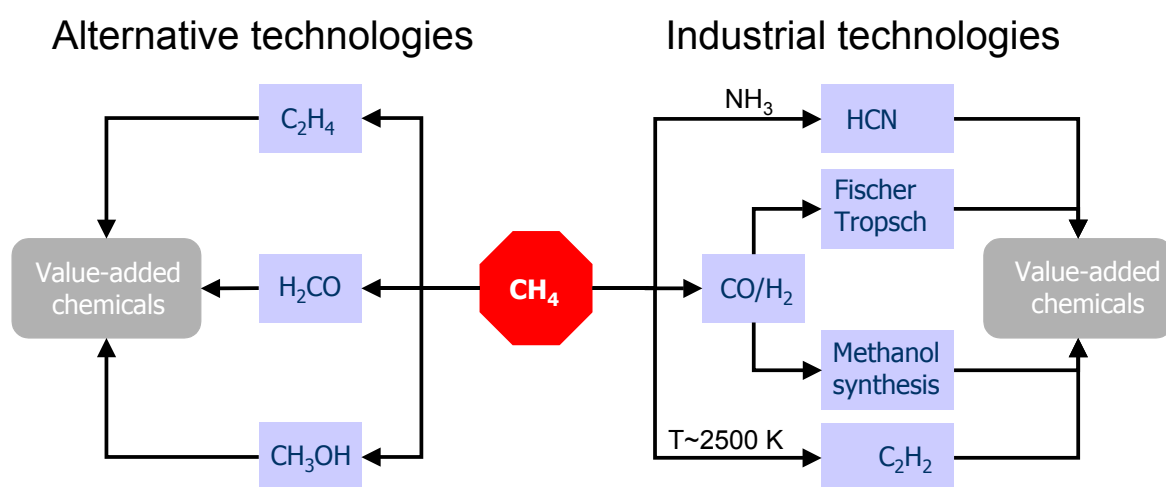

Figure 3.1 Conversions of methane into value-added chemicals.

Steam reforming of methane is a mature technology, which is widely used for producing syngas, i.e. carbon monoxide and hydrogen.[2] An important industrial utilization of methane is the production of hydro cyanic acid via the Andrussow[3] or Degussa processes[3]. Hüls[4] and BASF[4] have developed processes for acetylene production from methane providing the required heat of this endothermic process either by an electric arc or by partial oxidation of natural gas above 1573 K in a special reactor at very short contact times for preventing cracking of acetylene formed. The most attractive alternative technologies for oxidative utilization of methane are shown in the left-hand side of Figure 3.1. These process routes employing novel technologies and catalysts could result in significant cost advantages for raw materials compared to current technologies.

3.3   Oxidative Coupling of Methane

3.3.1   Catalytic Materials and Modes of Process Operation

Catalytic materials for the oxidative coupling of methane (OCM) can be divided into four
groups according to the systematisation of Lee and Oyama:[5]

 i)   reducible metal oxides, e.g. $NaMnO_4/MgO \cdot SiO_2$;

 ii) non-reducible metal oxides, e.g. Li/MgO, SrO/La_2O_3;

 iii) halogen-containing oxide materials, e.g. BaF_2/Y_2O_3;

 iv) solid electrolytes, e.g. $SrCe_{0.9}Yb_{0.1}O_{3-x}$.

Best OCM performances and catalytic materials reported in open and patent literature are
summarized in Figure 3.2. The black and grey lines illustrate upper bonds of C_2 (C_2H_4 +
C_2H_6) yields predicted for O_2 and CH_4 co-feeding[6] and alternating feeding[7] of the reactants;
the simulations have been performed on the basis of gas-phase and surface kinetics. Various
engineering means have been suggested to improve product separation and overall C_2 yields.
These are the counter-current moving-bed chromatographic reactor,[8] staged catalytic fixed-
bed reactors with distributed and co-feed oxygen addition,[9] and product removal over several
stages,[10] oxygen-conducting membrane reactors,[11-13] recycling reactors with continuous
removal of ethylene over 5A zeolite [14] or as an aqueous silver ion complex via a membrane
contactor.[15] None of these approaches appear presently economically viable due to the recycle
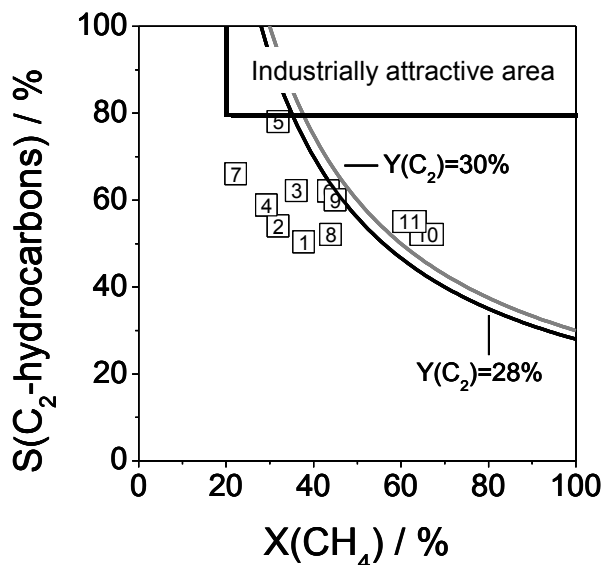of huge amounts of unconverted methane and expensive product separation.

Figure 3.2   OCM performance per pass over selected catalytic materials: 1 – Li/MgO[16], 2 – 30%BaO/Ga$_2$O$_3$[17], 3 - 95mol%BaF$_2$/Y$_2$O$_3$[18], 4 - La/MgO[19], 5- Rb$_2$WO$_4$/SiO$_2$[20], 6 - Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$[21], 7 - La$_2$O$_3$-CeO$_2$[22], 8 - Na$_2$WO$_4$/SiO$_2$[20], 9 - 10%Y$_2$O$_3$-89%ZrO$_2$-1%TiO$_2$ membrane   with   Li$_2$O/MgO/ZrO$_2$[23], 10 - Ba(1-0.5x)TiO$_3$SnCl$_2$(0.05x) (x is 1 mol)[24], 11 – Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-d}$[25].

3.3.2   Interaction of Methane on Solid Catalytic Surfaces

From a fundamental point of view the oxidative coupling of methane is an interesting reaction; it occurs via a mechanism including heterogeneous and homogeneous steps coupled with each other. Since a methane molecule does not possess any functional groups but four equivalently strong C-H bonds as pointed out above, the OCM reaction is initiated by breaking one of these bonds by oxygen species on the surface of the catalyst. For the mechanism of C-H bond activation, two concepts exist:

(1) The assumption of heterolytic breaking of the C-H bond is based on the well-established experimental observation that selective catalytic materials are of basic nature.[26, 27] According to this concept a proton is abstracted by the basic surface site of O^{2-}, while the remaining

methyl anion CH_3^- is linked to the surface cation M^{n+} (Equation 3.1)). Thus, it may be concluded, that there is no change of the valence state of the metal centre and that methane is reversibly activated as suggested by the experimental measurement of the extent of CH_4/CD_4 isotopic equilibration.[28] Moro-oka, however, concluded that no such strong acid/base pairs exist on most metal oxide catalysts and that heterolytic cleavage would be less preferable on most metal oxide surfaces.[29] In fact, there was no direct experimental evidence for the heterolytic cleavage of the C-H bond in the rate-determining step on metal oxide catalysts.

$$CH_4 + M^{n+}O^{2-} \rightarrow M^{n+}CH_3^- + O^{2-}H^+ \qquad \text{(Equation 3.1)}$$

(2) In the homolytic cleavage mechanism (Equation 3.2), there is still an open question whether the initial oxidation step involves a two-electron (2e) transfer or single-electron (1e) transfer. Haber postulated,[30, 31] that in the activation of a C-H bond on oxide surfaces, the proton would attach to the surface oxygen to form a hydroxyl group (OH), while the alkyl cation would attach to the surface oxygen forming an alkoxy group (OR). Two electrons originally localized in the C-H bond would be injected into the conductive band of the solid.[30] The presence of hydroxyl and alkoxy groups detected by IR spectroscopy on oxide surfaces was interpreted as experimental support of the Haber's mechanism.[32] In support of the homolitic cleavage, Sinev, who has applied kinetic and thermochemical analysis of the OCM reaction, suggested that a single electron transfer process involving the free radical formation was likely to be the most favourable process.[33]

$$CH_4 + M^{n+}O^{2-} \rightarrow CH_3^\bullet + M^{(n-1)+} + OH^- \qquad \text{(Equation 3.2)}$$

In contrast to the mechanism of breaking C-H bond in CH_4, there are no doubts that methyl radicals are primary gas-phase products. Lunsford and associates[34, 35] observed methyl radicals by means of matrix-isolation electron-spin resonance over various catalytic materials. The formation of gas-phase methyl radicals via heterogeneous reaction of methane with

adsorbed oxygen species on MgO and Sm_2O_3 was also proven by Buyevskaya et al.[36] using the temporal analysis of products (TAP) reactor operated under Knudsen-diffusion conditions. Later, methyl radicals were observed in situ upon methane oxidation over platinum at temperatures between 1273 and 1573 K.[37]

3.3.3   Mechanistic Insights into Ethane, Ethylene and CO_x Formation

Methyl radicals generated on the catalyst surface recombine in the gas phase to ethane. In the presence of gas-phase O_2, these radicals can react to $CH_3O_2\cdot$ or/and $CH_3O\cdot$ radicals, which are precursors of CO_x. Alternatively, methyl radicals can undergo heterogeneous transformations to CO_x. Ethylene is formed either via homogeneous or heterogeneous ethane dehydrogenation. As reported in[38] methane inhibits homogeneous oxidation of ethane. Similar to methane oxidation, the initial step of heterogeneously catalysed ethane oxidation to ethylene is breaking a C-H bond of the molecule by a surface-oxygen species. Thus, this reaction competes with methane activation. Due to the lower bonding energy of the C-H bond in C_2H_6 compared to CH_4, the rate of ethane consumption is 5-20 times higher than that of methane consumption.[39, 40] Ethylene is even more reactive than ethane. Due to the strong difference in the reactivities of C_1 and C_2 hydrocarbons, consecutive oxidation of ethane and ethylene is the main reaction pathway leading to CO_x at high methane conversions. These non-selective reactions occur via homogeneous and heterogeneous pathways, the latter playing the most significant role. Therefore, the main challenge of the OCM reaction is minimizing CO_x formation. Since the non-selective gas-phase reactions are difficult to control, significant improvements in the OCM performance may presumably be only achieved by controlling heterogeneous reaction pathways, which are influenced by various physico-chemical properties of the catalysts applied. Therefore, possible approaches for developing novel selective catalytic materials comprise knowledge on fundamental relationships between

selectivity and activity on one hand and physico-chemical properties on the other hand as well as on additional knowledge on reaction mechanism and micro-kinetic parameters.

3.3.4 Oxygen Species in the OCM Reaction

The most essential reaction step of the OCM reaction is the generation of active oxygen species from gas-phase oxygen on the catalyst surface. The type of oxygen species formed from O_2 on the catalyst surface and the physico-chemical properties of solids are essential selectivity-governing factors. Therefore, establishing relationships between these properties and individual selective and non-selective reaction pathways of the OCM reaction is a highly important requirement for designing novel selective catalytic materials. The diversity of oxygen species, which can exist on the catalyst surface and participate in the formation of selective and non-selective reaction products, is illustrated in Figure 3.3. However, the nature of selective and non-selective oxygen species in the OCM reaction is still debated. This is due to the variety of OCM catalysts and due to the experimental limitations for an unambiguous identification of active sites at high temperatures (> 873 K), which are required for methane activation. According to[41], the following physico-chemical properties of solid materials are required for generation of active oxygen species:

i) the presence of oxygen vacancies or impurity metal ions or interstitial sites;

ii) the catalysts should be p-type semiconductors with a band gap of 5-6 eV.

The latter requirement is due to the fact that the band gap determines the concentration of charge carriers. If the band gap is too low, a high concentration of adsorbed oxygen species is expected, which favour total oxidation over the selective formation of C_2-products. The poor performance of n-type conductors is ascribed to their low ability for generating methyl radicals but their high activity for total oxidation of the radicals.
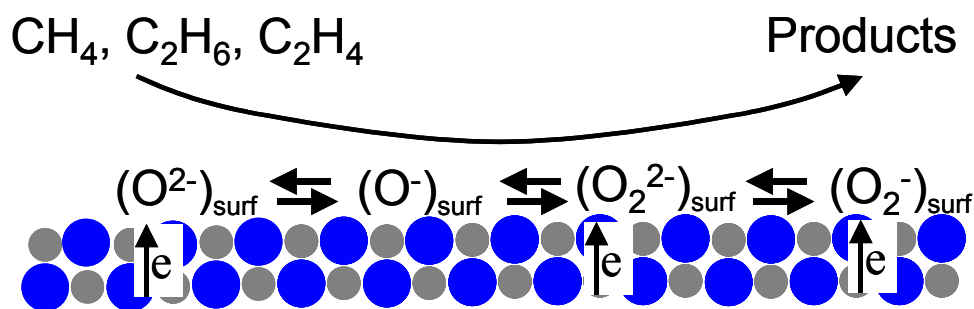
CH$_4$, C$_2$H$_6$, C$_2$H$_4$ → Products

$(O^{2-})_{surf}$ ⇌ $(O^-)_{surf}$ ⇌ $(O_2^{2-})_{surf}$ ⇌ $(O_2^-)_{surf}$

Figure 3.3   Oxygen species stabilized on the surface of oxide catalysts upon activation of gas-phase O$_2$[42-44].

Irrespective of the nature of the OCM catalysts, oxygen adsorption takes place on defects in the structural lattice, if the oxide structure enables oxygen to enter these sites[41]. Lattice oxygen (O^{2-}) is directly formed from gas-phase O$_2$ upon its interaction with reducible metal oxides: the metal cation changes its oxidation state with simultaneous electron transfer to oxygen. Since the band gap in oxides of non-reducible metals is high compared to the reducible ones, differently charged oxygen species (O^-, O_2^-, O_2^{2-}, and O^{2-}) can exist on the catalyst surface. Intrinsic factors (anion vacancies, interstitial sites) and impurity defects in these oxides play a significant role in electronic transfers, since the metal cations of the host oxide matrix cannot change their oxidation state.

O^- is the most discussed oxygen species in the OCM reaction. Lunsford and associates[34, 45] identified M(Li or Na)$^+$O$^-$ centres in Li/MgO, Li/ZnO and Na/CaO catalysts by means of ESR (electron spin resonance) spectroscopy. Since M$^+$O$^-$ centres were identified in the bulk of the catalysts, these authors suggested that there exists equilibrium between bulk and surface species. The high reactivity of O$^-$ oxygen species in the OCM reaction was supported by periodic DFT (density functional theory) calculations over La$_2$O$_3$.[46, 47] However, the authors suggested a mechanism considering the participation of O$_2^{2-}$ in the breaking of a C-H bond in the methane molecule. The role of O$^-$ was not completely excluded.

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The ability of O_2^{2-} species for methane activation was supported by the results of methane oxidation over Na_2O_2 and BaO_2 in the absence of gas-phase oxygen.[48, 49] By means of in-situ Raman analysis, O_2^{2-} species were identified over Na/La_2O_3 and Sr/La_2O_3[50] at 973 K and over BaO/MgO[51] at 973 and 1023 K upon methane oxidation with oxygen. In addition to O_2^{2-}, O_2^- species were also observed over catalytic materials based on rare-earth oxides in a recent in-situ Raman study.[52] It was suggested that O_2^- and O_2^{2-} originate from O_3^{2-}. The latter species is formed via reversible coupling of O_2 with a neighbouring O^{2-}. A correlation between the rate of the disappearance of the O_2^- species and C_2H_4 formation was observed over a SrF_2/La_2O_3 catalyst.[53] This result suggests that O_2^- may be an active oxygen species responsible for the oxidative coupling of methane.

In previous studies,[54-56] it was demonstrated that the presence of Na content in Na/CaO catalysts influenced the nature of surface oxygen species originating from gas-phase O_2 as well as catalytic performance in the OCM reaction and in the oxidative dehydrogenation of ethane (ODE) to ethylene. The latter reaction occurs also under conditions of the OCM reaction. For all the catalysts, C_2 (C_2H_4 and C_2H_6) and C_2H_4 selectivity in the OCM and ODE reactions, respectively, are affected by the alkane-to-oxygen ratio and sodium concentration. Some of the dependencies are illustrated in Figure 3.4.
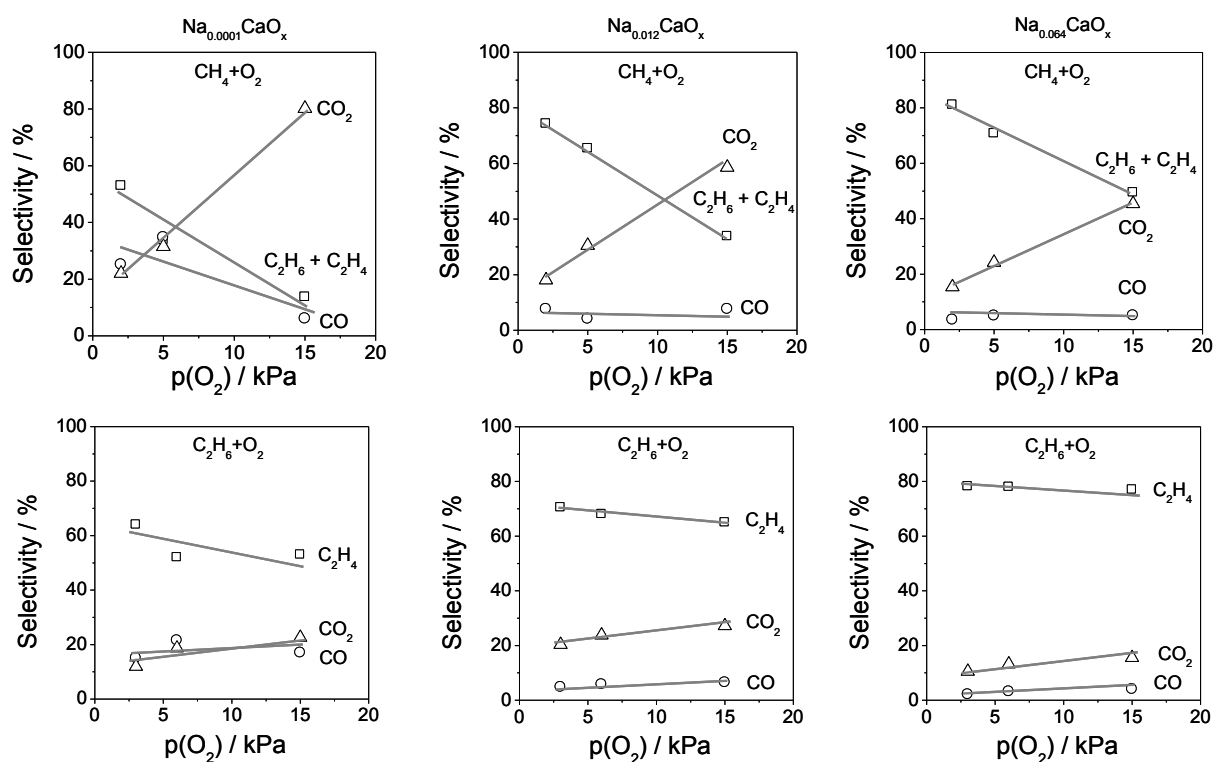
Figure 3.4   Effect of oxygen partial pressure on selectivity of the OCM and ODE reactions over an Na-CaO catalyst at 1023 K and 923 K, respectively (X(CH$_4$)~10%, p(CH$_4$)=30 kPa, X(C$_2$H$_6$)~10%, p(C$_2$H$_6$)=30 kPa). Data are from[54-56].

An increase in oxygen partial pressure results in a decrease in selectivity towards desired products; this was accompanied by an increase in CO$_x$ selectivity. CO$_2$ formation prevails over CO production in the whole range of oxygen partial pressures. This indicates that C$_2$H$_6$ and C$_2$H$_4$ are oxidized to CO$_2$. Besides the oxygen effect, selectivity towards C$_2$ products increases with an increase in sodium loading at a constant oxygen partial pressure as shown in Figure 3.4. In contrast to C$_2$ selectivity, the selectivity towards CO and CO$_2$ decreases with an increase in Na content. Therefore, it can be concluded that non-selective consecutive oxidation of C$_2$ hydrocarbons to CO$_x$ is inhibited upon doping of CaO with Na. Based on the results of measurements of the electrical conductivity and work function of electrons,[56] it was concluded that the incorporation of Na$^+$ into the cationic sub-lattice of CaO results in the creation of anion vacancies in the anionic sub-lattice. The latter are active sites for O$_2$

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adsorption. The concentration of surface anion vacancies in Na/CaO materials was determined from multi-pulse O_2 experiments performed in the TAP reactor;[56] the higher the Na loading, the higher the concentration of anion vacancies. In order to derive additional insights into the effect of Na in Na/CaO materials on the mechanism of O_2 activation, a detailed micro-kinetic analysis of O_2 activation on the basis of elementary reaction steps including surface intermediates was performed.[55] From this micro-kinetic analysis it was concluded that the alkali dopant does not change the mechanism of oxygen activation and the state of surface oxygen species. Gas-phase O_2 adsorbs over anion vacancies reversibly and dissociatively via a molecular-adsorbed precursor. Only the catalyst ability for dissociation of bi-atomic oxygen species seems to distinguish differently doped Na/CaO catalysts; the higher the sodium loading, the faster the dissociation. This is related to the creation of additional anion vacancies in the lattice of CaO upon incorporation of Na^+ into cationic lattice positions.

By taking into account the micro-kinetic knowledge of O_2 adsorption, the ability of the catalyst for fast transformation of bi-atomic oxygen species into atomic ones was identified as a key catalyst property for achieving high C_2 selectivity. It was suggested that mono-atomic oxygen species are responsible for selective oxidation (ethane and ethylene formation), while bi-atomic oxygen species take part in consecutive oxidation of C_2 hydrocarbons to CO_x. The dissociation of bi-atomic oxygen species can be accelerated by creation of anion vacancies in the oxide lattice upon adding low-valence additives into the host oxide matrix. This statement was experimentally proven by doping of CaO with Na_2O,[56] CeO_2 with CaO[57] and Nd_2O_3 with SrO.[58]

Comparing the results of the OCM reaction using O_2 and N_2O as oxidizing agents indirectly supports the importance of the nature of oxygen species. In[59-63], higher C_2 selectivity was found over Na/CaO and Li/CaO catalytic materials with low (< 2 at.%) Li and Na loading with N_2O than with O_2. The difference was related to the different oxygen species generated from O_2 and N_2O. Adsorption of gas-phase O_2 was suggested to occur via a molecular

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precursor followed by its dissociation to O^{2-}_{cus} (cus: coordinatively unsaturated sites) and non-charged atomic oxygen (O). The latter one is selective and also generated upon N_2O activation. The O^{2-}_{cus} species was assumed to participate in CO formation, since the rate of CO formation strongly decreased upon replacing O_2 by N_2O.

3.3.5 Selectivity and Activity Governing Factors

The importance of structural defects of catalytic materials for generating selective and non-selective oxygen species as well as for achieving high C_2 selectivity has been repeatedly reported for the OCM reaction.[41, 55, 56, 58, 64-66] The authors[64] divided all known OCM catalysts into two groups: i) multiphase catalysts and ii) single phase catalysts. For the former group of catalysts, particular phases appear to be required for good performing catalysts. Oxygen vacancies and ions of transitional metals as impurities are the main defects of single-phase catalysts. Structural defects influence the type of electrical conductivity of solid materials. The electrical properties play an essential role in the OCM reaction.[66] However, the defect structure is changed under OCM conditions as outlined in.[60, 61, 64, 67] These reaction-induced defects influence the catalytic performance. For M/CaO (M=Li or Na < 2 at.%), $[MCO_3]^-$, CO_2^{2-} and O_3^{2-} defects were identified in the volume of the CaO lattice after the OCM reaction took place at 1023 K. An increase in the fraction of the $[M(Li \text{ or } Na)CO_3]^-$ centres in doped CaO resulted in a rise of C_2 selectivity using an O_2-containing reaction feed.[60, 61] CO_2^{2-} species were considered as precursors for CO, while O_3^{2-} was assumed to be a non-selective oxygen species for consecutive oxidation of C_2 products. However, when N_2O was used as oxidant, no structural changes in the catalyst volume were observed. The differences in catalytic performance were related to the nature of oxygen species generated from O_2 and N_2O.

Nagy et al.[67] demonstrated the importance of reaction-induced changes in the silver-catalysed

OCM reaction. Ag faceting promotes the formation of O_γ species (nucleophilic oxygen embedded in the uppermost layer of silver atoms) as determined by the authors. These species were suggested to be responsible for improved catalytic performance.

Based on past and more recent characterization studies, it has been suggested that the catalytic performance of various solid materials for selective oxidative transformation of light hydrocarbons was negatively affected by surface acidity[68, 69] but positively by basicity.[70] However, Choudhary and co-workers [71] did not observe a direct relationship between surface basicity and catalytic activity/selectivity over CaO doped with alkali metal oxides. For example, a Na/CaO catalyst (Na/Ca=0.1 before calcination) showed better OCM performance (C_2 selectivity of 68.8% at 24.7% methane conversion) than Rb/CaO materials. In a recent OCM study with CO_2,[72] it was suggested that the strength and distribution of surface basic sites are important factors determining the OCM performance. According to them, selective OCM catalysts should possess low concentrations of very strong basic sites (CO_2 desorption above 923 K).

Based on the above background it is clear that the OCM reaction is influenced by various physico-chemical properties, which, however, have not been previously considered together for deriving a final conclusion on their relevance for catalyst design. Therefore, a better understanding of the various physico-chemical properties and their effect on reaction mechanism, micro-kinetics and, as results thereof, on catalytic performance would certainly allow controlling the overall process of methane conversion and, hence providing useful guidelines for a rational catalyst design and development. It needs to be seen, whether there are synergistic or possibly even adverse effects of different solid-state properties on the desired catalytic performance. This can be achieved by systematic catalyst characterization using modern surface and bulk techniques as well as micro-kinetic analysis.

3.4   Methane Oxidation to Methanol and Formaldehyde

3.4.1   Interaction of Oxygen and Methane on Transition Metal Oxides

The direct oxidation of methane into methanol and/or formaldehyde is even more challenging than the OCM reaction. In contrast to the heterogeneously catalysed methane oxidation, the natural enzyme catalyst monooxygenase in methanotrophic bacteria demonstrates that highly selective methane oxidation to methanol is possible even at room temperature.[73] This is an enticing example of what could be achieved with other catalytic materials. Also, as proven by theoretical analysis and experimental data, methyl radicals and methanol were formed after the interaction of methane with gaseous $[NiO^+]$ [74], $[FeO]^+$ [74], $[MoO_3]^+$ [75], $[OsO_n]^+(n=0-4)$ [76], $[V_4O_{10}]^+$ [77], and $[MgO]^+$ [78] clusters. This leads to a recent review by Fu et al. [79] who analysed different C-H activation pathways over terminal $[=O]$ and bridged $[-O-]$ oxygen species. On this basis, Mo_3O_9 was used as model system to support previous findings. The results provide some additional insights into the fundamental issues with respect to C-H activation by metal oxo-species involved in many heterogeneous, homogeneous and enzymatic catalytic processes.

In the direct conversion of methane and oxygen to methanol and formaldehyde, activation of the reactants is of fundamental and practical importance. Two issues need to be solved:

- Firstly, the chemical inertness of methane as demonstrated by the high C−H bond strength (104.8 kcal/mol), high ionisation potential (12.5 eV), low proton affinity (4.4 eV), and low acidity ($pK_a = 48$) of the molecule has to be overcome.

- Secondly, the propensity for full oxidation in the presence of oxygen is to be surmounted.

The authors[79] refer to various studies on the mechanisms of alkane oxidation by transition metal oxides. A detailed and final mechanism of C-H bond activation on these catalysts remains, however, elusive.[80-85]

Some interesting but partly contradictory results were obtained in recent years on the mechanism of the oxidation of methane. Lunsford et al.[86] reported that MoO_3 supported on silica was a catalyst for the selective oxidation of methane to methanol and formaldehyde when N_2O is the oxidant. The O^- ions coordinated to Mo^{VI} at the surfaces were claimed to be the active species, capable of abstracting a hydrogen atom from methane. The methyl radicals formed reacted rapidly with the oxidic surface to form methoxide complexes, which then decompose to HCHO, or react with water to form CH_3OH. Barbaux et al.[87] investigated the properties of surface oxygen species generated by different oxidants on the MoO_x systems. They found that O^- generated by O_2 led to the formation of CO_x, while O^{2-} generated by N_2O led to higher selective oxidation to HCHO. Smith and Ozkan examined the partial oxidation of methane to formaldehyde over MoO_3/SiO_2.[88] Emphasis was on the surface species formed on the supports and their effects on reactivity and selectivity: low MoO_3 loadings led to the formation of silicomolybdic species with terminal Mo=O sites, while higher loadings gave rise to the formation of polymolybdate species with Mo-O-Mo bridges, the former having a better selectivity for HCHO than the latter.[88, 89] Interestingly, other experiments seem to support the opposite view: it was concluded that bridge oxygen [-O-] was responsible for selective oxidation, while terminal oxygen [=O] was related to total oxidation.[90]

3.4.2 Methane to Methanol

3.4.2.1 Homogeneous and Heterogeneous Methanol Formation

Methanol can be directly formed from methane via homogeneous gas-phase reactions of radical nature at high pressures (50-100 bar) in the temperature range from 573 to 973 K.[82] The methanol yields achieved are rather low and cannot be easily tuned, since radical reactions are difficult to be controlled. Therefore, heterogeneously catalysed methane oxidation has been intensively investigated besides liquid-phase oxidation. Methanol

selectivities up to 80 % at methane conversions below 4 % have been reported over Mo-, Fe-, and V-based catalytic materials.[80, 91-94] From a mechanistic point of view, methanol formation occurs either via direct insertion of active oxygen species into a C-H bond in CH_4 or via oxidative abstraction of H atom yielding methyl radical and OH group. The methyl radical formed undergoes further surface or gas-phase oxidations to methoxide species. The latter can react with water to form methanol or can decompose to formaldehyde. Both these oxygenates are easily oxidized to carbon oxides. This gives rise to a fundamental problem of selective CH_4 conversion to CH_3OH (similar to OCM) without its further consecutive oxidation to CO_x via H_2CO. This situation results into the need to isolate the selective reaction products before side products are formed. The extent of such isolation depends on the relative rates of formation and further oxidation of CH_3OH. As shown schematically in Figure 3.5, methanol over-oxidation can be avoided by continuous removal of methanol from the reactive zone or generating methyl derivatives, which are chemically protected from over-oxidation to carbon oxides. Hereafter, these derivatives might be transformed to methanol or directly used for industrial purposes.
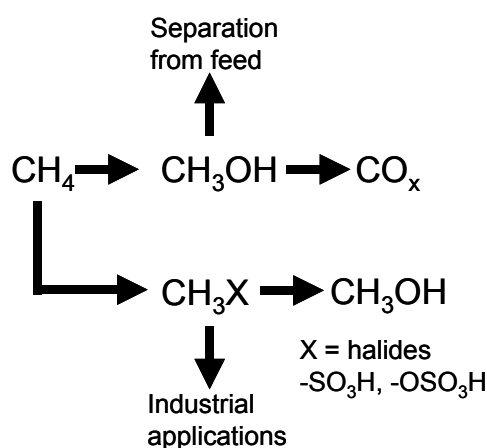

Figure 3.5   Possible alternatives for preventing methanol over-oxidation to CO_x.

Chemical protection for liquid-phase conversion of methane to methanol has been originally demonstrated by Periana et al.[95, 96] via the formation of methyl bisulphate in oleum at 373 K. A bipyrimidyl platinum (II) complex has been identified as the most efficient and highly

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selective catalyst resulting in the formation of methyl bisulphate with an one-pass yield of 72 % (81 % selectivity based on methane). Although the achieved catalytic performance appears to be attractive, this process scheme suffers from the production of large amounts of diluted sulphuric acid, on and hydrolysing the methyl ester to methanol. Muehlhofer et al.[97] have alternatively reported the formation of trifluoroacetic acid methyl ester upon methane oxidation in a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride at a methane pressure of 20-30 bar and 353-373 K. In this case, Palladium (II) complexes with N-heterolytic carbine ligands were used as catalysts. The authors mentioned that trifluoroacetic acid methyl ester can be easily hydrolysed and the acid recovered can be used for the reaction, although this was not demonstrated.

Inspired by the studies of liquid-phase methane oxidation to methanol derivatives, Li and Yuan[98] suggested a process scheme for gas-phase methane oxidation to methanol using various solid materials as catalysts: $Pt(SO_4)_2$, $HgSO_4$, $Ce(SO_4)_2$ and $Pd(SO_4)_2$ supported over $BaSO_4$ nanotubes. Methanol yields up to 28 % were reported in the presence of gas-phase oxygen as oxidant in the temperature range from 443 to 503 K. The catalysts were pre-treated in concentrated sulphuric acid at 393 K for 3 hours before they were applied for methane oxidation. Among the catalysts investigated, $Pt(SO_4)_2/BaSO_4$ showed the best performance; methanol selectivities of about 70% at methane conversions of around 40 % were achieved.

The authors suggested that sulphuric acid deposited on the catalysts is used for methane activation yielding methyl bisulphate followed by its hydroxylation to methanol and sulphuric acid. Gas-phase O_2 oxidizes SO_2 formed during the methane activation by SO_3. Although this latter approach might be interesting for possible industrial application, the authors did not provide any data on the time-on-stream performance, which may be influenced by possible removal the acid during the reaction course. Moreover, corrosion problems have to be taken into account.

CH_3OH selectivity above 55 % and CO_2 selectivity below 10 % at 14 % CH_4 conversion were

reported by F. Li and G. Yuan[99] upon gas-phase oxidation of CH_4 by O_2 over

$MoO_2Br_2(H_2O)$/Zn-MCM-48 at 493 K and 10 bar. Other reaction products were dimethyl

ether and methane bromides. This high catalytic performance was, however, not stable with

time-on-stream and depended on the content of ZnO in the catalyst; the higher the ZnO

loading, the more stable the performance and the higher is the production of dimethyl ether.

Catalyst deactivation with time-on-stream was related to bromine leaching as bromine fumes

and methane bromides. This leaching is a significant drawback. In order to overcome this

drawback, the catalyst ability for converting methane bromides to methanol and MoO_x to

MeO_xBr_2 (x=0-2) should be significantly improved.

The abstraction of hydrogen from methane can be facilitated upon feeding gaseous radical

initiators like NO_x (x=1, 2) into CH_4-O_2 feeds. Previous literature dealing with the effect of

NO_x on methanol and formaldehyde production from methane has been thoroughly reviewed

in 2002.[80] In general, NO increases the catalyst activity and selectivity towards oxygenates.

Up to now, the highest overall yield of methanol and formaldehyde of 16 % was achieved

over a low surface area V_2O_5/SiO_2 catalyst.[100] Methane was oxidized with O_2 in the presence

of NO_x. The positive effect of NO_x is related to acceleration of gas-phase reactions leading to

methanol and formaldehyde.

3.4.2.2 Enzymatic Conversion of Methane to Methanol

As opposed to the various types of chemical conversions of methane to methanol as

mentioned above, also its enzyme-catalysed reaction to methanol may be of high interest due

to the studies on a molecular level. The knowledge derived from such investigations may

contribute to possible new routes in designing novel and improved inorganic catalysts for the

reaction of methane to methanol.

X. Shan and L. Que[101] outlined in a review article that the initial step in the enzymatic

(biomimetic) oxidation of alkanes is the activation of oxygen. High-valent iron-oxo species

(Fe^{IV}=O or Fe^{V}=O) are often invoked as the key oxidizing agents in the catalytic cycles of

oxygen activating nonheme iron enzymes. A principal mechanistic scheme of oxygen

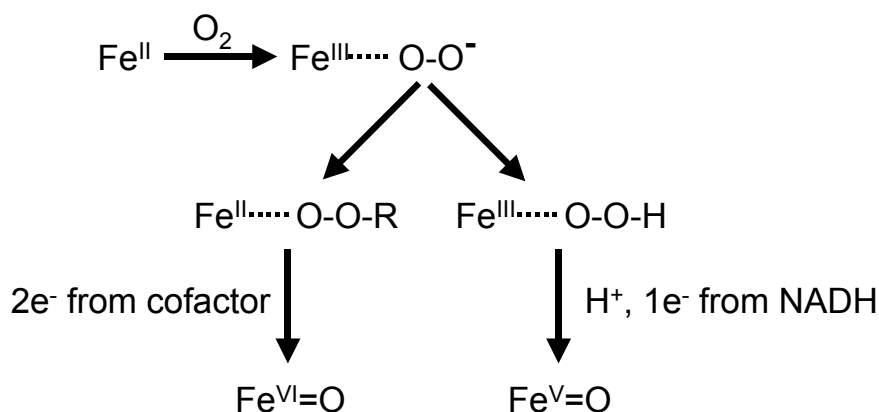activation at biological iron sites is shown in Figure 3.6.

$$Fe^{II} \xrightarrow{\; O_2 \;} Fe^{III} \cdots O\text{-}O^-$$

$$Fe^{II} \cdots O\text{-}O\text{-}R \qquad Fe^{III} \cdots O\text{-}O\text{-}H$$

$$2e^- \text{ from cofactor} \qquad\qquad H^+,\ 1e^- \text{ from NADH}$$

$$Fe^{VI}\text{=}O \qquad\qquad Fe^{V}\text{=}O$$

Figure 3.6   Mechanistic scheme for oxygen activation at biological iron sites [   ]; Fe^{IV}=
O(porph*) for heme enzymes, $Fe^{IV}_2O_2$ for MMO, Fe^{V}= O(OH) for Rieske
dioxygenases.[102]

Arguments in support of a metal-based oxidant instead of oxygen radical are ascribed to the

high degree of conversion of the feed molecule and the nature of the reaction products. E.g., it

has been assumed that among the mononuclear non-heme iron enzymes one class, i.e. the

Rieske dioxygenases, involves an formal Fe^{V}=O oxidant in the oxygen activation

mechanism.[102]

Recently Rinaldo et al.[103] dealt in a theoretical study with the intermediates in dioxygen

activation by soluble methane monooxygenase (MMO) for oxidation of methane to methanol.

They combined QM/MM and broken-symmetry DFT methods. The work revealed that two

iron sites (see above) need a distinct environment. A protein environment helps driving the

reactants toward products along the reaction path. In summary, various reaction steps are

required for converting methane to methanol on Fe=O sites as illustrated in Figure 3.7.
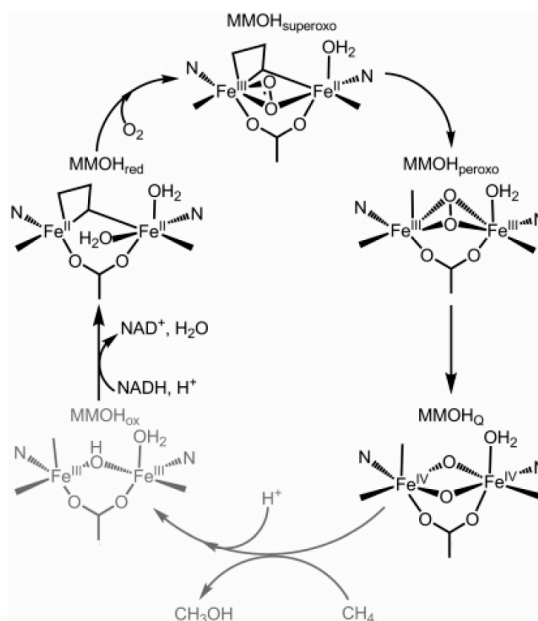
Figure 3.7   The catalytic cycle of MMO (in its various forms). The part of the cycle corresponding to activation of dioxygen is shown in black while the oxidation of the substrate (hydroxylation of methane to methanol *in vivo*) is in light gray. The data are from.[103]

Despite of their common oxidation state of the two iron atoms the electronic structure reveals that they are not equivalent. They are in different environments with one iron having an octahedral geometry and the other one being in a square pyramidal environment; hereby, their interaction with oxygen, and hence, with methane via the attached oxygen is supposed to be different.

From the above results as obtained by Shan and Que[101] as well as by Rinaldo et al.[103] indications may be derived for developing novel or modifying known catalytic solid materials for the gas-phase oxidation of methane to methanol.

3.4.3 Methane to Formaldehyde

Various catalytic materials have been tested for methane oxidation to formaldehyde. It is generally suggested that the active and selective catalysts should fulfil a double role: i) dehydrogenation of methane and ii) oxygen addition. Most of the catalysts studied are supported ones; most often silica or silica-alumina are used as support, while oxides of vanadium, molybdenum, iron, tungsten, and nickel are the active components. It is suggested that the effectiveness of silica is related to its low ability for consecutive formaldehyde conversion to CO_x. Figure 3.8 compares formaldehyde selectivities obtained over different materials as a function of methane conversion; catalysts yielding less than 2 % of CH_4 conversion and formaldehyde selectivities below 20% are not included in this figure. It should be stressed that these data were obtained under various reaction conditions using both O_2 and N_2O as oxidizing agents and NO_x as gas-phase dopants. None of the catalysts investigated up to now led to formaldehyde yields of at least 20%. The low formaldehyde selectivity is due to heterogeneous reaction steps, which occur on both, active components and supports and by homogeneous formaldehyde combustion.
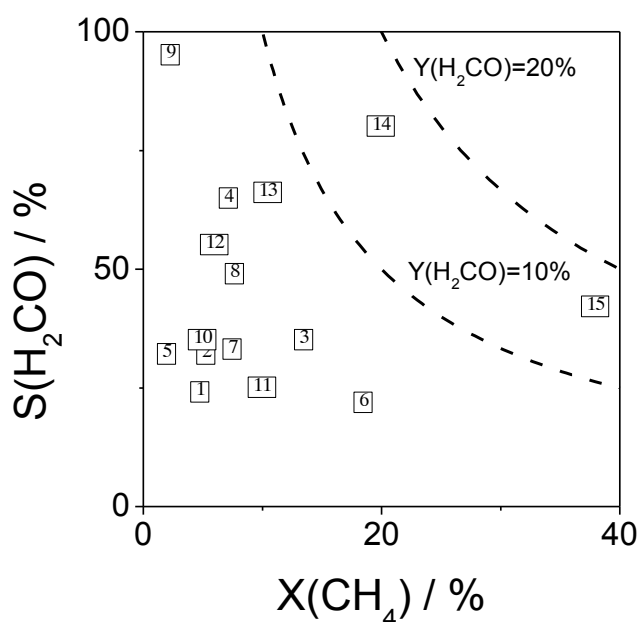
Figure 3.8   Formaldehyde selectivity versus methane conversion over selected catalytic materials: 1 – SiO_2[104], 2 – MoO_3/SiO_2[105], 3 – V_2O_5/SiO_2[106], 4 – $MoSnP/SiO_2$[107], 5 – $Zr-P-O_x$[108], 6 – $Zn-Fe_2(MoO_4)_3$[109], 7 – TiO_2 + CH_2Cl_2[110], 8 – V_2O_5/SiO_2[111], 9 – VO_x(3 wt.%)/SBA-15[111], 10 – SiO_2 4-5P[112], 11 – $Sn_{0.8}Ge_{0.2}O_2$[113], 12 - MoO_3/SiO_2 with N_2O[114], 13 - 40% $FePO_4$/MCM-41 with N_2O[115], 14 - $MoCl_5$/R4Sn/SiO_2 R is an alkyl group[116], 15 – total selectivity of H_2CO and CH_3OH over V_2O_5/SiO_2 with NO addition[100].

Aiming at fundamental knowledge for developing novel well-performing catalytic materials, the effect of physico-chemical properties but also reaction mechanisms and kinetics have been widely investigated. A key parameter for good formaldehyde selectivity is the dispersion of MoO_x, VO_x and FeO_x species on the support surface.[111, 117-123] A deeper kinetic analysis of direct methane oxidation to formaldehyde has been performed by Bell and co-workers[124] who used a MoO_x/SiO_2 catalyst with a nominal surface density of molybdenum of 0.44 Mo nm^{-1}. The gas-phase reactions did not contribute significantly to the product distribution between 848 and 923 K. Formaldehyde formation from methane occurs predominantly over MoO_x species, while formaldehyde combustion takes place additionally over bare silica. Since methane and formaldehyde compete for the same active sites (lattice oxygen of MoO_x), the highest single-pass yield of formaldehyde can be achieved, when the rate of methane conversion is increased compared to the one of consecutive formaldehyde consumption. The kinetics predicts that the rate of methane consumption depends more strongly on the coverage by oxidized sites than the rate of the consecutive formaldehyde reaction. Moreover, the activation energy of the reaction of methane conversion to formaldehyde is higher than that of formaldehyde consumption. Therefore, the maximal formaldehyde yield is predicted, when the methane oxidation is performed at high CH_4/O_2 ratios and reaction temperatures as high as possible where gas-phase reaction can be still avoided.

3.5   Outlook

Although oxidative methane conversion towards the coupling products ethane and ethylene as well as to methanol and formaldehyde are of significant industrial interest the fundamentals of its heterogeneous catalysis is still not satisfactory for designing highly selective catalysts. Thorough studies including experimental as well as theoretical work are still needed; the results on the bio catalytic conversion of methane to methanol as mentioned above might be supportive.

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