Fluctuating Storage of the Active Phase in a Mn-Na$_2$WO$_4$/SiO$_2$ Catalyst for the Oxidative Coupling of Methane

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Abstract: Structural dynamics of a Mn-Na$_2$WO$_4$/SiO$_2$ catalyst were detected directly under reaction conditions during the oxidative coupling of methane via in situ XRD and operando Raman spectroscopy. A new concept of fluctuating storage and release of an active phase in heterogeneous catalysis is proposed that involves the transient generation of active sodium oxide species via a reversible reaction of Na$_2$WO$_4$ with Mn-SiO$_2$. The process is enabled by phase transitions and melting at the high reaction temperatures that are typically applied.

Introduction

The oxidative coupling of methane (OCM) to ethane and ethene represents an attractive alternative to current crude-oil-based processes in order to access value-added chemicals.\cite{1} Since the pioneering works of Keller and Bhasin,\cite{2} Hinsen and Baerns,\cite{3} and Ito and Lunsford\cite{4} in the early 1980s, the multi-phase Mn-Na$_2$WO$_4$/SiO$_2$ catalyst has established itself as a high-performance system that exhibits extended on-stream stability at high reaction temperatures.\cite{5} Despite extensive investigations, both the active site and working mechanism of the catalyst remain much debated.\cite{6} In general, most research has been directed towards the structural characterization of the catalyst before and after the reaction or in a quenched state.\cite{7} Only limited efforts have, however, been made to elucidate the nature of the catalyst under working conditions.

In this report, a Mn-Na$_2$WO$_4$/SiO$_2$ catalyst (Supporting Information, Table S1, Figures S1–S3), synthesized in large scale by Simon et al.,\cite{8} was investigated with the aim of identifying structural motifs and phase transitions directly under relevant reaction conditions. A multi-method approach, featuring electron microscopy (SEM-EDX), thermal analysis (TG-DTA-MS), in situ and operando Raman spectroscopy and in situ X-ray diffraction, was adopted. Reference compounds, in form of Na$_2$WO$_4$·2H$_2$O, MnWO$_4$, and natural braunite (Mn$_2$SiO$_4$)\cite{9} were also examined (Supporting Information, Figures S4–S13). With pure Na$_2$WO$_4$ known to undergo a phase transition from solid to liquid at 695°C (Supporting Information, Figure S11),\cite{9} the formation of a catalytically active liquid component, containing alkali and transition metal oxides, was investigated.

Results and Discussion

The as-synthesized catalyst is a macro-porouos material with low specific surface area (2.9 m$^2$g$^{-1}$) (Supporting Information, Figure S3). Its crystalline fraction is constituted by α-cristobalite (92 wt%), quartz (0.5 wt%), Na$_2$WO$_4$ (4.1 wt%), and mixed-valent Mn$_3$SiO$_4$ (3.4 wt%) (Supporting Information, Figure S1). The manganese silicate mostly contains the transition metal in the oxidation state +3 (Mn$^{3+}$Mn$^{4+}$SiO$_4$). Another phase, MnWO$_4$, which only features Mn in the oxidation state +2, was sporadically detected at certain spots by Raman spectroscopy (Figure 1A, bottom, Supporting Information, Figure S2). By investigating the aforementioned reference compounds using Raman spectroscopy (Supporting Information, Figures S4–S10), all observed bands were successfully allocated for the multi-phase Mn-Na$_2$WO$_4$/SiO$_2$ catalyst system. The low concentration of MnWO$_4$ is expected to arise from the higher stability of Mn$_3$SiO$_4$, relative to MnWO$_4$, under oxidizing conditions.

SEM-EDX revealed an inhomogeneous distribution of manganese, sodium, and tungsten on the catalyst surface and inside the silica support, with Na$_2$WO$_4$ preferentially forming separate domains (appearing in yellow-orange in Figure 1B). Furthermore, large areas of the catalyst are only constituted by manganese, silicon and oxygen. Higher concentrations of Mn, in close vicinity to the Na$_2$WO$_4$ phase, may suggest a structural interaction of the Mn-containing phases with Na$_2$WO$_4$. Freely existing W can also be observed, suggestive of silica-supported WO$_4$ species. However, typical bands for WO$_4$ species dispersed on silica do not appear in the Raman spectrum of the catalyst (Figure 1A).\cite{10} Surface inhomogeneities are also reflected in the Raman spectra recorded at different spots, which evidently feature varying concentrations of Na$_2$WO$_4$ and Mn$_3$SiO$_4$ (Figure 1A, top and middle).

After testing the catalyst under relatively mild conditions (Supporting Information, Figure S14), a slightly increased concentration of quartz was observed, yet the general phase composition of the catalyst remained unaltered (Supporting Information, Figure S1). Both the support (in its high-temper-
above the melting point of Na$_2$WO$_4$ (Figure 1A, top). Both, Takanabe et al. [60] and Yu et al. [11] reported similar observations, describing a reversible disappearance and intensity loss of the characteristic Raman bands for Na$_2$WO$_4$ supported on TiO$_2$ and CeO$_2$, respectively. Raman spectroscopy at different sampling positions clearly proves that the melt does not completely wet the catalyst surface. While in some areas only signals of β-cristobalite and Mn$_3$SiO$_5$ were evident (Figure 1A, top, gray spectrum), other areas also featured a broadened spectrum of Na$_2$WO$_4$ (Figure 1A, top, black spectrum). In summary, melting of the crystalline Na$_2$WO$_4$ phase in the Mn-Na$_2$WO$_4$/SiO$_2$ catalyst was clearly observed in synthetic air by in situ XRD and TG-DTA analysis. However, according to Raman spectroscopy, a full wetting of the catalyst surface with molten Na$_2$WO$_4$ does not occur, that is, surface inhomogeneities clearly persist at temperatures higher than 700°C.

In contrast to this, the structural evolution changes drastically in inert atmosphere. Cubic Na$_2$WO$_4$ disappears at 600°C in favor of an unknown transient phase (Figure 2B; Supporting Information, Figure S17), which only partially resembles the transient phase formed in air at 600°C (Figure 2A). Instead of detecting the formation of orthorhombic Na$_2$WO$_4$ at 650°C, as observed in synthetic air (Figure 2A), the patterns of the transient peaks are subject to further change. The intensity of the reflection near 3° 2θ, assigned to Mn$_3$SiO$_5$, starts to decrease, while peaks due to MnWO$_4$ arise (Figure 2B). The development of the MnWO$_4$ peaks occurs simultaneously with the complete disappearance of the Mn$_3$SiO$_5$ reflection. A significant formation of MnWO$_4$, by reaction of Mn$_3$SiO$_5$ with Na$_2$WO$_4$ and/or WO$_3$, was also evident via Raman spectroscopy for nitrogen feed...
(Figure 3A). The band of Mn$_7$SiO$_{12}$ at 958 cm$^{-1}$ is no longer distinguishable at higher temperatures due to shift or broadening of the band of Na$_2$WO$_4$ at 927 cm$^{-1}$. The latter is most likely caused by phase transition and melting of Na$_2$WO$_4$ or by formation of tetrahedrally coordinated, silica-supported WO$_x$ species. The disappearance of Mn$_7$SiO$_{12}$ and cubic Na$_2$WO$_4$ in the XRD, starting at 600°C, is therefore, most likely connected to a partial or complete conversion of the two phases to MnWO$_4$. Thermal analysis of the Na$_2$WO$_4$, MnWO$_4$, and Mn$_7$SiO$_{12}$ reference compounds (Supporting Information, Figures S11–S13) only revealed a significant oxygen release ($m/z = 32$) at elevated temperatures for the Mn$_7$SiO$_{12}$ phase, with an onset at 807°C (Figure 3B; Supporting Information, Figure S13). Several different thermal events were observed for the Mn$_7$SiO$_{12}$/SiO$_2$ catalyst system in argon (Figure 3B; Supporting Information, Figure S18). The DTA curve features an endothermic event (1) at 226°C, which is assigned to the phase transition of the α-cristobalite support to β-cristobalite.$^{[12]}$ Oxygen evolution from the catalyst is shifted to significantly lower temperatures when compared to the Mn$_7$SiO$_{12}$ reference, with the onset recorded at 653°C (2). This could be associated with the phase transition of cubic Na$_2$WO$_4$ into unknown transient phases at 600°C, the commencing formation of MnWO$_4$ at 650°C as well as the disappearance of Mn$_7$SiO$_{12}$, also observed from 650°C onwards (Figure 2B). Instead of a well-defined endothermic peak, the DTA curve only displays minor irregularities in the temperature regime between 600°C and 700°C (Figure 3B; Supporting Information, Figure S18). It is possible that the superposition of the melting and redox processes, as observed via in situ XRD in the absence of air in this temperature range, limits the ability of DTA to clearly detect melting.

Progressive surface mobility, initiated by restructuring of supported Na$_2$WO$_4$ above 600°C and facilitated by melting of residual Na$_2$WO$_4$ at higher temperatures, can enable the reaction between Mn$_7$SiO$_{12}$ and Na$_2$WO$_4$ as shown in...
Equation (1). This, in turn, leads to the reduction of Mn$^{4+}$ (in Mn$_3$SiO$_{12}$) to Mn$^{2+}$ (in MnWO$_4$), the release of molecular oxygen with its maximum at 927°C (3) and (4) in Figure 3 B), and the formation of amorphous or dispersed sodium oxide.

\[
\text{Mn}^{4+}\text{SiO}_{12}^{-} \text{+ 7NaWO}_4 \rightarrow 7\text{MnWO}_4 + \text{7NaO + SiO}_2 + \text{1.5O}_2
\]  

(1)

The broad temperature range for the oxygen release covers the onset temperature of oxidative coupling of methane (650°C) as well as the reaction temperatures that are typically applied (700–800°C). A weight loss of 0.2% (0.22 mg) was caused by the event, with the DTA curve indicating endothermicity (4). It is postulated that the process described in Equation (1) provides mobile lattice oxygen under steady-state operation of the catalyst. This is in agreement with O$_2$-TPD experiments performed by Gordienko et al.\[13\] who identified two forms of lattice oxygen that may potentially contribute to catalysis upon desorption at relevant temperatures. The source of oxygen has been attributed to manganese oxide.\[6,7\] or any unspecified lattice oxygen.\[14\] Potentially more decisive is the release of an active form of sodium oxide species that has been proposed to catalyse the oxidative coupling of methane by generation of OH radicals at high temperatures.\[16,17\] presumably under involvement of homogeneous gas-phase reactions\[15\] due to the high volatility of sodium compounds under operation conditions\[18\].

Evidence, that the redox process described in Equation (1) occurs under reaction conditions and is indeed reversible, was provided by operando Raman spectroscopy at different reaction temperatures and feed compositions (Figure 4; Supporting Information Figure S19). In all operando spectra (Figures 4 A and B), the region of 100–400 cm$^{-1}$ is dominated by a broad band of the β-cristobalite support, which is formed via phase transition from α-cristobalite at 225°C.\[12a,17\] The spectra recorded under steady-state conditions in a CH$_4$/O$_2$/N$_2$ (4:1:4) feed at various temperatures (Figure 4 A) predominantly feature bands of β-cristobalite and the remaining steady-state concentrations of Mn$_3$SiO$_{12}$ (450–700 cm$^{-1}$) and Na$_2$WO$_4$ (920–930 cm$^{-1}$). At the highest reaction temperature, the formation of MnWO$_4$ becomes apparent, as indicated by a very weak band at 874 cm$^{-1}$. Carbon oxides, ethane, and water were identified as the main reaction products via online mass spectrometry and gas chromatography in the effluent gas of the Raman cell (Supporting Information, Figures S20, S21). Significant formation of coke was not observed (Figure 4 A). The selectivity to C$_2$ products was much lower compared to analogous experiments conducted in a quartz fixed bed reactor without dilution of the catalyst (Supporting Information, Figure S14), which is attributed to consecutive reactions of the desired C$_2$ products on the hot stainless-steel walls of the operando cell and the inadequate reactor geometry. However, comparison of the catalytic tests conducted with the empty operando cell and the same cell filled with the catalyst under identical reaction conditions clearly showed a lower activity and selectivity to C$_2$ products for the empty reactor (Figure 4 C).

Changes to the spectral composition were observed upon switching to a reducing CH$_4$/N$_2$ (4:5) feed at 700°C (Figure 4 B). This was accompanied by a significant decline in catalyst performance and the formation of hydrogen and carbon monoxide as main products, suggesting that lattice oxygen is consumed and gas-phase reactions as well as methane pyrolysis prevail under these conditions (Supporting Information, Figures S20 and Figure S21). The complete removal of oxygen leads to the formation of MnWO$_4$, as indicated by the band at 878 cm$^{-1}$ (Figures 4 B and D). Thus, a reaction of Na$_2$WO$_4$ and/or WO$_3$ with Mn$_3$SiO$_{12}$ and/or MnO$_2$ to yield MnWO$_4$ occurs under reducing conditions. The formation of coke is excluded here based on Raman spectroscopy (Figure 4 A). During catalyst regeneration using the initial reaction feed (CH$_4$/O$_2$/N$_2$ = 4:1:4), braunite is suddenly reformed at the expense of MnWO$_4$ after approximately 8 h (Figure 4 D). Moreover, due to this reversible phase transformation, the formation of C$_2$ products is re-initiated (Supporting Information, Figure S20 and Figure S21 after 8 h), thereby highlighting the significance of the Mn$_3$SiO$_{12}$ phase in maintaining catalytic activity. The presence of Mn$_3$SiO$_{12}$ is also clearly responsible for the formation of CO$_2$ in place of CO (Supporting Information, Figure S21). As can be seen in Figure 4 A, the spectrum initially observed under steady-state conditions, is restored entirely by switching back to a CH$_4$/O$_2$/N$_2$ feed (Figure 4 A, red spectrum).

**Conclusion**

In conclusion, the present in situ and operando experiments disclosed reversible redox activity of the Mn$_3$SiO$_{12}$, MnWO$_4$ and Na$_2$WO$_4$ phases under operation conditions in the oxidative coupling of methane over Mn-Na-WO$_4$/SiO$_2$. A new concept is proposed that involves the fluctuating storage and release of an active phase in heterogeneous catalysis. According to Equation (1), active sodium oxide species, which are responsible for high activity and selectivity in the oxidative coupling of methane,\[6\] are generated in the catalytically relevant temperature regime in small amounts. The extent of this reaction is controlled by the oxygen partial pressure in the gas phase and the redox chemistry on the surface (Scheme 1). While the structural synergy of all phases is responsible for the high stability and activity of the catalyst, the supported Na$_2$WO$_4$ phase acts as storage phase responsible for transient generation of active sodium oxide species that would, in absence of the stabilizing Mn$_3$SiO$_{12}$-MnWO$_4$ redox couple, suffer from steady sublimation,\[19\] thus leading to catalyst deactivation.\[20,21\] As long as the oxygen partial pressure in the reactor is not too low, a small steady-state concentration of the active phase is formed according to Scheme 1.

Phase transitions and melting of Na$_2$WO$_4$ enable the generation of the active phase by providing mobile sodium species. Furthermore, the supported Mn$_3$SiO$_{12}$ phase was observed to function as oxygen-donor at working temperatures, which further enhances sodium oxide formation and, thus, has implications for the reactivity. However, the availability of adsorbed or lattice oxygen due to the presence of
redox-active elements alone\textsuperscript{6j,7,13,14} cannot be responsible for the outstanding performance of the Mn-Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2} catalyst and does not explain the mechanistic role and importance of Na in this system. On the other hand, a pure silica-supported sodium oxide would rapidly deactivate under the severe reaction conditions applied in the oxidative coupling of methane.\textsuperscript{6g} Only the chemical complexity of the Mn-Na\textsubscript{2}WO\textsubscript{4}/SiO\textsubscript{2} catalyst guarantees long-term stability. The synergistic element combination discovered by chance is so successful because melting and redox reactions occur in the same temperature window (Figure 2 and Figure 3).

In the presence of gas-phase oxygen, the phase transition of Mn\textsubscript{7}SiO\textsubscript{12} and Na\textsubscript{2}WO\textsubscript{4} into Na\textsubscript{2}O and MnWO\textsubscript{4} is largely impeded and generates only transient amounts of active sodium oxide species. Apparently, only a small concentration of oxygen is necessary to keep the system in this highly active state (>88\% oxygen conversion in the steady state, see Supporting Information, Figure S21, t > 8 h). Such a low concentration of oxygen in the gas phase is beneficial in terms of the selectivity. Only in total absence of oxygen is the system disturbed and MnWO\textsubscript{4} formed in
noticeable amounts. The oxygen donor Mn$_2$SiO$_4$ (Figure 3B), however, evidently hinders a complete and rapid transformation into MnWO$_4$ and Na$_2$O (Figure 4B), which would lead to a loss of Na$_2$O due to sublimation and progressive catalyst deactivation. The described scenario may also be considered as displacement of the redox chemistry from the organic to the inorganic part of the hybrid reaction system. Therefore, in future concepts of catalyst design it might be reasonable to take into account that the activation of methane could also proceed via an acid-base reaction by using the strong base O$_2$ as catalyst avoiding radical chemistry in the selective pathway.

Our experiments clearly show that MnWO$_4$ is a product of catalyst deactivation, which is formed under strongly reducing reaction conditions. However, regeneration by increasing the partial pressure of oxygen in the feed again is possible (Figures 4D and Supporting Information, Figure S21).

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Conflict of interest

The authors declare no conflict of interest.

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