

Short communication

Enhancement and limits of the selective oxidation of methane to formaldehyde over V-SBA-15: Influence of water cofeed and product decomposition

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ABSTRACT

The possibility of a selective catalytic oxidation of methane to formaldehyde has been known for decades, and positive influences of water added to the reaction mixture and ultra-short contact times have been reported. In the present work, the complexity of interdependencies has been revealed. Specific parameter variations can increase conversion and selectivity of the target product. Surprisingly, formaldehyde formation over VO_x species and its decomposition in gas phase were equally dependent on the partial pressure of the added water, so that the sweet spot can only be found by varying the residence time.

1. Introduction

Methane is the most inert alkane due to its symmetry and stability of the low polarized C-H bonds in combination with the higher reactivity of its oxidized products (e.g., methanol, formaldehyde, and formic acid). These properties cause methane to be the most difficult alkane to upgrade [1]. Hence, processes directly yielding oxygenates from methane are challenging and often referred as the holy grail of heterogeneous catalysis. Within the possible oxygenates which can be directly obtained, formaldehyde can be produced from methane and oxygen with a highest productivity of $13.6 \text{ kg}_{\text{CH}_2\text{O}} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$. When using a selective V-SBA-15 catalyst, it is the ultra-short residence time that becomes decisive in achieving such high values [2].

Short residence times, however, cause low conversions. A reduction in gas-hourly space velocity ($\text{GHSV}, \text{h}^{-1}$) consequently leads to an increase in conversion, but the longer contact time is responsible for further oxidation and thus reduction in selectivity for formaldehyde [3]. Hence, different attempts aiming to improve the selectivity of reaction were made and reported. In previous studies, optimized catalysts as well as reaction conditions were discussed [4–7], which made use of new reactor set-ups, like continuous recycling [8,9] and rapid quenching [10,11], or the addition of cofeeds. Especially, the latter offers promising opportunities due to the variety of possible additives, namely, H_2O [5,12–14], NO_2 [15], NO [16], N_2O [17], HCl [18], CH_2Cl_2 [19,20] or H_2 [21], which all do affect the reaction network in different ways. But not all of these molecules are really

trendsetting. Only water presents an attractive option due to its availability and non-toxicity. Its influence when cofed already became evident in three different ways: i) equilibria are shifted to less oxidized C1-compounds when water is a reaction product, ii) the structure of the catalyst is altered by forming additional Brønsted acid sites via hydrolysis, and iii) water competes for adsorption on active catalytic sites [22].

We have previously reported on the impact of different reaction parameters on the selective oxidation of methane to formaldehyde over an in situ prepared V-SBA-15 catalyst [2]. Therein, the addition of water to the reaction mixture was demonstrated to have a high influence on the reaction as it drastically increased methane conversion, while improving the selectivity to formaldehyde. Therefore, we investigated the influence of water on the selective oxidation of methane to formaldehyde in more detail and how water alters the consecutive oxidation of the desired product of formaldehyde. Herewith, we provide new information of how the yield of the target product can be increased by adding water, and what one needs to know about the stability of the same under the reaction conditions applied.

2. Experimental

2.1. Catalyst preparation

For the synthesis of the V-SBA-15 catalyst, an upscaled version of a previously described procedure was used [2]. In short, 16 g Pluronic P123 (Sigma Aldrich) were dissolved in 480 g of deionized water at

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room temperature under stirring. Afterwards, 0.59 g NH_4VO_3 (Merck, 99%) were added followed by further stirring for 1 h. Subsequently, 34.7 g tetraethyl orthosilicate (Sigma Aldrich, 98%) were added dropwise. The pH value was adjusted to 2.5 using an aqueous HCl and checked with a pH meter (Multilab 540, WTW, Weilheim, Germany). The reaction mixture was then heated to 40 °C. After stirring for 24 h, the suspension was transferred into a PTFE inlet for hydrothermal treatment at 100 °C for 48 h. Finally, the precipitate was filtered, washed with water, dried at 80 °C overnight and calcined at 625 °C for 16 h (heating rate 1 K min^{-1}) yielding 10 g of V-SBA-15.

Plain SBA-15 was synthesized by dissolving 16 g Pluronic P123 in 480 g 2 M HCl with subsequent stirring at room temperature. When dissolved, the solution was heated to 40 °C followed by dropwise addition of 34.7 g tetraethyl orthosilicate. After further stirring at 40 °C for 24 h, the suspension was transferred into a PTFE inlet for a hydrothermal treatment at 100 °C for 24 h. Subsequent steps were equal to the synthesis of V-SBA-15.

2.2. Catalyst characterization

The amount of vanadium in V-SBA-15 was determined via inductively coupled plasma-optical emission spectrometry (Varian 715-ES spectrometer). Prior to analysis, the sample was dissolved by microwave irradiation at 200 °C and 80 bar in a mixture of aqua regia and hydrofluoric acid. Powder XRD data were collected using the X'Pert Pro (Panalytical) diffractometer with Ni-filtered $\text{Cu-K}\alpha$ radiation. Nitrogen sorption was carried out after removal of water at 400 °C under reduced pressure in ASAP2010 (Micromeritics) apparatus, and analyzed by the BET method. Ultraviolet-visible spectra were measured using an Ava Spec-2048 spectrometer equipped with a FCR-7UV400C-2 reflection probe. V-SBA-15 was diluted with three parts SBA-15 and measured prior and after dehydration at 350 °C for 1 h in flowing synthetic air (100 mL min^{-1}) with BaSO_4 as white standard.

2.3. Catalytic oxidation of methane and formaldehyde

Measurements of the catalyst performance were carried out using a homemade fixed-bed plug-flow quartz reactor. The reactor had an inner diameter of 8 mm that decreased to 4 mm in the middle at which the catalyst bed was placed and kept in place by quartz wool. The temperature was measured and controlled at the middle of the catalyst bed. The amount of catalyst was 25 mg diluted with 225 mg of quartz sand. The total flow rate was 200 mL min^{-1} resulting in a GHSV of 480,000 $\text{L kg}^{-1} \text{h}^{-1}$. Effects of residence time variation were investigated by varying the total volume flow rate and catalyst mass (see Table S1, ESI). The composition of the detected C1 components in the product gas stream during the experiments are given in Fig. S1 (ESI). The mass flow rates of the respective gases were adjusted by means of mass flow controllers (MKS-Instruments, Andover, USA). Water was added by means of a syringe pump which injected liquid water into a heated (150 °C) transfer line. Formaldehyde was added via a heated reactor filled with paraformaldehyde through which a mixture of nitrogen/oxygen was passed. Product analysis was performed by means of IR gas analyzers (Matrix MG01, Bruker, Ettlingen, Germany). Spectra of the carbonyl stretching region with and without water cofeed are given in Fig. S2 (ESI) along with an example illustrating the C1-balance over the course of an experiment (Fig. S3, ESI). The residence time for the experiments in the empty reactor was calculated as the ratio of the reactor volume in the isothermal zone (6.6 mL) to the respective flow. Further formulae for the calculation of catalytic properties are given in the ESI as well as a scheme of the used experimental set-up (Scheme S1, ESI).

3. Results and discussion

3.1. Influence of water on the oxidation of methane

The V-SBA-15 catalyst used in this study exhibits a Vanadium content of 1.74 wt% and specific surface area of 762 $\text{m}^2 \text{g}^{-1}$. Powder XRD data,

nitrogen sorption curves as well as UV-vis spectra of the catalyst at ambient conditions and after dehydration are given in Figs. S4 and S5 (ESI). A more in-depth characterization and interpretation of this material can be found elsewhere [2].

The influence of water cofeeding on the selective oxidation of methane was investigated in the 560–640 °C range as shown in Fig. 1, and the partial pressure of water was varied in the 0–10 kPa range. At 560 °C and 0 kPa of water cofeed, the observed methane conversion was 0.1% and increased to 0.2% at $p_{\text{H}_2\text{O}} = 1.7$ kPa, followed by a further decrease to 0.02% at $p_{\text{H}_2\text{O}} = 10$ kPa. While the overall conversion of methane increases with increasing reaction temperature, the maximum in activity was broadened and shifted to higher amounts of water cofeed in the reaction gas mixture. At 580 °C, the maximum in activity was observed at $p_{\text{H}_2\text{O}} = 3.4$ kPa, and at 600 °C at $p_{\text{H}_2\text{O}} = 7.2$ kPa. Slightly above this temperature the maximum lies out of the investigated range.

As reported in previous studies, the addition of water leads to the hydrolysis of V–O–Si and V–O–V bonds in the catalyst structure, forming V–OH groups which were reported to be highly active in methane oxidation [23,24]. Upon further addition of water, more and more of these moieties are blocked by water molecules leading to the observed decrease in activity - and increased selectivity to oxygenates - at constant reaction temperature. Since hydrolysis and blocking of the active sites are no entropically favored processes, the sweet spot between hydrolysis and blocking by water is shifted to higher partial pressures of water with increasing temperature. Previous theoretical studies already investigated the thermodynamics of the hydration of VO_x species on silica [25,26]. Just like the conversion, the water cofeed has an influence on the different production rates of CH_2O , CO, CH_3OH and CO_2 as shown in Fig. S6 (ESI).

In catalytic reactions, however, it is crucial to increase the selectivity, while maintaining the reactant conversion. In an isothermal catalytic performance test series, both the GHSV and the water content were specifically varied to demonstrate the decisive influences in this main criterion. Fig. 2 shows selectivity versus conversion plots at 640 °C for all products (the set of conditions is given in Table S1, ESI). At this temperature, the positive influence of water increases with increasing addition of water. In Fig. 2, curve a, the partial pressure of water was varied at a constant GHSV of 480,000 $\text{L kg}^{-1} \text{h}^{-1}$. With increasing partial pressure of water, the conversion increases from 1.4 to 4.7% but the selectivity decreases from 59 to 42%, which is obviously due to the consecutive oxidation/combustion of formaldehyde.

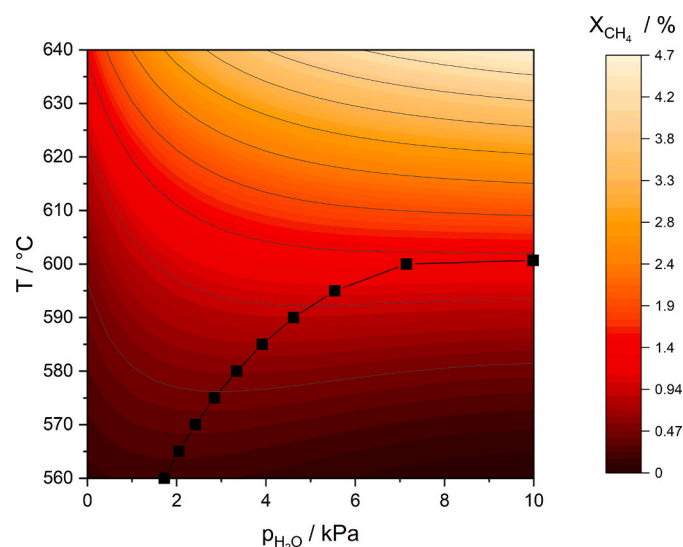


Fig. 1. Methane conversion over V-SBA-15 (1.74 wt% V) in the 560–640 °C range at water levels between 0 and 10 kPa. Reaction conditions: GHSV = 480,000 $\text{L kg}^{-1} \text{h}^{-1}$, 20 kPa CH_4 , 10 kPa O_2 , x kPa H_2O and 70-x kPa N_2 . The squares show the concentration of water with the maximum methane conversion at the respective reaction temperature.

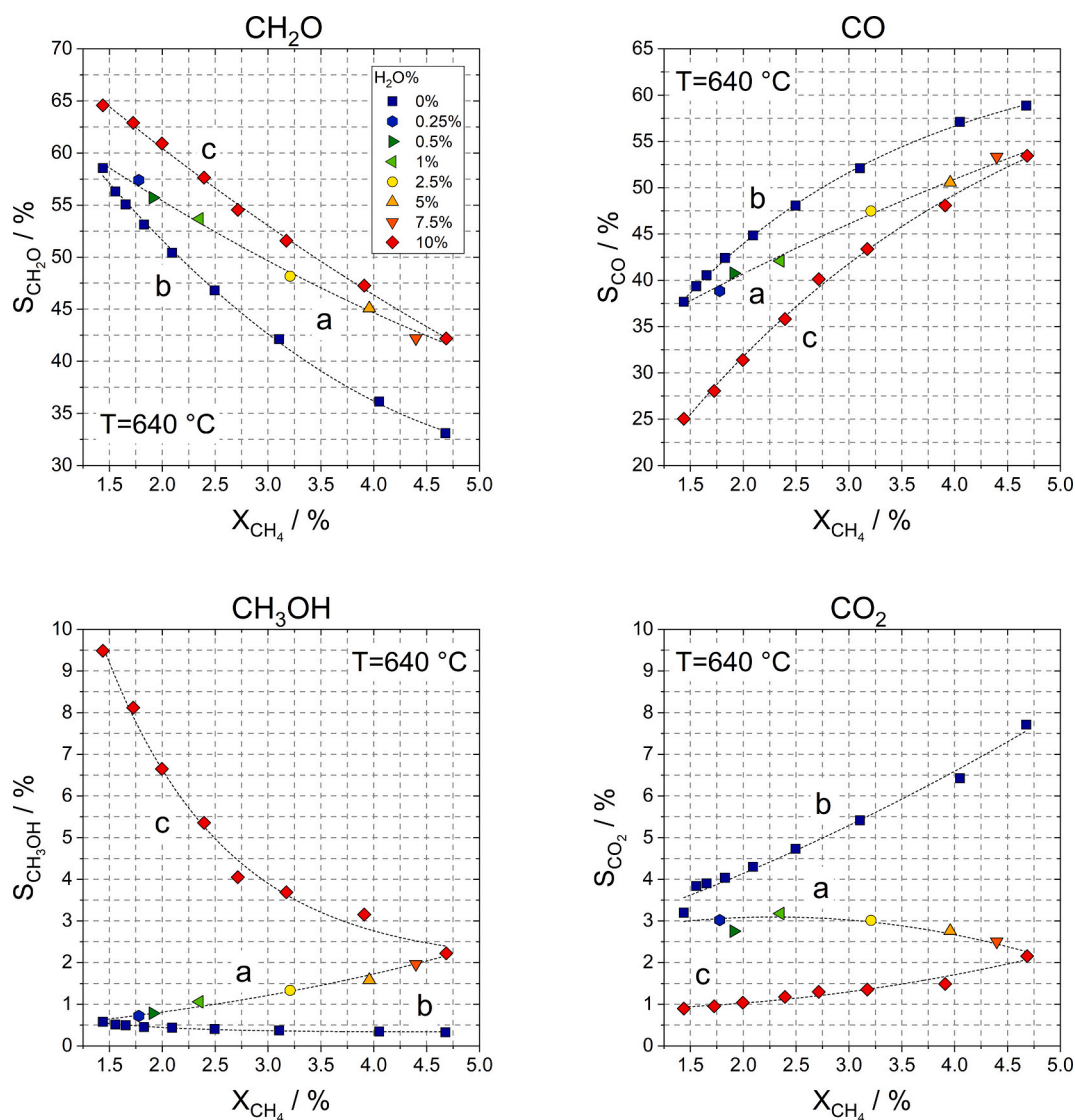


Fig. 2. Selectivity toward CH_2O , CO , CH_3OH and CO_2 versus methane conversion at 640 °C , $20\text{ kPa } CH_4$ and $10\text{ kPa } O_2$ in the feed obtained over V-SBA-15 (1.74 wt % V). Reaction conditions: (a) $GHSV = 480,000\text{ L kg}^{-1}\text{ h}^{-1}$, $x\text{ kPa } H_2O$, $70-x\text{ kPa } N_2$; (b) $GHSV = 168,000\text{--}480,000\text{ L kg}^{-1}\text{ h}^{-1}$, $0\text{ kPa } H_2O$ and $70\text{ kPa } N_2$; (c) $GHSV = 480,000\text{--}1,500,000\text{ L kg}^{-1}\text{ h}^{-1}$, $10\text{ kPa } H_2O$ and $60\text{ kPa } N_2$. Dotted lines represent a visual guidance.

In Fig. 2, curve b and c, the GHSV was varied at constant partial pressure of water, either 0 or 10 kPa. At a conversion of 4.7%, the selectivity without water is 33% leading to a yield of 1.55%, while at $p_{H_2O} = 10\text{ kPa}$, a yield of 1.97% formaldehyde was reached. Moreover, at the lowest probed conversion of 1.4%, the difference in selectivity is 6% in favor of water-rich conditions.

These findings are somewhat contradictory to previous studies, which reported no strong effect of selectivity enhancement for the V-SBA-15 systems [5,13], while it was stated the opposite for example, for silica supported iron-phosphate [12] or molybdenum [27,28]. Obviously, the addition of water can increase the selectivity of VO_x species toward formaldehyde at the same conversion level of methane. The fact that a molecular change of the VO_x centers could be causal for this behavior has already been shown by Launay et al. [24], who detected the hydroxylation of the VO_x species by infrared spectroscopy and postulated an improved electron delocalization between the V–O bond initiated by this. Thus, the prerequisite for a much more favored methane activation is given, namely, electrophilic oxygen species favor homolytic C–H cleavage and lead to the formation of $VOCH_3$ species. It can be seen that under increased water partial pressure the oxygenates, which are thermodynamically unstable under these reaction conditions,

do not continue to react as strongly as when no water is added in the feed. Even significant amounts of methanol are formed with ultra-short residence times. Probably, methanol is the direct precursor of formaldehyde. Due to the catalytic suitability of the V-species, methanol is oxidized to formaldehyde [29,30], especially with increasing residence time. However, the latter cannot be prevented in any way, as the following series of experiments on formaldehyde stability under reaction conditions showed.

3.2. Influence of water on the oxidation of formaldehyde

Besides of the activation of methane, the preservation of the produced formaldehyde presents the major challenge in the selective oxidation. Hence, the stability of formaldehyde was probed under reaction conditions over V-SBA-15 and in an empty reactor (Fig. 3) as well as over SBA-15 alone (Fig. S7, ESI).

As shown in Fig. 3 (a), there is a relatively sharp drop in the conversion of formaldehyde over V-SBA-15 between 0 and 1 kPa of water partial pressure. This can be explained based on the competitive adsorption of formaldehyde and water on the same active sites, which has already been shown via IR spectroscopy with the example of

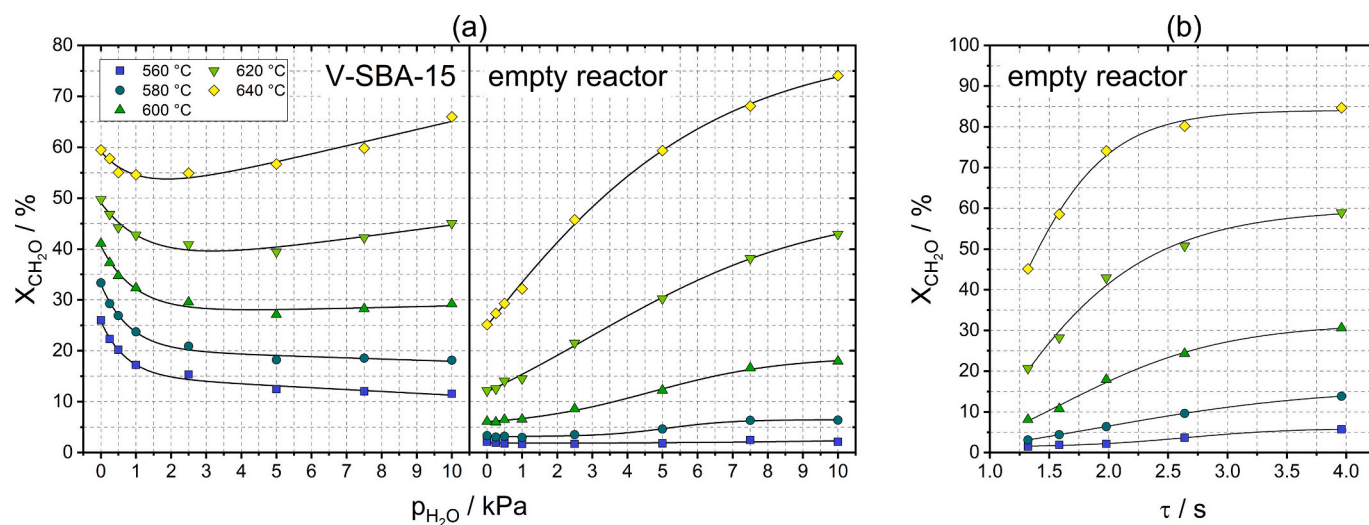


Fig. 3. (a) Formaldehyde conversion in the 560–640 °C range over V-SBA-15 (1.74 wt% V) and in an empty reactor at water levels between 0 and 10 kPa. Reaction conditions: GHSV = 480,000 L kg⁻¹ h⁻¹, 1 kPa CH₂O, 10 kPa O₂, x kPa H₂O and 89-x kPa N₂. (b) Formaldehyde conversion in the 560–640 °C range at different residence times. Reaction conditions: 1 kPa CH₂O, 10 kPa O₂, 10 kPa H₂O and 79 kPa N₂.

molybdenum oxide surfaces [31]. Moreover, since methane activation is increased by water addition and formaldehyde oxidation is suppressed, one can conclude that both processes require different sites, and the addition of water promotes the formation of active centers for methane activation. Below 600 °C, this picture seems valid over the whole $p_{\text{H}_2\text{O}}$ range, namely, the conversion slowly decreases with increasing water partial pressure. However, at higher temperatures, this statement loses its validity, therefore, there must be another effect to counteract it.

The cause is evident from stability experiments without catalyst (empty reactor). The conversion, while being unaffected at 560 °C, increases at elevated temperatures by the addition of water. Remarkably, at 640 °C the conversion in the empty reactor exceeds the conversion over V-SBA-15 at $p_{\text{H}_2\text{O}} \geq 5$ kPa. This observation suggests for a predominance of gas phase decomposition at high water partial pressure, which may proceed via the formation of highly labile methanediol intermediate species, offering new reaction paths with subsequent dehydrogenation to formic acid and dehydration toward carbon monoxide and water formation. Indeed, formic acid was observed in small quantities, up to 50 ppm in formaldehyde oxidation experiments, and for formic acid dehydration, water was identified as a catalyst that significantly reduces activation barriers, as shown by previous DFT studies [32–34]. This gas phase reaction can only be suppressed by lowering the residence time as shown in Fig. 3 (b). However, it should be stated that the results from formaldehyde decomposition experiments are not completely transferable to the methane oxidation case, since formaldehyde fed can be decomposed over the whole length of the reactor. In contrast to that, in methane oxidation, formaldehyde is first produced within the catalyst bed and decomposed within and after the catalyst bed at the exit of the reactor. Hence, the formaldehyde decomposition is somewhat overestimated in these experiments. To complete, at $p_{\text{H}_2\text{O}} < 2.5$ kPa, SBA-15 alone (Fig. S7, ESI) converts more formaldehyde than the empty reactor. Similarly, for the V-SBA-15, a decrease of formaldehyde conversion is observed at low water partial pressure as well as a nearly linear increase at higher partial pressure.

In all experiments, carbon monoxide was detected as main product, and carbon dioxide as by-product. The respective formation rates over V-SBA-15 are given in Fig. S8 (ESI). As main product, the carbon monoxide formation rates follow the trend of formaldehyde conversion. Contrary to that, carbon dioxide production is continuously suppressed with increasing water addition. This result also shows a consecutive

mechanism of methane activation and transformation of the oxygenates toward CO when high water partial pressures are applied. On the other hand, the formation of CO₂ from direct total oxidation is suppressed.

4. Conclusions

In the present study, the influence of water cofed in the selective oxidation of methane to formaldehyde was investigated over a wide temperature range and water partial pressures in the 0–10 kPa range. A temperature-dependent maximum in activity was found for methane oxidation which was shifted to higher water partial pressures as the temperature was increased. In contrast, formaldehyde conversion over V-SBA-15 was suppressed with low water addition, suggesting the presence of different active sites for methane and formaldehyde oxidation. At high water partial pressures, an enhanced contribution of gas phase formaldehyde oxidation was observed. The interplay between activity enhancement in methane activation and lower formaldehyde decomposition rate can lead to an improved but limited selectivity in the investigated reaction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2021.106317>.

References

- [1] R. Horn, R. Schlögl, Methane activation by heterogeneous catalysis, *Catal. Lett.* 145 (2015) 23–39.
- [2] B. Kunkel, A. Kabelitz, A.G. Buzanich, S. Wohlrab, Increasing the efficiency of optimized V-SBA-15 catalysts in the selective oxidation of methane to formaldehyde by artificial neural network Modelling, *Catalysts* 10 (2020) 1411.
- [3] E.V. Kondratenko, T. Peppel, D. Seeburg, V.A. Kondratenko, N. Kalevaru, A. Martin, S. Wohlrab, Methane conversion into different hydrocarbons or oxygenates: current status and future perspectives in catalyst development and reactor operation, *Catal. Sci. Technol.* 7 (2017) 366–381.
- [4] D. Seeburg, U. Bentrup, B. Kunkel, T.T. Ha Vu, T.T.H. Dang, S. Wohlrab, Influence of hydrothermal ageing time on the performance of in situ prepared VMCM-41 catalysts in the selective oxidation of methane to formaldehyde, *Microporous Mesoporous Mater.* 288 (2019) 109581.
- [5] L.D. Nguyen, S. Loridant, H. Launay, A. Pigamo, J.L. Dubois, J.M.M. Millet, Study of new catalysts based on vanadium oxide supported on mesoporous silica for the partial oxidation of methane to formaldehyde: catalytic properties and reaction mechanism, *J. Catal.* 237 (2006) 38–48.
- [6] D.A. Ruddy, N.L. Ohler, A.T. Bell, T.D. Tilley, Thermolytic molecular precursor route to site-isolated vanadia-silica materials and their catalytic performance in methane selective oxidation, *J. Catal.* 238 (2006) 277–285.
- [7] K. Shimura, T. Fujitani, Effects of promoters on the performance of a VOx/SiO2 catalyst for the oxidation of methane to formaldehyde, *Appl. Catal. A Gen.* 577 (2019) 44–51.
- [8] I.C. Bafas, I.E. Constantinou, C.G. Vayenas, Partial oxidation of methane to formaldehyde with 50% yield in a continuous recycle reactor separator (CRRS), *Chem. Eng. J.* 82 (2001) 109–115.
- [9] A. Parmaliana, F. Arena, F. Frusteri, A. Mezzapica, High yields in the catalytic partial oxidation of natural gas to formaldehyde: catalyst development and reactor configuration, in: A. Parmaliana, D. Sanfilippo, F. Frusteri, A. Vaccari, F. Arena (Eds.), *Studies in Surface Science and Catalysis*, Elsevier, 1998, pp. 551–556.
- [10] L.P. Didenko, V.R. Linde, V.I. Savchenko, Partial catalytic oxidation and condensation of methane by oxygen and Sulphur, *Catal. Today* 42 (1998) 367–370.
- [11] L. Yu, S. Yuan, Z. Wu, J. Wan, M. Gong, G. Pan, Y. Chen, Partial oxidation of methane into formaldehyde on a catalysis-separation reactor, *Appl. Catal. A Gen.* 171 (1998) L171–L175.
- [12] G.O. Alptekin, A.M. Herring, D.L. Williamson, T.R. Ohno, R.L. McCormick, Methane partial oxidation by unsupported and silica supported Iron phosphate catalysts: influence of reaction conditions and co-feeding of water on activity and selectivity, *J. Catal.* 181 (1999) 104–112.
- [13] H. Berndt, A. Martin, A. Brückner, E. Schreier, D. Müller, H. Kosslick, G.U. Wolf, B. Lücke, Structure and catalytic properties of VOx/MCM materials for the partial oxidation of methane to formaldehyde, *J. Catal.* 191 (2000) 384–400.
- [14] C.-B. Wang, R.G. Herman, C. Shi, Q. Sun, J.E. Roberts, V2O5-SiO2 xerogels for methane oxidation to oxygenates: preparation, characterization, and catalytic properties, *Appl. Catal. A Gen.* 247 (2003) 321–333.
- [15] J. Zhang, V. Burklé-Vitzthum, P.M. Marquaire, An investigation on the role of NO2 in the oxidation of methane to formaldehyde, *Combust. Sci. Technol.* 187 (2015) 1139–1156.
- [16] M.A. Bañares, J.H. Cardoso, G.J. Hutchings, J.M. Correa Bueno, J.L.G. Fierro, Selective oxidation of methane to methanol and formaldehyde over V2O5/SiO2 catalysts. Role of NO in the gas phase, *Catal. Lett.* 56 (1998) 149–153.
- [17] M.M. Khan, G.A. Somorjai, A kinetic study of partial oxidation of methane with nitrous oxide on a molybdena-silica catalyst, *J. Catal.* 91 (1985) 263–271.
- [18] L.Z. Meltser, T.A. Garibyan, R.R. Grigoryan, A.A. Muradyan, L.N. Kurina, Effect of homogeneous initiator on heterogeneous-homogeneous oxidation of methane, *React. Kinet. Catal. Lett.* 38 (1989) 229–236.
- [19] T.R. Baldwin, R. Burch, G.D. Squire, S.C. Tsang, Partial oxidation of methane to formaldehyde on chlorine-promoted catalysts, *Appl. Catal.* 75 (1991) 153–178.
- [20] R.S. Mann, M.K. Dosi, Partial oxidation of methane to formaldehyde over halogen modified catalyst, *J. Chem. Technol. Biotechnol.* 29 (1979) 467–479.
- [21] Y. Wang, K. Otsuka, Structure of catalytic active site for oxidation of methane to methanol by H2-O2 gas mixture over iron-containing catalysts, *J. Mol. Catal. A Chem.* 111 (1996) 341–356.
- [22] T.V. Andrushkevich, E.V. Ovchinnikova, The role of water in selective heterogeneous catalytic oxidation of hydrocarbons, *Molecular Catalysis* 484 (2020) 110734.
- [23] H. Launay, S. Loridant, A. Pigamo, J.L. Dubois, J.M.M. Millet, Vanadium species in new catalysts for the selective oxidation of methane to formaldehyde: specificity and molecular structure dynamics with water, *J. Catal.* 246 (2007) 390–398.
- [24] H. Launay, S. Loridant, D.L. Nguyen, A.M. Volodin, J.L. Dubois, J.M.M. Millet, Vanadium species in new catalysts for the selective oxidation of methane to formaldehyde: activation of the catalytic sites, *Catal. Today* 128 (2007) 176–182.
- [25] M.M. Islam, D. Costa, M. Calatayud, F. Tielens, Characterization of supported vanadium oxide species on silica: a periodic DFT investigation, *J. Phys. Chem. C* 113 (2009) 10740–10746.
- [26] J. Sauer, M. Pritzsche, J. Döbler, Catalytically active Vanadia species on silica: effect of oxygen and water, *J. Phys. Chem. C* 118 (2014) 29159–29163.
- [27] H.F. Liu, R.S. Liu, K.Y. Liew, R.E. Johnson, J.H. Lunsford, Partial oxidation of methane by nitrous oxide over molybdenum on silica, *J. Am. Chem. Soc.* 106 (1984) 4117–4121.
- [28] T. Sugino, A. Kido, N. Azuma, A. Ueno, Y. Udagawa, Partial oxidation of methane on silica-supported Silicomolybdic acid catalysts in an excess amount of water vapor, *J. Catal.* 190 (2000) 118–127.
- [29] G. Deo, I.E. Wachs, Reactivity of supported vanadium oxide catalysts: the partial oxidation of methanol, *J. Catal.* 146 (1994) 323–334.
- [30] H. Zhang, Z. Liu, Z. Feng, C. Li, Effective silica supported Sb-V mixed oxide catalyst for selective oxidation of methanol to formaldehyde, *J. Catal.* 260 (2008) 295–304.
- [31] W.-H. Cheng, Methanol and formaldehyde oxidation study over molybdenum oxide, *J. Catal.* 158 (1996) 477–485.
- [32] B. Wang, H. Hou, Y. Gu, New mechanism for the catalyzed thermal decomposition of formic acid, *J. Phys. Chem. A* 104 (2000) 10526–10528.
- [33] S. Inaba, Theoretical study of water cluster catalyzed decomposition of formic acid, *J. Phys. Chem. A* 118 (2014) 3026–3038.
- [34] M.E. Wolf, J.M. Turney, H.F. Schaefer, High level ab initio investigation of the catalytic effect of water on formic acid decomposition and isomerization, *Phys. Chem. Chem. Phys.* 22 (2020) 25638–25651.