### Methane Valorization Hot Paper

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# Selective Production of Carbon Monoxide via Methane Oxychlorination over Vanadyl Pyrophosphate

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Abstract: A catalytic process is demonstrated for the selective conversion of methane into carbon monoxide via oxychlorination chemistry. The process involves addition of HCl to a  $CH_4-O_2$  feed to facilitate C-H bond activation under mild conditions, leading to the formation of chloromethanes, CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub>. The latter are oxidized in situ over the same catalyst, yielding CO and recycling HCl. A material exhibiting chlorine evolution by HCl oxidation, high activity to oxidize chloromethanes into CO, and no ability to oxidize CO, is therefore essential to accomplish this target. Following these design criteria, vanadyl pyrophosphate (VPO) was identified as an outstanding catalyst, exhibiting a CO yield up to approximately 35% at 96% selectivity and stable behavior. These findings constitute a basis for the development of a process enabling the on-site valorization of stranded naturalgas reserves using CO as a highly versatile platform molecule.

Methane, the principal constituent of natural gas, is an important energy resource and an attractive feedstock for the manufacture of chemicals and fuels.<sup>[1]</sup> However, >30% of abundant natural-gas reserves are allocated in small reservoirs and/or remote areas, wherein the high transportation costs of methane and marked capital expenditure of the existing syngas-based gas-to-liquid (GTL) technologies hamper their efficient exploitation.<sup>[1a,b,2]</sup> Consequently, copious amounts of natural gas retrieved from these stranded wells are nowadays burned to reduce anthropogenic greenhouse gas emissions-the global warming potential of CH<sub>4</sub> is > 21 times higher than that of CO<sub>2</sub>. Disparagingly, the socalled "flaring" wastes around 3.5% of the global natural gas production-a quantity worth approximately 13 billion USD and comparable to the current fraction of the world's natural gas supply used for the manufacture of commodities (<10%).<sup>[1d,3]</sup> This alarming situation calls for the development of modular, decentralized processes for the economical harvesting of stranded gas.[1b,2a]

The catalytic oxyhalogenation of methane, comprising its reaction with a hydrogen halide (HCl or HBr) and oxygen, is an attractive approach to satisfy these objectives as it enables

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direct methane functionalization under moderate operating conditions (ca. 1 bar, < 853 K).<sup>[4-6]</sup> This route has traditionally targeted the production of methyl halides (CH3Cl and CH<sub>3</sub>Br), platform molecules equivalent to methanol that can be transformed into a wide spectrum of value-added chemicals and fuels via a halogen elimination step (hydrogen halide is liberated). Recent reports demonstrate the high selectivity to halomethanes over LaOCl and CeO<sub>2</sub> in oxychlorination, and over CeO<sub>2</sub> and vanadyl pyrophosphate (VPO) in oxybromination.<sup>[4-6]</sup> Moreover, the oxyhalogenation of methane over catalysts with mild oxidizing properties, such as LaOCl in oxychlorination and FePO4 and VPO in oxybromination, led to CO as the dominant oxidation product, with only marginal CO<sub>2</sub> production.<sup>[4a,5-7]</sup> These findings hint at the extra potential of the route as an effective method to exploit the natural gas feedstock for on-purpose production of CO, which is a key building block in the manufacture of numerous commodities.<sup>[8]</sup> In this way, the highly endergonic steam reforming and coal gasification processes, commonly practiced today to obtain CO, could be substituted by an exergonic halogen-mediated process. Nevertheless, this application of the oxyhalogenation reaction has not been considered to date; this is probably due to the fact that CO was never produced at a selectivity exceeding  $50\,\%,^{[4,6,7]}$  which would necessitate a complex downstream separation train. Alternatively, a two-step process can be sought, involving selective methane oxyhalogenation over one catalyst, followed by oxidation/hydrolysis into CO over a second catalyst.<sup>[9]</sup> Although the latter step was typically studied with an aim to convert halomethanes into CO<sub>2</sub>, catalysts such as alumina and La-based materials could yield CO with a relatively high selectivity, which however depends on the nature of the halomethane.<sup>[9c]</sup> Nonetheless, integration of halomethane formation with their subsequent oxidation/ dehydrohalogenation into CO over a single catalyst is highly desirable in view of process intensification. However, a tandem process of this type is rather challenging from the point of view of catalyst design as it requires a fine balance between the catalyst activities in two reactions. In such a hypothetical process, the use of HCl as a halogenating agent would be desirable instead of HBr because of the lower corrosiveness and the much higher availability of the former.<sup>[10]</sup>

Herein, we present the one-step selective conversion of  $CH_4$  into CO via oxychlorination chemistry (Figure 1). This alternative methane valorization route 1) generates the versatile feedstock CO,<sup>[8]</sup> 2) allows for in situ HCl recycling, and 3) enables heat integration in other processing steps. Consequently, it is essential to find a catalyst showing high activity for oxychlorination of methane to chloromethanes

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**Figure 1.** CO is the chief carbonylating agent for production of a wide variety of commodities such as acids, alcohols, and isocyanates. Integration of methane oxychlorination with the selective oxidation of the thus obtained chloromethanes into CO, over a single catalytic material, is an attractive route to valorize stranded natural gas.

and strong propensity for the selective oxidation of the latter into CO under oxychlorination conditions (Figure 1).

To approach the above targeted catalytic process, a series of bulk materials with different oxidation properties,<sup>[6,11]</sup> comprising RuO<sub>2</sub>, CeO<sub>2</sub>, LaVO<sub>4</sub>, Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, and VPO, were prepared and characterized by X-ray diffraction and N<sub>2</sub> sorption, respectively (Supporting Information, Figure S1, Table S2). Their performance in the oxychlorination of methane is compared by taking the temperature at which approximately 15% CH<sub>4</sub> conversion is achieved,  $T_{15}$ , as a relative measure of their overall catalytic activity (Figure 2, top), while product distribution at this relatively low conversion level was used to fingerprint their inherent reaction kinetics (Figure 2, bottom). The results are presented on the basis of an increasing selectivity to CO, which is considered here as the principal descriptor of the catalyst performance. Based on their activity patterns, the catalysts can be classified into four different categories. The first class is represented by RuO<sub>2</sub>, a well-established HCl oxidation catalyst,<sup>[10a]</sup> exhibiting the highest activity for methane conversion as inferred from its lowest value of  $T_{15}$ . Nevertheless, the oxychlorination reaction over this material leads to a pronounced CO<sub>2</sub> formation, as can be expected from its strong propensity to oxidize CH<sub>4</sub>, chloromethanes, and possible CO intermediate, into  $CO_2$ .<sup>[6,12]</sup> On the other hand,  $CeO_2$  predominantly produces chloromethanes, in line with previous studies reporting its outstanding selectivity to these products in the oxyhalogenation reaction.<sup>[5,6]</sup> The third class of catalysts comprises mild oxidizers such as LaVO<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub>,<sup>[11]</sup> exhibiting low activity for CH<sub>4</sub> conversion (the highest values of  $T_{15}$ ; Figure 2). Although CO is the dominant oxidation product, a significant part of the chloromethanes remains unconverted even at high reaction temperatures, thus hampering the closure of the HCl loop. Finally, TiO<sub>2</sub> and VPO show inherently high selectivity to CO and moderate activity in converting CH<sub>4</sub>. The unprecedentedly suppressed CO<sub>2</sub> formation over VPO ( $\leq 1\%$  in selectivity) coupled to the low residual amounts of chloromethanes, make it a highly attractive catalyst for selective CO production from methane via oxychlorination chemistry. This unique performance of VPO and TiO<sub>2</sub> is understood with a series of catalytic tests (Supporting Information, Figure S2; Figure 3). In contrast to



**Figure 2.** Selectivity to product *j*, *S*(*j*), in the oxychlorination of methane over various catalysts at ca. 15% of CH<sub>4</sub> conversion, which is obtained at temperature *T*<sub>15</sub> indicated in the top plot. A full set of experiments is presented in Figure S2 (Supporting Information). Conditions:  $F_T/W_{cat} = 100 \text{ cm}^3 \text{ min}^{-1} \text{ g}^{-1}$ , feed molar composition CH<sub>4</sub>:HCl:O<sub>2</sub>:Ar:He = 6:6:3:4.5:80.5, and *P* = 1 bar.

CeO<sub>2</sub> and RuO<sub>2</sub>, where evolution of CO<sub>2</sub> is enhanced at high reaction temperatures (Supporting Information, Figure S2), in the oxychlorination of methane over TiO<sub>2</sub> and particularly VPO, the production of CO<sub>2</sub> remains low in a very broad temperature range (Figures 3 a,b). In the case of VPO, 33 % vield and 96% selectivity for CO are achieved at 836 K. Only trace amounts of H<sub>2</sub> are detected, while HCl conversion is <1.5% (Supporting Information, Table S3), which suggests that the biggest part of HCl is recycled in situ in a single reactor pass. The selectivity to CO and CO<sub>2</sub> generally increases and that to halomethanes decreases (Supporting Information, Figure S2; Figures 3a,b) upon raising the reaction temperature, suggesting the consecutive oxidation of the chloromethanes generated in the first oxychlorination step as the plausible pathway of CO formation. Nevertheless, the latter products might in principle evolve from the direct oxidation of methane over a catalyst. To elucidate the contribution of these two routes to the CO formation over VPO and TiO<sub>2</sub>, the direct oxidation of methane (Figure 3a, open symbols) as well as the impact of feed HCl concentration on reaction performance (Supporting Information, Figure S3) were also studied. The negligible CH<sub>4</sub> conversion over both VPO and TiO<sub>2</sub> in the direct oxidation, at temperatures which are significantly higher compared to those applied in the oxychlorination reaction, and an increase in CH<sub>4</sub> conversion upon increasing the inlet HCl concentration, demonstrates the pivotal role of HCl in activating methane and corroborates the oxidation of halomethanes as the

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*Figure 3.* Conversion of reactant *i*, *X*(*i*), and selectivity to product *j*, *S*(*j*), over VPO (blue) and TiO<sub>2</sub> (red) versus temperature in: a, b) methane oxychlorination (CH<sub>4</sub>:HCl:O<sub>2</sub>:Ar:He = 6:6:3:4.5:80.5) and oxidation (CH<sub>4</sub>:O<sub>2</sub>:Ar:He = 6:3:4.5:86.5); c, d) CH<sub>3</sub>Cl oxidation (CH<sub>3</sub>Cl:O<sub>2</sub>:Ar:He = 1:3:4.5:91.5); e, f) CH<sub>2</sub>Cl<sub>2</sub> oxidation (CH<sub>2</sub>Cl<sub>2</sub>:O<sub>2</sub>:HCl:Ar:He = 1:3:0(6):4.5:91.5(85.5)); g) HCl oxidation (HCl:O<sub>2</sub>:He = 6:3:91); and h) CO oxidation (CO:O<sub>2</sub>:HCl:Ar:He = 1:3:0(6):4.5:91.5(85.5)); g) HCl oxidation (HCl:O<sub>2</sub>:He = 6:3:91); and h) CO oxidation (CO:O<sub>2</sub>:HCl:Ar:He = 1:3:0(6):4.5:91.5(85.5)). Open symbols denote the points taken in the absence of HCl in the feed. Conditions:  $F_T/W_{cat}$  = 100 cm<sup>3</sup>min<sup>-1</sup>g<sup>-1</sup> and *P* = 1 bar.

principal source of CO over these two catalysts. To support the above-indicated consecutive pathway, the activities of VPO and TiO<sub>2</sub> in the oxidation of chloromethanes were further assessed, as presented in Figures 3c-f. In good agreement with the oxychlorination tests, CO is produced with very high selectivity (>99%) in both  $CH_3Cl$  and  $CH_2Cl_2$ oxidation over VPO (Figures 3d,f), while in the case of TiO<sub>2</sub>, the selectivity to CO observed in the oxidation of CH<sub>3</sub>Cl (ca. 90%) is lower than that obtained in the oxidation of  $CH_2Cl_2$ (>99%). Besides, the light-off curves for the conversion of chloromethanes over TiO<sub>2</sub> are shifted to lower temperatures than that over VPO, indicating its higher activity in these reactions, which at first glance contrasts the results presented in Figures 2 and 3b. This might be explained by the substantially higher activity of VPO in the HCl oxidation reaction (Figure 3h), indicating the higher propensity of this catalyst to evolve chlorine, and thus the enhanced production of the precursor chloromethanes, leading to a higher CO productivity. Inhibition of chloromethanes oxidation by HCl poisoning of TiO<sub>2</sub> (which has been reported often in the catalytic abatement of chlorocarbons over oxide materials) might also contribute to the difference in performance among the two catalysts.<sup>[9c,13]</sup> To check for the latter effect, HCl was co-fed with CH2Cl2 and O2 in the corresponding oxidation test to simulate the conditions of the oxychlorination reaction (Figures 3 e,f). The results demonstrate a significant drop in CH<sub>2</sub>Cl<sub>2</sub> conversion over TiO<sub>2</sub> in the presence of HCl, thus corroborating the inhibitory role of HCl, contributing to the inferior activity of this material compared to VPO in the oxychlorination of methane.

The differences in performance of VPO and TiO<sub>2</sub> in the oxychlorination reaction, as well as those in the oxidation of halomethanes, are further explained by evaluating their activities in CO oxidation (Figure 3h, open symbols). VPO shows much lower conversion of CO into CO<sub>2</sub> than TiO<sub>2</sub> (Figure 3h), which is likely caused by its inherently low propensity to adsorb CO.<sup>[14]</sup> Nevertheless, in analogy to the CH<sub>2</sub>Cl<sub>2</sub> oxidation, CO conversion over TiO<sub>2</sub> is substantially suppressed in the presence of HCl (Figure 3h, closed symbols), which might explain the low CO<sub>2</sub> productivity observed in the oxychlorination of methane.

Based on these results, CO production from CH<sub>4</sub> over VPO can be rationalized by a mechanism comprising HCl oxidation into Cl<sub>2</sub>, followed by gas-phase methane chlorination, which is analogous to that proposed for methane oxybromination over this material.<sup>[6]</sup> This is supported by the ability of VPO to oxidize HCl into Cl<sub>2</sub> (Figure 3g), and its low activity in the direct oxidation of methane (Figure 3a), indicating its minor propensity to cleave C-H bonds. Moreover, the temperature window of the HCl oxidation coincides with that of methane oxychlorination, suggesting that the evolved Cl<sub>2</sub> readily reacts with methane. This is in line with literature reports testifying the vigorous kinetics of methane chlorination already at 673 K,<sup>[1c]</sup> and it is also corroborated by the low Cl<sub>2</sub> concentration detected at the reactor outlet (Supporting Information, Table S3). The ability of VPO to oxidize HCl at temperatures that are comparable or even

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higher than those needed for chloromethanes oxidation is uniquely combined with its inherent propensity to suppress the oxidation of CO into CO<sub>2</sub>, eventually resulting in a highly selective production of CO from methane via the oxychlorination reaction. Notably, the oxybromination reaction over VPO yields CO as the principal oxidation product. Still, the generation of CO is generally overwhelmed by the formation of bromomethanes, even at high reaction temperatures,<sup>[6]</sup> which might be explained by significantly faster HBr oxidation compared to bromomethanes oxidation (Supporting Information, Figure S4). The exceptional CO production via methane oxychlorination over VPO is shown to be stable by a 100 h on-stream test (Figure 4a). X-ray diffraction (XRD)



**Figure 4.** a) Methane conversion and product selectivity versus timeon-stream (tos) in the oxychlorination of methane over VPO. b) <sup>31</sup>P nuclear magnetic resonance spectra by spin-echo mapping of fresh and used VPO recovered after *x* h on stream. Conditions:  $F_T/W_{cat}$ = 100 cm<sup>3</sup>min<sup>-1</sup>g<sup>-1</sup>, CH<sub>4</sub>:HCI:O<sub>2</sub>:Ar:He = 6:6:3:4.5:80.5, T = 803 K, and P = 1 bar.

analysis of the fresh and used samples recovered after different time-on-stream durations (Supporting Information, Figure S5) indicated the equilibration of the starting  $(VO)_2P_2O_7$  structure within the first 1 h of operation, which remains unaltered over the whole evaluated period of time. <sup>31</sup>P nuclear magnetic resonance by spin-echo mapping (Figure 4b) showed a major peak centered at around 2500 ppm, which is characteristic for a  $(VO)_2P_2O_7$  phase.<sup>[15]</sup> This peak is slightly broader in the case of the fresh catalyst sample, but shows no significant changes among the used catalyst, in line with XRD data. No peaks ascribed to  $V^{3\scriptscriptstyle +}$ phases (located at ca. 4700 ppm) could be observed, while a small peak located around 0 ppm, which is more pronounced in the case of used catalyst samples, indicates the presence of  $V^{5+}$  sites. This is further corroborated by temperature-programmed reduction with H<sub>2</sub> (Supporting Information, Figure S5) and X-ray photoelectron spectroscopy (Supporting Information, Table S4, Figure S6), which also point to the presence of  $V^{\text{5+}}$  sites in the surface region of all catalyst samples.

The unique performance of VPO opens a way for the development of a novel process for natural gas upgrading by exploiting CO as a versatile platform molecule. In particular, if coupled with the well-established production of formic acid, a valued chemical and highly prospective energy carrier,<sup>[16]</sup>

it could provide an effective means of bringing carbon, hydrogen, and/or energy equivalents of stranded methane reserves to the market in a liquid form. Alternatively, the onsite water-gas shift reaction of the CO–H<sub>2</sub>O mixture could generate hydrogen.<sup>[17]</sup> In this way, traditional syngas-to-chemicals transformations, such as methanol production or Fischer–Tropsch (F-T) hydrocarbon synthesis, can be practiced by circumventing steam-reforming (1073–1273 K, 20–30 bar) or auto-reforming (> 2273 K, < 100 bar) processes, which are the most energy- and capital-demanding steps of the commercial syngas generation technologies.<sup>[1,18]</sup> Moreover, H<sub>2</sub> derived from renewable sources, such as photocatalytic water splitting or biomass reforming,<sup>[19]</sup> might also be utilized.

In conclusion, we have demonstrated the first example of highly selective one-step CO production from methane via oxychlorination chemistry. Following simple catalyst design criteria-requiring that the optimal catalyst for this process should exhibit the chlorine evolution activity essential to support the formation of chloromethanes and the ability to selectively oxidize the latter into CO-various materials families possessing different redox properties were evaluated in the oxychlorination of methane. VPO, which exhibited a high selectivity to halomethanes in methane oxybromination, emerged as an outstanding catalyst for CO production via methane oxychlorination, demonstrating the complexity and versatility of oxyhalogenation chemistry. A yield of CO up to approximately 35% at 96% selectivity was achieved over this catalyst under ambient pressure and temperatures < 835 K. The exceptional performance of VPO, which was stable over 100 h on stream, constitutes the basis for development of a modular, decentralized process for the valorization of stranded natural gas by exploiting CO as a well-established platform molecule for the manufacture of value-added commodities.

#### **Experimental Section**

Commercial CeO<sub>2</sub> was treated at 1173 K, while rutile TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> were treated in static air at 873 K, respectively, prior to their use in the catalytic tests. RuO2 was prepared by thermal decomposition of RuCl<sub>3</sub> at 823 K in static air. LaVO<sub>4</sub> was synthetized by coprecipitation of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O with NH<sub>4</sub>VO<sub>4</sub>, followed by hydrothermal synthesis at 453 K for 24 h. After filtration and washing with water and methanol, the powder was dried in vacuum at 373 K and calcined at 873 K. VPO was prepared by refluxing a slurry containing V<sub>2</sub>O<sub>5</sub>, benzyl alcohol, and isobutyl alcohol for 3 h. Subsequently,  $H_3PO_4$  was added (P:V=1.2) and the slurry was refluxed for 16 h, followed by drying in vacuum at 373 K and thermal treatment at 873 K under flowing nitrogen. A heating rate of 5 K min<sup>-1</sup> and holding time of 5 h were applied in all thermal treatments of the catalysts. The catalytic tests were performed at 1 bar in a continuous-flow fixed-bed reactor set-up (Supporting Information, Scheme S1) using a catalyst weight  $W_{cat} = 1.0 \text{ g}$  (particle size = 0.4–0.6 mm) well-mixed with quartz (particle size = 0.2–0.3 mm) and a total gas flow  $F_{\rm T}$  =  $100 \text{ cm}^3 \text{STPmin}^{-1}$  at bed temperatures, T, in the range of 423– 875 K. The molar composition of the mixtures in methane oxychlorination (CH<sub>4</sub>:HCl:O<sub>2</sub>:Ar:He = 6:6:3:4.5:80.5), methane oxidation (CH<sub>4</sub>:O<sub>2</sub>:Ar:He = 6:3:4.5:86.5), and the oxidation of CH<sub>3</sub>Cl/  $CH_3Br$  ( $CH_3Cl/CH_3Br:O_2:Ar:He = 1:3:4.5:91.5$ ),  $CH_2Cl_2/CH_2Br_2$ (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Br<sub>2</sub>:O<sub>2</sub>:HCl:Ar:He = 1:3:0(6):4.5:91.5(85.5)), HCl/HBr  $(HCl:O_2:Ar:He = 6:3:4.5:86.5), and CO (CO:O_2:HCl:Ar:He = 6:3:4.5;86.$ 

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1:3:0(6):4.5:91.5(85.5)) were set using digital mass flow controllers to feed the gases, while CH2Cl2 or CH2Br2 were fed by syringe pump and a homemade evaporation unit. Concentrations of the carboncontaining compounds at the reactor inlet and outlet were analyzed online using a gas chromatograph coupled to a mass spectrometer. The concentration of H<sub>2</sub> was determined by an off-line gas chromatograph equipped with a thermal conductivity detector. The Cl<sub>2</sub> concentration was quantified using an off-line iodometric titration of the absorbing KI solution, while the HCl concentration was determined by acid-base titration after its absorption into H<sub>2</sub>SO<sub>4</sub> solution. The errors of carbon and chlorine balances were lower than 5%. The fresh and used catalysts were characterized by means of X-ray diffraction, N<sub>2</sub> sorption, X-ray fluorescence, temperatureprogrammed reduction with H<sub>2</sub>, <sup>31</sup>P nuclear magnetic resonance spinecho mapping, and X-ray photoelectron spectroscopy. More details on catalyst preparation, characterization, and testing are provided in the Supporting Information.

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## **Communications**



### **Communications**

#### Methane Valorization

V. Paunović, G. Zichittella, R. Verel, A. P. Amrute, J. Pérez-Ramírez\* \_\_\_\_\_

Selective Production of Carbon Monoxide via Methane Oxychlorination over Vanadyl Pyrophosphate



**Natural value**: Highly selective carbon monoxide production from methane over vanadyl pyrophosphate, via oxychlorination chemistry, offers a credible route by which stranded natural gas may be exploited. On-site manufacture of valueadded chemicals and fuels from a carbon monoxide feedstock is readily foreseeable.

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