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Letter

Carbon Dioxide Origin during High-Yield Partial Oxidation of Methane to Protected Methyl Esters

Andrea N. Blankenship, Alexandru-Tudor Toderaşc, Vladimir Paunović, and Jeroen A. van Bokhoven*

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ABSTRACT: Mn/TiO_2 catalysts are highly active for the partial oxidation of methane using dioxygen in acidic media to form oxidation-protected methyl esters. Nonetheless, the formation of carbon dioxide in these systems remains significant. In this study, we used ^{13}C isotope-labeled methane to trace the origin of the carbon dioxide formation. These experiments showed that carbon dioxide primarily stems from acid degradation rather than product overoxidation in this system, confirming the high-yield methane partial oxidation of the esterification approach. Evaluation of activities and selectivities of the catalysts with different initial manganese distributions under different methane partial pressures and reaction temperatures revealed that ester selectivity within the liquid products remains nearly constant, while lower temperatures minimize the parasitic overoxidation of solvent. Using this knowledge, we demonstrated that a Mn/TiO_2 catalyst synthesized via coprecipitation can provide 90% ester selectivity at 21% methane conversion within 3 h at 215 °C, representing the best reported heterogeneously catalyzed system for methane partial oxidation with molecular oxygen. This study identifies the road ahead for this chemistry, entailing further optimization of solid catalysts for improved ester productivity and high product yields while curtailing undesired side reactions unrelated to methane conversion.

$^{13}CH_4 + O_2 \rightarrow CF_3COO^{13}CH_3$ + acid, Mn/TiO_2, Selectivity; $^{12}CO_2 \gg {}^{13}CO_2$

KEYWORDS: methane, methyl trifluoroacetate, manganese, carbon dioxide, heterogeneous catalysts
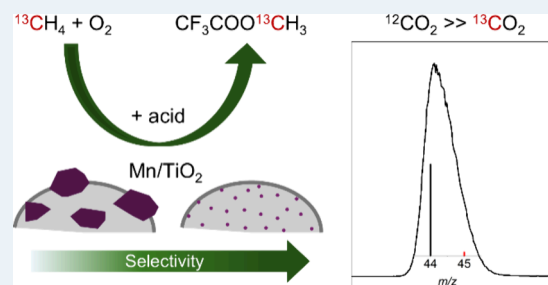
1. INTRODUCTION

Methane partial oxidation to liquid oxygenates is a highly desired pathway to produce commodity chemicals such as methanol from underutilized sources of natural gas.[1−4] Still, this reaction is constrained by several fundamental and technoeconomic challenges, most notably the steep selectivity-conversion tradeoff and requirement of affordable oxidants, such as dioxygen.[5,6] One of the only demonstrated pathways that breaks out of the selectivity-conversion limit to achieve high single-pass product yields is a protective esterification approach that preserves produced methanol within oxidation-resistant methyl esters during reaction.[4,7,8] Using this approach, we obtain ester selectivities essentially independent of methane conversion. This results in the best product yields reported for methane partial oxidation, even exceeding 70% in the case of the original Periana-Catalytica system that selectively produced methyl bisulfate with a platinum complex in concentrated H_2SO_4.[9]

Despite the promising performance of this protective pathway, little work has been done on developing practical heterogeneous catalysts that are active and use dioxygen for this chemistry.[10] Previously, we introduced two solid catalysts for the methane-to-methyl-ester (MtME) chemistry, silica-supported cobalt and titania-supported manganese, capable of producing high yields of methyl trifluoroacetate from methane. The use of diluted trifluoroacetic acid that reduces solvent

corrosivity and the use of dioxygen as the terminal oxidant are particularly attractive features.[11,12] Side reactions unrelated to methane oxidation, such as solvent degradation, have been previously reported or suspected, which may affect the overall process performance of these approaches.[13−17] In this contribution, we evaluate the contribution of the main methane partial oxidation pathway and potential side reactions toward the observed carbon dioxide production using catalytic tests and ^{13}C isotope-labeled methane for the active Mn/TiO_2 system. Through this rigorous assignment, the high selectivity of Mn/TiO_2 materials at high levels of methane conversion to methyl esters is verified.
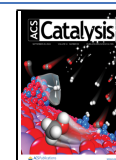
2. RESULTS AND DISCUSSION

Here, we further examine the active Mn/TiO_2 catalyst system by preparing two series of catalysts using common preparation methods, resulting in significantly different Mn incorporation and distribution over the support. Based on the originally published Mn/TiO_2 system, TiO_2 currently remains the best

candidate for the support due to its apparent ability to stabilize Mn and preclude significant leaching of Mn, thereby heterogeneously catalyzing the MtME reaction. The catalysts in this study were first prepared via wetness impregnation, denoted Mn/TiO_2-WI. Both STEM EDS and XRD show large manganese aggregates on the titania surface at both 4.4% and 8.7% Mn loadings (Figure 1a-d, Figure S1). To further
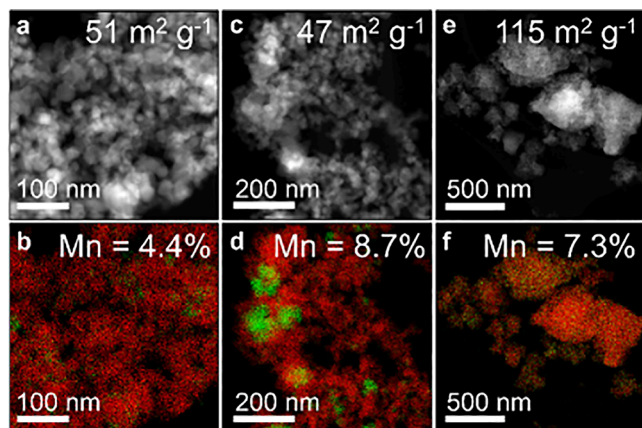

Figure 1. HAADF STEM (top) and corresponding STEM EDS map overlays (bottom) of Ti K-edge (red) and Mn K-edge (green) for Mn/TiO_2 catalysts: (a-b) 4.4% Mn/TiO_2-WI; (c-d) 8.7% Mn/TiO_2-WI; (e-f) 7.3% Mn/TiO_2-CP.

investigate the effects of Mn speciation and Mn-Ti proximity on performance, manganese and titanium precursors were coprecipitated to create a catalyst with Mn embedded in the bulk titania matrix, denoted Mn/TiO_2-CP. In contrast to the large Mn aggregates on Mn/TiO_2-WI, the 7.3% Mn/TiO_2-CP material contains a highly dispersed but not fully uniform mixture of Mn within the titania matrix, with no observable manganese oxide phases via STEM EDS and XRD (Figure 1e-f, Figure S1). At the 8.7% loading, Mn/TiO_2-WI produces both methyl trifluoroacetate (MTFA) and formic acid within the liquid fraction, with a total liquid oxygenate productivity of 1200 μmol g^{-1} h^{-1} and 89% selectivity to MTFA within the liquid products under the standard reaction conditions at 215 °C (Figure 2a). Nearly 200 μmol of CO_2 evolved during the reaction, which was the only gas phase product detected in quantifiable amounts. With the 7.3% Mn/TiO_2-CP catalyst, the liquid product productivity substantially improved by ca. 20% to 1430 μmol g^{-1} h^{-1}, with 90% selectivity to MTFA in the liquid fraction (Figure 2c). The increased formation of product in combination with a lower concentration of Mn in 7.3% Mn/TiO_2-CP suggests improved utilization of Mn at high loadings when finely dispersed within high surface area TiO_2 (ca. 115 m^2 g^{-1}). Resolving specific active Mn structures on the surface of both catalyst types with advanced spectroscopic methods is outside the scope of this letter. Again, CO_2 evolved during the reaction in similar quantities as the 8.7% Mn/TiO_2-WI (210 μmol). Insignificant levels of manganese were detected postreaction in the filtered reaction medium, confirming the heterogeneous character of both catalysts.

The necessity of trifluoroacetic acid (TFA) as a protecting agent is confirmed by the observation that no liquid oxygenates are formed in the absence of this component. Without TFA in the reaction medium, only CO_2 is formed at a productivity of ca. 630 μmol g^{-1} h^{-1}, which is less than half of the MTFA

productivity in the presence of TFA for 7.3% Mn/TiO_2-CP. The absence of any liquid oxygenates, such as methanol and formic acid, confirms the expectation that any unprotected products will quickly undergo further oxidation under the reaction conditions. Therefore, to preserve the partial oxidation products, even at low methane conversion levels below 1%, the protective esterification approach using TFA is essential. Lower CO_2 production in the absence of TFA than MTFA formation in the presence of TFA also implies that TFA has an influence on the catalyst activity beyond its role as an esterification agent.

Previous studies using homogeneous transition metal complexes for the MtME reaction have attributed CO_2 production to solvent degradation via TFA decarboxylation.[13,16,17] Coutard et al. have even proposed solvent degradation as a step in the MtME catalytic cycle with Mn-complexes derived from Mn-oxides.[17] However, no definite studies exist of solvent degradation during MtME using heterogeneous catalysts, for which the support material and its interaction with active Mn may be influential. Upon replacing methane in the feed with an inert for both 8.7% Mn/TiO_2-WI and 7.3% Mn/TiO_2-CP, CO_2 production significantly increases by ca. 37% and 77%, respectively, while no liquid products are formed (Figure 2a,c). These observations strongly suggest that the primary origin of CO_2 is from side reactions unrelated to methane oxidation. The increase in CO_2 formation upon the removal of methane may further suggest competition between methane and other present species, such as TFA, for available active Mn sites.

Given that a key attribute of MtME chemistry is the ability to preserve MTFA selectivity at high levels of methane conversion, we sought to unambiguously assign the origin of CO_2 and gain an accurate estimation of the total selectivity to MTFA using isotopically labeled methane ($^{13}CH_4$). The WI and CP catalysts were tested under methane-limited conditions for extended reaction times to evaluate product selectivity under high conversion conditions, for which the proportion of CO_2 evolving from product overoxidation is expected to be at its highest. For both 4.4% Mn/TiO_2-WI and 7.3% Mn/TiO_2-CP, the produced quantity of CO_2 exceeds the $^{13}CH_4$ input, which clearly indicates that CO_2 is formed from another carbon source rather than methane. The percentage of $^{13}CO_2$ in the gas-phase postreaction was determined via mass spectrometry to be 3.9% and 2.7%, respectively, and the ^1H NMR of the extracted liquid phase displays the characteristic C-H splitting of ^{13}C-containing MTFA (Figure 3a-d). Given the natural abundance of ^{13}C to be around 1.1% and $^{13}CH_4$ purity of 99%, the percentage of CO_2 originating from methane is calculated to be 2.9% and 1.6%, respectively. MTFA was the only liquid product formed under these conditions. These results show that only a very small fraction of produced CO_2 originates from methane overoxidation, and the methyl group of the product ester is derived from methane. Importantly, this result confirms that the catalyst does not readily further oxidize protected MTFA, in contrast to the catalytic trials at lower conversion levels in the absence of the TFA protectant, in which CO_2 was the only final product (Figure 2c). Accounting for methane-derived CO_2 results in a total selectivity to MTFA of ca. 64% and 90% for 4.4% Mn/TiO_2-WI and 7.3% Mn/TiO_2-CP, respectively, at 215 °C and low methane partial pressures. Therefore, both Mn/TiO_2 catalysts are highly active for methane conversion and successfully preserve partial oxidation products with selectivity
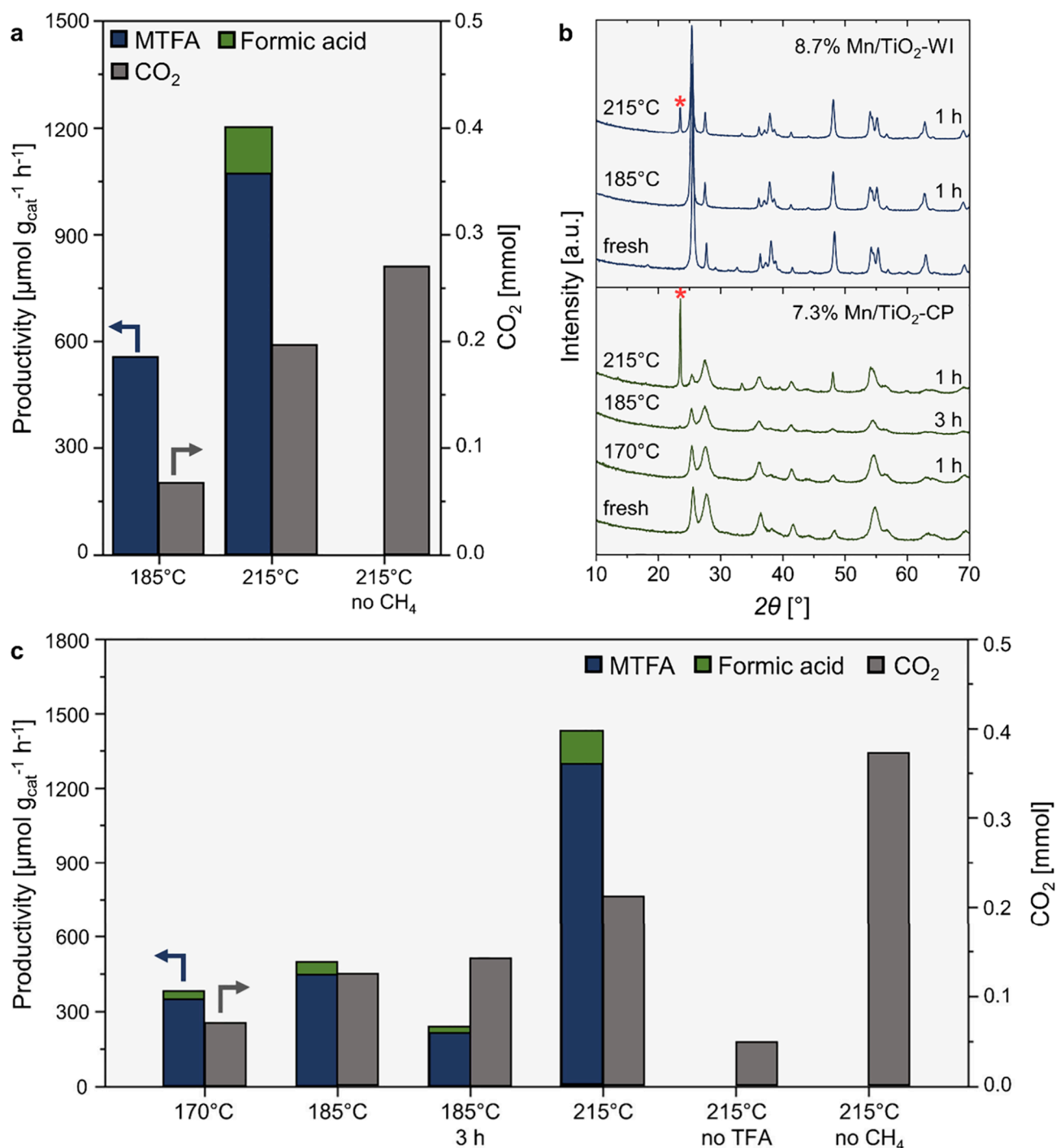
Figure 2. (a) Productivity and CO_2 production of 8.7% Mn/TiO_2-WI under various reaction conditions; (b) XRD of 8.7% Mn/TiO_2 and 7.3% Mn/TiO_2-CP fresh and postreaction under various condition, red marker indicates the main Bragg reflection of $TiOF_2$; (c) Productivity and CO_2 production of 7.3% Mn/TiO_2-CP under various reaction conditions.

above 60% at extents of methane conversion exceeding 20%, which notably surpasses the achieved yields of all other recently published heterogeneous catalysts for methane conversion using only dioxygen within the field of thermocatalysis (Figure 4).[10] Therefore, Mn/TiO_2 catalysts are excellent candidates for applying the protective esterification approach. An obvious disadvantage, however, is the solvent degradation, which is significant, especially under the conditions for high levels of methane conversion.

Although solvent degradation has been previously observed in homogeneous systems, very little has been done to understand how catalysts and reaction conditions may influence the contribution of this undesired side reaction. Compared to a homogeneous Mn complex under similar conditions, heterogeneous Mn/TiO_2 catalysts demonstrate substantial reduction of TFA degradation normalized to both Mn content and turnovers (TO). Under high conversion conditions, $Mn_2(TFA)_4(HTFA)_4$ produces excessive CO_2 resulting from primarily TFA degradation, around 15.25
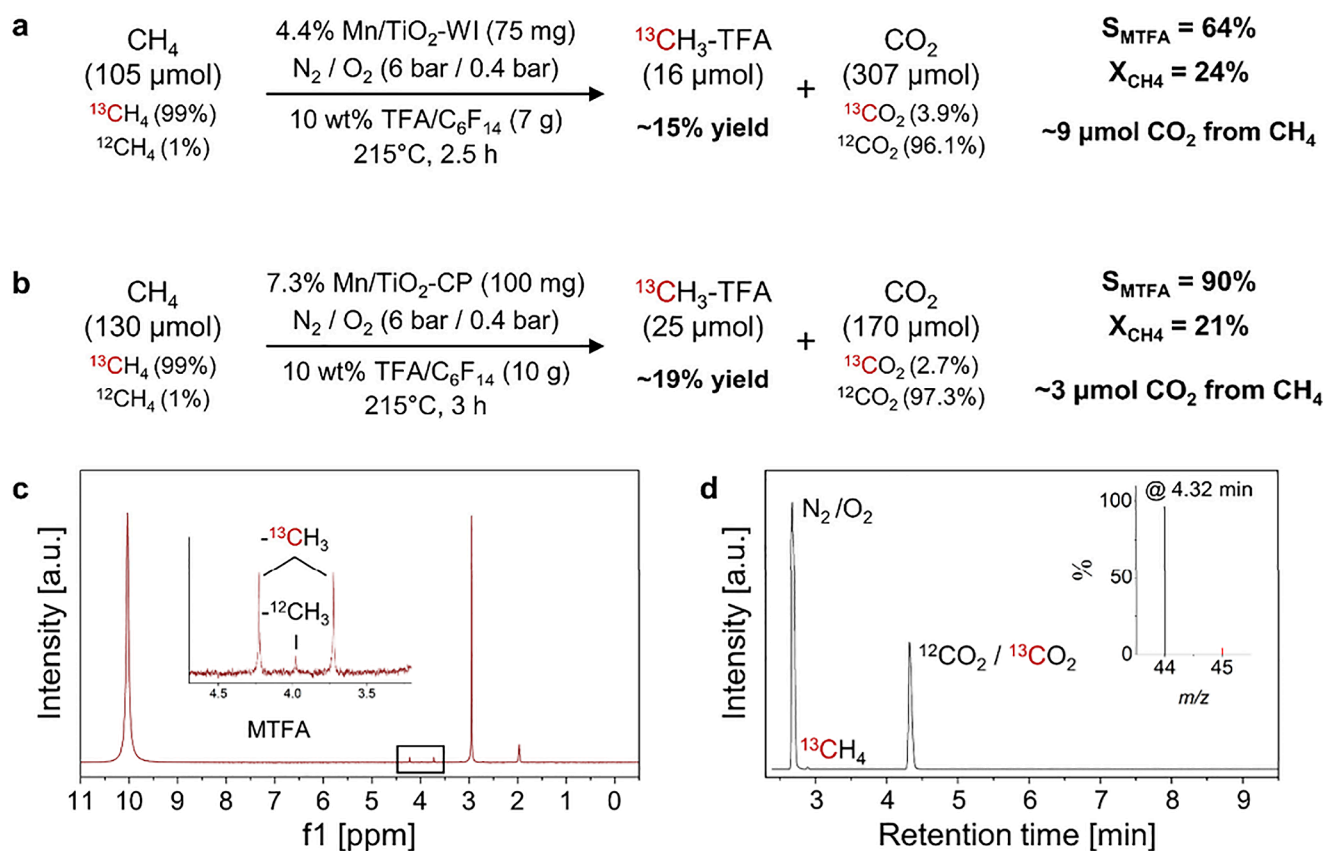
Figure 3. Summary of high conversion $^{13}CH_4$ trials for a) 4.4% Mn/TiO$_2$-WI and b) 7.3% Mn/TiO$_2$-CP; c) ^{1}H NMR of the extracted liquid products; d) GC-MS chromatogram of the collected gas products.
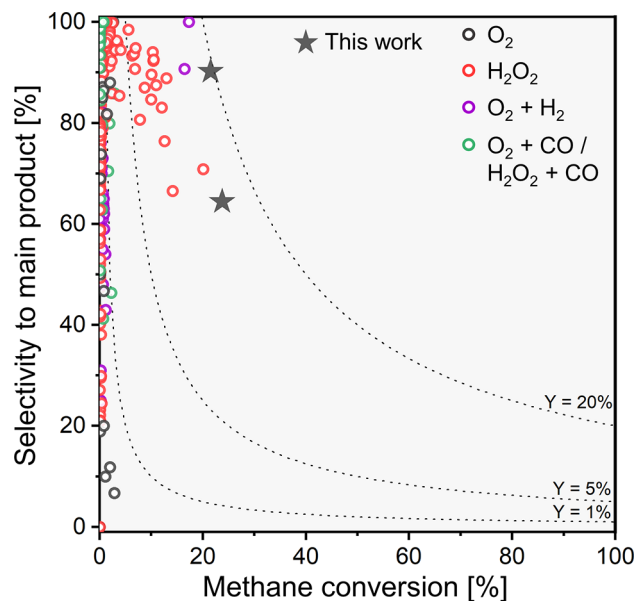

Figure 4. Selectivity versus methane conversion for heterogeneous catalytic systems delineated by terminal oxidant, adapted with permission from ref 10. Copyright 2023 Springer Nature. Performance of Mn/TiO$_2$ from this study is denoted with stars.

mol_{CO_2} mol_{Mn}^{-1} or 2.77 mmol per TO (TO = $mol_{product}$ mol_{metal}^{-1}) at ∼ 20% methane conversion (Table 1). In contrast, 7.3% Mn/TiO$_2$-CP selectively produces MTFA with less tangential CO$_2$ production, around 1.26 mol mol_{Mn}^{-1} and 0.88 mmol per TO also at ∼21% methane conversion, despite

an increased reaction temperature and O$_2$/CH$_4$ ratio that would be expected to favor increased product and TFA degradation.[14] Under the original methane-excess conditions, the amount of CO$_2$ produced relative to MtME activity is even lower, around 0.19 mmol per TO. The compatibility of Mn/TiO$_2$ performance in terms of MTFA yields and CO$_2$ produced per turnover under conditions with a high excess of dioxygen is particularly promising, as other high-interest methane partial oxidation systems tend to be particularly sensitive to the high oxidant concentrations required for high single pass yields.[18] Although a detailed mechanistic understanding of solvent degradation during MtME conditions remains challenging, these findings provide the first insights into facile ways to reduce the TFA degradation side-reaction without compromising MtME activity by using supported transition metal catalysts in dilute acid solvents.

In addition, the relationship between productivity, CO$_2$ production, and reaction temperature was investigated for Mn/TiO$_2$-WI and Mn/TiO$_2$-CP. Under the original methane-excess conditions, 8.7% Mn/TiO$_2$-WI and 7.3% Mn/TiO$_2$-CP were further screened at temperatures between 170 and 215 °C (Figure 2a, c). Notably, both catalysts remain considerably active even upon a decrease in reaction temperature of 45 °C. The selectivity to MTFA in the liquid products remains constant around 90% upon a temperature increase from 170 to 215 °C. However, the CO$_2$ production from side reactions decreases from about 210 μmol to 70 μmol upon a decrease of 45 °C for 7.3% Mn/TiO$_2$-CP and from 195 μmol to 65 μmol upon a decrease of 30 °C for 8.7% Mn/TiO$_2$-WI. For 7.3% Mn/TiO$_2$-CP, extending the reaction time from 1 to 3 h at 185 °C results in an increase in yield for all products and a similar

Table 1. Comparison of Total Carbon Dioxide Production for Manganese Catalysts Using Dioxygen as Oxidant in MtME

Catalyst	Experimental Conditions	Methane Conversion [%]	CO_2 [mol mol_{metal}^{-1}]	CO_2 [mmol TO^{-1}][a]
7.3% Mn/TiO_2-CP	$T = 215$ °C $O_2/CH_4 = 3.24$ $t = 3$ h	~21	1.26	0.88
7.3% Mn/TiO_2-CP	$T = 215$ °C $O_2/CH_4 = 0.07$ $t = 1$ h	<5	2.11	0.19
4.4% Mn/TiO_2p-WI	$T = 215$ °C $O_2/CH_4 = 4.35$ $t = 2.5$ h	~24	4.96	1.12
8.7% Mn/TiO_2-WI	$T = 215$ °C $O_2/CH_4 = 0.07$ $t = 1$ h	<5	1.64	0.25
8.7% Mn/TiO_2-WI	$T = 185$ °C $O_2/CH_4 = 0.07$ $t = 1$ h	<5	0.56	0.19
$Mn_2(TFA)_4(HTFA)_4$[17]	$T = 180$ °C $O_2/CH_4 = 0.73$ $t = 2$ h	~20	15.25	2.77

[a]$TO = mol_{product}\ mol_{metal}^{-1}$

ratio of MTFA to formic acid within the liquid fraction (90.6% and 88.7%, respectively), excluding the significant product overoxidation at extended reaction times. However, the average productivity to liquid oxygenates decreases from 490 μmol g^{-1} h^{-1} after 1 h to 290 μmol g^{-1} h^{-1} after 3 h.

Furthermore, reaction temperature has a large influence on the TiO_2 support observed postreaction via XRD. Postreaction at 215 °C, a fraction of the original anatase TiO_2 in the materials is converted to a new $TiOF_2$ phase. Notably, this phase is hardly observed postreaction at the lower temperatures, even for extended reaction periods up to 3 h (Figure 2b), implicating increased stability of the initial TiO_2 anatase phase in the acidic environment. Based on the available catalytic data, no direct correlation between the $TiOF_2$ phase and catalyst deactivation can be observed. All together, these observations positively suggest that parameters such as methane partial pressure, reaction temperature, and the reaction medium may be further optimizable along with catalyst properties to enhance MtME activity while reducing the influence of side-reactions on the overall product distribution and catalyst structure.

Scheme 1 summarizes proposed general mechanisms for methane conversion in the presence of TFA over Mn/TiO_2. Metal oxides are capable of activating methane via heterolytic splitting of the C−H bond to form surface methyl and hydroxyl groups, with the former further reacting with oxygen species to form a methoxy group.[19,20] In the absence of the TFA protectant, the surface methyl and methoxy species can readily undergo further oxidation to CO_2. Based on our observations of an increase in the level of CO_2 upon the removal of methane, we propose the competitive adsorption of TFA onto metal oxide surface sites, which may further form other surface trifluoroacetate species. Neighboring methoxy and trifluoroacetate species are expected to form the protected methyl ester, and this process should proceed quickly in alignment with the isotopic $^{13}CH_4$ tests that demonstrated the predominance of esterification over overoxidation pathways under high conversion conditions. Finally, we observe that the dominant pathway for CO_2 production is via TFA degradation, which others have proposed may proceed with the assistance

Scheme 1. Proposed Mechanisms for the MtME reaction over Mn/TiO_2
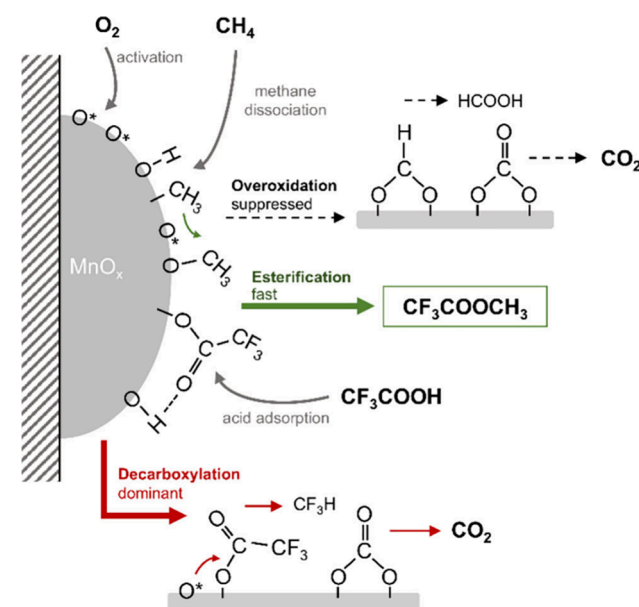
of surface oxides.[21] However, especially in comparison to the considerable CO_2 concentrations we observe postreaction, we could only detect CF_3H in very trace amounts.

Other degradation pathways for TFA not detailed may account for the formation of $TiOF_2$ with the anatase TiO_2 phase. Further study of this system is necessary to refine the mechanisms, especially the TFA degradation pathways that should be minimized for viable process concepts based on the MtME reaction.

3. CONCLUSION

In conclusion, the evidence provided in this study of Mn/TiO_2 catalysts strongly confirms that they are highly active and compatible with a protective esterification approach. The protection of methyl derivatives during reaction with TFA remains an effective product protection strategy for dioxygen-

using heterogeneous catalysts, with a record high methane-based product yield of around 19% achieved within 3 h. Mn/TiO$_2$ catalysts with highly dispersed manganese in a TiO$_2$ matrix show improved MTFA productivity under methane-excess conditions and demonstrate exceptional ester selectivity of ca. 90% at 21% conversion. Isotopic labeling experiments reveal that carbon dioxide evolved during the reaction predominately arises from TFA decomposition that is independent of the main methane oxidation pathway, which is a known challenge for the MtME reaction. This study shows that key conditions, such as methane partial pressure and reaction temperature, can be modified to reduce the impact of this side reaction relative to MtME activity. Importantly, the conversion of Mn/TiO$_2$ in dilute acid solvents already shows robust improvements while also functioning at much higher dioxygen concentrations compared to homogeneous analogues. These results provide insights into directions to further improve the promising MtME chemistry to achieve high yield methane valorization using dioxygen, while addressing the remaining challenges of this pathway in developing active solid catalysts and minimizing undesired side reactions. Addressing the structure and nature of active sites present on both Mn/TiO$_2$-WI and Mn/TiO$_2$-CP should be undertaken in future work. To accomplish this, further development of spectroscopic setups to be compatible with the MtME conditions is needed to identify and monitor the relevant surface intermediates and active sites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.4c04105.

Methods and materials, characterization details, XRD patterns of fresh catalysts (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

MtME   methane-to-methyl-ester
TFA   trifluoracetic acid
MTFA   methyl trifluoroacetate
NMR   nuclear magnetic resonance
XRD   X-Ray diffraction
HAADF   high-angle annular dark-field imaging
STEM   scanning transmission electron microscopy
EDS   energy-dispersive X-ray spectroscopy

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