Discovery of a Fischer-Tropsch Hybrid Reaction: Hydrogenation of Methylformate to Long-Chain Hydrocarbons with Anderson-Schulz-Flory Chain Length Distribution

Viacheslav lablokov^[a] and Norbert Kruse^{*[a]}

We report on the formation of chain-lengthened hydrocarbons through hydrogenation of methyl formate over a Co/MgO heterogeneous catalyst and provide time-dependent product spectra through Chemical Transient Kinetics. The results bear striking similarities with the CO hydrogenation over the same catalyst under essentially identical reaction conditions. Accordingly, hydrocarbons are mainly composed of straight paraffins besides smaller amounts of iso-products and olefins. The kinetic analysis demonstrates methyl formate to undergo dissociative chemisorption and reaction rather than hydrogenation as a molecule. The initiation of C₂₊ hydrocarbon chain lengthening occurs time-delayed and is correlated with gaseous CO and CO₂ formation. Straight paraffins appear sequentially with about 1... 2 s time increments between successive homologues. The chain growth follows polymerization-type kinetics according to Anderson-Schulz-Flory, similar to the Fischer-Tropsch reaction of CO hydrogenation.

One of the most striking examples where advanced engineering know-how meets insufficient understanding of the underlying chemical reaction mechanisms is the Fischer-Tropsch (FT) synthesis of chain-lengthened hydrocarbons. This synthesis, dating back to original work in the twenties of the past century,^[1,2] leads to fuel-type products (synfuel) in one procedural step starting from carbon monoxide-hydrogen gas mixtures (syngas) and using a solid catalyst on the basis of either cobalt or iron metal in large-scale industrial applications. While there is general agreement that a polymerization-type reaction mechanism is in operation, the question for the chemical nature of the inserting monomer and the respective target chemical bonds have been a matter of debate for decades.[3-5] This lack of established knowledge is particularly inhibiting in view of emerging FT process variants which aim at directing the synthesis to light olefins,^[6,7] for example, or long-chain alcohols^[8] and aldehydes^[9] through the use of advanced catalyst

[a] Dr. V. lablokov, Prof. N. Kruse
Voiland School of Chemical Engineering and Bioengineering
Washington State University
155 A Wegner Hall
Pullman, WA 99164-6515 (USA)
E-mail: norbert.kruse@wsu.edu

preparation techniques. Notwithstanding the deficits in molecular-level understanding, the various opinions on the mechanistic pathways may be categorized by either claiming immediate or delayed carbon monoxide dissociation while composing hydrocarbon skeletons along with their functionalization. In a previous communication by our group, evidence was reported from in-operando transient response measurements that, while carbon monoxide (CO) may undergo immediate (or hydrogenassisted)^[10] dissociation to construct the active phase of the cobalt-based catalyst, a CO insertion mechanism is in operation involving formate- and carboxylate-derived species as key intermediates of the FT synthesis. In this case, chain-lengthened hydrocarbons are formed from delayed intramolecular C-O bond dissociation during hydrogenation of such intermediates. It would therefore appear congruous to investigate the hydrogenation of organic esters containing O-C-O moieties from the start, to either support or discard the "late version" of CO dissociation in hydrocarbon production. We chose formic acid methyl ester, O=CH-O-CH₃ (methyl formate or "Mf") for this purpose and will demonstrate that chain-lengthened hydrocarbons can indeed be formed from Mf with high yield under mild reaction conditions.

From the perspective of synthetic organic chemistry, the hydrogenation of organic esters is actually an important reaction and can be designed to produce alcohols with high selectivity under mild and environmentally benign conditions. Homogeneous catalysts based on ruthenium hydride complexes with NPN pincer ligands demonstrated that this reaction occurred in the absence of solvents and other additives.[11,12] More recently, NP non-pincer manganese complexes have also been demonstrated to turn esters into alcohols.^[13] The hydrogenation of methyl formate is of particular interest, since it may be designed to produce methanol with high yields under considerably less stringent conditions^[11] than those applied in the high-pressure synthesis using heterogeneous Cu/ZnO-based catalysts. Furthermore, methyl formate may be considered a potentially important C1 building block for a variety of processes.^[14] Interesting examples of the large-scale use as a C1 supplier are the (non-catalytic) carbonylation of ammonia and dimethylamine to produce formamide or dimethyl formamide, respectively. Carbonyl transfer during heterogeneous methyl formate decomposition and reaction to produce C_{2+} chainlengthened chemicals has never been reported, to the best of our knowledge. The present communication will demonstrate that straight hydrocarbons up to C_8H_{18} (and beyond) can be

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.201802045

formed through hydrogenation according to a polymerizationtype growth mechanism following the Anderson-Schulz-Flory (ASF) formalism. Our observations are in agreement with CO playing the role of the inserting monomer as suggested for the homogeneous hydroformylation process over ligand-substituted transition metal carbonyl complexes^[15] or, more recently, for the CO hydrogenation over heterogeneous Co-based catalysts.^[16]

ChemPubSoc

Our experiments have been carried out under atmospheric pressure conditions using a Co/MgO (atomic ratio Co:Mg=10) catalyst. We note that MgO here plays the role of a dispersant rather than that of a generic support material (for details of the catalyst preparation see the Methods). To provide insight into the reaction steps enabling methyl formate hydrogenation to long-chain hydrocarbons, we applied Chemical Transient Kinetics (CTK) as a relaxation-type method allowing the construction ("build-up") of the catalytically active phase to be followed with time until the steady-state of the reaction is reached. Catalytic action is thereby triggered by switching the molecular flow abruptly from a non-reactive gas mixture (H_2, H_2) using Ar as reference) to a reactive one (methyl formate $+ H_{2}$, using helium as reference). Conversely, once steady-state conditions of the catalytic reaction are reached, the reactive gas flow can be swiftly replaced by a non-reactive one to monitor the decay of the catalytic process and the scavenging of the catalytically active phase. Characteristic time constants for the formation and the decay of reaction products become measurable during build-up or scavenging, respectively.[17,18] In the present communication, which aims at demonstrating a Fischer-Tropsch-akin valorization of methyl formate hydrogenation, we will focus on the build-up phase and scrutinize the sequence of product formation. He and Ar references help calibrate the molecular flow conditions and characterize the reactor response behavior.

Figure 1 shows CTK results for the hydrogenation of methyl formate over Co/MgO (10:1 at% of metal) at 220 °C. As can be seen, all reactant and product gases appear delayed as



Figure 1. CTK build-up for the hydrogenation of methyl formate (Mf) hydrogenation over Co/MgO. Reaction conditions: 220 °C, atmospheric pressure, $D_{tot} = 50 \text{ cm}^3 \text{min}^{-1}$, $H_2/Mf = 2 \text{ Mf}_{theor}$ describes the scaled Ar reference response.

compared to the theoretical methyl formate signal that represents the scaled He response of the reaction vessel. Remarkably, parent methyl formate only appears about 90 s after its introduction into the reaction vessel (since the H_2 molecular flow is kept constant during the entire experiment, we do not show it in Figure 1).

Methyl formate (Mf) conversion under steady-state conditions is about 68% (reaction rate = 9.4 μ mol_{Mf}g_{Co}⁻¹s⁻¹, or turnover frequency $TOF = 0.07 \text{ s}^{-1}$, see SI). Various reaction products appear earlier during CTK, meaning that a direct hydrogenation of molecularly adsorbed methyl formate can be discarded. Instead, Mf must be assumed to dissociate before reaction. The first product seen in the mass spectrometer is methane (besides much smaller amounts of water). Its delay time relative to the theoretical Mf signal (scaled He) is short. The easiest way to explain early methane formation would be to assume O-CH3 bond dissociation in O=CH-O-CH3 and hydrogenation of the resulting methyl groups. However, such a scenario is neither compatible with earlier surface science work of Mf adsorption on Ni^[19] nor with CTK studies in which methyl formate is subject to reaction with deuterium rather than hydrogen (see SI). In this case fully deuterized methane appears first while mixed $CD_{4-x}H_x$ (x=1-3) appear in sequence, with CH₄ not being formed at all. To explain this finding, "deep" decomposition of methyl formate to provide carbon (and oxygen/hydrogen) atoms must occur during the early stages of the adsorption process, similar to conclusions by Zahadi et al.^[19]

Remarkably, methane production in Figure 1 reaches a maximum after about 25 s (with respect to the He reference) before decreasing to steady-state levels for reaction times longer than 90 s. This behavior is very similar to measurements with CO/H₂ reactive feeds published earlier^[16] and suggests different formation mechanisms are in operation before (early) and beyond the maximum (late). Such mechanistic change with time is understandable since selective methane formation through carbon hydrogenation at short times entrains an enrichment of the catalyst surface with adsorbed O atoms (see below). To gain more information about the chain lengthening mechanism and the order of appearance of hydrocarbon products, we replaced simple mass spectrometry (MS) by combined MS/gas chromatographic (GC) analytics using a 16 positions-valve at the reactor outlet with a time resolution of about 1...3 s and optimized sensitivity.

According to the respective CTK data, methyl formate hydrogenation to chain-lengthened hydrocarbons can be followed up to n-decane. The reaction occurs stepwise, in agreement with a polymerization-type process. Since C_{2+} gaseous products appear in sequence of their carbon number, the chain lengthening process must involve a C_1 monomer, which would be the case for CO. Previous CO hydrogenation studies brought forth similar results, albeit showing lower chain lengthening probabilities for a Co/MgO catalyst with the same 10:1 Co/Mg atomic ratio as used here. Figure 2 demonstrates chain-lengthened hydrocarbons to appear with time increments of +/-2 s. The detection of hydrocarbons $> C_8$ is hampered by condensation in the gas sampling loops. Interestingly, hydrocarbon formation through methyl formate hydrogenation is



Figure 2. CTK sequence of appearance of hydrocarbons during methyl formate hydrogenation over Co/MgO (10:1) at 220 °C. Same conditions as in Figure 1.

characterized by an Anderson-Schulz-Flory (ASF) distribution (up to n-octane). Linear ASF plots for C₂₊ products are typical for the Fischer-Tropsch process. The chain lengthening probability α is about 0.57, which characterizes an optimized C₅–C₉ slate of hydrocarbon formation. Thus, the catalytic hydrogenation of methyl formate under the chosen experimental conditions leads to a fuel-type mix of hydrocarbons close to the gasoline fraction (C₅–C₁₂)^[20] in one procedural step. Interestingly, methane fits the linear ASF dependence shown in Figure 3.

We also note that methanol was formed with an overall selectivity of about 2% at 220 °C. In some of our studies – they are preliminary and need to be complemented by including varying reaction temperatures – we actually also found higher amounts of methanol and olefins. This is interesting in that both homogeneous^[11,12] and heterogeneous^[21,22] hydrogenation



Figure 3. Anderson-Schulz-Flory plot for chain-lengthened products at steady-state of methyl formate hydrogenation over Co/MgO (10:1). Same reaction conditions as in Figure 1 $W_n = n (1-\alpha)^2 \alpha^{n-1}$, where W_n is the mass fraction of hydrocarbon molecules containing n carbon atoms, and $\alpha = 0.57$ is the chain lengthening probability. Deviations from linearity at high n are due condensation in the sampling loops.

of methyl formate were reported to mainly produce methanol besides lesser amounts of carbon monoxide.

As mentioned above, adsorbed fragments of dissociative methyl formate chemisorption have to be considered to form active intermediates for initiating and maintaining hydrocarbon chain growth. While the main incentive of this short communication is to report on the feasibility of methyl formate hydrogenation to long-chain hydrocarbons, similar to the Fischer Tropsch reaction, some preliminary conclusions on possible reaction scenarios may be drawn from both the absolute and relative onsets of product formation during transient experiments. As already noted, early and late methane formation seem to follow different pathways. To develop a molecular picture of possible reaction scenarios, both absolute and relative onsets of product formation must be examined. As already noted, early and late methane formation most probably follow different pathways. Only the early route seems to involve hydrogenation of surface carbon liberated during Mf decomposition. Asymmetric product formation - the quantities of methane are not balanced by those of water, although both products appear with an identical delay time, see Figure 1 lead to the accumulation of surface oxygen (and hydrogen). Only after another ~25 s reaction products other than methane and water are detected. These general statements suggest a rather complex chemical "conditioning" of the catalytically active phase to take place involving the formation of C_xO_yH_z moieties. Assuming high reactive sticking probabilities for methyl formate adsorption,^[19] time-integrated outlet flows (Figure 1) indicate saturated surface coverages are being built up within the first 25 s time-on-stream. Hydrocarbon chain lengthening therefore essentially takes place under conditions of high surface coverages.

Very similar to our CO hydrogenation results over Co/MgO catalysts,^[16] a remarkable feature in Figure 1 is the coincidence of CO appearance in the gas phase and chain lengthening to C2+ hydrocarbons. Furthermore, methane formation reaches a maximum once gaseous CO transients start forming. Last but not least, both CO and CO₂ formation are triggered after identical delay times. These observations lead us to hypothesize that, similar to CO hydrogenation, a CO insertion mechanism is responsible for chain lengthening, with formate-type species playing the role of the most abundant surface intermediate ("masi"). Such species have been previously reported in IR vibrational studies of methyl formate adsorption on Ni(111),[19] Cu/SiO₂^[22,23] or, respectively, during CO hydrogenation over Co/ MgO (10:1 at% of metal).^[24] To the best of our knowledge, there have been no such studies of methyl formate adsorption using Co-based catalysts. According to Zahidi et al.,^[19] surface layers generated by sole methyl formate adsorption on Ni (111) contain $H_{ad},\ CO_{ad}$ and $CH_{3}O_{ad}.$ On Co particle surfaces, at a reaction temperature of 220 $^\circ\text{C},\ \text{CO}_{ad}$ (or $\text{COH}_{ad})$ will partly dissociate to form CH_{ad} and OH_{ad} in the presence of hydrogen.^[10] Such a reaction mechanism would give way to (early) methane formation via CH_{ad} hydrogenation. As previously argued, in the absence of balancing water formation, O_{ad} and OH_{ad} participate in the chemical construction of the catalytically active phase during CTK build-up. While some O_{ad} may undergo



reaction with CO_{ad} to form CO_2 , OH_{ad} may be suggested to suffer CO insertion to form $C_xO_yH_z$ species (for x = 1, y = 2 and z = 1, these would correspond to formate) which can be either hydrogenated to (late) methane or transformed into higher carboxylate-type homologues. Chain lengthening according to this scenario would then essentially come down to repetitive CO insertion into the O–R bond of alkoxy according to Equation (1):

$$R-O_{ad} + CO \rightarrow RCOO_{ad} \tag{1}$$

followed by hydrogenation to R'H and formation of water, as suggested previously.^[16] Although incomplete and subject to further investigations, the mechanistic considerations presented above are in agreement with the detailed time dependence observed in Figure 1. To elucidate the fairly complex mechanistic pathways, we suggest performing further measurements with isotope-labelled methylformate, DCOOCH₃ and H¹³COOCH₃, using either H₂ or D₂ to induce hydrogenation. Preliminary CTK results of methyl formate hydrogenation with deuterium to isotope-exchanged methane are discussed in the SI.

It should also be noted that the observed hydrogenation activity of methyl formate is dependent on temperature, with an onset of C_{2+} hydrocarbon formation at about 190 °C. We have noticed that the minor presence of oxygen and/or water may lead to significant methanol production. The operational conditions under which methanol is formed are always milder than those reported earlier for the hydrogenolysis of methyl formate^[21] or the transformation of fatty acid esters to the corresponding alcohols using heterogeneous catalysts.^[25] With regard to possible support effects, essentially the same CTK response as that shown in Figure 1 has been observed for Co/ SiO_2 catalysts at 220 °C (see SI). While there are activity and selectivity changes, the occurrence of chain lengthening seems to be independent of the nature of the support. In contrast, however, exchanging the Co/MgO catalyst for silicon carbide in the absence of any catalytically active material provided no catalytic reactivity at all.

In summary, we discovered the catalytic hydrogenation of methyl formate to chain-lengthened hydrocarbons and provided insight into the microkinetics of this unprecedented reaction. The interpretation of transient response times is straightforward since the chemical reactor used in our studies is operated under nearly gradient-free conditions. This is a clear advantage over previous designs that entrained a plug-flow through-catalyst behavior of the reaction zone. In the absence of such significant "chromatographic effects", our CTK data evaluation needs no "compartmental" treatment as suggested by Biloen and Sachtler in their classical study of transient effects in isotope exchange under steady state reaction conditions.^[26] Instead, the catalyst bed reacts uniformly, which enabled us to measure characteristic time constants for individual reaction steps without data "aftertreatment". The CTK response patterns for methyl formate and carbon monoxide hydrogenation are strikingly connatural and suggest similar reaction mechanisms for hydrocarbon chain lengthening to apply in both types of reactions. Our future efforts will include a rigorous kinetic analysis of back-transient behaviors in terms of decay times for the scavenging of the catalytically active phase. Isotope labelling experiments will be carried out and the absolute coverages in terms of carbon, oxygen and hydrogen atoms ("atom counting") at any instant of the transient response will be determined according to well established procedures previously developed.^[16] The results obtained so far demonstrate that the classical "C–C" coupling concepts used to explain the Fischer-Tropsch product distribution do not apply to methyl formate hydrogenation. Instead, a CO insertion mechanism seems to be in operation, similar to our previous studies of the CO hydrogenation over Co/MgO catalysts.^[16]

From a more general viewpoint, the discovery of chainlengthened hydrocarbon synthesis, as described in the present communication, clearly broadens the perspectives of using methyl formate as a C₁ building block in catalytic chemistry.^[14] On the one hand, methyl formate has the potential of playing a key role in the "methanol economy" of the future.[27] Its formation from methanol through formal CO insertion into the methanolic O-H bond, already proposed in 1919 by Christiansen,^[26] is a large-scale process mainly conduced to formic acid production. Beyond that, the physical properties of liquid methyl formate make it a convenient transport medium of carbon monoxide or syngas (CO/H₂), in explicit context with the present communication. Its decomposition can actually be managed to produce mixtures of CO and H₂ with 1:1 ratios at $300\,^\circ\!C$ to $350\,^\circ\!C$ using alkali earth metal oxides. $^{[29]}$ We have demonstrated here that methyl formate can be turned into long-chain hydrocarbons in one procedural step, i.e. without intermediate recovery of CO/H₂ mixtures for synfuel production. We anticipate that our results will effectively reorient the present-day mechanistic understanding of the Fischer-Tropsch reaction mechanism and guide the development of new process variants leading to functionalized chain-lengthened hydrocarbons as chemical feedstock.

Acknowledgements

We would like to thank the National Science Foundation for partial financial support under contract no. CBET-1438227. One of us (N.K.) acknowledges fruitful discussions with Mathias Beller (Rostock, Germany) on the possible use of alkyl formates in mechanistic studies.

Conflict of interest

The authors declare no conflict of interest.

Keywords: Fischer-Tropsch · reaction mechanism · Chemical Transient Kinetics · methyl formate hydrogenation · cobalt

 [1] F. Fischer, H. Tropsch, Ber. Dtsch. Chem. Ges. (A and B series) 1926, 59, 830–831.



- [2] BASF. Verfahren zur Darstellung von Kohlenwasserstoffen und deren Derivaten. German patent 293,787, 1913.
- [3] B. H. Davis, Fuel Process. Technol. 2008, 71, 157–166.
- [4] R. A. van Santen, A. J. Markvoort, I. A. W. Filot, M. M. Ghouri, E. J. M. Hensen, Phys. Chem. Chem. Phys. 2013, 15, 17038–17063.
- [5] R. B. Anderson, R. A. Friedel, H. H. Storch, J. Chem. Phys. 1951, 19, 313– 319.
- [6] F. Jiao, J. Li, X. Pan, J. Xiao, H. Li, H. Ma, M. Wei, Y. Pan, Z. Zhou, M. Li, S. Miao, J. Li, Y. Zhu, D. Xiao, T. He, J. Yang, F. Qi, Q. Fu, X. Bao, *Science* 2016, *351*, 1065–1068.
- [7] H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan, K. P. de Jong, *Science* **2012**, *335*, 835–838.
- [8] Y. Xiang, V. Chitry, P. Liddicoat, P. Felfer, J. Cairney, S. Ringer, N. Kruse, J. Am. Chem. Soc. 2013, 135, 7114–7117.
- [9] Y. Xiang, N. Kruse, Nat. Commun. 2016, 7, 13058.
- [10] M. Ojeda, R. Nabar, A. U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, J. Catal. 2010, 272, 287–297.
- [11] E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* 2011, 3, 609–614.
- [12] J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, Angew. Chem. Int. Ed. 2006, 45, 1113–1115.
- [13] R. van Putten, E. A. Uslamin, M. Garbe, C. Liu, A. Gonzalez-de-Castro, M. Lutz, K. Junge, E. J. M. Hensen, M. Beller, L. Lefort, E. A. Pidko, Angew. Chem. Int. Ed. 2017, 56, 7531–7534.
- [14] J. S. Lee, J. C. Kim, Y. Kim, Appl. Catal. 1990, 57, 1–30.
- [15] R. F. Heck, D. S. Breslow, J. Am. Chem. Soc. 1961, 83, 4023-4027.
- [16] J. Schweicher, A. Bundhoo, N. Kruse, J. Am. Chem. Soc. 2012, 134, 16135–16138.
- [17] N. Kruse, J. Schweicher, A. Bundhoo, A. Frennet, T. Visart de Bocarme, *Top. Catal.* **2008**, 48, 145–152.

[18] A. Bundhoo, J. Schweicher, A. Frennet, N. Kruse, J. Phys. Chem. C 2009, 113, 10731–10739.

CHEMCATCHEM

Communications

- [19] E. Zahidi, M. Castonguay, P. McBeren, J. Am. Chem. Soc. 1994, 116, 5847–5856.
- [20] G. P. van der Laan, A. A. C. M. Beenackers, *Catal. Rev.* **1999**, *41*, 255–318.
- [21] R. J. Gormley, V. U. S. Rao, Y. Soong, E. Micheli, Appl. Catal. A 1992, 87, 81–101.
- [22] D. M. Monti, N. W. Cant, D. L. Trimm, M. S. Wainwright, J. Catal. 1986, 100, 17–27.
- [23] G. Millar, C. H. Rochester, K. C. Waugh, J. Chem. Soc. Faraday Trans. 1991, 87, 2785–2793.
- [24] J. Schweicher, A. Bundhoo, A. Frennet, N. Kruse, H. Daly, F. C. Meunier, J. Phys. Chem. C 2010, 114, 2248–2255.
- [25] Y. Pouilloux, F. Autin, J. Barrault, Catal. Today 2000, 63, 87–100.
- [26] P. Biloen, J. N. Helle, F. G. A. van den Berg, W. M. H. Sachtler, J. Catal. 1983, 81, 450–463.
- [27] G. A. Olah, A. Goeppert, G. K. S. Prakash in Beyond oil and gas: the methanol economy, ed. 2, Wiley-VCH, Weinheim, 2009.
- [28] J. A. Christiansen, Method of producing methyl alcohol from alkyl formats. U. S. Patent 1, 302,011, 1919.
- [29] T. Hiratani, S. Noziri, Chem. Econ. Eng. Rev. A 1985, 17, 21-24.

Manuscript received: December 14, 2018 Accepted manuscript online: December 18, 2018 Version of record online: January 25, 2019