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Homogeneous copper-catalyzed conversion of methane to methyl trifluoroacetate in high yield at low pressure.

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Abstract: The direct catalytic oxidation of methane to oxygenates, a reaction that garners significant scientific and industrial interest, is plagued by poor methane-based yields. Some of the best homogeneous catalytic systems reported to date convert methane to methyl esters using catalysts with complex organic ligands to reach high yields at relatively high temperature (>423 K) and pressure (20-70 bar). In our study, we used a simple copper compound, copper (II) oxide, to selectively convert methane to methyl trifluoroacetate at 363 K and low pressure (5 bar) resulting in yields as high as 63% at a methane conversion of 71%. The catalyst is easily recovered by treating the spent reaction mixture with a base, and the catalytic performance of the recovered material is highly comparable to that of the fresh catalyst. In terms of turnover, copper oxide (TON=33 for ester yield of 56%) ranks higher than other simple metal compounds and is comparable to catalysts with NHC ligands. Thus, this work demonstrates the possibility of using a simple catalyst devoid of complex ligands to convert methane in high yields at low pressure.

Methane, the major component of natural gas, is, for the most part, an underused resource.^[1] The challenges in methane transportation and conversion render its valorization economically unfeasible leaving flaring as the solitary option. Industries, which use methane as a feedstock, produce methanol indirectly, first converting methane to synthesis gas (CO and H₂) and the subsequent synthesis of methanol. This two-step process is energy-intensive, requiring hiah temperatures and pressure.^[2] Hence, the quest for direct methane-conversion routes has captivated the interest of the scientific and industrial community for more than a century. One such method of methane valorization is the selective oxidation of methane to oxygenates such as methanol. However, the direct oxidation of methane to methanol (DMTM) in high yield is difficult due to the facile over-oxidation of primary oxygenates to carbon dioxide. Systems that stabilize or derivatise methanol during methane oxidation clearly outperform systems that do not incorporate specific measures for methanol protection.^[3-8] The protection of methanol in the form of an ester, such as methyl bisulfate and methyl trifluoroacetate, enables liquid homogeneous methane oxidation systems to reach high yields. Methyl ester yields of 43% and 72% were reported with mercuric bisulfate^[3] and [(2,2'-bipyrimidine)PtCl₂]^[4], respectively, as catalysts in sulfuric acid medium at 453 K and 35 bar. A more recent study demonstrated the high catalytic activity and stability of potassium tetrachloroplatinate (K₂PtCl₄) to selectively convert methane to methyl bisulfate in oleum. Under the suitable conditions, primarily dictated by the concentration of sulfur trioxide, the turnover frequency of the inorganic platinum salt was significantly higher than that of the original homogeneous version.^[7] It is particularly noteworthy that potassium tetrachloroplatinate in low concentrations with suitable concentrations of sulfur trioxide did not deactivate until

termination of the reaction. Much like the sulfuric acid-based systems, there are a number of reports on trifluoroacetic acidbased systems.^[5, 9] Palladium(II) complexes with chelating bis(NHC) ligands catalyze the conversion of methane to methyl trifluoroacetate in yields up to 980% relative to palladium in the presence of potassium persulfate.^[6] The NHC complexes were very resistant under the acidic conditions required for methane C-H activation. Methyl trifluoroacetate yields of 37% and 50% were reported with manganese oxide^[10] and cobalt acetate^[11], respectively, as catalysts in a mixture of trifluoroacetic acid and trifluoroacetic anhydride. The stoichiometry of methane oxidation to methyl trifluoroacetate with potassium persulfate as the oxidant is as follows: $CH_4 + CF_3COOCH + K_2S_2O_8 \rightarrow CF_3COOCH_3 + 2KHSO_4$

We report the homogeneous copper-catalyzed conversion of methane to methyl trifluoroacetate in high yield at low temperature and pressure. Unlike many other homogeneous systems, which use complex organic ligands, this study relies on copper (II) oxide, a simple copper compound. The activity of numerous transition metal-based catalysts, such as maganese,^[10] vanadium^[12] and cobalt^[11], was tested in the oxidation of methane to methyl trifluoroacetate. However, studies of copper-based catalysts for this process are scarce and do not aim at high methane-based yields.^[13, 14] In this contribution, we report a catalytic system that demonstrates the possibility of reaching ester yields as high as 63%. Copper(II) oxide is as an efficient pre-catalyst for the selective oxidation of methane to methyl trifluoroacetate (Table 1, Fig. 1) and dissolves easily in trifluoroacetic acid to form copper(II) trifluoroacetate. We refrained from using copper salts with organic counter-ions due to possible interferences under reaction conditions designed for C-H activation. The conversion of methane to methyl trifluoroacetate and methyl acetate esters with copper acetate as the catalyst has been reported.^[15] However, the stability of the catalyst under oxidizing conditions was mediocre. We tested the stability of copper acetate under typical reaction conditions in the absence of methane and found that more than 3 mol% of the catalyst disintegrated to form methyl trifluoroacetate and a proportionate amount of formic acid within two hours. This is undesirable in a catalytic process, which typically lasts for long periods of time. Furthermore, the ester product results not only from methane but also from side reactions that consume the catalyst, thereby distorting the actual yield. This has also been reported for palladium acetate catalysts^[16] and, hence, we abstained from using catalysts with an acetate counter-ion in oxidation reactions. In this regard, precatalysts without C-H bonds, such as cupric oxide, are attractive alternatives.

Potassium persulfate as the oxidant enables the continuous conversion of methane over long periods of time. Studies with other oxidants, such as hydrogen peroxide, often report a

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Table 1. Catalytic results of copp	er-based homogenous c	catalysts for the oxidation	of methane. [a
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Entry	Temp. [K]	K2S2O8 [M]	Catalyst [mMcu]	Reaction time [h]	Methyl ester Selectivity [%]	Methane conversion [%]
1	363	0.30	CuO (9.4)	17	91.6	43.8
2	383	0.30	CuO (9.4)	17	86.0	66.0
3	363	0.06	CuO (9.4)	17	90.6	29.1
4 ^[b]	363	0.06	CuO (9.4)	17	92.5	26.0
5	363	0.30	CuO (9.4)	3	89.5	9.3
6 ^[c]	363	0.30	CuO (9.4)	3	100	<2
7 ^[d]	363	0.30	CuO (9.4)	3	100	<1
8	363	0	CuO (9.4)	17	0	tr.
9	363	0.30	-	17	52.1	6.0
10	363	0.30	CuO (18.8)	17	88.9	71.2
11	363	0.06	Cu ₂ O (10.4)	17	91.6	35.1
12 ^[e]	363	0.15	CuO (18.8)	17	91.5	66.4
13 ^[f]	363	0.15	CuO (18.8)	17	73.6	21.7

[a] Standard reaction conditions: 5.2 bar CH₄, 23 g TFA, 5 g TFAA, 875 rpm.

[b] Using regenerated copper oxide catalyst.

[c] In presence of 0.02 M benzophenone, selectivity for methyl ester in liquid phase recorded.

[d] In presence of 0.05 M hydroquinone, selectivity for methyl ester in liquid phase recorded.

[e] 19 g TFA, 9 g TFAA

[f] Spent reaction mixture of entry 12 recycled for a second pass.

saturation in product yield within a few hours due to the much faster rate of decomposition of hydrogen peroxide.^[17] Our approach with potassium persulfate is particularly rewarding due to the stability of methyl trifluoroacetate, which is the primary product under reaction conditions. A nearly constant selectivity to the ester, independent of methane conversion (Fig. S1), indicates that the over-oxidation of the ester to carbon dioxide is strongly suppressed, facilitating the accumulation of the product during methane oxidation. Under the tested conditions, there was a linear relationship between catalyst mass and methane conversion with ester selectivity remaining fairly independent of the amount of catalyst used (Fig. S2).

At high oxidant loadings, the increase in methane conversion is not proportional to the increase in the amount of the oxidant (Fig. S3). This leveling-off suggests that the oxidant does not govern the rate-limiting step of methane oxidation at higher loadings. At high oxidant loadings (Entry 1, Table 1), the conversion in the oxidant to potassium hydrogen sulfate is approximately 15%. It is striking that, under these oxidant concentrations, the amount of catalyst has a more tangible effect on methane conversion (Fig. S2), demonstrating its role in accelerating the rate-limiting step. While most of the reactions in this study were carried out at 363 K, increasing the temperature to 383 K resulted in a significant increase in methane conversion (Entries 1-2, Table 1). The methyl ester remained stable at higher temperature, as the selectivity to methyl trifluoroacetate decreased to a minor extent (92% at 363 K and 86% at 383 K). This translates to an increase in ester yield by more than 37%. We employed a sodium hydroxide-based procedure to regenerate and recover the spent catalyst. The X-ray diffraction pattern of the regenerated catalyst closely resembles that of copper(II) oxide (Fig. S4).



 Figure 1. Comparison of product selectivity-methane conversion performance

 of the copper oxide-based catalytic system with other homogeneous systems

 reported
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 Figure
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 from^[8].

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Table 2. Comparison of homogeneous catalysts for the oxidation of methane to methyl trifluoroacetate.

Entry	Catalyst	P [bar]	TON ^[a]	Methyl ester yield [%]	Ref.
1	Pd(acac) ₂	20	3.8	n.a.	[5]
2	N N N Br N	30	30.0	n.a.	[5]
3	EuCl ₃	10	5.3	n.a.	[18]
4	FeCl ₃	10	<0.5	n.a.	[18]
5	Pd(OAc)₂/ benzoquinone/ H₅PMo₁₀V₂O₄₀	25	0.7-3	n.a.	[19]
6	[Pd(hfacac) ₂]	25-30	39.0 ^[b]	<13.7	[14]
7	[Cu(hfacac) ₂ (H2O) ₂]	25-30	13.0 ^[b]	<3.1	[14]
8	VO(acac) ₂	50	18.5	0.3	[12]
9	$H_4PV_1Mo_{11}O_{40}$	50	290	<4.4	[12]
10	$H_5PV_2Mo_{10}O_{40}$	10	128	60.2	[20]
11	CuO	5.2	33.0	56	This work

[a] Moles of product / moles of catalyst, [b] Moles of methyl trifluoroacetate / moles of catalyst.

The catalytic performance of the regenerated material was comparable to that of fresh copper oxide in terms of methane conversion and ester selectivity (Entries 3-4, Table 1).

Studies with potassium persulfate in alkane oxidation generally propose a radical mechanism due to the high probability of generating KSO4° radicals from K2S2O8. Such a radical mechanism seems to govern our system, because methane conversion was strongly suppressed in the presence of benzophenone and hydroquinone, known radical scavengers (Entries 5-7, Table 1). Control experiments performed in the absence of the oxidant showed no conversion of methane (Entry 8, Table 1). This implies that copper (II) cannot stoichiometrically oxidize methane by reducing to copper (I) and underscores the importance of potassium persulfate in methane activation. Thus, it is likely that KSO4° abstracts a hydrogen from methane to form the methyl radical. UV-visible spectroscopy is a useful technique to investigate changes in the oxidation state of copper. Cull is characterized by a d-d transition in the region of 600-800 nm which is not present in Cu¹ since it has a d¹⁰ configuration.^[21] On the other hand, absorbance at around 400 nm is associated with a metal-to-ligand charge transfer transition in Cu^I species.^[22] A UV-visible spectrum of the solution after reaction indicates Cu^{II}to Cu^I conversion during the reaction, as indicated by the appearance of an absorption band at 440 nm (Fig. S5). Thus, we postulate that copper (II) oxidizes the methyl radical to methyl trifluoroacetate and potassium persulfate facilitates the re-oxidation of Cu^I to Cu^{II} to complete a catalytic cycle. This suggests that Cu^I can also be used as a catalyst. The conversion of methane and the selectivity to the ester achieved

with cuprous oxide (Entry 11, Table 1) was comparable to that with cupric oxide (Entry 3, Table 1).

A significant reason for the non-commercialization of a direct methane-to-methanol process is poor methane-based yields. One way to address this issue is to synthesize methanol derivatives such as methyl esters to achieve yields that may suggest the feasibility of commercialization.^[8] Fig. 1 places the results of this work in the context of the numerous other homogeneous systems reported in the past and illustrates the impressive performance of this catalytic system to retain high product selectivity at high methane conversion (the sources for the data points are in Ref.^[8]). This performance was achieved at relatively low temperature and pressure compared to many of the other methane oxidation processes reported to date. Furthermore, the catalyst is a commercially available copper compound with no complex organic ligands, which are usually required to ensure the solubility of the active species by preventing the precipitation of the metal.

The copper oxide pre-catalyst achieved turnovers (TON) of up to 33. Table 2 ranks the performance of this catalytic system with a number of other catalysts for the oxidation of methane to methyl trifluoroacetate. Quantities such as conversion, yield and selectivity are well defined, making it possible to compare systems. However, TON and TOF cannot be compared directly, often due to the pronounced effects of temperature and pressure on these quantities.^[23] Our experiments were performed at considerably lower methane pressure (Table 2). Notwithstanding this limitation, Table 2 shows that copper oxide has a higher TON than other simple metal compounds. Furthermore, this is comparable to values reported for catalysts with NHC complexes. However, heteropoly acid-based catalysts have a considerably higher TON. Notably, the TON of 33 is achieved at high methane conversion and ester yield, unlike many of the systems listed in Table 2. Furthermore, the stability of the copper oxide catalyst against deactivation is realized by testing the activity of the spent reaction mixture for the oxidation of methane without adding fresh catalyst or oxidant. On the second pass, a methane conversion above 20% was observed, implying that the catalyst did not deactivate completely by the end of the first cycle. (Entries 12-13, Table 1)

Besides high yields, industrial processes produce the desired product in high concentrations to minimize the costs of separation and recovery of the product. Our experiments show the possibility of reaching methyl trifluoroacetate concentrations of 0.12 M in two cycles of low-pressure reactions. Such or higher concentrations of the ester were achieved only at higher temperature and pressure (Table S1).

The catalytic system in this study leads to relatively high ester yields due to the stability of the product and the catalyst under the reaction conditions. The homogeneous catalyst can be recovered by a simple base-involved procedure and re-used for the oxidation of methane. The resistance of methyl trifluoroacetate against over-oxidation enables the maintenance of high selectivity, while the stability of the copper catalyst over long time periods, renders high methane conversion feasible. This reinforces the necessity to target a primary product, which is less vulnerable to over-oxidation with a catalyst that does not deactivate quickly for a yield-efficient approach of methane oxidation. Compensating on any one of these fronts will have a palpable effect on the yield of the desired product.

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Keywords: C-H activation • Homogeneous catalysis • Methane oxidation • Methyl trifluoroacetate • Copper catalysis

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Entry for the Table of Contents

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High-yield methane oxidation: This work demonstrates the possibility of using copper oxide, a simple catalyst devoid of complex ligands, to convert methane in high yield to methyl trifluoroacetate at low pressure.



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