Selective Methane Oxidation Catalyzed by Platinum Salts in Oleum at Turnover Frequencies of Large-Scale Industrial Processes

Tobias Zimmermann,[†] Mario Soorholtz,[†] Marius Bilke, and Ferdi Schüth*

Max-Plank-Institut für Kohlenforschung, Mülheim an der Ruhr D-45470, Germany

S *Supporting Information*

ABSTRACT: Direct catalytic methane functionalization, a "dream reaction", is typically characterized by relatively low catalyst activities. This also holds for the η^2-(2,2′-bipyrimidyl)-dichloroplatinum(II) [(bpym)PtCl$_2$, **1**] catalyst which oxidizes methane to methyl bisulfate in sulfuric acid. Nevertheless, it is arguably still one of the best systems for the partial oxidation of methane reported so far. Detailed studies of the dependence of activity on the SO$_3$ concentration and the interplay with the solubility of different platinum compounds revealed potassium tetrachloroplatinate (K$_2$PtCl$_4$) as an extremely active, selective, and stable catalyst, reaching turnover frequencies (TOFs) of more than 25,000 h^{-1} in 20% oleum with selectivities above 98%.

SO$_3$ concentration changes activity by orders of magnitude

CH$_4$ + SO$_3$/H$_2$SO$_4$

CH$_3$OSO$_3$H + H$_2$O + SO$_2$

K$_2$PtCl$_4$ outperforms Pt(bpym)Cl$_2$ activity in the range of industrial processes

The TOFs are more than 3 orders of magnitude higher compared to the original report on (bpym)PtCl$_2$ and easily reach or exceed those realized in commercial industrial processes, such as the Cativa process for the carbonylation of methanol. Also space-time-yields are on the order of large-scale commercialized processes.
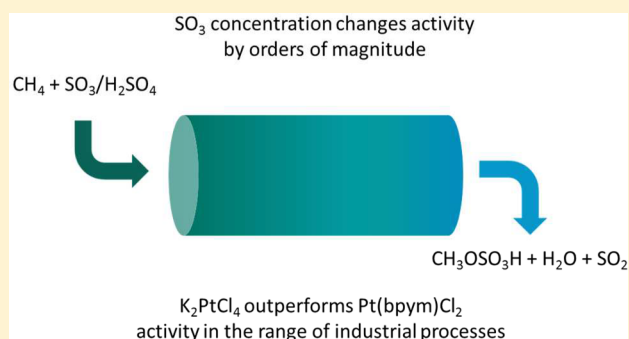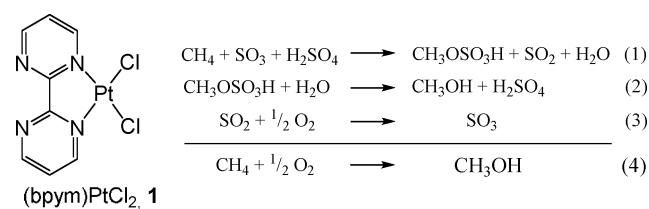
INTRODUCTION

C−H functionalization, and, in particular, methane functionalization, is one of the great challenges in catalysis.[1,2] It is not only of high fundamental interest but also of highest industrial importance, especially with the advent of the shale gas boom.[3,4] Industrial methane valorization currently relies on the conversion to syngas as an initial step, which is in turn transformed into numerous other compounds. Direct conversion of methane to value-added products without intermediate production of syngas is commercially currently not feasible, despite the numerous approaches undertaken in the last 50 years.[1,5,6] We show in this contribution that under well-chosen conditions, the reaction of methane to methyl bisulfate (MBS) can be effected by the simple platinum compound potassium tetrachloroplatinate (K$_2$PtCl$_4$), over which turnover frequencies (TOFs) in the same range as in large-scale industrial processes are reached, at selectivities exceeding 98% and good catalyst lifetimes.

While there are first reports on heterogeneously catalyzed oxidative coupling of methane on demonstration scale,[7] methane functionalization based on C−H activation with dissolved metal complexes still awaits a game changing discovery.[8] Substantial understanding of transition-metal-catalyzed C−H activation, that is the cleavage of a C−H bond by the action of a transition metal, has been developed, but closed catalytic cycles, including functionalization of the hydrocarbon and regeneration of the catalytically active species, are rarely realized, especially not for aliphatic molecules.[9−11] One of the most interesting reported systems is the Catalytica/Periana System, a true benchmark due to its reported one pass

yield of 72%,[12] which is based on the chemistry originally developed by Shilov.[11] This system utilizes η^2-(2,2′-bipyrimidyl)dichloroplatinum(II) [(bpym)PtCl$_2$, **1**] as catalyst in concentrated or fuming sulfuric acid (oleum) to oxidize methane to MBS. H$_2$SO$_4$/sulfur trioxide (SO$_3$) act also as transfer oxidants and are reduced to sulfur dioxide (SO$_2$). When MBS is subsequently hydrolyzed to methanol and sulfuric acid, the sulfur dioxide can be reoxidized to sulfur trioxide, closing the cycle to a net oxidation of methane to methanol by oxygen (Scheme 1). At 220 °C and a pressure of 34 bar, 90% of methane is converted with 81% selectivity in 2.5 h by a 50 mM solution of **1** in 102% sulfuric acid, which corresponds to 9% oleum and a SO$_3$/CH$_4$ ratio of 1.5. The final solution reaches an MBS concentration of 1 mol L^{-1}.[12]

Scheme 1. Structure of η^2-(2,2′-Bipyrimidyl)dichloroplatinum(II) and Partial Oxidation of Methane to Methanol with Sulfur Trioxide As Transfer Oxidant

$$CH_4 + SO_3 + H_2SO_4 \longrightarrow CH_3OSO_3H + SO_2 + H_2O \quad (1)$$

$$CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4 \quad (2)$$

$$SO_2 + {}^1\!/_2\, O_2 \longrightarrow SO_3 \quad (3)$$

$$CH_4 + {}^1\!/_2\, O_2 \longrightarrow CH_3OH \quad (4)$$

(bpym)PtCl$_2$, **1**

However, in spite of the unrivaled high selectivity at high conversion, the system could not be commercialized. This can be attributed to (i) difficulties in process layout, associated with recycling sulfuric acid and sulfur dioxide, (ii) problems with respect to separation of MBS, respectively methanol, from the reaction solution, and (iii) insufficient activity of the catalyst. It is estimated that TOFs should be increased from the current level of around 10 h^{-1} to at least 1000 h^{-1}.[1,13−15] Our study addresses the latter problem where no improvement has been achieved since the introduction of the system almost 20 years ago. As a result of the reinvestigation of the system over a broader range of parameters, TOFs >25,000 h^{-1} are demonstrated, a value in the range of commercial large-scale processes in homogeneous catalysis. These findings are expected to spark renewed interest in this system with the goal of commercial application.

■ RESULTS AND DISCUSSION

Our previous studies on solid analogs of **1**[16,17] triggered a reinvestigation of the original system, since we observed TOFs for **1** that were 2−3 orders of magnitude higher compared to Periana's original publication. Several factors can be responsible for these deviations, since the reaction system is very complex and difficult to analyze: (i) H$_2$SO$_4$/SO$_3$ participate in the reaction, thus, an effect of the SO$_3$ concentration is expected; (ii) solubilities of different catalysts can differ widely so that for some compounds, which are not completely soluble, rates do not reflect intrinsic activity at high nominal catalyst loadings; and (iii) in published studies normally integral rates were determined, i.e., rates averaged over the entire reaction time, which is typically fixed. If conversion is appreciable, rates over the course of the reaction will potentially differ drastically. This problem has been solved by our experimental approach, see Experimental Section and Supporting Information (SI). These factors were studied systematically, which led to realization of unprecedented catalytic activity.

Influence of the SO$_3$ Concentration. Sulfur trioxide as the transfer oxidant is a key compound in the reaction, and thus a substantial influence of its concentration on the rate of methane oxidation—not only on the rate of H/D exchange—is expected. There is current agreement that an increase in the Hammett acidity function leads to acceleration of the rate of H/D exchange, respectively, C−H activation,[14,18] but influence on the oxidation and functionalization steps have largely been ignored, although there is experimental evidence for that.[19] The activity of **1** in methane oxidation versus SO$_3$ concentration is shown in Figure 1.

Going from 96% sulfuric acid to ~44.9% oleum leads to an increase in the TOF by a factor of approximately 100. Further increase in the sulfur trioxide concentration leads to a decrease of the TOF by a factor of 2. The highest observed TOF in these experiments is ~1250 h^{-1}, 35 times higher than in the original report, and selectivities in oleum are well above 90% (vide infra).

Potassium Tetrachloroplatinate. Due to the strong influence of the sulfur trioxide concentration and the possibility to reach substantial rates at very low catalyst concentrations, the investigation of less soluble, inorganic platinum salts, such as potassium tetrachloroplatinate, seemed also worthwhile. Inorganic salts of platinum are believed to be active for methane oxidation, but unselective and prone to deactivation, with only very low turnover numbers (TONs), due to formation of polymeric Pt compounds, e.g., platinum (II)
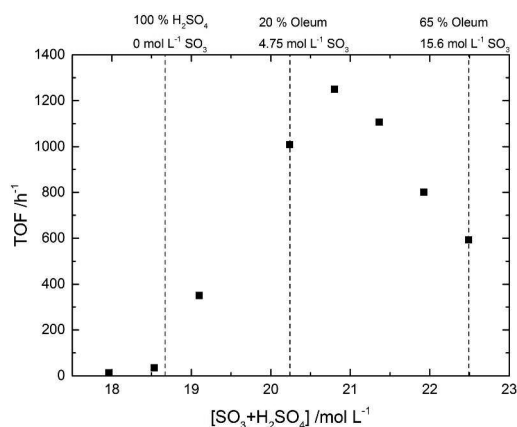
Figure 1. Dependence of TOF for methane oxidation with **1** on sulfur trioxide concentration at 215 °C. TOF in mol$_{MBS}$ mol$_{Pt}^{-1}$ h^{-1}; MBS determined by ^{1}H NMR; 15 mL solution, [**1**] 600 μM, conversion of methane <30%, TOFs extrapolated to methane partial pressure of 50 bar. See SI for detailed explanation and raw data.

chloride (PtCl$_2$), or "Pt black",[12] which is in fact not the case. At low catalyst concentration, deactivation of K$_2$PtCl$_4$ is not found, and the catalysts operated without sign of deactivation until the experiments were terminated (turnovers (TOs) > 500, to be distinguished from TONs, which are defined as the turnovers until the catalyst is deactivated). The overall activity of K$_2$PtCl$_4$ is substantially higher than that of **1**, and a similar dependence on SO$_3$ concentration is observed (Figure 2). The
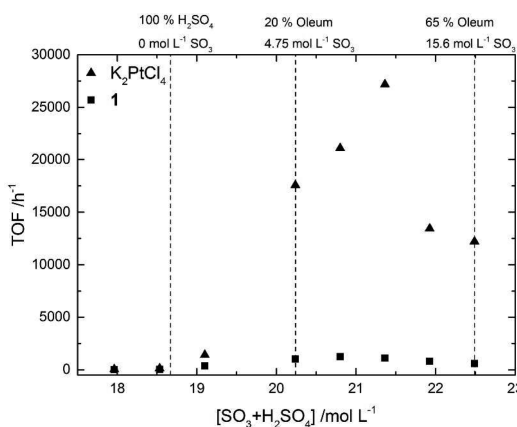
Figure 2. Dependence of TOF for methane oxidation with potassium tetrachloroplatinate on sulfur trioxide concentration at 215 °C (**1** shown for comparison). Conditions and remarks identical to Figure 1.

maximum TOF is ~27,000 h^{-1} which is 3−4 orders of magnitude higher compared to the original report and still more than 20 times higher compared to **1**, measured under similar conditions (see Figure 1). Such a value is much higher than any other activity value reported for the selective oxidation of methane and clearly reaches the range necessary for a large-scale process based on this chemistry (usually reported TOFs for partial oxidation of methane are <10 h^{-1} with the exception of copper-promoted Fe-ZSM-5 which reaches TOFs higher than 10,000 h^{-1} with H$_2$O$_2$ as oxidant, but at relatively low volumetric productivity).[20]

Since both, **1** and potassium tetrachloroplatinate, show the same trends upon increasing SO$_3$ concentration, the reason seems to be linked to the properties of the solvent/oxidant.

Table 1. Performance of Platinum Compounds for Methane Oxidation in 20% Oleum at 215 °C[a]

entry	compd, conc (μM)	TOF[b] (h^{-1})	TOs[b,c]	S_{MBS}[d] (%)	r_{MBS}[b,e] (mol h^{-1})	reaction time (h:min:s)
1	**1**, 600	1280	650	96	0.012	0:29:15
2	**1**/bpym, 600/3000	560	760	91	0.005	1:22:09
3	$(NH_3)_2PtCl_2$, 600	19,200	650	98	0.173	0:02:02
4	$PtCl_2$, 600	15,300	770	97	0.138	0:03:02
5	$(bipy)PtCl_2$[f], 600	14,400	840	97	0.130	0:03:30
6	Pt black, 680	20,200	840	98	0.206	0:02:30
7	$Pt(acac)_2$, 680	22,500	880	97	0.230	0:02:21
8	K_2PtCl_4, 600	22,800	940	98	0.205	0:02:28
9	K_2PtCl_4, 670	23,400	770	99	0.235	0:01:56
10	K_2PtCl_6, 670	24,100	780	98	0.242	0:01:59
11	control reaction, 0	n.a.	n.a.	67	0.0003	2:30:00

[a]Reaction conditions: 15 mL 20% oleum, conversion of methane <30%, $p_{CH_4,215\ °C} \sim 65$ bar, $p_{total,215\ °C} \sim 72$ bar. [b]Values rounded. [c]Differences in TOs are a result of slightly different conversion (20−30%) and catalyst concentrations. [d]S_{MBS} is selectivity to MBS. [e]r_{MBS} is rate of MBS formation. [f]Bipy stands for 2,2′-bipyridyl.

This is also indicated by the fact that major changes in TOF are observed at prominent points in the $H_2O/H_2SO_4/SO_3$ system, where properties of the solvent significantly change, i.e., the transition from sulfuric acid to oleum and close to 44.9% oleum, the formal composition of disulfuric acid, $H_2S_2O_7$.

The variation of the TOF could be explained by a typical rate law with a positive reaction order in SO_3. At the transition from 100% sulfuric acid to oleum the concentration of "free SO_3", respectively, di- or polysulfuric acid, increases considerably. Such species may be the actual oxidant, and the observed rates thus would be proportional to their concentration. In general, also Hammett acidity function[21] and oxidation potential[22] increase with SO_3 concentration and thus correlate with TOF, too.

The decrease of TOF at high sulfur trioxide concentrations is most probably due to decreasing methane solubility and a kinetic phenomenon. Integral experiments (reaction time >2 h) with excess of methane show that the final concentration of MBS is higher in 65% oleum compared to 20% where the TOF is higher. A lower solution concentration of methane at high SO_3 concentration would explain the decrease in TOF. This proposal is supported by solubility data in aqueous sulfuric acid,[23] and additional experiments where bi- and disulfate salts were added to oleum (Table S4). In general, addition of salt (>0.5 M) leads to a decrease of TOF, and the influence is stronger in 65% oleum.

Other Simple Platinum Compounds. Since the results with K_2PtCl_4 revealed that the bpym ligand is not mandatory for high activity under well-chosen conditions, other simple Pt compounds were also studied for their performance, including cis-$(NH_3)_2PtCl_2$ and $PtCl_2$, which had already been discussed and investigated in the context of this system at higher concentrations of the catalyst and lower oleum concentrations.[12] The activity of the compounds in 20% oleum is given in Table 1. The activity of all tested systems is at least 1 order of magnitude higher compared to **1**. Moreover, all of them exhibit a decent stability with TOs > 500, and deactivation does not seem to be a considerable issue. The TOs given are lower thresholds for the TON which could be achieved in this system, since the reaction was stopped after a predetermined conversion, and TOs were calculated for this point in time. In comparison to the original report,[12] the higher activity in oleum compensates the 2 orders of magnitude lower catalyst concentration, and the volumetric productivities are even higher by up to a factor of 5 compared to[12] (8.7−16.1 vs

3.6 mol L^{-1} h^{-1} at ∼0.5 M vs ∼1 M final MBS concentrations). Selectivity of the highly active simple platinum compounds is in all cases higher than the selectivity of **1** and above 97% in 20% oleum, the reason for which is discussed below.

Interestingly, all platinum compounds show high reactivity, irrespective of whether the oxidation state of platinum in the starting compound is 0, II, or IV. Pt(0) does not seem to play any role, also not for deactivation, since oleum is capable of oxidizing Pt black to Pt(IV).[24] However, this capability and the activity of K_2PtCl_6 open room for controversy: While this is no definitive proof for the activity of Pt(IV), commonly believed to be inactive for C−H activation,[18] the mechanism postulated in literature needs more experimental support, and it remains to be answered if contamination,[25] a self-repair mechanism,[18] or Lewis acid catalysis is responsible for the observed activity.[26−28]

Inspection of the different compounds in Table 1 reveals that the bpym ligand actually seems to be detrimental for high activity under the conditions chosen. In order to check this, an experiment with added bpym ligand was carried out (entry 2), in which additionally 3000 μM concentration of bpym was present. As one can see, this reduces the activity of **1** by approximately a factor of 2, suggesting indeed that bpym blocks the catalyst. For the other compounds it appears that under reaction conditions more or less similar states are reached, irrespective of the nature of the starting compound. The chloro complexes may undergo speciation, which may account for the small differences observed. Speciation is a phenomenon generally observed for reactions catalyzed by transition-metal halides and in particular by the related Shilov system.[13,25,29,30] Further investigation, however, is complicated in sulfuric acid, as chloride reacts to hydrochloric acid therein, and the exact amount of chloride is difficult to control.

Clearly, the ligand sphere influences the reactivity of the complexes. Computational studies predict the oxidation step to be easier with cis-$(NH_3)_2PtCl_2$,[31,32] which at least suggests that the bpym ligand might actually not be optimal. Although this has to be interpreted with care, the detrimental effect of excess bpym (Table 1, entry 2) in combination with the significantly higher activity of the other compounds actually raises the question, if **1** is indeed the active species for methane oxidation. At least at high SO_3 concentration it might instead be a dormant species, and an unligated or underligated Pt center would be the active catalyst. Interestingly, in Periana's original report free ligand was observed at 200 °C in 20% oleum.[12] Addition of excess ligand would shift the equilibrium of

complex formation to the side of ligated platinum and reduce the amount of catalytically active species, explaining the reduced activity in the presence of free bpym. However, further studies are needed for clarification of this point.

Selectivity. The selectivity for MBS in oleum is always above 90% and higher than in sulfuric acid (Figure S4). In Figure 3, selectivities obtained in a high number of experiments
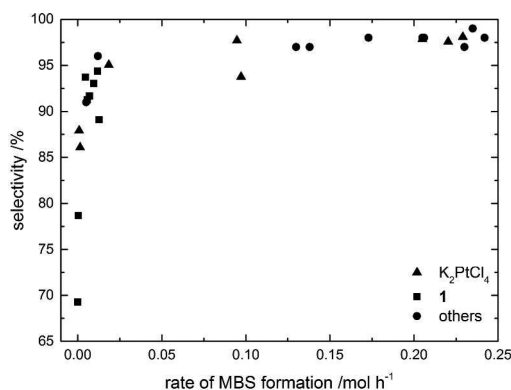
Figure 3. Selectivity as a function of the rate of MBS formation at 215 °C for different catalysts in sulfuric acid and oleum.

using different catalysts are plotted over the rate of MBS formation. This suggests a predominantly consecutive reaction pathway (simplified: $CH_4 \rightarrow MBS \rightarrow CO_2$) as the main process. If the rate of the first step is increased, then the selectivity will increase for identical conversion. However, the experiments plotted in Figure 3 were not strictly run at identical conversion (generally ~20%, but lower for rates <0.001 mol h^{-1}), and thus the data need to be interpreted with care. Influences on selectivity should be further investigated, e.g., effects of deprotection due to hydrolysis of MBS and oxidation of free methanol in more dilute acid.[33] As for any partial oxidation, the full reaction network is expected to be more complex than the simple sequence given above and potentially consists of parallel and consecutive reactions which can be catalyzed or uncatalyzed. Nevertheless, stability of MBS under reaction conditions is high, since selectivity only drops for very low rates of MBS formation, indicating the power of product protection.

Catalyst Stability. With a reaction like the one investigated here, catalyst lifetime is a serious issue, and many platinum compounds were not considered suitable due to their perceived instability. Indeed, a half-life of 15 min at 180 °C was reported for cis-$(NH_3)_2PtCl_2$.[12] However, TOs in the current study typically exceed 500, and this is a lower limit for the TON, because the reaction was stopped while the catalyst was still active. The reaction solutions remained clear up to this point, also suggesting that no deactivation via precipitation of insoluble compounds had occurred. However, TOs of 500 are by far not sufficient for industrial processes, and thus additional experiments to assess stability were carried out. K_2PtCl_4 was kept for 5 h at 215 °C before starting the reaction by pressurizing with methane. Within experimental error, there is no difference between this experiment and the reference where the reaction is started directly after reaching 215 °C (320 μM, 20% oleum, TOF$_{without\ preheating}$ 25,600 h^{-1}, TOF$_{5\ h\ preheating}$ 27,800 h^{-1}). In addition, separate experiments demonstrate more than 16,000 TOs for K_2PtCl_4 (40 μM, 20% oleum, 2 h). The continuing decrease in pressure indicates catalytic activity

over the whole reaction time, although it is reduced significantly over the course of the reaction. This can be expected, due to consumption of sulfur trioxide and the dependency shown in Figures 1 and 2 and does not have to be due to deactivation. Consequently, the quoted TOs can be considered as lower limit and should be significantly higher at a constant sulfur trioxide concentration. Thus, in contrast to the common view presented in the literature, platinum salts are generally not prone to deactivation, but stable, selective, and unprecedentedly active.

Catalyst Solubility. The selectivity and especially the stability of inorganic platinum salts are clearly in conflict with accepted views of the scientific community, although there is scattered evidence for this in the literature.[34−36] This conflict can be rationalized, if closer attention is paid to the influence of catalyst concentration, and the interplay with sulfur trioxide concentration. Reviewing the patent preceding the 1998 publication reveals that in the vast majority of examples, reactions were carried out in 96% sulfuric acid and at catalyst concentrations higher than 25 mM.[34] As shown above, the activity in sulfuric acid is generally lower, but at 600 μM potassium tetrachloroplatinate is still slightly more active than 1. In order to check the influence of solubility, reactions were carried out at high formal catalyst loadings of 50 mM in 98% sulfuric acid (Table 2, pressure vs time curves in Figure S7).

Table 2. Comparison of the Catalytic Performance of 1, PtCl$_2$, and K$_2$PtCl$_4$ in 98% H$_2$SO$_4$ at low (600 μM, entry 1−3) and high (50 mM, entry 4−6) catalyst concentration at 215 °C^a

entry	catalyst	r_{MBS}^{b} (mol h^{-1})	C_{CH_4}^{c} (%)	S_{MBS} (%)
		98% H$_2$SO$_4$ 600 μM		
1	**1**	0.0004	2.9	79
2	PtCl$_2$	0.0006	3.6	87
3	K$_2$PtCl$_4$	0.0015	8.8	86
		98% H$_2$SO$_4$ 50 mM^d		
4	**1**	0.0046	46.1	87
5	PtCl$_2$	0.0018	15.3	96
6	K$_2$PtCl$_4$	0.0004	4.1	83

^{a}Reaction conditions: 15 mL solution, total pressure of 55 (50 mM), respectively, 67 bar (600 μM). Experiments stopped after 2.5 h (50 mM), respectively, 2 h (600 μM). ^{b}Values rounded. ^{c}C_{CH_4} is conversion of methane ^{d}Care has to be taken in comparing the values in this series: r_{MBS} of **1** is underestimated due to oxidation of MBS. Selectivity should not be compared because conversions and absolute amount of CO$_2$ formed are significantly different.

Clearly, in agreement with the literature, higher rates are achieved with **1** compared to potassium tetrachloroplatinate and platinum chloride, which is at least partly due to the different solubilities of the respective compounds. Potassium tetrachloroplatinate and platinum chloride are basically insoluble in concentrated sulfuric acid and oleum, whereas **1** is reasonably well soluble, although in some experiments, also precipitation was observed (e.g., from 50 mM solutions of **1** in 96% sulfuric acid in the absence of methane upon heating to 215 °C). Other effects of catalyst concentration may play a role, but catalyst solubility is a crucial factor in this system which can outweigh effects of intrinsic activity. Development of catalysts with high solubility is an important target, still, since performance could be further improved, and the scope of conditions with high activity extended.

Table 3. Comparison of Parameters for Industrial Processes and Methane Oxidation in Sulfuric Acid/Oleum

entry	parameter	Periana et al., 1998[12]	guideline[14,15]	our work	Cativa process[38]	MeOH synthesis[39]
1	rate (mol L^{-1} h^{-1})	3.6	3.6	>15	40	20−30
2	[catalyst] (mM)	50	1	0.6	18	n.a.
3	TOF (h^{-1})	10	3600	>25,000	>2000	n.a.
4	TON	1000	10^5−10^6	>16,000	>10^5	n.a.
5	selectivity (%)	81	>90	>95	99	>99
6	conversion (%)	90	20	20−30	n.a.	15−50
7	separation[a]	to be developed	simple	to be developed	distillation	distillation

[a]Starting with 65% oleum, a final concentration of 2.7 M MBS was reached. Based on guidelines,[14,15] product concentration should be around 2 M (this is ≪10 wt % MeOH) which seems to be unfavorable for distillation compared to MeOH or acetic acid synthesis where product concentrations are well above 50 wt %. Not applicable is n.a.

CONCLUSION

In conclusion, we have obtained new insight into the factors influencing methane functionalization with platinum catalysts in sulfuric acid and oleum and shown that **1** is generally not the most effective catalyst. In fact, simple platinum salts are stable, selective, and unprecedentedly active, and under most conditions superior to **1**. TOFs and space time yields, respectively, volumetric productivities, compare favorably to those achieved in large-scale commercial processes. However, the difficulty of separating MBS and recycling sulfur dioxide are still important problems to be solved, which currently prohibit industrial realization (Table 3). Also, while corrosion is clearly a severe disadvantage of this chemistry, this does not seem to pose an unsurmountable challenge. In fact, oleum is less corrosive than sulfuric acid, and handling of such conditions is standard in modern sulfuric acid and oleum production.[37]

EXPERIMENTAL SECTION

Caution. Sulfuric acid, oleum, and SO_3 are strongly oxidizing agents and pose potential hazards. MBS is potentially methylating. Dimethylsulfate is carcinogenic and might be formed under the conditions used, but has never been observed in our experiments.

Catalytic Experiment. Catalytic methane oxidation was carried out in a two autoclave setup which had been described previously.[17] Both autoclaves were connected via two valves and a short capillary. One autoclave served as a heated CH_4 reservoir. The other autoclave, denoted reactor, was used for the actual reaction. Usually, the CH_4 reservoir was filled with methane to a pressure of 53 bar at room temperature. The reactor was filled with sulfuric acid or oleum and catalyst and purged with argon before closure. Both autoclaves were heated to 215 °C, and the reaction was started by pressurizing the reactor with preheated methane.

The reaction was run until a certain pressure drop—a consequence of the oxidation of methane—was reached or in the case of slow rates after a certain time, mostly 2 h. By this, the conversion of methane was limited to approximately 30% which ensures comparison under similar conditions and maintains the SO_3 concentration at a sufficient level. The reaction was stopped by quenching it in a water bath under stirring.

The relative composition of the gas phase was analyzed by IR spectroscopy, and the liquid phase by ^{1}H nuclear magnetic resonance (NMR) spectroscopy as well as high-performance liquid chromatography (HPLC) after hydrolysis of an aliquot of the reaction solution. Finally, the reactor was rinsed with acetone and water, dried overnight in a drying oven, and checked for its tightness before the next experiment.

TOFs are calculated by dividing the molar amount of MBS formed by the molar amount of platinum put in the reactor and the reaction time. This does not necessarily reflect intrinsic activity, and the values are apparent, especially for high catalyst loadings if solubility is low. TOs are used instead of TONs since reactions were stopped at a point in time when there was still catalytic activity. TOs are thus a lower limit for TONs.

Reproducibility. Due to the amount of sources contributing to experimental error, quantitative assessment is difficult. Nevertheless, all trends are reproducible, and typical experiments (20% oleum, 600 μM **1**), carried out by two different operators over the course of one year, during which pressure meters had to be recalibrated, autoclaves reworked, and different batches of chemicals used, show deviations in TOFs below 5% from the average value (more information is given in the Table S2).

Details for each experiment, including amount of reactants and products and reaction times are given in the SI.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05167.

Experimental and methodological details, raw data of SO_3 concentration series, description of extrapolation, selectivity vs SO_3 concentration and conversion, pressure-dependent measurements, pressure time curves at high catalyst loading, catalytic activity after salt addition, stirring dependency, IR spectra of degassing, and raw data (PDF)

AUTHOR INFORMATION

Corresponding Author
*schueth@mpi-muelheim.mpg.de
Present Address
†hte GmbH, Heidelberg, D-69123, Germany
Notes
The authors declare no competing financial interest.

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