

## Supporting Information

### **Influence of Catalyst Concentration on Activity and Selectivity in Selective Methane Oxidation with Platinum Compounds in Sulfuric Acid and Oleum**

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## General

All chemicals were purchased from Sigma Aldrich Corp. and used without further purification. The specifications of the chemicals were as indicated in brackets: oleum (puriss p.a.), concentrated sulfuric acid (extra pure),  $K_2PtCl_4$  (99.9%), bpym (95%), all other chemicals (98% or better). Methane of the specification N25 (>99.5%) was purchased from Air Liquide.

Elemental analysis was carried out by Mikroanalytisches Laboratorium Kolbe, Mülheim, Germany, via atomic absorption spectroscopy. NMR spectra were measured using a Bruker AV-300 spectrometer. Spectra were referenced to residual protons of DMSO- $d_6$  which was added in a coaxial capillary to the NMR tube. Chemical shifts are stated in parts per million downfield of tetramethylsilane. The reaction mixture after hydrolysis was analyzed by HPLC using a Shimadzu LC-20 chromatograph equipped with an organic acid column and a refractive index detector. The eluent was 10 mM trifluoroacetic acid. IR spectra of the gas phase were collected with a Thermo Nicolet Avatar 370 FT-IR spectrometer. For each spectrum 32 scans were accumulated with a resolution of  $2\text{ cm}^{-1}$ . Background spectra were collected before each sample spectrum and automatically subtracted. Before integration all spectra were subjected to automatic baseline correction. Titrations were done with 848 titrino plus automatic titrator from Metrohm using 0.1 M NaOH standard solution the exact concentration of which was determined separately. Volumes of autoclaves were determined with ASAP 2010 sorption analyzer from Micromeritics. X-ray diffraction (XRD) was measured using a Stadi P diffractometer by Stoe with a theta/theta stage in reflection geometry with  $Cu\ K_\alpha$  radiation.

## Experimental Details

### Synthesis of $\eta^2$ -(2,2'-bipyrimidyl)dichloroplatinum(II) [(bpym)PtCl<sub>2</sub>, **1**]

**1** was synthesized in a similar way as reported previously.<sup>1</sup> In brief 0.4453 g of  $K_2PtCl_4$  was dissolved in 50 mL distilled water at room temperature under air. 0.170 g bpym, dissolved in 4 mL water, was added in less than 1 min under stirring. An orange precipitate formed quickly and the solution was filtered after 30 min. The mother liquor was stirred overnight and filtered for a second time. Both times the precipitate was washed with water and acetone and dried at 90 °C overnight and afterwards in a vacuum drying oven at 50 °C. The yield amounted for 93% (The yield of the first filtration was 80%). Characterization was done by elemental analysis and  $^1H$  NMR.

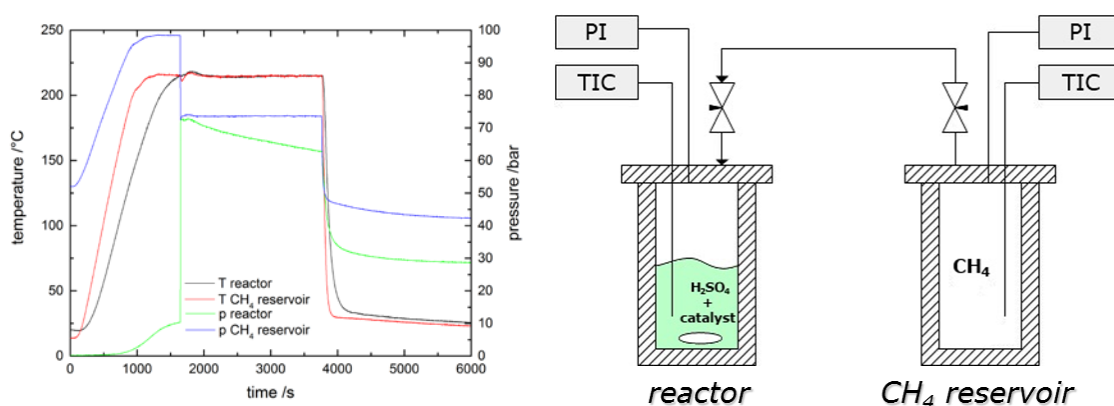
$^1H$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  8.0 (dd, 2H, bpym H<sub>5/5'</sub>), 9.4 (dd, 2H, bpym H<sub>4/4'</sub>), 9.7 (dd, 2H, bpym H<sub>6/6'</sub>)

Analytical data for **1**: Calculated: 22.7% C, 1.4% H, 13.2% N, 16.7% Cl, 46.0% Pt; Found: 22.3% C, 13.5% N, 16.4% Cl, 45.0% Pt.

### Description of catalytic experiments

Catalytic methane oxidation was carried out in a two autoclave setup described previously<sup>2</sup> and is shown in scheme S1 (all autoclaves are of in-house design). Both autoclaves of the setup were equipped with pressure meter (JUMO dTrans p30; the pressure meter suffers from corrosion and has to be controlled and recalibrated from time to time) and thermocouple (type K; the metal housing was additionally protected by a Teflon hose), heated separately via external heat supply, controlled by a previously optimized PID controller, and connected via two valves and a short capillary (dead volume of the capillary and valves 0.9 respectively 1.3 mL). One autoclave made of stainless steel

(1.4571, 54.6 mL) was exclusively filled with methane and served as preheating reservoir. The other autoclave, named reactor, consisted of Hastelloy G-35 (balance Ni, 33% Cr, 8% Mo,  $\leq 2\%$  Fe,  $\leq 0.6\%$  Si,  $\leq 0.5\%$  Mn,  $\leq 0.4\%$  Al,  $\leq 0.05\%$  C) and was used for the actual reaction. Two different autoclaves were used for this purpose (the volumes, reduced by their glass inlet and magnetic stir bar amounted 36.2, 37.3 mL for reactor 1 and 30.4, 32.9, 34.8 mL for reactor 2; several values are given for each reactor as corrosion made remachining necessary from time to time). All volumes were analyzed with a physisorption analyzer by measurement of the pressure difference between the calibrated known volume manifold and the sum of manifold and autoclave after opening the in house made connection to the autoclave. Helium was used as gas and the measurement was done at room temperature and a pressure ranging from 0.5 to 1 bar. The ideal gas law was used for calculation. In order to reduce contact of the reaction mixture with the reactor wall a glass inlet was used for all reactions. Stirring was achieved by magnetic stirring with a Teflon stir bar. Sealing materials consisted of gold or Teflon. Teflon was used at less demanding connections and had to be replaced more frequently. In case of 65% oleum Teflon sealing proved to be inappropriate. Valves and connections were made of stainless steel and were replaced upon observation of leakage. The use of Hastelloy valves resulted in prolonged valve lifetime but did not sufficiently prevent corrosion. Pressure and temperature of both autoclaves were monitored and recorded throughout heat-up, reaction and until after quenching and release of the gas by a LabView program of in house design.



Scheme S1: p,T-t profiles of a typical experiment (left) and schematic representation of the experimental setup (right).

Usually, the preheating autoclave was filled with methane to a pressure of 53 bar at room temperature. The reactor was filled with, unless otherwise stated, 15 mL of sulfuric acid or oleum and catalyst, respectively other substances if indicated, and purged with Argon before closure. Both autoclaves were connected via the capillary, but still separated by valves, and placed in their heating blocks. Heating was started, in case of the reactor together with stirring. It usually took 30 min until reaction temperature was reached. Before pressurizing the reactor temperature was allowed to stabilize for  $\sim 5$  min. The reaction was started by opening the valves to the preheating autoclave for  $\sim 10$  s which led to a total pressure of  $\sim 70$  bar in the reactor. The reaction was run until a certain pressure drop was reached or in case of slow rates after a certain time, mostly 2 h. The pressure drop was 8.3 bar in case of reactor 1 and 10 bar in case of reactor 2 and most experiments were performed with a drop of the pressure volume product of approximately 180 bar mL at reaction temperature. The reaction was stopped by removing the reactor from the heating block and quenching it in a water bath under stirring. The temperature and pressure time profiles of the

reactor and preheating autoclave are shown in scheme S1 (left) with the heat up period (until ~1600 s) leading to autogenous pressure increase of ~10 bar in the reactor due to evaporation of SO<sub>3</sub> from the solution. Upon pressurizing the pressure of reactor and preheating autoclave are identical, i.e., ~70 bar. The reaction however leads to a pressure drop in the reactor. At the beginning of the last period (~4000 s), pressure and temperature of both autoclaves drop rapidly due to quenching in a water bath. After room temperature was reached, the gas phase was vented into a gas sampling bag and part of it transferred with a gas tight syringe into the gas cell of the IR spectrometer and the relative composition analyzed. An aliquot (~1 mL) of the liquid phase was mixed with a weighted amount of methane sulfonic acid (MSA) as standard and analyzed by <sup>1</sup>H NMR (It was separately verified that MSA is not formed under the used conditions.). The amount of MBS formed during the reaction was determined based on the integrals of the methyl resonances of MBS (3.6 ppm) and MSA (2.9 ppm). The exact positions of the resonances depend on the acidity (lower acidity leads to up field shifts). Another aliquot (10 mL) of the reaction solution was added slowly to 20 mL of chilled distilled water under stirring and heated to 90 °C for 3 h. This mixture was afterwards analyzed by HPLC for its methanol content. In most cases hydrolysis was not complete and only 80% of MBS was converted to methanol. NMR of the hydrolysate showed that the remainder stayed unaffected. In some cases an aliquot (1 mL) of the oleum/sulfuric acid was titrated after and or prior to reaction. To lower the concentration of protons 1 mL of the solution was mixed with distilled water to give a volume of 100 mL. 3 mL of this solution were mixed with distilled water to give a solution of 50 mL and half of this solution was finally titrated. Due to the amount of dilution steps, unknown contributions from MBS and SO<sub>2</sub> and the vigorous reaction in the first dilution step titrated SO<sub>3</sub> concentrations should be taken with care. Anyway, the results of the titrations correlated with the calculated SO<sub>3</sub> concentration as well as with the SO<sub>3</sub> partial pressure. The SO<sub>3</sub> concentration of mixtures was calculated based on the volumes of the stock solutions disregarding density changes upon mixing with densities of the stock solutions of 1.8355 (96% sulfuric acid), 1.9 (20% oleum) and 1.925 g mL<sup>-1</sup> (65% oleum). Titration and fuming of the reaction solutions indicate that experiments with 20% oleum in quasi differential mode stay in the oleum region. Rough estimation based on an average titration value of 20.2 mol L<sup>-1</sup> for the concentration of SO<sub>3</sub> equivalents (calculated value of 20.23 mol L<sup>-1</sup>), a MBS concentration of 0.5 mol L<sup>-1</sup> and a 2:1 stoichiometry for the reaction indicates the same (100% sulfuric acid has a concentration of 18.67 mol L<sup>-1</sup>). Finally, the reactor was rinsed with acetone and water, dried overnight in a drying oven and checked for its tightness before the next experiment.

## Calculations

The amount of methane introduced in the reactor was calculated based on the measured volume of the preheating autoclave and temperatures and pressures before heat up and after quenching. The Benedict-Webb-Rubin (BWR, (1), see table S1 for constants) equation of state was used for the calculations.<sup>3-4</sup> The solver add in of Excel was used for numerical solution of the BWR equation. Using the ideal gas law differences up to 10% can easily be obtained. The amount of methane and CO<sub>2</sub> after the reaction was calculated with the BWR equation too under assumption of Dalton's law, i.e. the sum of the partial pressures of methane and CO<sub>2</sub> equals the total pressure. The partial pressures are obtained from integration of IR spectra (2800-3200 cm<sup>-1</sup> for CH<sub>4</sub> and 2150-2550 cm<sup>-1</sup> for CO<sub>2</sub>). Apparent integral attenuation coefficients were separately determined and resulted in a 10.55 times higher integral absorption of CO<sub>2</sub> in the indicated spectral range which was used accordingly in the calculation of the partial pressures.

$$p = RT \frac{n}{V} + \left( B_0 RT - A_0 - \frac{C_0}{T^2} \right) \frac{n^2}{V^2} + (bRT - a) \frac{n^3}{V^3} + a\alpha \frac{n^6}{V^6} + \frac{c}{T^2} \frac{n^2}{V^2} \left( 1 + \gamma \frac{n^2}{V^2} \exp \left( -\gamma \frac{n^2}{V^2} \right) \right) \quad (1)$$

Table S1: BWR constants for methane and carbon dioxide (Units in atm, L, mol and K; R 0.08207 atm L mol<sup>-1</sup> K<sup>-1</sup>)

	a	A <sub>0</sub>	b	B <sub>0</sub>	c	C <sub>0</sub>	α 10 <sup>5</sup>	γ 10 <sup>3</sup>
CH <sub>4</sub>	0.0494	1.855	0.00338004	0.0426	2545	22570	12.4359	6
CO <sub>2</sub>	0.24204855	1.8367101	0.00625361	0.03201493	19008.12	176028.05	4.878407	4.280822

Reported TONs are calculated as the ratio of the amount of MBS in the crude reaction mixture, determined by <sup>1</sup>H NMR spectroscopy, and amount of Platinum used as catalyst for the reaction. TOFs are calculated by division of the respective TONs by the reaction time. The observed rate of MBS formation,  $r_{\text{MBS}}$ , is calculated as amount of MBS divided by the reaction time. Volumetric productivities are based on the liquid phase volume, i.e., 15 mL.

Conversion is defined as: 
$$C_{\text{CH}_4} = \frac{n_{\text{CO}_2} + n_{\text{MBS}}}{n_{\text{CH}_4 \text{ initial}}} \cdot 100\%$$

Selectivity is defined as: 
$$S_{\text{MBS}} = \frac{n_{\text{MBS}}}{n_{\text{MBS}} + n_{\text{CO}_2}} \cdot 100\%$$

These definitions of conversion and selectivity are not biased by deviations in the carbon balance which was usually between 90 and 100%. In case of low conversion influences by a not fully closed carbon balance can become significant.

## Experimental error

Due to the amount of sources contributing to experimental error quantitative assessment is difficult and error bars are not shown in the graphs. Anyway trends are reproducible although errors under different conditions are different. As a general measure of precision the average value and the standard deviation of experiments under “standard conditions” are as follows: 4 experiments of methane oxidation with **1** (600 μM, 20% oleum; both reactors used; different batches of **1**) resulted in a value of the TOF of 1281 h<sup>-1</sup> with a standard deviation of 39 h<sup>-1</sup>, i.e. the relative standard deviation is 3%. Extending this set of experiments with two more experiments from another operator gives, based on HPLC measurements for all experiments, a TOF of 1011 h<sup>-1</sup> and a standard deviation of 31 h<sup>-1</sup> (Note that as mentioned before hydrolysis is not complete and TOFs based on HPLC are usually only 80% of the value based on NMR). These experiments were done over the course of one year during which pressure meters had to be recalibrated, autoclaves remachined and different batches of chemicals used. This shows a generally high precision and reproducibility. Higher errors were observed for measurements with K<sub>2</sub>PtCl<sub>4</sub>, especially at high catalyst concentration. 4 measurements with 50 mM of K<sub>2</sub>PtCl<sub>4</sub> as precursor, albeit with different pretreatments (grinding and waiting time at 215 °C before the reactor was pressurized) resulted in an average  $r_{\text{MBS}}$  of 0.0654 mol h<sup>-1</sup> with a standard deviation of 0.0176 which corresponds to a relative standard deviation of 27%.

## Supplementary results

### Concentration dependency

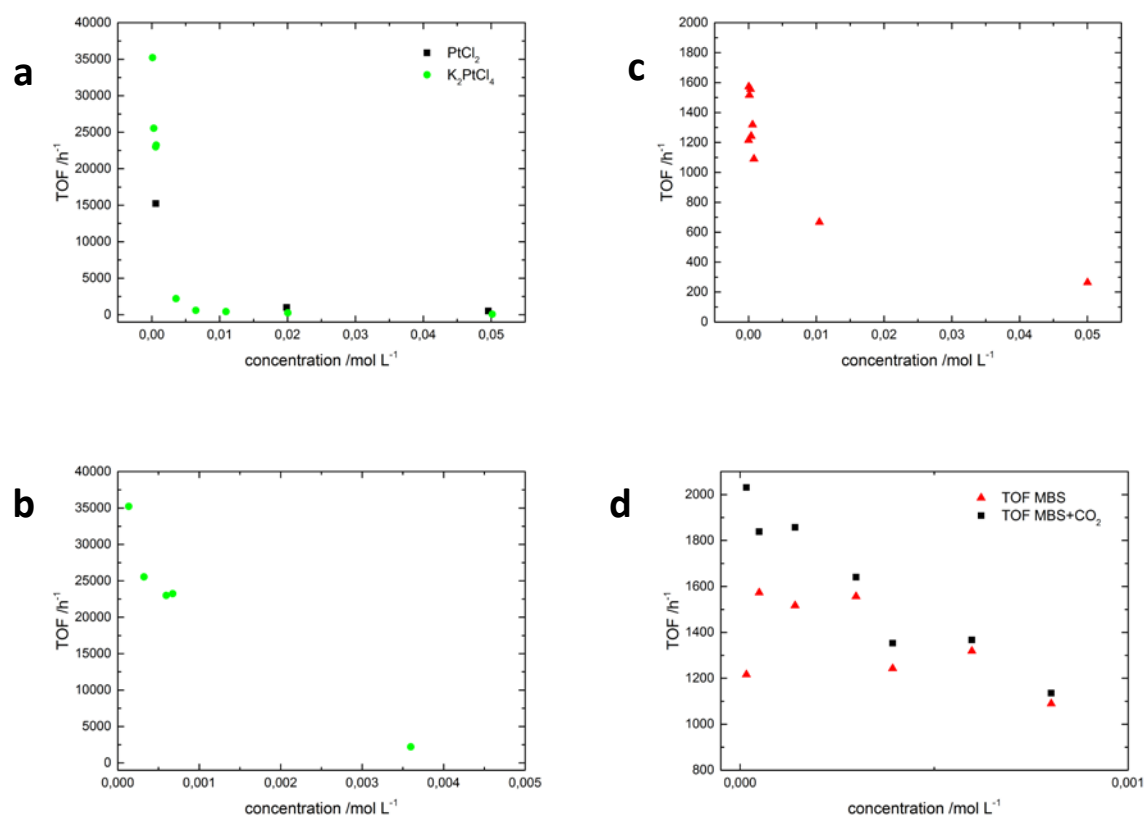


Figure S1: Dependency of TOF on catalyst concentration in 20% oleum (15 mL) at 215 °C for a)  $\text{PtCl}_2$  and  $\text{K}_2\text{PtCl}_4$ , b)  $\text{K}_2\text{PtCl}_4$  and c) **1** ( $C_{\text{CH}_4}$  20-30%,  $p_{\text{total}}$  72 bar,  $p_{\text{CH}_4}$  65 bar). d) For **1** a comparison between the TOF based on MBS only and the sum of MBS and  $\text{CO}_2$  is shown.

### Stirring dependency

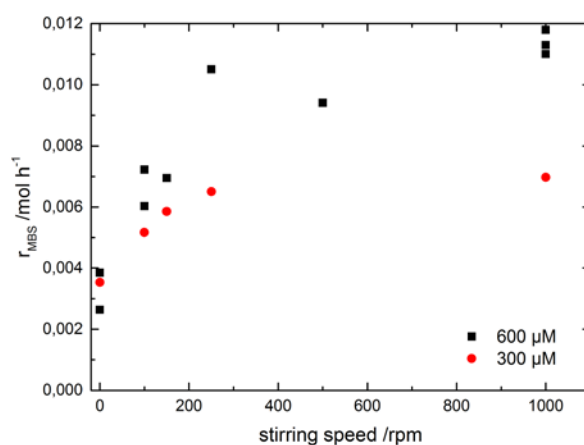


Figure S2: Dependency of the rate of MBS formation on the stirring speed in 20% oleum at 215 °C with **1** ( $C_{\text{CH}_4}$  20-30%,  $p_{\text{total}}$  72 bar,  $p_{\text{CH}_4}$  65 bar).

At low stirring speed the rate is within error margin identical for both concentrations of **1** which proves gas liquid mass transfer to be limiting. Increasing the stirring speed above 300 rpm does not increase the rate anymore. From 300 rpm on the differences in rate between the two different catalyst concentrations become significant.

### Pressure dependency

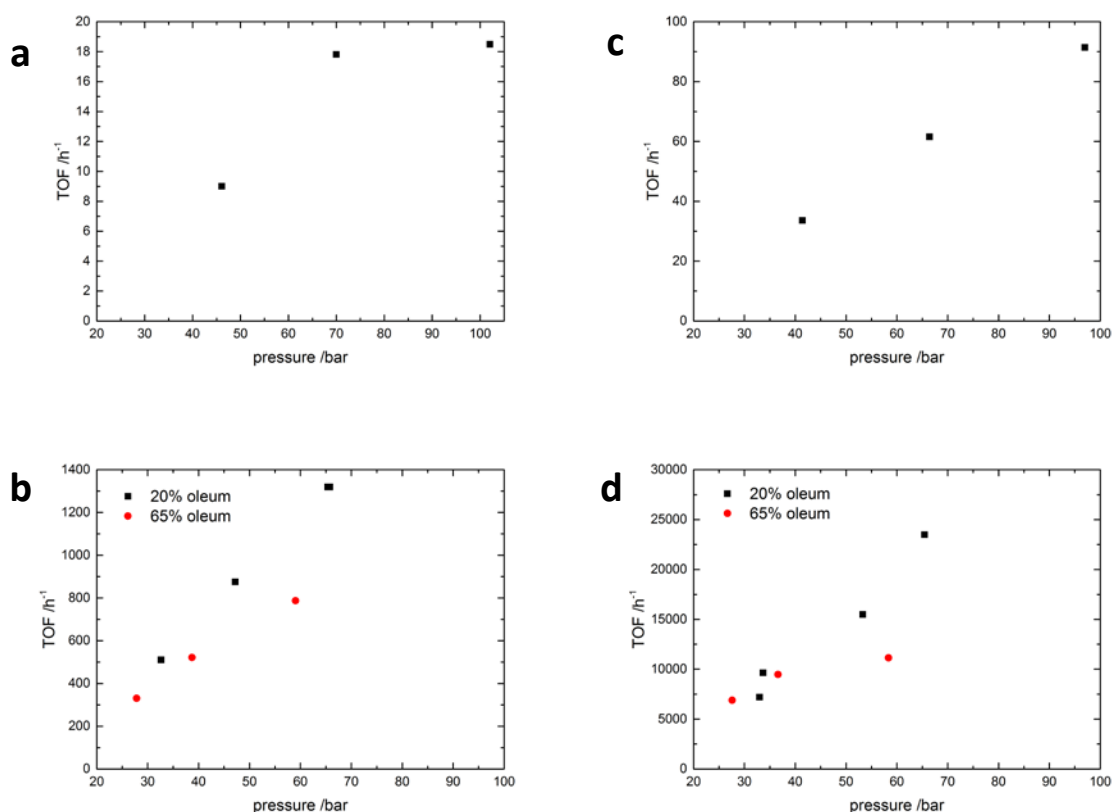


Figure S3: Pressure dependency of the TOF for a) **1** in 15 mL 96% sulfuric acid, b) **1** in 15 mL 20% as well as 65% oleum c)  $\text{K}_2\text{PtCl}_4$  in 15 mL 96% sulfuric acid and d)  $\text{K}_2\text{PtCl}_4$  in 15 mL 20% as well as 65% oleum at 215 °C with a catalyst concentration of 600  $\mu\text{M}$ . The ranges of methane partial pressure are different due to the increasingly higher  $\text{SO}_3$  partial pressures limiting the experimentally accessible window. The total pressure, the calculated methane partial pressure, TOF and temperature of the respective experiments can be found in table S2.

The pressure in figure S3 is the calculated partial pressure of methane at reaction temperature and was obtained in the same way as for the  $\text{SO}_3$  dependency series. Comparison of the data in 20 and 65% oleum supports a lower solubility of methane in 65% oleum, where the TOF values are lower, respectively level of towards higher pressure. In 96% sulfuric acid with **1** as catalyst (upper left graph, S3a) the TOF seems to become saturated with increasing pressure. However, the TOF is based on MBS found in the crude reaction mixture, and the  $\text{CO}_2$  formed in the experiment with the highest pressure is higher compared to the other experiments of this series. This illustrates the problem of underestimation of TOF if  $r_{\text{MBS}}$  is low in general. It might be in this case that the rate of MBS decomposition already equals  $r_{\text{MBS}}$ . In case of the pressure dependent experiments in 96% sulfuric acid the conversion of methane was below 5%. In 20% oleum conversion ranged from 15 to 40% and in 65% oleum it was  $\sim 10\%$  in case of **1** and  $\sim 30\%$  for  $\text{K}_2\text{PtCl}_4$ . Due to the differences in conversion these results should be seen qualitatively. Due to the interdependencies of the parameters it is



difficult to perform a clean and distinct pressure series, respectively the experimental setup should be further modified that operation under constant pressure is possible, i.e., methane should be continuously fed into the reactor and the conversion of SO<sub>3</sub> limited.

Table S2: TOFs, calculated partial pressure of methane ( $p_{\text{theo}}$ ), measured total pressure and temperature for the pressure dependency series.

<b>1</b>				<b>K<sub>2</sub>PtCl<sub>4</sub></b>			
TOF /h <sup>-1</sup>	P <sub>calc</sub> /bar	p <sub>tot</sub> /bar	T /°C	TOF /h <sup>-1</sup>	p <sub>calc</sub> /bar	p <sub>tot</sub> /bar	T /°C
96% sulfuric acid							
9.0	46.1	39.7	215.9	32.9	41.4	38.3	215.9
17.8	70.0	66.0	216.2	60.3	66.4	67.5	215.5
18.5	102.1	92.4	215.9	89.5	97.0	90.5	215.9
20% oleum							
510	32.6	41.0	215.5	7204	33.0	40.7	215.2
875	47.2	53.7	215.4	9442	33.7	40.8	215.5
1319	65.4	70.1	214.8	15165	53.3	58.3	216.0
1319	65.8	72.8	214.9	22998	65.4	69.9	215.3
65% oleum							
330	27.8	83.2	216.4	6742	27.6	86.5	217.9
522	38.7	>100	225	9271	36.6	96.6	219.1
787	59.1	>100	224	10898	58.4	>100	230

### Observations with respect to solubility

In order to find out if solubility might be significantly higher perhaps as a result of conversion to more soluble species at reaction temperature solutions of K<sub>2</sub>PtCl<sub>4</sub> and PtCl<sub>2</sub> in 20% oleum with a formal concentration of 50 mM were heated to 215 °C in glass vials. Compared to room temperature no difference was observed and black sediment was visible (appearance is black because the material is wet). However, the same experiment with 50 mM solutions of **1** in 96% sulfuric acid and 20% oleum showed a difference: In oleum the solution is yellow and the optical appearance does not change during heating to 215 °C and subsequent cool down to room temperature. In 96% sulfuric acid though the solution is orange at room temperature and at 215 °C an orange-reddish precipitate is formed which does neither redissolve upon cooling to room temperature nor does it dissolve in DMSO, H<sub>2</sub>SO<sub>4</sub> or 20% oleum. There might be also some influence due to the presence of methane and/or the time at 215 °C: In case of 20% oleum the solution after methane oxidation is also clear and yellow, viz no clear difference. If methane oxidation with a 50 mM solution of **1** is conducted in 98% sulfuric acid the reaction solution has a dark blue-yellow appearance and no precipitate is observed directly after the reaction. Only after leaving the reaction solution for two days some orange-green-brown precipitate is observed. The solution has still the dark blue-yellow appearance. In any case, experiments in concentrated sulfuric acid seem to be sensitive to the presence of methane. Actually theoretical investigations suggest that Cl<sup>-</sup> is exchanged for HSO<sub>4</sub><sup>-</sup> during the first cycle of catalytic methane oxidation.<sup>5</sup> This could be the reason for the observed differences in case of the presence of methane but further experiments investigating the influence of the SO<sub>3</sub> concentration on the solubility of **1** as well as the role of methane are needed.

## Derivation of a simplified mathematical expression for rate of MBS formation

$$r_{MBS} = \frac{dMBS}{dt} = k_{MBS} * PtCH_4 \quad (1)$$

$r_{MBS}$ , is based on scheme 1 described by equation (1) (as functionalization and C-H activation - the cleavage of the C-H bond - are expected to be facile, mechanistic details are ignored and these steps neglected for simplicity of the formulas.). The problem is, that only the initial amount of platinum can be changed easily, and neither the concentration of dissolved methane nor the concentration of the  $PtCH_4$  complex are accessible under reaction conditions. Thus, several simplifying assumptions are necessary to obtain an expression that relates the observed rates to the initial catalyst concentration.

By analogy to a so-called inverse Michaelis-Menten approach, which has for example been shown to well describe interfacial enzymatic reactions,<sup>6</sup> a quasi-steady-state concentration for the intermediate  $\sigma$ -complex  $Pt-CH_4$  is assumed at low methane conversion:

$$\frac{dPtCH_4}{dt} = k_{PtCH_4} * Pt * CH_{4,sol} - PtCH_4 * (k_{-PtCH_4} + k_{MBS}) = 0 \quad (2)$$

With  $K = \frac{k_{-PtCH_4} + k_{MBS}}{k_{PtCH_4}}$  and  $CH_{4,total} = CH_{4,sol} + PtCH_4$  (2) can be rewritten:

$$k_{PtCH_4} * Pt * (CH_{4,total} - PtCH_4) - PtCH_4 * (k_{PtCH_4} + k_{MBS}) = 0 \quad (3)$$

$$Pt * (CH_{4,total} - PtCH_4) - PtCH_4 * \frac{k_{-PtCH_4} + k_{MBS}}{k_{PtCH_4}} = 0 \quad (4)$$

$$Pt * (CH_{4,total} - PtCH_4) - PtCH_4 * K = 0 \quad (5)$$

Reordering (5) and putting it into (1) gives:

$$PtCH_4 = \frac{Pt * CH_{4,total}}{Pt + K} \quad (6)$$

$$r_{MBS} = k_{MBS} \frac{Pt * CH_{4,total}}{Pt + K} \quad (7)$$

The requirement for the derived rate equation to be valid is a large excess of Pt in solution. Rigorous analyses have found that this may be expressed mathematically as  $CH_{4,total} \ll Pt + K$ .<sup>7-9</sup> Although the exact concentration of  $CH_4$  in solution under reaction conditions is not known, values between 1 and 33 mM are reported, with 33 mM most probably being a very high upper bound, since this value has been determined at 100°C in concentrated sulphuric acid.<sup>10-11</sup> With a K of 0.014 M obtained by the fit (see below), it can be concluded that particularly for higher catalyst concentrations equation (7) provides a decent approximation. In the limiting case of  $CH_{4,total} = PtCH_4$  the maximum possible rate for a given methane concentration will be observed. Thus:

$$r_{max} = k_{MBS} * CH_{4,total} \quad (8)$$

And:

$$r = r_{max} \frac{Pt}{Pt + K} \quad (9)$$

Linearization of (9) in a double reciprocal plot yields the following relationship:

$$\frac{1}{r} = \frac{1}{r_{max}} + \frac{K}{r_{max}} \frac{1}{Pt} \quad (10)$$

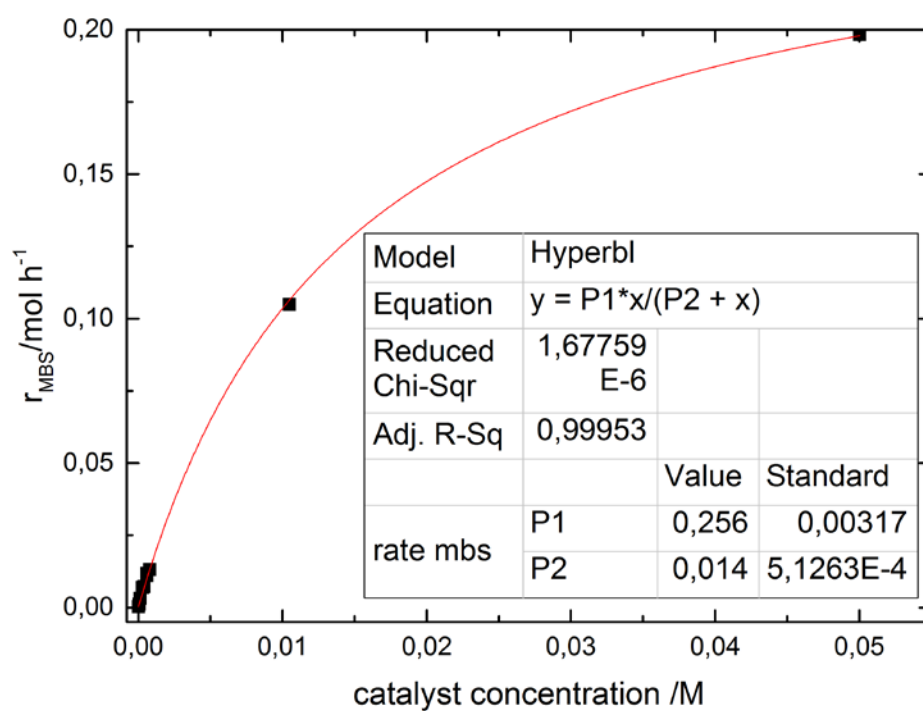


Figure S4: Hyperbolic fit of dependency of  $r_{MBS}$  on catalyst concentration.

## Dependency of selectivity

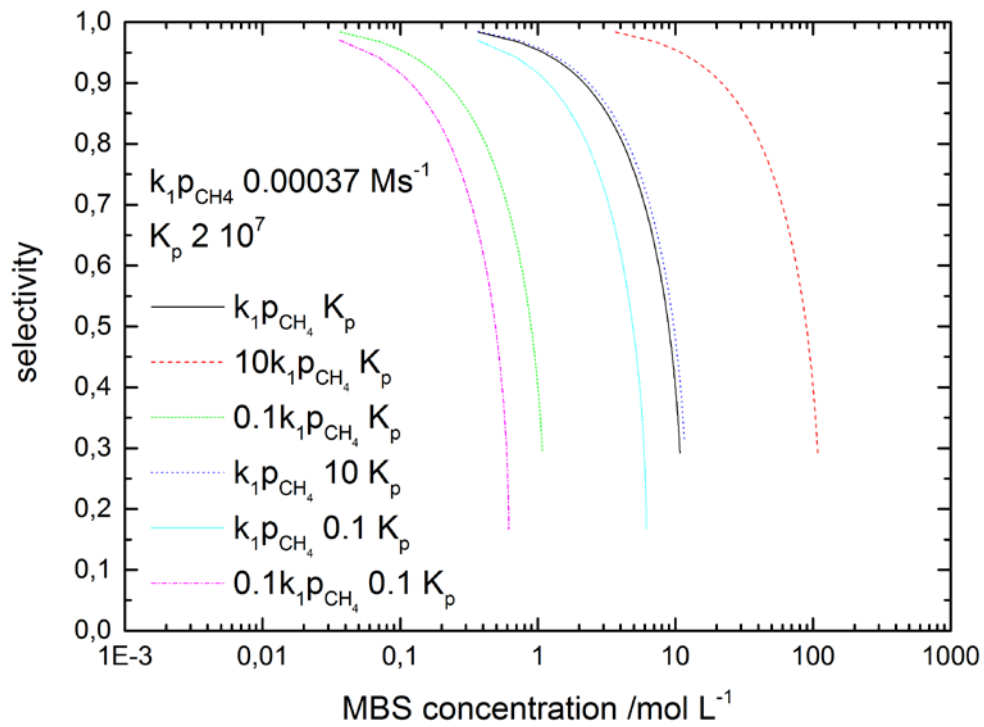


Figure S5: Reassessment of the dependency of selectivity on MBS concentration changing  $k_1$  and  $K_p$  independently using the identical model, formulas and values described and given in reference<sup>12</sup>.

$$K_p = \frac{MBS}{MeOH}$$

$$k_{ox} = \frac{k_2}{1 + K_p} + \frac{k_3 K_p}{1 + K_p}$$

$$k_2 \ 60 \text{ s}^{-1}, k_3 \ 0.00003 \text{ s}^{-1}$$

$$S = \frac{1 - e^{-k_{ox}t}}{k_{ox}t}$$

$$[MBS] = \frac{k_1 p_{CH_4} (1 - e^{-k_{ox}t})}{k_{ox}}$$

Equations used for figure S6 (basic model of a consecutive first order reaction in a batch reactor):

$$C_{CH_4} = (1 - e^{-k_1 t}) * 100$$

$$Y_{MBS} = \frac{k_1}{k_{ox} - k_1} * \frac{e^{-k_1 t} - e^{-k_{ox} t}}{1} * 100$$

Equation used for figure S7:

$$[MBS] = \frac{k_1 c_{CH_4,0}}{k_{ox} - k_1} (e^{-k_1 t} - e^{-k_{ox} t})$$

$[CH_4]_0 = 0.115 \text{ mol}/0.08 \text{ L} = 1.4375 \text{ M}$ ;  $k_1 p_{CH_4}$  and  $k_1$  are interconverted by this factor;  $k_{ox}$  identical to figure S5.

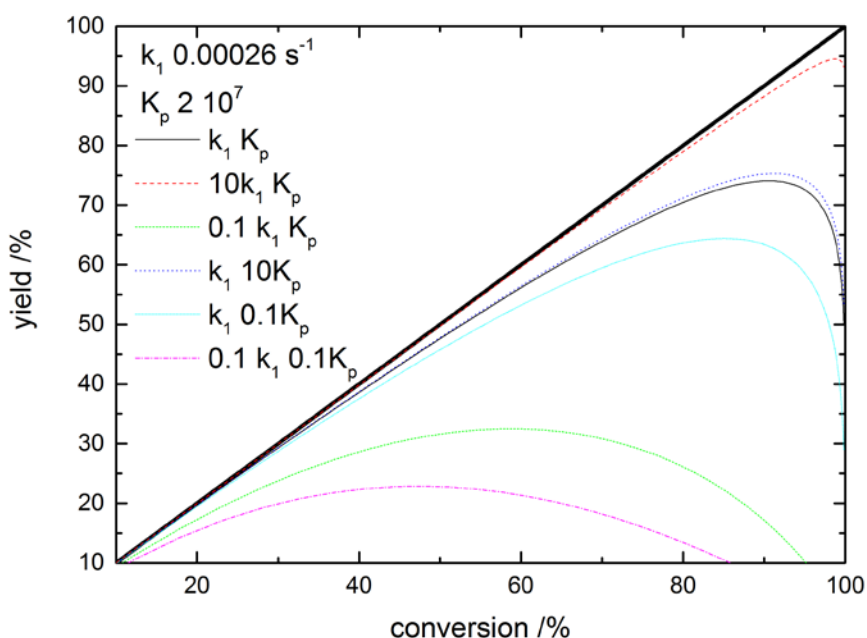


Figure S6: Optimum performance envelope for methane oxidation with further oxidation of MBS and unprotected methanol. The thick black line represents the limit without subsequent oxidation.

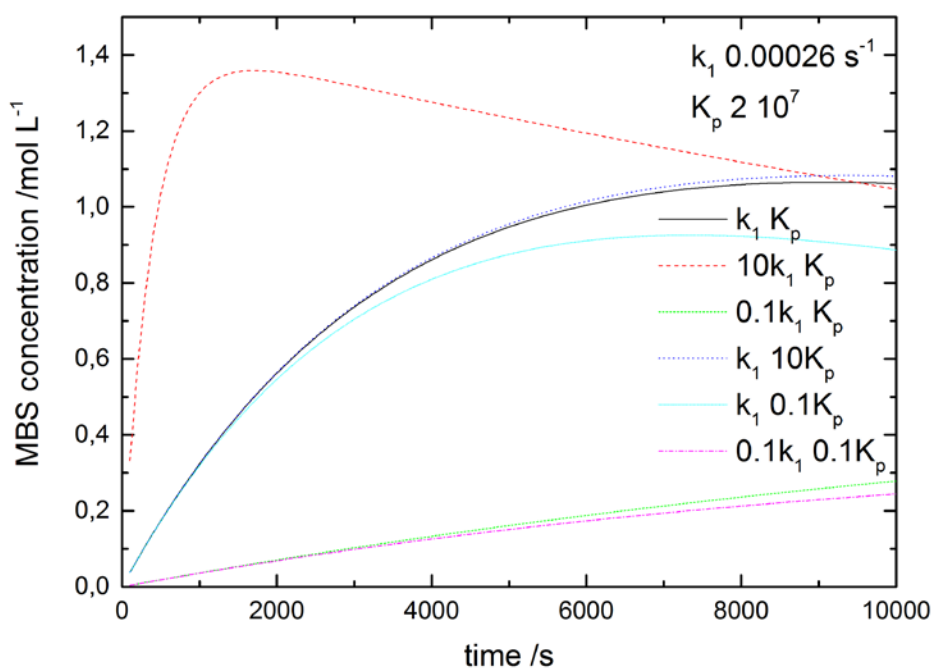


Figure S7: Dependency of MBS concentration on time for methane oxidation with oxidation of MBS and unprotected methanol.

Formula for the fit used in Figure 5:

$$S_{MBS} = \frac{k_{1,apparent}}{(k_{ox,apparent} - k_{1,apparent})} \frac{0.75 - 0.75 \frac{k_{ox,apparent}}{k_{1,apparent}}}{0.25} * 100$$

$r_{MBS}$  is variable (as methane partial pressure was identical in all experiments  $r_{MBS}$  equals  $k_{1,apparent}$ ) and  $k_{ox,apparent}$  is fit parameter assuming first-order reactions regarding methane and MBS, respectively (fit results in a value of  $0.00123 \text{ mol h}^{-1}$ , respectively  $0.082 \text{ mol L}^{-1} \text{ h}^{-1}$ ; a plot of the dependency of selectivity for a consecutive first order reaction on  $k_1$  for a set of  $k_{ox}$  and conversion is given below:

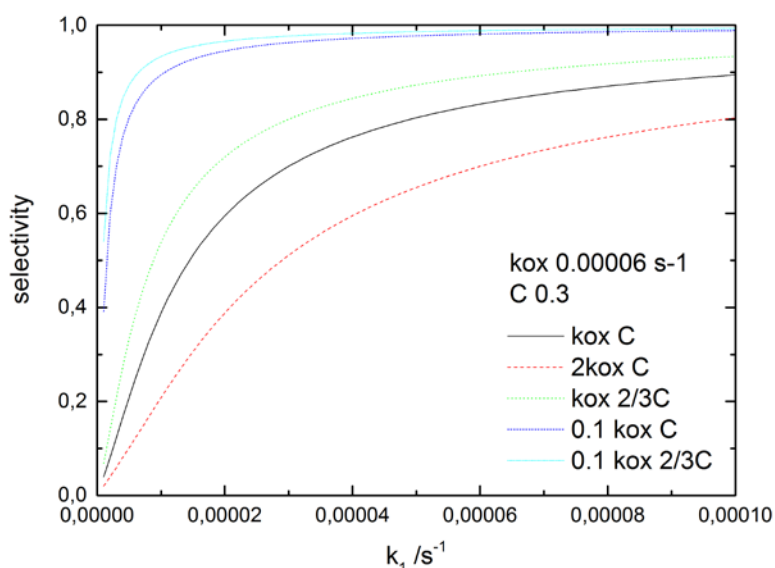
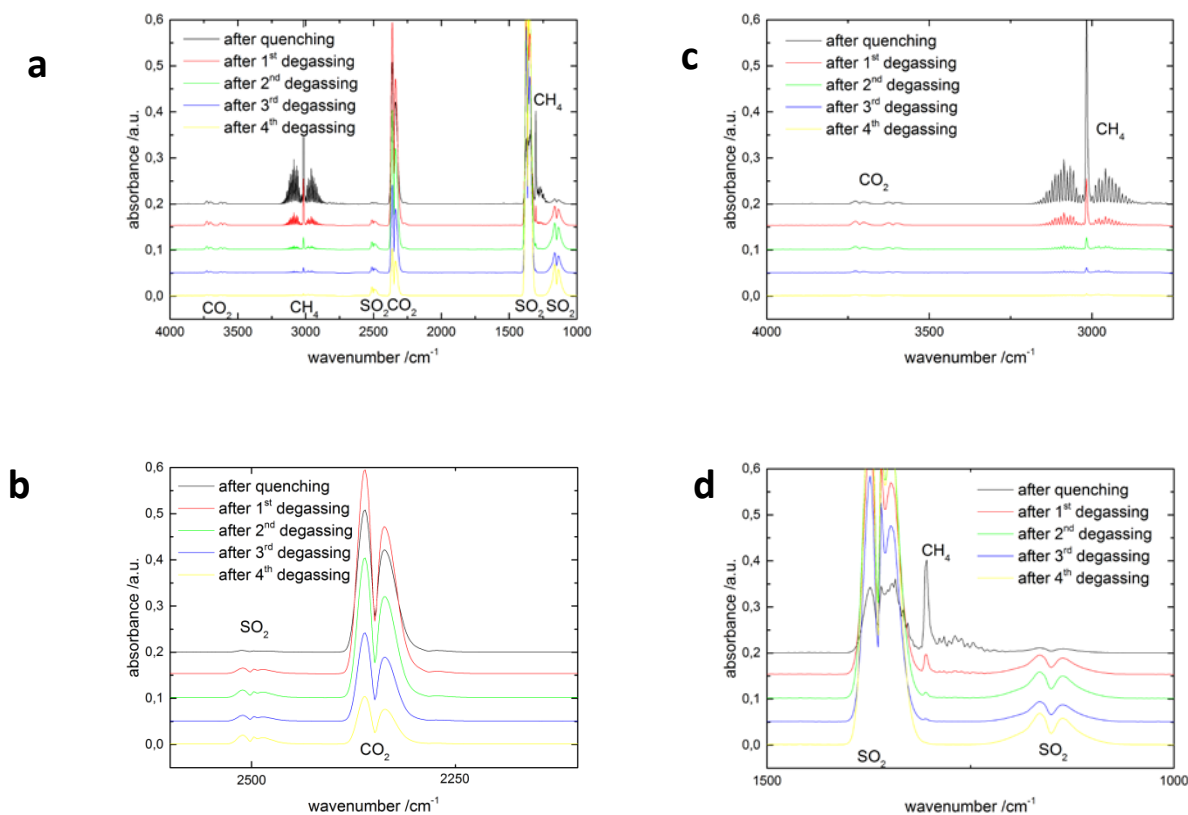


Figure S8: Dependency of selectivity on  $k_1$  for a first order consecutive reaction (Same formula as used for fit in figure 5 but adjusted for conversion).  $k_{ox,apparent}$  from the fit in figure 5 is under assumption of first order in MBS and 1 M concentration  $0.082 \text{ h}^{-1}$  which lies between  $k_{ox}$  and  $0.1k_{ox}$  in figure S8.

## Degassing after reaction



Figures S9: IR spectra (spectral regions: a) 1000-4000 cm<sup>-1</sup>, b) 2000-2750 cm<sup>-1</sup>, c) 2750-4000 cm<sup>-1</sup>, d) 1000-1500 cm<sup>-1</sup>) of gas release and four subsequent degassing cycles of methane oxidation at 215 °C with 50 mM **1** and 100 mM KHSO<sub>4</sub> in 98% sulfuric acid (15 mL) for 2.5 h ( $p_{\text{CH}_4} \approx p_{\text{total}} \approx 50$  bar,  $C_{\text{CH}_4}$  46.7%). Compared to an experiment without addition of K<sup>+</sup>, CO<sub>2</sub> was released easier from the solution. Generally, the spectra shown here originate from experiments with high conversion and thus higher amounts of CO<sub>2</sub> and SO<sub>2</sub>.

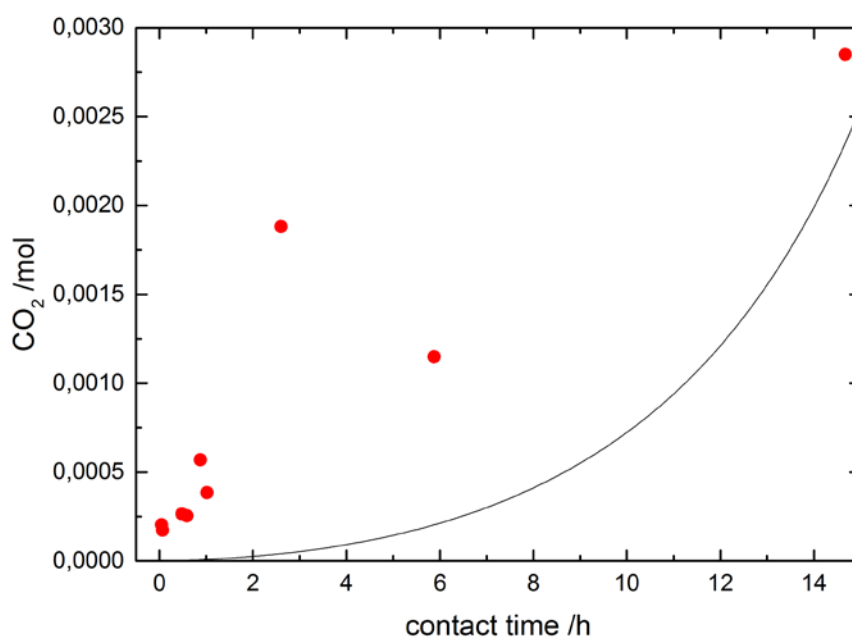


Figure S10: Amount of CO<sub>2</sub> as a function of the contact time in 20% oleum (15 mL) at 215 °C. All reactions stopped after the same pressure drop;  $p_{\text{total}}$  72 bar  $p_{\text{CH}_4}$  65 bar  $C_{\text{CH}_4}$  20-30% [1] varied. The black line corresponds to the amount of CO<sub>2</sub> at 25% conversion for a consecutive reaction.

Deviations from the expected trend can be manifold: Different pathways of CO<sub>2</sub> formation, changes in rate constant for undesired oxidation reactions and systematic errors in the determination of CO<sub>2</sub>, e.g., insufficient degassing. However, the correlation with a consecutive reaction is striking and contributions from other effects are expected to refine the picture.



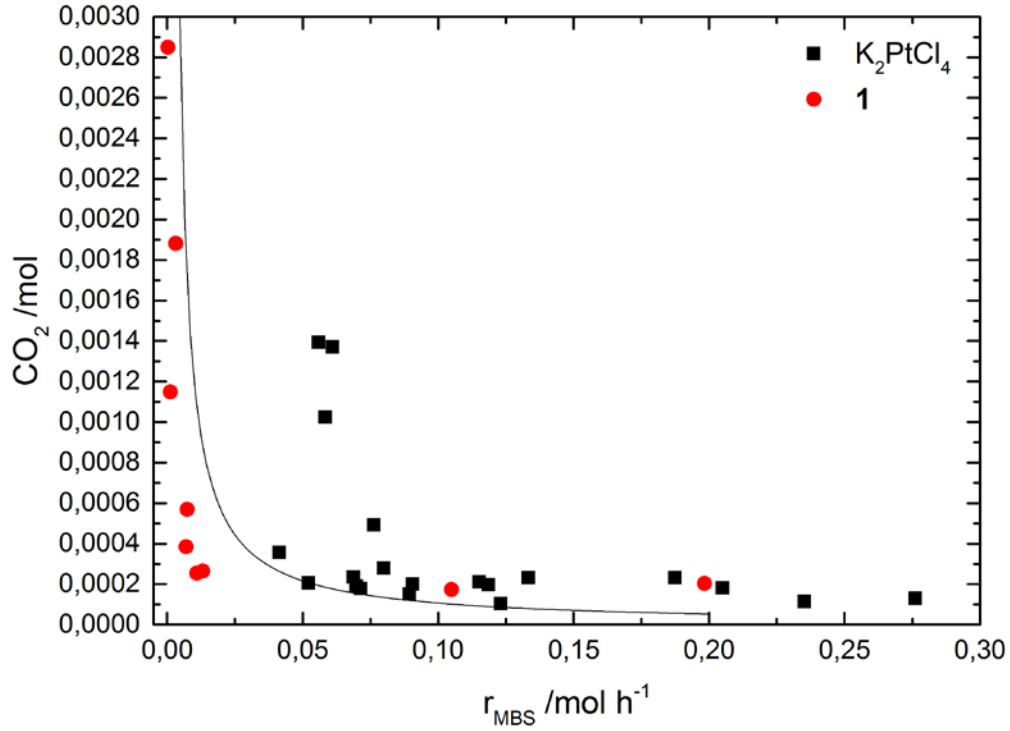


Figure S11: Amount of CO<sub>2</sub> as a function of  $r_{MBS}$  in 20% oleum (15 mL) at 215 °C. All reactions stopped after the same pressure drop;  $p_{total}$  72 bar  $p_{CH_4}$  65 bar  $C_{CH_4}$  20-30% [1, K<sub>2</sub>PtCl<sub>4</sub>] varied. The black line corresponds to the amount of CO<sub>2</sub> at 25% conversion for a consecutive reaction.

With respect to the formed amount of CO<sub>2</sub> the SO<sub>3</sub> concentration series are ambiguous as outlined. Thus only for the catalyst concentration series this analysis was done.

Equations for simulated consecutive first order reaction in figures S10 and S11:

$$n_{CO_2, 25\% conversion}(k_1) = n_{CH_4, 0} + \frac{k_1 n_{CH_4, 0}}{k_{ox} - k_1} 0,75^{\frac{k_{ox}}{k_1}} - \frac{k_{ox} n_{CH_4, 0}}{k_{ox} - k_1} 0,75$$

$$n_{CO_2, 25\% conversion}(t_{contact}) = n_{CH_4, 0} + \frac{-\frac{\ln 0,75}{t} n_{CH_4, 0}}{k_{ox} - \frac{\ln 0,75}{t}} e^{-k_{ox} t} - \frac{k_{ox} n_{CH_4, 0}}{k_{ox} + \frac{\ln 0,75}{t}} 0,75$$

With  $n_{CH_4, 0}$  0.03 mol and  $k_{ox, apparent}$  0.00123 mol h<sup>-1</sup>.

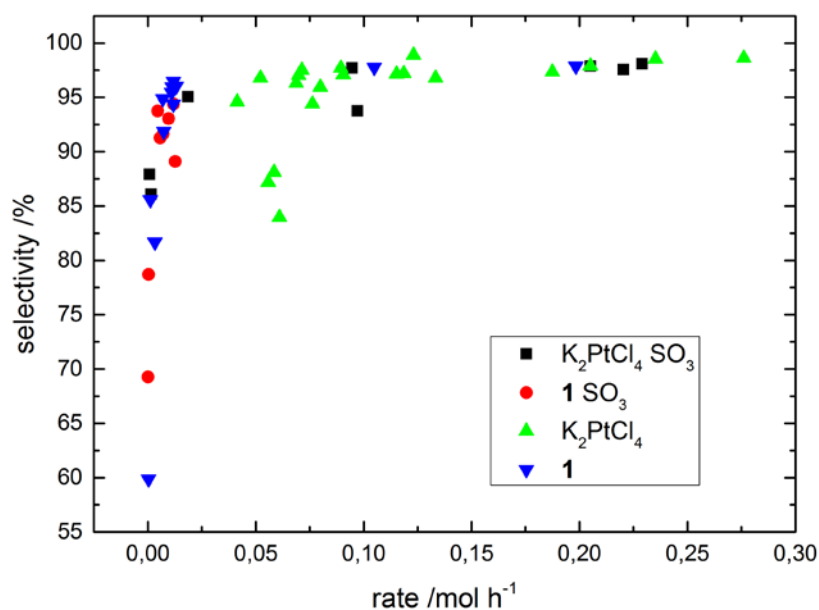


Figure S12: Dependency of selectivity on the rate of MBS formation for the catalyst concentration series (denoted **1** and  $\text{K}_2\text{PtCl}_4$ , same as in figure 5) and the  $\text{SO}_3$  concentration series (denoted **1**  $\text{SO}_3$  and  $\text{K}_2\text{PtCl}_4 \text{ SO}_3$ ).

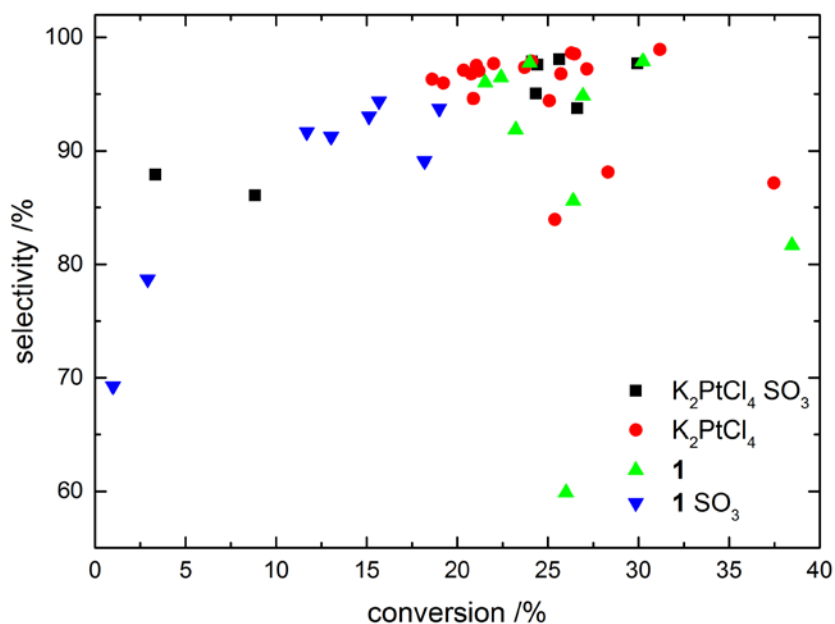


Figure S13: Plot of selectivity versus conversion. The increase in conversion is an artefact attributed to low  $r_{\text{MBS}}$  in concentrated sulfuric acid, data points which were taken at low conversion. On the other hand the catalyst concentration series might indicate that normal behavior, i.e., decrease of selectivity with conversion exists (especially for the concentration series with  $\text{K}_2\text{PtCl}_4$  where contact times and  $r_{\text{MBS}}$  did not cover orders of magnitude).

## MBS decomposition

In order to get a better understanding of the possible roles of the oxidation potential and  $K_p$  for selectivity and to which extent a change in  $SO_3$  concentration influences  $k_{ox}$  the decomposition of MBS was investigated in concentrated sulfuric acid and 20% oleum separately, by subjecting the sodium salt of MBS (NaMBS) which is commercially available to different treatments. 1 M solutions of NaMBS were reacted in a Hastelloy autoclave at 215 °C for 2.5 h in different media as well as with and without addition of 20 mM of **1**. The results are shown in table S3 together with the rate of  $CO_2$  formation in blind experiments. The amount of decomposed NaMBS increased in the following order: Concentrated sulfuric acid < 20% oleum < concentrated sulfuric acid with **1** (20 mM) < 20% oleum with **1** (20 mM). In none of the experiments methane was observed, indicating that functionalization is irreversible.

Table S3: Decomposition of NaMBS and  $CO_2$  formation in blind experiments

entry	conditions <sup>a</sup>	r <sub>ox, total</sub> /mol L <sup>-1</sup> h <sup>-1</sup>	r <sub>ox, cat only</sub> /mol L <sup>-1</sup> h <sup>-1</sup>	r <sub>ox, cat only</sub> /r <sub>ox, total</sub>
1	96% H <sub>2</sub> SO <sub>4</sub>	0.049		-
2	20% oleum	0.065		-
3	96% H <sub>2</sub> SO <sub>4</sub> , 20 mM <b>1</b>	0.119	0.070	0.59
4	20% oleum, 20 mM <b>1</b>	0.137	0.072	0.53
entry	conditions <sup>a</sup>	r <sub>CO<sub>2</sub>→CH<sub>4</sub></sub> <sup>b</sup> /mol L <sup>-1</sup> h <sup>-1</sup>		r <sub>CO<sub>2</sub>→CH<sub>4</sub></sub> / r <sub>ox, total, 20 mM</sub>
5	blind test 96% H <sub>2</sub> SO <sub>4</sub>	0.0058		0.049
6	blind test 20% oleum	0.0072		0.053

<sup>a</sup>215 °C, 2.5 h, 15 mL, 1 M NaMBS <sup>b</sup>based on 15 mL reaction volume excluding gas phase oxidation

These experiments show that uncatalyzed decomposition of MBS (or catalyzed by non Pt compounds, vide infra) has a significant contribution to over oxidation to  $CO_2$ , i.e., uncatalyzed decomposition proceeds with almost the same rate as decomposition catalyzed by 20 mM of **1** in oleum. Furthermore, uncatalyzed decomposition is slightly faster in oleum which might be due to the higher oxidation potential. Catalytic decomposition, however, seems to be rather insensitive to the  $SO_3$  concentration. Finally, entries 5 and 6 show that direct  $CO_2$  formation from  $CH_4$  is around one order of magnitude slower than  $CO_2$  formation via MBS (It cannot be excluded that  $CO_2$  is generally formed via MBS with an extremely low steady state concentration of MBS. Indeed, traces of MBS were found in oleum without addition of catalyst.<sup>13</sup>).

Due to the various contributions the most general description of selectivity in this system is given by equation (1) with integral rates and selectivity.

$$S = \frac{n_{MBS}}{n_{MBS} + n_{CO_2}} = \frac{r_{MBS} - r_{ox, cat} - r_{ox, noncat}}{r_{MBS} + r_{CH_4 \rightarrow CO_2}} \quad (1)$$

Thus, fitting selectivity as a function of  $r_{\text{MBS}}$  with constant  $k_{\text{ox,apparent}}$  is partially justified: Due to the relatively big contribution of noncatalytic decomposition the ratio of  $k_1/k_{\text{ox}}$  increases with increasing catalyst concentration (at least for **1**). This holds especially at low catalyst concentration since decomposition can almost exclusively be attributed to noncatalytic decomposition. Anyway, comparing the value of  $0.082 \text{ mol L}^{-1} \text{ h}^{-1}$  obtained for  $k_{\text{ox,apparent}}$  from the fit in figure 3 and correcting it with a factor of four due to the lower concentration of MBS (final concentration of MBS was around  $0.5 \text{ mol L}^{-1}$ ) shows that these values are in the same ballpark but by far not similar, a result of the rough model.

Actually, the values of catalytic decomposition show that the concept of protection works much better than assumed so far: Transforming the value, under assumption of MBS being first order in catalytic decomposition, of  $0.07 \text{ mol L}^{-1} \text{ h}^{-1}$  into TOF gives a value of  $3.5 \text{ h}^{-1}$  compared to the TOF for methane oxidation with 50 mM of **1** in 20% oleum of  $264 \text{ h}^{-1}$  (vide second part of this back to back series). This is already two orders of magnitude faster which gives if a two orders of magnitude lower methane concentration is assumed (10 mM) around 10000-fold higher intrinsic reactivity towards methane as a lower limit. This comparison also shows that part of the protection is dumbed down by the low solution concentration of methane since the rate constants are convoluted by the solution concentrations. Increasing the concentration of methane in the solution should lead to improvements in selectivity.

It is remarkable that decomposition in 96% sulfuric acid proceeds slower although methanol can be observed in NMR and a part of the ester was obviously saponified. It might be that methanol itself is protonated and still sufficiently protected. Anyhow, as decomposition of NaMBS is slower in concentrated sulfuric acid it does not seem likely that  $K_p$  already dropped to an alarming value in 96% sulfuric acid. Thus, if oxidation potential and solubility of methane could be increased in concentrated sulfuric acid it might be possible to achieve reasonable activity still with high selectivity. The determination of  $K_p$  as well as  $k_{\text{ox}}$  as a function of  $\text{SO}_3$  concentration, especially in more dilute acid (50 – 100%), could be an important goal in order to define a region where methane oxidation could be viable in terms of product protection.

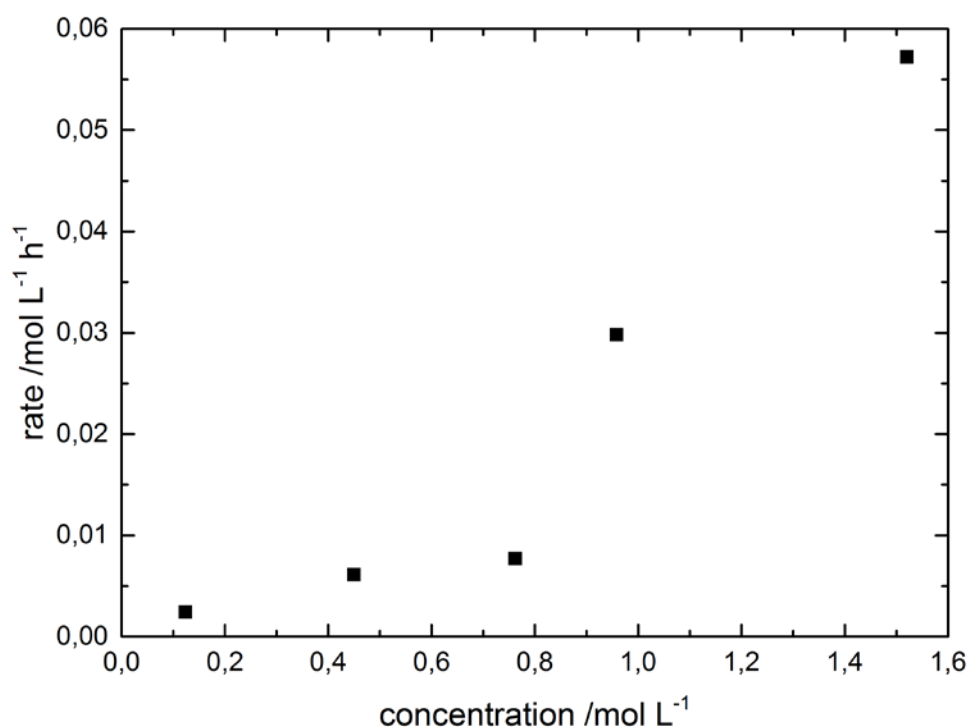


Figure S14: Concentration dependency of NaMBS decomposition in glass vials: 1 mL 96% sulfuric acid, glass vials, no catalyst, 2.5 h, 215 °C,  $C_{\text{NaMBS}} < 10\%$ . Double logarithmic plot does not give a clear linear correlation.

Table S4: Raw data (For some datasets deviations <1% exist due to rounding errors and the solving of BWR by numerical procedure)

SO <sub>3</sub> concentration, liquid phase 15 mL, 215 °C, 600 μM catalyst								
mixing ratio <sup>a</sup>	[SO <sub>3</sub> ] /mol L <sup>-1</sup> (titrated)	CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol	p <sub>SO<sub>3</sub></sub> /bar	time /h:min:s	V <sub>gas</sub> /mL
K <sub>2</sub> PtCl <sub>4</sub>								
3:1:0	18.53 (18.0)	0.038381	0.031151	0.002915	0.000472	1.2	2:00:00	21.2
1								
3:1:0	18.53 (17.8)	0.038660	0.032340	0.000884	0.000239	1.2	2:00:00	21.2
PtCl <sub>2</sub>								
3:1:0	18.53 (18.2)	0.038286	0.035300	0.001191	0.000174	1.0	2:00:00	22.3
catalyst concentration series, 15 mL 20% oleum, 215 °C								
catalyst	[catalyst] /mM	CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol	time /h:min:s	V <sub>gas</sub> /mL	
K <sub>2</sub> PtCl <sub>4</sub>	0.135	0.034019	0.023490	0.006990	0.000178	0:05:53	19.8	
K <sub>2</sub> PtCl <sub>4</sub>	0.321	0.030802	0.019409	0.009504	0.000104	0:04:38	17.9	
K <sub>2</sub> PtCl <sub>4</sub> <sup>b</sup>	0.321	0.028125	0.021405	0.006999	0.000232	0:03:09	17.9	
K <sub>2</sub> PtCl <sub>4</sub>	0.594	0.035708	0.025629	0.008428	0.000182	0:02:28	21.2	
K <sub>2</sub> PtCl <sub>4</sub>	0.594	0.036077	0.026596	0.009358	0.000131	0:02:02	21.9	
K <sub>2</sub> PtCl <sub>4</sub>	0.675	0.029793	0.019321	0.007775	0.000115	0:01:59	17.9	
K <sub>2</sub> PtCl <sub>4</sub>	0.675	0.036981	0.022709	0.008538	0.000232	0:02:44	19.8	

K <sub>2</sub> PtCl <sub>4</sub>	3.598	0.026067	0.018385	0.006881	0.000198	0:03:29	15.4	
K <sub>2</sub> PtCl <sub>4</sub>	3.630	0.029898	0.017993	0.006429	0.000152	0:04:19	15.4	
K <sub>2</sub> PtCl <sub>4</sub>	6.505	0.029014	0.016878	0.009482	0.001394	0:10:12	15.4	
K <sub>2</sub> PtCl <sub>4</sub>	6.505	0.030487	0.017391	0.007607	0.001025	0:07:19	15.4	
K <sub>2</sub> PtCl <sub>4</sub>	10.95	0.030249	0.018467	0.006226	0.000189	0:05:21	15.4	
K <sub>2</sub> PtCl <sub>4</sub>	10.95	0.030886	0.018325	0.006209	0.000206	0:07:09	15.4	
K <sub>2</sub> PtCl <sub>4</sub>	20.06	0.036196	0.025823	0.006678	0.000280	0:05:01	22.3	
K <sub>2</sub> PtCl <sub>4</sub>	20.08	0.035336	0.025784	0.007228	0.000211	0:03:46	22.3	
K <sub>2</sub> PtCl <sub>4</sub>	50.16	0.031667	0.021300	0.006257	0.000357	0:09:04	17.9	
K <sub>2</sub> PtCl <sub>4</sub> c	50.13	0.034420	0.026036	0.006168	0.000236	0:05:23	21.9	
K <sub>2</sub> PtCl <sub>4</sub> d	50.00	0.033837	0.025502	0.006688	0.000200	0:04:26	21.9	
K <sub>2</sub> PtCl <sub>4</sub> e	50.24	0.033668	0.025207	0.007176	0.001371	0:07:04	21.9	
<b>1</b>	0.0159	0.027300	0.015834	0.004250	0.002849	14:40:22	15.4	
<b>1</b>	0.0492	0.030167	0.016295	0.006814	0.001148	5:52:21	15.4	
<b>1</b>	0.142	0.026690	0.015063	0.008387	0.001882	2:36:15	15.4	
<b>1</b>	0.299	0.027846	0.021562	0.007114	0.000385	1:01:12	17.9	
<b>1</b>	0.393	0.030047	0.018674	0.006410	0.000568	0:52:29	15.4	
<b>1</b>	0.597	0.031585	0.019452	0.005309	0.000252	0:28:57	15.4	
<b>1</b>	0.597	0.028838	0.018981	0.005796	0.000244	0:30:47	17.9	
<b>1</b>	0.597	0.032120	0.021268	0.006943	0.000255	0:35:15	17.9	
<b>1</b>	0.597	0.035743	0.025042	0.005279	0.000314	0:26:48	21.2	
<b>1</b>	0.802	0.030774	0.018848	0.006367	0.000264	0:29:08	15.4	
<b>1</b>	10.47	0.032159	0.019337	0.007546	0.000173	0:04:19	15.4	
<b>1</b>	50.03	0.031638	0.019868	0.009365	0.000203	0:02:50	17.9	
PtCl <sub>2</sub>	0.602	0.034839	0.026973	0.006940	0.000235	0:03:02	22.3	
PtCl <sub>2</sub>	19.87	0.033660	0.021409	0.009722	0.000113	0:01:59	22.3	
PtCl <sub>2</sub> <sup>f</sup>	49.60	0.033113	0.021012	0.009561	0.000209	0:01:32	22.3	
high TON, high MBS concentration 215 °C								
conditions		CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol	time /h:min:s	V <sub>gas</sub> /mL	
K <sub>2</sub> PtCl <sub>4</sub> (40.6 μM), 15 mL 20% oleum		0.029698	0.016180	0.009805	0.000856	2:00:00	17.9	
influence of K <sup>+</sup> and Cl <sup>-</sup> on PtCl <sub>2</sub> , 215 °C, 15 mL 20% oleum								
conditions		CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol	time /h:min:s	V <sub>gas</sub> /mL	
50 mM PtCl <sub>2</sub> , 100 mM KHSO <sub>4</sub>		0.034710	0.024229	0.009114	0.000121	0:01:21	21.9	
50 mM PtCl <sub>2</sub> , 100 mM KCl		0.033687	0.022146	0.007699	0.000294	0:31:54	19.5	
50 mM catalyst, 15 mL 98% sulfuric acid, 215 °C								
catalyst	CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol		time /h:min:s	V <sub>gas</sub> /mL	
<b>1</b>	0.028421	0.010040	0.011402	0.001699		2:30:00	17.9	
K <sub>2</sub> PtCl <sub>4</sub>	0.026610	0.021120	0.000914	0.000185		2:30:00	17.9	
PtCl <sub>2</sub>	0.030725	0.023778	0.004521	0.000188		2:30:00	19.8	
pressure dependency, 600 μM catalyst, 15 mL solution, 215 °C								
conditions	p <sub>total</sub> /bar	p <sub>theo</sub> /bar	CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol	time /h:min:s	V <sub>gas</sub> /mL

K <sub>2</sub> PtCl <sub>4</sub> , 96% H <sub>2</sub> SO <sub>4</sub>	38.3	41.4	0.023181	0.019302	0.000587	0.000092	0:02:00	21.9
K <sub>2</sub> PtCl <sub>4</sub> , 96% H <sub>2</sub> SO <sub>4</sub>	67.5	66.4	0.037339	0.034208	0.001074	0.000171	0:02:00	21.9
K <sub>2</sub> PtCl <sub>4</sub> , 96% H <sub>2</sub> SO <sub>4</sub>	90.5	97.0	0.054214	0.046712	0.001595	0.000220	0:02:00	21.9
<b>1</b> , 96% H <sub>2</sub> SO <sub>4</sub>	39.7	46.1	0.023518	0.018477	0.000161	0.000072	0:02:00	19.5
<b>1</b> , 96% H <sub>2</sub> SO <sub>4</sub>	66.0	70.0	0.035879	0.030400	0.000319	0.000117	0:02:00	19.5
<b>1</b> , 96% H <sub>2</sub> SO <sub>4</sub>	92.4	102.1	0.052069	0.043291	0.000332	0.000164	0:02:00	19.5
K <sub>2</sub> PtCl <sub>4</sub> , 20% oleum	40.7	33.0	0.016244	0.007815	0.006778	0.000163	0:06:20	17.9
K <sub>2</sub> PtCl <sub>4</sub> , 20% oleum	40.8	33.7	0.018482	0.010852	0.006360	0.000157	0:04:32	21.2
K <sub>2</sub> PtCl <sub>4</sub> , 20% oleum	58.3	53.3	0.029141	0.019277	0.007210	0.000237	0:03:12	21.2
K <sub>2</sub> PtCl <sub>4</sub> , 20% oleum	69.9	65.4	0.035727	0.025628	0.008428	0.000183	0:02:28	21.2
<b>1</b> , 20% oleum	41.0	32.6	0.016101	0.007564	0.006360	0.000265	1:24:00	17.9
<b>1</b> , 20% oleum	53.7	47.2	0.023065	0.013250	0.006646	0.000210	0:50:50	17.9
<b>1</b> , 20% oleum	70.1	65.4	0.035698	0.025013	0.005279	0.000314	0:26:48	21.2
<b>1</b> , 20% oleum	72.8	65.8	0.032056	0.021277	0.006943	0.000255	0:35:15	17.9
K <sub>2</sub> PtCl <sub>4</sub> , 65% oleum	86.5	27.6	0.016148	0.008358	0.005008	0.000219	0:05:00	21.2
K <sub>2</sub> PtCl <sub>4</sub> , 65% oleum	96.6	36.6	0.021775	0.011825	0.006887	0.000241	0:05:00	21.9
K <sub>2</sub> PtCl <sub>4</sub> , 65% oleum	>100	58.4	0.032624	0.017400	0.008095	0.000538	0:05:00	21.2
<b>1</b> , 65% oleum	83.2	27.8	0.016267	0.013677	0.001480	0.000187	0:30:00	21.2
<b>1</b> , 65% oleum	>100	38.7	0.022900	0.017060	0.002376	0.000164	0:30:30	21.9
<b>1</b> , 65% oleum	>100	59.1	0.032961	0.021512	0.003529	0.000320	0:30:00	21.2
dependency on stirring speed, 15 mL 20% oleum, 215 °C								
catalyst	stirring speed /rpm	CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol	time /h:min:s	V <sub>gas</sub> /mL	
<b>1</b> , 600 μM	0	0.029538	0.018681	0.006952	0.000362	2:38:06	15.4	
<b>1</b> , 600 μM	100	0.029243	0.016493	0.009256	0.001105	1:32:09	15.4	
<b>1</b> , 600 μM	150	0.030007	0.018690	0.005700	0.000310	0:49:13	15.4	
<b>1</b> , 600 μM	250	0.029111	0.018727	0.009267	0.000313	0:52:55	15.4	
<b>1</b> , 600 μM	500	0.028177	0.017810	0.006708	0.000805	0:42:47	15.4	
<b>1</b> , 600 μM	1000	0.031628	0.019447	0.005309	0.000252	0:28:57	15.4	
<b>1</b> , 600 μM	0	0.029804	0.019543	0.006999	0.000464	1:49:12	17.9	

1, 600 $\mu$ M	100	0.026289	0.019978	0.006448	0.000281	0:53:33	17.9
1, 600 $\mu$ M	1000	0.028864	0.018980	0.005796	0.000244	0:30:47	17.9
1, 300 $\mu$ M	0	0.028658	0.021201	0.005901	0.000413	1:40:13	17.9
1, 300 $\mu$ M	100	0.029029	0.021749	0.005932	0.000367	1:08:52	17.9
1, 300 $\mu$ M	150	0.030870	0.021752	0.005840	0.000355	0:59:48	17.9
1, 300 $\mu$ M	250	0.029230	0.021641	0.006350	0.000346	0:58:36	17.9
1, 300 $\mu$ M	1000	0.027848	0.021571	0.007114	0.000385	1:01:12	17.9
blindtests, 215 °C, 15 mL solution							
	CH <sub>4,in</sub> /mol	CH <sub>4,out</sub> /mol	MBS /mol	CO <sub>2</sub> /mol	time /h:min:s	V <sub>gas</sub> /mL	
96% H <sub>2</sub> SO <sub>4</sub>	0.037711	0.035352	0.000032	0.000174	2:00:00	21.9	
20% oleum	0.033493	0.027156	0.000875	0.000271	2:32:00	19.5	
20%oleum	0.034952	0.028364	0.000712	0.000346	2:30:00	19.5	
65% oleum	0.015692	0.011908	0.000108	0.000131	0:05:00	21.2	

<sup>a</sup>mixing ratio is the ratio of the volumes used for preparing the reaction solution and is given as the ratio of 96% sulfuric acid: 20% oleum: 65% oleum <sup>b</sup>5 h at 215 °C before pressurizing with methane <sup>c</sup>K<sub>2</sub>PtCl<sub>4</sub> ground <sup>d</sup>K<sub>2</sub>PtCl<sub>4</sub> ground; 5 h at 215 °C before pressurizing with methane <sup>e</sup>K<sub>2</sub>PtCl<sub>4</sub> ground; 20 h at 215 °C before pressurizing with methane <sup>f</sup>temperature increased to 223 °C after pressurizing with methane



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13. Catalytically active contaminations might be present. Teflon parts, e.g. the coating of stir bars, can soak up reaction solution (with catalyst) and release it in the next experiment. Because tiny amounts of catalytically active material show substantial activity in oleum this has to be considered and taken care of (Experiments with I<sub>2</sub> (30 mM) as catalyst changed the appearance of Teflon parts to purple. These parts showed substantial activity without additional catalyst). Consequently, care has to be taken and Teflon parts have to be frequently replaced.