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# Enhanced catalytic activity of $(DMSO)_2PtCl_2$ at the methane oxidation in SO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> system

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#### ABSTRACT

Among the various methane activation reactions, oleum  $(SO_3-H_2SO_4)$  mediated methane oxidation to methyl bisulfate (MBS), a methanol precursor, is one of the best methods in terms of methane conversion and product selectivity. In this report, we investigated the effect of the catalyst concentration on the MBS yield using the catalyst systems, (bpym)PtCl<sub>2</sub>, K<sub>2</sub>PtCl<sub>4</sub>, and (DMSO)<sub>2</sub>PtCl<sub>2</sub> at 180 °C for 3 h. (bpym)PtCl<sub>2</sub> showed a very high stability as well as a high MBS yield of over 84%, but its catalytic activity expressed in terms of turnovers for 3 h was in the ranges of 50 - 500. K<sub>2</sub>PtCl<sub>4</sub> showed very high catalyst turnovers of over 17,000 at a low catalyst concentration; however, it deactivated rapidly to PtCl<sub>2</sub> which prevents achieving a high MBS yield that was achieved by (bpym)PtCl<sub>2</sub>. However, (DMSO)<sub>2</sub>PtCl<sub>2</sub> showed an enhanced catalytic performance for both the MBS yield and the turnovers. An MBS yield of over 84% with a selectivity of 94% was obtained at a catalyst concentration of 3.0 mM, and its turnovers reached over 19,000 at a low catalyst concentration. This higher catalytic performance of (DMSO)<sub>2</sub>PtCl<sub>2</sub> compared to the other chloride-ligated Pt compounds is due to the DMSO ligand on the Pt, which increases the solubility of the Pt species in oleum. Furthermore, as the DFT study revealed, the low dissociation energy of DMSO from the Pt center can facilitate the coordination of methane on Pt reaction center. Although (DMSO)<sub>2</sub>PtCl<sub>2</sub> was deactivated to PtCl<sub>2</sub> after the reaction like the other Pt compounds with chloride ligand, it can be reactivated to some extent by adding DMSO.

KEYWORDS: methane, oxidation, Pt, oleum, oxidation, methylbisulfate, methanol

# INTRODUCTION

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Catalytic activation of methane to get more valuable chemical such as methanol is an important issue from both a practical and academic standpoint.<sup>1-6</sup> For the conversion of methane to methanol, one of the four C-H bonds in the methane should be selectively oxidized. Due to its abundance and innocuous property, molecular oxygen-mediated direct oxidation of methane using a heterogeneous catalyst has been studied extensively.<sup>7-10</sup> However, a high reaction temperature above 600 °C and the trade-off between conversion and selectivity limit this method. Other kinds of oxidants such as H<sub>2</sub>O<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, SeO<sub>3</sub> and iodates, which can oxidize methane at a milder condition with high selectivity, have also been used. <sup>11-23</sup> In particular, SO<sub>3</sub> is attracting much attention because it can be regenerated using oxygen from the reduced state, SO<sub>2</sub>, and is used in the commercialized process for sulfuric acid production.

The first pioneering work, in which oleum (SO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>) was used as an oxidant for methane oxidation, was carried out by Periana et al. who used Hg(SO<sub>4</sub>) and sulfuric acid as a catalyst and a solvent, respectively.<sup>15</sup> In this reaction, methane is oxidized to methyl bisulfate (MBS) which can be converted to methanol by hydrolysis with water in a separate process (Scheme 1). This SO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> oxidation system was further evolved by the development of the Catalytica/Periana system, (bpym)PtCl<sub>2</sub>, which showed a methane conversion of 90%, a selectivity of over 80% and a catalyst turnover of over 20.<sup>16</sup> The prominent feature of this catalyst is the bipyrimidyl ligand which stabilizes the Pt species so as not to be precipitated in the form of polymeric PtCl<sub>2</sub>. Since then, Pt-catalyzed methane oxidation reactions to MBS have been studied in various ways.<sup>24-29</sup> Cheng et al. used an ionic liquid such as 1-methylimidazolium chloride to dissolve less-soluble Pt catalysts such as PtCl<sub>2</sub> and PtO<sub>2</sub> in a sulfuric acid system.<sup>30</sup> The use of ionic liquid was found to increase the catalytic activities of the Pt compounds by coordination and/or intermolecular interaction with Pt as well as by increasing the Pt solubility in the reaction system. Palkovits et al. and Soorholtz

et al. had immobilized PtCl<sub>2</sub> on a covalent triazine-based framework (CTF) and nitrogen-doped carbon (NDC), respectively, and showed that the PtCl<sub>2</sub>-immobilized solid catalysts had very high catalytic activities, which were superior to the homogeneous Pt(bpym)<sub>2</sub>Cl<sub>2</sub>.<sup>31-32</sup> However, the catalytic activities of the solid catalysts decreased during reuse due to the leaching of the Pt component on the solid catalyst, suggesting the probability of a homogeneous reaction. This assumption was further supported by the same research group that showed that a very small amount of homogeneous Pt species can act as a catalyst.

Zimmermann et al. reported that the performance of Pt compounds in this oleum-mediated oxidation of methane was on the order of large-scale commercialized processes.<sup>33</sup> They showed that the turnover frequency (TOF, h<sup>-1</sup>) of platinum compounds including (NH<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>, Pt black, and Pt(acac)<sub>2</sub> reached over 20,000, which was measured in a reaction condition with a very low catalyst concentration ~ 0.6 mM and a short reaction time less than 5 min. In that report, K<sub>2</sub>PtCl<sub>4</sub> showed the highest turnovers (TOs) of 940 with a product selectivity of 98% for 2.5 min, while, (bpym)PtCl<sub>2</sub> showed TOs of 650 for 30 min, which is a much higher value compared to the previously reported value of 20 obtained with a higher catalyst concentration of 50 mM and a longer reaction time of 2.5 h.<sup>33</sup> Zimmermann et al. ascribed the difference of these two results to (i) the effect of the SO<sub>3</sub> concentration, (ii) a different catalyst solubility at a high catalyst loading, and (iii) the difference in the reaction time. They also showed that PtCl<sub>2</sub> had a comparable activity to (bpym)PtCl<sub>2</sub>.

It seems that the formation of  $PtCl_2$  from the chloride-ligated Pt catalyst is inevitable during the reaction, which leads to catalyst deactivation for any chloride-ligated Pt catalyst in a sulfuric acid system. Because  $PtCl_2$  precipitates in the form of a polymer, the catalyst concentration is one of the important factors that affect the MBS yield. To prevent catalyst deactivation in the form of

PtCl<sub>2</sub>, one solution could be to conduct the reaction at a low catalyst concentration as reported by Zimmermann.<sup>33</sup> Another method might be to introduce a ligand that can stabilize the chloride-ligated platinum catalyst like in the Catalytica system, (bpym)PtCl<sub>2</sub>. However, the strong bidentate ligand does not appear to increase the catalytic activity compared to its precursor K<sub>2</sub>PtCl<sub>4</sub>. These results motivated us to investigate a new chloride-ligated Pt compound with a ligand that can not only increase the stability of the Pt species but also increase the catalytic activity under these harsh reaction conditions.<sup>33</sup>

Herein, we investigated the effect of the catalyst concentration on the catalytic activities of Pt compounds including K<sub>2</sub>PtCl<sub>4</sub>, PtCl<sub>2</sub>, and (bpym)PtCl<sub>2</sub>. Understanding the catalytic behavior of the conventional system according to the catalyst concentration prompted us to introduce a new catalyst system, (DMSO)<sub>2</sub>PtCl<sub>2</sub>, which is widely used as an intermediate for the synthesis of a Pt-based organometallic catalyst because of its good solubility in various solvents as well as easy synthesis method <sup>34-36</sup>. As expected, (DMSO)<sub>2</sub>PtCl<sub>2</sub> exhibited the highest catalytic performance among the tested catalysts. A DFT calculation was conducted to understand the high activity of (DMSO)<sub>2</sub>PtCl<sub>2</sub>, and a potential energy profile for the catalytic cycle of this chloride-ligated Pt(II) was presented.

## **EXPERIMENTAL SECTION**

*General Information.* All chemicals were of analytical reagent grade and used without further purification. K<sub>2</sub>PtCl<sub>4</sub> was obtained from STREM Chemicals Inc. Dimethyl sulfoxide DMSO, oleum (20%wt SO<sub>3</sub>), PtCl<sub>2</sub> and other chemicals for the synthesis of catalyst were purchased from Sigma Aldrich Chemical Co. High-purity methane containing 1% of Ar was supplied from Shinyang Gas Co (Korea).

*Oxidation reaction.* Partial oxidation of methane was conducted using bomb reactor (SUS316, 100 ml) equipped with glass liner, thermocouple, and heating jacket. Glass liner containing catalyst and 30 g of 20%wt oleum (SO<sub>3</sub> 75 mmol) was positioned into the reactor and pressurized with 25 bar of  $CH_4$  at room temperature. With the solution stirred by using teflon-coated magnetic stirrer with 800 rpm, reactor was heated to 180 °C and the resulting mixture was stirred for 3 h. During the reaction, the pressure was maintained to 35 bar. After the reaction, the reactor was cooled to room temperature and the remaining gas was vented in the hood.

*Catalyst synthesis.* Periana catalyst, (bpym)PtCl<sub>2</sub> ( $\eta^2$ -(2,2'-Bipyrimidyl)dichloroplatinum(II)) shown in Figure 1, was synthesized according to the previous method.<sup>16</sup> Potassium tetrachloroplatinate (II) K<sub>2</sub>PtCl<sub>4</sub> (0.223 g, 0.54 mmol) was dissolved in water (2 mL), then 2, 2'-bipyrimidine (0.085 g, 0.54 mmol) was added. This solution was stirred for 12 h at room temperature. An orange precipitation was filtered, washed with acetone and dried in a drying vacuum system at 60 °C. Yield: 92%, <sup>1</sup>H NMR (D<sub>2</sub>SO<sub>4</sub>),  $\delta$  9.81 (d, *J* = 6.0 Hz, 2H), 9.34 (dd, *J* = 5.4, 1.8 Hz, 2H), 8.22 (t, *J* = 5.8 Hz, 2H).

*cis*-Dichlorobis(dimethyl sulfoxide)platinum(II)  $(DMSO)_2PtCl_2$  shown in Figure 1 was synthesized from K<sub>2</sub>PtCl<sub>4</sub> (0.83g, 2.00mmol) and dimethyl sulfoxide (0.44 mL, 6.00 mmol) in water (2 mL) at room temperature with a gentle stirring for 12 h. The white solid was filtered off,

#### ACS Catalysis

washed with ethanol and diethyl ether several times and dried under the vacuum condition. Yield: 92%, <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  3.54 (t, *J* = 11.0 Hz, 6H)

*Product Analysis.* Liquid product containing methyl bisulfate was analyzed using <sup>1</sup>H NMR spectroscopy (400 MHz, Varian). Calibration curve was made using sodium bisulfate (CH<sub>3</sub>OSO<sub>3</sub>Na) and methane sulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H) as an external standard in D<sub>2</sub>SO<sub>4</sub>. In order to evaluate the CO<sub>2</sub> formation, the gas phase product was captured, washed with distilled water, and analyzed using GC-MS (HP 6890 GC with a 5973 Mass spectrometer selective detector) equipped with capillary column (Poraplot Q 30 m x 25 um). The peak areas of Ar which was included in methane (1%) was used as a reference to determine the concentration of CO<sub>2</sub>. The Platinum concentration in the liquid phase was also examined by ICP-OES technique (Thermo scientifiv iCAP 700 series-ICP spectrometer). The X-ray diffraction patterns (XRD) were recorded on a Shimazu X-ray diffractometer (XRD-6000, Japan) using nickel-filtered CuKα radiation with 20 angle from 10 to 90°.

After the reaction, yield and selectivity of MBS were calculated as follows. According to the eq. (3) in Scheme 1. Catalyst turnovers (TOs) were obtained from the synthesized amount of MBS and used catalyst amount after 3 h reaction.

Yield (MBS, %) =  $100 \times \frac{\text{MBS produced (mmol)} \times 2}{\text{SO}^3 \text{ used (mmol)}}$ 

Selectivity (MBS, %) =  $100 \times \frac{\text{MBS produced (mmol)}}{\text{MBS produced (mmol)} + \text{CO}^2 \text{ produced (mmol)}}$ 

Turnovers (TOs, MBS) = MBS produced (mmol)/catalyst used (mmol)

The mass balance of the reaction was calculated by conducting the reaction in a closed condition. The pressured drop by the methane conversion to MBS and CO2 was measured and the consumed amount of methane was calculated using the Benedic-Webb-Rubin equation.<sup>33</sup> The results in Table S3 shows that the produced amounts of MBS and CO<sub>2</sub> were almost equal to the consumed amount of methane which was calculated from the pressure decrease.

*Computational Details.* All calculations were carried out using Gaussian 16 (Revision A.03. Gaussian, Inc., Wallingford CT). All ground-state and transition-state geometries were optimized at the B3LYP level of theory. Basis sets selected for these calculations are the 6-31G(d,p) for C, H, N, O, S, and Cl and LANL2DZ for Pt. Geometries were confirmed as minima or transition-state structures by normal-mode vibrational frequency analysis. Exhaustive conformational searching was performed for all ground-state and transition state structures, but only the lowest-energy structures are reported. Calculations were performed for reactions in the liquid phase, so the SMD polarizable continuum solvent model<sup>37</sup> augmented with parameters for sulfuric acid (static (eps = 101) and optical (epsinf = 2.042) dielectric constants)<sup>38</sup> was used.

# **RESULTS AND DISCUSSION**

When methane is oxidized to methyl bisulfate (MBS) with  $SO_3/H_2SO_4$ , two reactions can happen in the reaction system (Scheme 1). The first reaction is the oxidation of methane to MBS in the presence of a catalyst and oxidant/solvent,  $SO_3/H_2SO_4$  (eq. (1) in Scheme 1). At this reaction, water is co-produced, which rapidly reacts with  $SO_3$  to form  $H_2SO_4$  (eq. (2) in Scheme 1). Therefore, the net reaction of the oxidation of methane to MBS can be expressed as eq. (3) in Scheme 1; one mole of methane reacts with 2 moles of  $SO_3$  to make 1 mole of MBS and  $SO_2$ , respectively. MBS can be hydrolyzed to methanol and sulfuric acid as eq. (4) in Scheme 1. Besides MBS,  $CO_2$  is also formed by this oxidation (eq. (5) in Scheme 1). Irrespective of the formation route, 6 equiv. of  $SO_3$ are consumed for the formation of  $CO_2$  from  $CH_4$ . Therefore, the yield of MBS, the selectivity to MBS, and the turnovers (TOs) for MBS were calculated as described in the experimental part.

*Methane Oxidation using Conventional Pt(II) Catalysts.* First, we did a methane oxidation reaction using the previously studied chloride-ligated catalysts, (bpym)PtCl<sub>2</sub>, K<sub>2</sub>PtCl<sub>4</sub>, and PtCl<sub>2</sub> in the presence of 30 g of 20wt% oleum at 180 °C for 3 h under a methane pressure of 35 bar. The effects of the catalyst concentrations were investigated at ranges between 0.15 to 50 mM, which cover the experimental condition of the previous reports by Periana and Zimmermann.<sup>16, 33</sup> Figure 2 and Tables S4 – S7 showed that the tested catalysts had very different yields of the methane oxidation product, methyl bisulfate (MBS) according to the catalyst concentration.

At a very low catalyst concentration of 0.015 mM,  $K_2PtCl_4$  showed a quite high MBS yield of 11.5% corresponding to near 18,000 turnovers (TOs) during a 3 h reaction. With an increasing catalyst concentration up to 0.77 mM, the yield also rapidly increased to 61.6%; however, the yield of MBS was maximum at this concentration and decreased thereafter. At a concentration between

1.54 and 50 mM, the yields were nearly 50%. The comparison reaction depicted in Figure 3 shows that the MBS yield for a 0.77 mM K<sub>2</sub>PtCl<sub>4</sub> solution is always higher than that of for a 50 mM K<sub>2</sub>PtCl<sub>4</sub> solution for a reaction from 1 - 5 h, and, after 12 h, the MBS yields reached about 74% in both cases. This unexpected phenomenon can be ascribed to the formation of PtCl<sub>2</sub> under a high catalyst concentration condition. It was already reported that the chloride-ligated Pt complex is transformed to  $\alpha$ -PtCl<sub>2</sub>, a polymeric form, which is known to be less soluble in oleum thereby comparatively less active.

However,  $\alpha$ -PtCl<sub>2</sub> showed a very interesting behavior according to the concentration (Figure 2 and Table S4). It had almost constant MBS yields at about 38% with a catalyst concentration from 0.77 ~ 4.8 mM, indicating that the concentration of the active catalytic component is similar in these concentration ranges. However, at a high catalyst concentration of 24.4 mM, it had quite a high MBS yield of 58.2%, and the yield was increased to 71.7% when 50 mM catalyst was used, which was undoubtedly higher compared to the K<sub>2</sub>PtCl<sub>4</sub>-catalyzed reaction.

Compared to K<sub>2</sub>PtCl<sub>4</sub> and PtCl<sub>2</sub>, (bpym)PtCl<sub>2</sub> showed a typical pattern as a homogeneous catalyst concentration (Figure 2 and Table S6); the MBS yield almost linearly increased with the increasing catalyst concentration. At 0.77 M, the MBS yield was 11.8%, which is the lowest value among the catalysts tested. With increasing catalyst concentrations, the yield of the product increased gently and reached the highest MBS yield of 84.2% at 12.6 mM in which the TOs was 158.

Overall, in terms of the catalytic activity, with TOs during a 3 h reaction,  $K_2PtCl_4$  showed a very prominent result, especially at the low catalyst concentration domain. However, in terms of the MBS yield, it has a limitation in reaching the highest MBS yield regardless of the catalyst concentration due to the instability of the catalyst. Although (bpym)PtCl<sub>2</sub> had the highest MBS

#### ACS Catalysis

yield at a high catalyst concentration, it was clear that the catalytic activity is much lower compared to those of  $K_2PtCl_4$  and  $PtCl_2$ .

*Methane Oxidation using (DMSO)*<sub>2</sub>*PtCl*<sub>2</sub>. At this point, we propose and demonstrate a new methane oxidation catalyst system, (DMSO)<sub>2</sub>PtCl<sub>2</sub> showing the highest catalytic performance in the production of MBS. Figure 2 and Table S6 show, at 0.015 mM of (DMSO)<sub>2</sub>PtCl<sub>2</sub>, the MBS yield was 12.2%, and the yield rapidly increased to 67.8% when the concentration of the catalyst reached 0.77 mM, which is almost similar with the value of K<sub>2</sub>PtCl<sub>4</sub>, 61.6%, obtained at the same reaction condition. However, unlike K<sub>2</sub>PtCl<sub>4</sub>, the MBS yield increased more with the increasing catalyst concentration and reached 84.6% at 3.0 mM. Under this condition, based on the amount of CO<sub>2</sub>, the MBS selectivity was 94.7% and the SO<sub>3</sub> conversion reached 98.7%. Further increases in the catalyst concentration, however, resulted in slight decreases of the MBS yield to 81.3% and the selectivity to 92.3% at 50.1 mM due to the increased formation of CO<sub>2</sub>. The highest turnovers of over 19,000 was reached at 0.015mM and the values decreased with increasing catalyst concentrations.

The catalytic activity and stability of  $(DMSO)_2PtCl_2$  could also be confirmed from the effect of the reaction time shown in Figure 3. At an early reaction time less than 3 h, the MBS yields of  $(DMSO)_2PtCl_2$  and  $K_2PtCl_4$  were almost similar at the catalyst concentration of 0.77mM, indicating that the intrinsic catalytic activities of these two catalyst are similar. However, when the reaction time was increased to 14 h, the MBS yield increased more and reached 90.6% with the  $(DMSO)_2PtCl_2$ , while the  $K_2PtCl_4$  had a 71.3% MBS yield after the same reaction time. Therefore, it can be concluded that  $(DMSO)_2PtCl_2$  is more active than  $(bpym)PtCl_2$  and is more stable than  $K_2PtCl_4$ .

*Extra Ligand Effect.* This unprecedented high catalytic performance of  $(DMSO)_2PtCl_2$  in this oleum-mediated methane oxidation reaction can be ascribed to the DMSO ligand on the Pt complex, which can stabilize the Pt species so as not to be converted rapidly to  $PtCl_2$  polymer at the reaction condition thus increasing the single molecular homogeneous Pt species in the oleum solution. Although the real concentration at a reaction condition of 180 °C in the presence of 20% oleum, is unknown, measurement of the dissolved Pt concentration in 20wt% oleum at room temperature revealed that the  $PtCl_2$  solubility increased 600 times when DMSO was dissolved together with it (Table S3).

The other role of DMSO is presumed to be to make a vacant site for methane coordination by dissociation from the Pt center during the reaction. With (bpym)PtCl<sub>2</sub>, its stability is much higher than any other chloride-ligated Pt complex; no precipitated PtCl<sub>2</sub> was observed even at a highly concentrated condition of 50 mM after the reaction. Nevertheless, the lower catalytic activity compared to (DMSO)<sub>2</sub>PtCl<sub>2</sub> might be due to the strong binding of the chloride ligand on the Pt. To confirm this explanation, a DFT calculation was conducted for the dissociation energy of the Pt-ligand. Figures 4 and 5 show that the dissociation energies of the Cl ligand for (bmpy)PtCl<sub>2</sub> and (DMSO)<sub>2</sub>PtCl<sub>2</sub> are 22.1 kcal/mol and 20.7 kcal/mol, respectively, which are very similar to each other, while the dissociation energy of the DMSO ligand from the (DMSO)<sub>2</sub>PtCl<sub>2</sub> was calculated to have a much lower value of 13.6 kcal/mol. Therefore, it is very reasonable to assume that, instead of chloride dissociation, DMSO dissociation occurs in the (DMSO)<sub>2</sub>PtCl<sub>2</sub>-catalyzed reaction for the methane coordination. The result shown in Table 1 that the addition of extra DMSO or chloride to (DMSO)<sub>2</sub>PtCl<sub>2</sub> resulted in a decreased yield of MBS also supports the dissociation of the ligand from the Pt center thereby making a vacant site for methane coordination as one of the important steps in this Pt-catalyzed reaction.

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The DMSO dissociation from (DMSO)<sub>2</sub>PtCl<sub>2</sub> in oleum condition could be observed at the <sup>1</sup>H-NMR study. Figure S5 shows when (DMSO)<sub>2</sub>PtCl<sub>2</sub> was dissolved in oleum, two peaks were appeared at 3.61 ppm and 4.04 ppm ((b) in Figure S5), which assumed to free DMSO that was dissociated from Pt center and Pt-bonded DMSO. Interestingly, adding DMSO to PtCl2 reagent also show a similar NMR pattern ((d) in Figure S5), indicating DMSO can also activate PtCl2 in oleum condition. This DMSO addition effect can be confirmed in the PtCl<sub>2</sub>-catalyzed reaction.

Table 1 shows when 2 equiv. of DMSO are added to the PtCl<sub>2</sub>-catalyzed reaction, the MBS yield increased from 30.7% to 58.2%, whereas the addition of extra Cl ligand resulted in the deterioration of the MBS yield. The addition of 2 and 4 equiv. of KCl to a 2.43 mM PtCl<sub>2</sub>-catalyzed reaction reduced the MBS yield to 18.3% and 13.3% from 30.7%, respectively. Furthermore, an excess amount of KCl completely suppresses oxidation. This extra chloride effect explains why  $K_2PtCl_4$  showed a maximum MBS yield at 0.77 mM and a lower MBS yields than those of PtCl<sub>2</sub> at a concentration higher than 10 mM.

Two kinds of PtCl<sub>2</sub> forms are known to exist. <sup>39-41</sup> One is the  $\alpha$  form, a polymeric structure, and the other is the  $\beta$  form, a hexameric PtCl<sub>2</sub>. After the K<sub>2</sub>PtCl<sub>4</sub>-calalyzed reaction with a highly concentrated solution of 50.1 mM, we could isolate the  $\beta$ -PtCl<sub>2</sub> from the solid catalyst (supporting information) and confirmed the structure using XRD. Figure 6 shows that the  $\beta$ -PtCl<sub>2</sub> isolated from the reaction had a very similar XRD pattern to the synthesized  $\beta$ -PtCl<sub>2</sub>. This result indicates that PtCl<sub>2</sub> exists not only in an insoluble polymeric form but also in a soluble monomer ~ oligomer structure in oleum media, which could act as a homogeneous oxidation catalytic species in the PtCl<sub>2</sub>-catalyzed reaction. Therefore, we can assume that, at a relatively low catalyst concentration range of 0.77 ~ 4.8 mM, irrespective of the added catalyst amount, the total active catalytic species might be similar in concentration due to the formation of various PtCl<sub>2</sub> oligomers. Over a 20 mM

concentration range, the dissolved oligomeric Pt species could increase with an increasing catalyst concentration. At the same time, a heterogeneous catalytic reaction on the surface of the solid  $PtCl_2$  cannot be excluded at the high catalyst concentration condition.

On the other hand, at a low catalyst concentration lower than 5 mM, the solubility of  $K_2PtCl_4$  would be higher than that of PtCl<sub>2</sub>. Furthermore, a low concentration of Pt as well as the presence of four chloride ligands on PtCl<sub>4</sub><sup>2-</sup> can prevent the immediate aggregation to the PtCl<sub>2</sub> oligomer or polymer. While, at a high concentration range, the PtCl<sub>2</sub> formation could be accelerated. In addition, the existence of two equiv. of free chloride ions dissociated from PtCl<sub>4</sub><sup>2-</sup> during the conversion to PtCl<sub>2</sub> can block the active catalytic site on PtCl<sub>2</sub>.

*Reactivation of deactivated (DMSO)*<sub>2</sub>*PtCl*<sub>2</sub>. Although (DMSO)<sub>2</sub>PtCl<sub>2</sub> exhibited the highest catalytic activity among the tested Pt catalysts, it was not stable enough like (bpym)PtCl<sub>2</sub>; when a large amount of (DMSO)<sub>2</sub>PtCl<sub>2</sub> was used, PtCl<sub>2</sub> formation was also observed after the reaction ((c) in Figure S6). However, this limitation could be overcome to some extent by adding DMSO to the deactivated system. After the oxidation of methane using (DMSO)<sub>2</sub>PtCl<sub>2</sub> at 180 °C for 3 h, more oleum was added, and methane oxidation was carried out again. Table 2 shows that the yield of MBS decreased to 53.2% in the second reaction, indicating that (DMSO)<sub>2</sub>PtCl<sub>2</sub> deactivated to PtCl<sub>2</sub> during the reaction. However, the addition of 2 equiv. of DMSO to the deactivated (DMSO)<sub>2</sub>PtCl<sub>2</sub> system increased the yield of MBS up to 78.4%, which is about 90% of the fresh catalyst yield. The reason for the decreased activity in the second reaction mainly due to the insufficient activation of the deactivated catalytic species and partially due to the increased volume of the solution thereby decreasing the catalyst concentration as well as the contact area between the liquid phase and gas phase.

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*Reaction mechanism.* Based on the above discussion, it seems that the (DMSO)<sub>2</sub>PtCl<sub>2</sub> turns into cationic sulfuric acid-coordinated Pt(II) species like I upon protonation of a facile ligand (Scheme 2). For the coordination of methane, a vacant coordination site has to be available through the dissociation of a coordinated solvent or DMSO. After the coordination of methane, the C-H bond of methane will be activated by oxidative addition to Pt, resulting in the formation of species III. Reductive elimination of sulfuric acid leading to species IV and successive addition of protonated SO<sub>3</sub> forms species V. From species V, OH of the pronated SO<sub>3</sub> is oxidatively added, and methyl bisulfate, sulfuric acid, SO<sub>2</sub>, and water are eliminated to form the starting species I. The energy diagram based on the DFT calculation is shown in Figure S7.

# CONCLUSION

Chloride-ligated Pt-catalyzed methane oxidation in oleum conducted at 180 °C for 3 h using various catalyst concentrations revealed that the ligand on the Pt catalysts controls the stability of the catalysts as well as the catalytic activity. The Catalytica system, (bpym)PtCl<sub>2</sub>, showed the lowest turnovers at low concentrations below 10 mM, but due to its stability, it had very high MBS yields over 84% at 12.6 mM. K<sub>2</sub>PtCl<sub>4</sub>, a recently reported highly active methane oxidation catalyst, showed a very high activity at a low catalyst concentration less than 1 mM; however, it showed a maximum MBS yield of 61.6% at 0.77 mM and decreased thereafter, indicating that catalyst deactivation in the form of PtCl<sub>2</sub> accelerated with the increasing catalyst concentration. This instability of K<sub>2</sub>PtCl<sub>4</sub> and the low catalyst activity of Pt(bmpy)Cl<sub>2</sub> could be overcome by introducing the DMSO ligand to chloride-ligated Pt catalysts; (DMSO)<sub>2</sub>PtCl<sub>2</sub> had a very high turnovers close to 20,000 and the highest MBS yield of 84.6% at 3.0 mM. The role of DMSO in

(DMSO)<sub>2</sub>PtCl<sub>2</sub> seems to be to increase the catalyst stability preventing deactivation to PtCl<sub>2</sub> during the reaction and to dissociate from the Pt center more easily than chloride in (bpym)PtCl<sub>2</sub> thereby facilitating methane coordination on the active center. We observed that (DMSO)<sub>2</sub>PtCl<sub>2</sub> was also deactivated to PtCl<sub>2</sub> after the reaction, but its activity could be restored to 90% of the activity of the fresh catalyst by adding 2 equiv. of DMSO.

#### ASSOCIATED CONTENT

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Author Contributions

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#### Notes

The authors declare no competing financial interest.

# **Supporting information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: Figures S1-S2 shows NMR spectra of synthesized (bpym)PtCl<sub>2</sub> and (DMSO)<sub>2</sub>PtCl<sub>2</sub>, respectively. More detailed explanation about experimentals was added, which showed reactor system, quantification and qualification for product, estimated error ranges. Procedures for the

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determination of Pt in sulfuric acid, isolation method for  $\beta$ -PtCl<sub>2</sub> from product solid, and synthesis of  $\beta$ -PtCl<sub>2</sub> according to the previous work were also contained. Table S4-S7 are tabulated values of Figure 2 showing TOs according to catalyst concentration.

# ACKNOWLEDGMENT

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Scheme 1. Reaction steps of methane oxidation to methanol via methylbisulfate ( $CH_3OSO_3H$ , MBS) using  $SO_3$ - $H_2SO_4$ .







**Figure 2**. Effects of catalyst concentration of various chloride-ligated Pt catalysts on methane oxidation. Condition: oleum (20wt%) 30g, CH<sub>4</sub> 35 bar, 180°C, 3 h.





**Figure 3.** Effect of reaction time and catalyst concentration at (DMSO)<sub>2</sub>PtCl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub>catalyzed methane oxidation. Condition: oleum (20wt%) 30g, CH<sub>4</sub> 35 bar, 180°C



**Figure 4.** Optimized structures showing the interactions of (bypm)PtCl<sub>2</sub> with  $H_2SO_4$ : (a) reactant ((bypm)PtCl<sub>2</sub> +  $H_2SO_4$ ), (b) transition state, and (c) product.



**Figure 5.** Optimized structures showing the interactions of  $(DMSO)_2PtCl_2$  with  $H_2SO_4$ : (a) reactant  $((DMSO)_2PtCl_2 + H_2SO_4)$ , (b1) transition state for chloride dissociation, and (c1) product, (b2) transition state for DMSO dissociation, and (c2) product.

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| Catalyst                              | Cat. Conc. | Additive (equiv.) <sup>b</sup> | MBS Yield (%) |
|---------------------------------------|------------|--------------------------------|---------------|
| (DMSO) <sub>2</sub> PtCl <sub>2</sub> | 3.08 mM    | -                              | 85.1          |
|                                       |            | DMSO (2)                       | 72.2          |
|                                       |            | DMSO (4)                       | 60.4          |
|                                       |            | KCl (2)                        | 70.3          |
|                                       |            | KCl (4)                        | 53.0          |
| PtCl <sub>2</sub>                     | 2.43 mM    | -                              | 30.7          |
|                                       |            | DMSO (2)                       | 58.2          |
|                                       |            | DMSO (4)                       | 48.9          |
|                                       |            | KCl (2)                        | 18.3          |
|                                       |            | KCl (4)                        | 13.3          |
|                                       |            | KCl (10)                       | tr.           |

Table 1. Effects of extra ligands on the methane oxidation reaction catalyzed by  $(DMSO)_2PtCl_2$  and  $PtCl_2^a$ 

<sup>a</sup> Condition: oleum (20wt%) 30g, CH<sub>4</sub> 35 bar, 180°C, 3 h. <sup>b</sup> Mole of additive / mole of catalyst.



**Figure 6.** XRD of  $PtCl_2$  isolated after the methane oxidation. (a) reagent  $\alpha$  -PtCl<sub>2</sub>, , (b) waterinsoluble solid, and (c) water-soluble solid isolated from  $K_2PtCl_4$ -catalyzed reaction, (d)  $\beta$ -PtCl<sub>2</sub> synthesized.

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| Catalys   | Additive (equiv.) <sup>b</sup> | MBS Yields (%) |
|---|--------------------------------|----------------|
| (DMSO) <sub>2</sub> PtCl <sub>2</sub>               |                                | 85.1           |
| (DMSO) <sub>2</sub> PtCl <sub>2</sub> (deactivated) |                                | 53.2           |
| (DMSO) <sub>2</sub> PtCl <sub>2</sub> (deactivated) | DMSO (2.0)                     | 78.4           |

 $^{\rm a}$  Condition: Catalyst 3.08 mM, CH\_4 35 bar, 180°C, 3 h.

<sup>b</sup> Mole of additive / mole of catalyst.



**Scheme 2.** Plausible reaction mechanism for oleum-mediated methane oxidation using (DMSO)<sub>2</sub>PtCl<sub>2</sub>.

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# TABLE OF CONTENTS



(Oleum 30 g (20wt%), CH4 35 bar, 3.0mM cat., 180°C, 3 h)

