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# CO-assisted direct methane conversion into C<sub>1</sub> and C<sub>2</sub> oxygenates over ZSM-5 supported transition and platinum group metal catalysts using oxygen as an oxidant

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**Abstract:** Conversion of methane towards chemical feedstocks such as oxygenates and hydrocarbons has been studied along with the development of natural gas technology. In this study, CO-assisted direct conversion of methane into C<sub>1</sub> and C<sub>2</sub> oxygenates was demonstrated over ZSM-5 supported transition and platinum group metal catalysts. Besides previously investigated Rh, other platinum group metals (e.g., Ru and Ir) were found to be a potential element as a catalyst. Presence of CO was critical for the reaction, which would work as a ligand, a reductant, and a reactant. On the other hand, the competing undesired CO oxidation toward CO<sub>2</sub> was found to be the major issue. Partial oxidation toward methanol or formic acid (C<sub>1</sub> oxygenates formation) was parallel to oxidative carbonylation to acetic acid (C<sub>2</sub> oxygenate formation).

Chemical industries have required a technology innovation to the demand of the times to follow the changes in the feedstocks. Since around 2010, the market price of natural gas has been decreasing due to the shale gas revolution, and the major feedstock for energy and base chemicals is shifting from crude oil to natural gas.<sup>[1,2]</sup> Because the main component of natural gas is methane (CH<sub>4</sub>, 70–90%), a lot of interest have been focused on methane conversion into valuable products such as C<sub>1</sub> oxygenates (i.e., methanol and formic acid), syngas (carbon monoxide with hydrogen), and resulting synthetic gasoline.<sup>[3–5]</sup> Methane conversion into liquid product would also contribute to the transportation problem of the combustible gas from isolated mines to consuming region.<sup>[6,7]</sup>

The two-step chemicals production via syngas has been industrialized for a long time although its high energy consumption due to the high temperature process (>1073 K) has been considered as a huge drawback and it limited the application only in a large-scale industry.<sup>[8]</sup> Formation of oxygenates via partial oxidation with several types of oxidants (e.g.,  $O_2$ ,  $H_2O_2$ , and  $N_2O$ ) is an alternative approach. Among them, low-temperature direct partial oxidation of methane using gaseous oxygen as an oxidant (i.e.,  $CH_4 + 1/2O_2 \rightarrow CH_3OH$ ) has been expected as the most desirable methane converting method to replace the current energy-intensive and large-scale approach.<sup>[9,10]</sup> A huge number of studies have been reported on the process and catalyst developments.<sup>[11–14]</sup> As far as we know, the highest one-pass yield (70%) of the C<sub>1</sub> oxygenates production was reported over homogeneous platinum-based catalyst by Periana et al.<sup>[15]</sup> Compared to this benchmark result, far low oxygenates yield has been achieved on heterogeneous catalysts.<sup>[13]</sup> In 2005, Groothaert et al. developed a heterogenous ZSM-5 supported copper catalyst and succeeded in the methanol synthesis with high selectivity by "chemical loop" system.<sup>[16]</sup> Because of the structural similarity in copper sites formed on zeolite to the enzyme, particulate methane monooxygenase (pMMO),<sup>[17–19]</sup> a lot of studies about zeolite supported copper catalysts have been reported and summarized in review papers.<sup>[14,20,21]</sup> However, together with the low oxygenates (i.e., methanol) yield (<< 1%), non-catalytic "chemical loop" process has also been a major drawback.

Another catalyst developed recently was single-atom Rh catalyst supported on ZSM-5 reported in 2017<sup>[22]</sup> and 2018<sup>[23]</sup> by two groups. It catalysed the methane conversion into methanol (CH<sub>3</sub>OH), formic acid (HCOOH), and acetic acid (CH<sub>3</sub>COOH) at 423 K under the assist of CO with production rate of 8.5, 1.6×10, and 3.1×10 mol·mol<sub>Rh</sub><sup>-1</sup>·h<sup>-1</sup>, respectively. The values were higher than the previous copper-based zeolite catalysts.<sup>[24–27]</sup> In the report of 2017, CO was denoted as a "cocatalyst".<sup>[22]</sup> This interesting reaction system was, however, not well-understood especially in the role of CO and the origin of C<sub>2</sub> oxygenates (i.e., CH<sub>3</sub>COOH). A new strategy for direct methane conversion would be established by a further investigation of this CO-assisted reaction system.

Herein, the CO-assisted methane conversion into  $C_1$  and  $C_2$  oxygenates was demonstrated over ZSM-5 supported transition and platinum group metals (i.e., Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir, and Pt). In the system, CO worked as a ligand to the transition metal and/or a reductant to form active oxo-species on the metal. Furthermore, it also worked as a co-reactant to form acetic acid via an oxidative carbonylation reaction. Competing simple oxidation of CO into CO<sub>2</sub>, however, suppressed the desired reactions. The detailed reaction route was investigated, and sequential partial oxidation from CH<sub>4</sub> to CH<sub>3</sub>OH to HCOOH was found parallel to oxidative carbonylation of CH<sub>4</sub> to CH<sub>3</sub>COOH.

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Metal catalysts supported on ZSM-5 were prepared by impregnation method. Practically, 600  $\mu$ L of metal nitrate or chloride salts solution were step-wisely added to 1 g of NH<sub>4</sub>-ZSM-5 (Si/Al = 11.9) powder and mixed homogeneously, and then pretreated by H<sub>2</sub> at 823 K for 3 h. Catalytic tests were conducted with a high-pressure batch reactor at 423 K under the presence of O<sub>2</sub>, CO, and CH<sub>4</sub> gases (0.2, 0.5, and 2.0 MPa, respectively) with 40 mg of catalyst and 8 mL of solvent water. Gaseous and liquid products were analysed by GC-FID equipped with methanizer and <sup>1</sup>H NMR with DANTE presaturation pulse,<sup>[28]</sup> respectively. For the detailed experimental procedures and product quantification, please see Supporting Information.

Besides previously tested Rh,[22,23] four other platinum group metals (i.e., Ru, Pd, Ir, Pt) supported on ZSM-5 were screened as a catalyst for CO-assisted direct methane conversion. In addition, transition metals including Cu were also tested as reference catalysts. Especially, Cu has previously been well-studied in the CO-free chemical loop system.<sup>[14,20,21]</sup> In the current study, all the tested metals demonstrated the formation of  $C_1$  and  $C_2$ oxygenates under the presence of CO (Fig. 1), and precious metals exhibited higher catalytic performance than Cu. In any case, only CH<sub>3</sub>OH and HCOOH were formed as C<sub>1</sub> oxygenates. and CH<sub>3</sub>COOH was formed as a C<sub>2</sub> oxygenate. Other potential chemicals, such as acetaldehyde (CH<sub>3</sub>CHO), were not observed either by <sup>1</sup>H NMR or GC-FID in our reaction conditions. Furthermore, it should be noted that CO was a critical additive and no oxygenates were formed without CO over precious metal catalysts (Fig. S7, in SI). In the case of Cu, small amount of CH<sub>3</sub>OH was formed (4.6 µmol·g<sup>-1</sup>) without CO (Fig. S7 in SI), maybe similar to a minor catalytic route found in the chemical loop system.[25,29]



Figure 1. Product formation rates  $[mol_{product} \cdot mol_{metal}^{-1} \cdot h^{-1}]$  of CH<sub>3</sub>OH (light blue dot), HCOOH (blue diagonal line), and CH<sub>3</sub>COOH (red filled) over ZSM-5 supported transition and platinum group metal (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir, Pt) catalysts (0.2 MPa O<sub>2</sub>, 0.5 MPa CO, 2.0 MPa CH<sub>4</sub>, 8 mL H<sub>2</sub>O, 40 mg catalyst, 423 K, 3 h).

Whereas the selectivity toward each product changes along with the metal atoms (Fig. 1), the reaction was not specific for Rh catalyst tested before.<sup>[22,23]</sup> And other precious metals could also be a potential candidate (especially Ru and Ir, because of their high production rates in CH<sub>3</sub>OH and HCOOH, respectively). If CH<sub>3</sub>OH and HCOOH formations are integrated as a C<sub>1</sub> oxygenates formation, the rates were in the same magnitude of order over Ru, Rh, Pd, and Ir catalysts (Fig. 1). These results would suggest that similar type of CO-assisted oxidation reaction proceeded over precious metals, implying the key factor is in the general feature of those atoms, which would explain their reactivity and selectivity.

Generally, under the presence of CO as a ligand, platinum group metals are thought to be reduced by the electron donation from coordinated CO, for instance Rh<sup>III</sup> is reduced by CO to Rh<sup>I</sup>–(CO)<sub>x</sub> over ZSM-5.[22] CO coordination is considered to make the electronic state around the metal more nucleophilic, and it enables electrophilic activation as a catalyst.<sup>[30,31]</sup> Because the presence of CO should be essential for the reaction (Figs. 1 and S7), the C-H activation might proceed over CO-coordinated metal site (i.e., CO works as a metal ligand). Another possibility might be the coordinated CO forms active oxo-species (dissociated single O atom, i.e., Rh=O) over metal site (i.e., CO works as a reductant, Rh–CO +  $O_2 \rightarrow CO_2$  + Rh=O). In either case, CO should preliminarily coordinate on the metal site. Detailed reaction mechanism was assumed in the end of present literature. The coordination of CO was confirmed by FTIR spectroscopy over Rh-ZSM-5 (Fig. S8 in SI). Two bands at 2112 and 2034 cm<sup>-1</sup> appeared after CO introduction, which was assigned as a symmetric and an asymmetric stretching of C=O in carbonyl species over Rh, respectively.<sup>[22]</sup> The investigation of other ligand instead of CO would be an approach for higher catalytic activity. However, as far as our attempts testing halogens and pyridines, a potential candidate has not been found yet (Table S1 in SI). It would be because the well-known unique interaction between metal and CO accompanied with both electron donation and backdonation.<sup>[32]</sup> We believe that the investigation of an alternative ligand is critical for the further catalyst development because the added CO was simply oxidized and consumed as discussed below, which hindered the desired reaction and formed a lot of byproduct (i.e.,  $CO_2$ ).

The consumption of CO into CO<sub>2</sub> was found to be the major issue in this catalysis system, as it was added as a "cocatalyst", [22] a catalyst ligand, a reductant, or a reactant. Fig. 2 showed CO consumption and CO<sub>2</sub> production along with the reaction time over representative metal catalysts, Ru and Rh supported on ZSM-5. Over both catalysts, the increase of CO consumption was corresponding to the CO<sub>2</sub> production along with the reaction time (Fig. 2). The right axis in Fig. 2 represented the theoretical conversion of CO, and it was approaching to 100% with the increase of reaction time (i.e., the theoretical maximum (4.6 mmol) limited by the initial O<sub>2</sub> amount in gas phase (2.3 mmol)). The results suggested that the CO2 was formed in a large amount mostly by CO oxidation. Therefore, qualitative investigation on the total oxidation of methane into CO2 would be difficult due to the far lower reactivity of methane conversion. Besides CO oxidation, water gas shift reaction (CO +  $H_2O \rightarrow CO_2 + H_2$ ) might also be possible, which can be critical in SCR reaction at higher temperature.<sup>[33]</sup> The route was, however, denied because CO<sub>2</sub> formation was not confirmed by a reference reaction of water and CO over Rh-ZSM-5 under the absence of O2 and CH4 (data not shown). Then, the issue was that the most of CO added as a "cocatalyst", [22] a catalyst ligand, a reductant, or a reactant was simply oxidized into CO2 via a side reaction. Again, finding an alternative instead of CO should be crucial for future catalyst development.

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Figure 2. CO consumption (grey open diamond) and CO<sub>2</sub> formation (black filled diamond) over ZSM-5 supported (a) Ru and (b) Rh catalysts (0.2 MPa O<sub>2</sub>, 0.5 MPa CO, 2.0 MPa CH<sub>4</sub>, 8 mL H<sub>2</sub>O, 40 mg catalyst, 423 K). Right axis shows the theoretical CO conversion limited by O<sub>2</sub> amount.

Because of the consumption of CO (Fig. 2), the catalytic reaction (i.e., oxygenates formation) might be suppressed especially over 50 h in our reaction condition. Fig. 3 showed the formation of oxygenates (i.e., CH<sub>3</sub>OH, HCOOH, and CH<sub>3</sub>COOH) along with reaction time over Ru and Rh catalysts. The formed amount of each product initially increased along with the time, and then those of CH<sub>3</sub>OH and HCOOH decreased whereas that of CH<sub>3</sub>COOH was maintained (Fig. 3). The behaviors of C<sub>1</sub> oxygenate products would be explained by the over oxidation toward CO<sub>2</sub> and the suppression of their formation due to the lack of CO at longer reaction time. On the other hand, CH<sub>3</sub>COOH was formed as like an apparent terminated product unaccompanied with further oxidation. Changes in the product selectivity along with the reaction time (Fig. 3 top) indicated that the formation of CH<sub>3</sub>OH and CH<sub>3</sub>COOH behaved as like primary products, on the other hand, that of HCOOH behaved like a secondary product over both catalysts. The results suggested the direct formation of CH<sub>3</sub>OH and CH<sub>3</sub>COOH and the subsequent oxidation of CH<sub>3</sub>OH to HCOOH. Furthermore, over oxidation toward CO2 would proceed from C<sub>1</sub> oxygenates.



Figure 3. Amount of formed CH<sub>3</sub>OH (light blue open circle), HCOOH (blue open square), and CH<sub>3</sub>COOH (red filled square) and their selectivities over ZSM-5 supported (a) Ru and (b) Rh catalysts (0.2 MPa  $O_2$ , 0.5 MPa CO, 2.0 MPa CH<sub>4</sub>, 8 mL H<sub>2</sub>O, 40 mg catalyst, 423 K). Selectivities were calculated by the amount of product divided by the sum amount of CH<sub>3</sub>OH, HCOOH, and CH<sub>3</sub>COOH. Dashed lines are meant to guide the eye.

One indicator for partial oxidation of methane is the yield of methanol, which has been often compared among catalyst.<sup>[13]</sup> The highest yield of methanol was 1.6% and 0.2% over Ru (96 h) and Rh (72 h) catalysts, respectively (Fig. S9 in SI). The value by Ru catalyst prepared in this study (yield of 1.6%) represented one of the highest yields compared with other heterogeneous catalysts reported before.<sup>[13]</sup>

In order to investigate the reaction pathway in this system, potential intermediates (i.e., CH<sub>3</sub>OH, HCOOH, CH<sub>3</sub>COOH and CH<sub>3</sub>CHO) were reacted with the presence of  $O_2$  and CO (Fig. 4). Starting from CH<sub>3</sub>OH as a reactant, the formation of HCOOH was observed along with its consumption (Fig. 4a), and from HCOOH, no liquid phase products were formed (Fig. 4b). In both cases, moles of the reactant consumed was larger than that of product formed in liquid phase, suggesting the over oxidation toward CO<sub>2</sub>. These results are in good agreement with the discussion above (Fig.3), in which CH<sub>3</sub>OH and HCOOH were assumed as primary and secondary products, respectively, in the sequential partial oxidation. Interestingly, formation of CH3COOH was not confirmed in both cases. This suggested that carbonylation (or CO insertion) of CH<sub>3</sub>OH to CH<sub>3</sub>COOH, similar to Monsanto process,<sup>[34]</sup> did not proceed in this system. Together with the results of CH<sub>3</sub>COOH formation as a primary product (Fig 3), we propose the direct oxidative carbonylation of methane as a plausible CH<sub>3</sub>COOH formation route (CH<sub>4</sub> + CO +  $1/2O_2 \rightarrow$ CH<sub>3</sub>COOH). Formation of acetaldehyde, CH<sub>3</sub>CHO, should also be considered, although its formation had not been experimentally confirmed (Fig. 3). By using CH<sub>3</sub>CHO as a starting reactant (Fig. 4d), it was found that the consumption of CH<sub>3</sub>CHO was much faster than any other reactant and formation of CH<sub>3</sub>COOH (in 80% carbon selectivity). Thus, even if it forms, CH<sub>3</sub>CHO assumed to be an unstable intermediate and quickly oxidized into CH<sub>3</sub>COOH. When the reaction started from CH<sub>3</sub>COOH, its consumption was much slower than any other reactants (Fig. 4c). Due to the slower oxidation (or decomposition) of CH<sub>3</sub>COOH, it observed as like an apparent terminated product in high yield (Fig. 3). As demonstrated in the Periana-Catalytica system,[35] in which activated methane was preserved in the form of  $CH_3-X$  (X = Cl, OSO<sub>3</sub>H), protecting a reactive product is an effective approach in partial oxidation of methane. Based on these results, the overall reaction pathways in this system were summarized in Scheme 1. For the further consideration about reaction mechanism, we speculated following mechanism as a more plausible case: 1) formation of oxo-species with using CO as a reductant, 2) C-H activation via o metathesis over surface oxo-species (M=O + CH4  $\rightarrow$  CH<sub>3</sub>–M–OH), and 3) subsequent oxygenates formation<sup>[30,36]</sup> (Scheme S1(a) in SI) rather than the C-H activation by metal and subsequent O (and CO) insertion (Scheme S1(b) in SI) discussed previously.<sup>[22]</sup> Although our speculation would agree with the no CH<sub>3</sub>CHO observation (Fig. 1) and the large CO consumption (Fig. 2), further studies should be necessary to elucidate the speculated reaction mechanism in the future.



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**Figure 4.** Reactant consumption and product formation via a reaction using (a) CH<sub>3</sub>OH (light blue open circle), (b) HCOOH (blue open square), (c) CH<sub>3</sub>COOH (red filled square), and (d) CH<sub>3</sub>CHO (green filled circle) as a reactant over ZSM-5 supported Rh catalysts (0.2 MPa O<sub>2</sub>, 0.5 MPa CO, 500 µmol reactant, 8 mL H<sub>2</sub>O, 40 mg catalyst, 423 K). CO consumption (grey open diamond) and CO<sub>2</sub> production (black open diamond) is also over plotted. Right axis shows the theoretical reactant conversion. Dashed lines are meant to guide the eye.



Scheme 1. Overall reaction pathways. Dashed arrow shows less plausible path.

In summary, it was demonstrated that ZSM-5 supported platinum group metals catalyzed methane conversion into C<sub>1</sub> and C<sub>2</sub> oxygenates under the assist of CO. In the reaction system studied here, the CO was unique and critical maybe as a ligand, a reductant, and a reactant. Partial oxidation of methane toward methanol or formic acid was parallel to oxidative carbonylation of methane to acetic acid. The major drawback of the system was the competing oxidation of CO into CO<sub>2</sub>. The design of another catalytic site without CO would improve the production of C<sub>1</sub> oxygenates. Another approach to develop the system would be a constructive use of CO as a reactant to form C<sub>2</sub> oxygenates as a terminated product.

The ZSM-5 supported metal catalysts were prepared via impregnation method as similar to the previous report.<sup>[22]</sup> Sodium-form ZSM-5 (Tosoh, Si/AI = 11.9) was preliminary ion-exchanged to NH<sub>4</sub>-form. Metal salt aqueous solution was added dropwise to the pre-dried NH<sub>4</sub>-form ZSM-5 powder and mixed by mortar and pestle. After the impregnation, the obtained powder was treated by H<sub>2</sub> gas (5 % balanced by Ar). Catalytic test was conducted with a batch reactor. Gaseous samples were quantitively measured by the on-line GC-FID, and liquid samples were measured by <sup>1</sup>H NMR with pre-saturation method. Please see details in supporting information.

**Keywords:** zeolite • Rh-ZSM-5 • Methane conversion • Partial oxidation • Methanol

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ZSM-5 supported platinum group metal catalysts achieved direct methane conversion into methanol, formic acid, and acetic acid under the assist of CO. Ru and Ir besides Rh were found to be the potential candidates. Presence of CO was critical for the reaction, whereas undesired CO oxidation into CO<sub>2</sub> also proceeded. C<sub>1</sub> formation route (i.e., partial oxidation) was parallel to C<sub>2</sub> formation route (i.e., oxidative carbonylation).