[Regular Paper]

Decomposition of Methanol on Supported Pd–Au Catalyst for Recovery of Unused Waste Heat at Low Temperature

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Decomposition of methanol into CO and H2 on supported Pd based catalyst was studied for recovery of unused heat at around 473 K. Decomposition of CH3OH into CO and H2 proceeded at lower temperature with greater endothermic heat compared with the CH3OH steam reforming reaction. Effects of additives to Pd were studied and it was found that the addition of Au or Pt was effective for increasing catalytic activity around 473-523 K. In particular, Pd with 30 wt% Au added was the most active for CH3OH decomposition into CO and H2, and H2 yield on Pd-Au(7 : 3)/Al2O3 was 51 % at 523 K. Although high H2 yield was achieved, yield of dimethyl ether (DME) was also high on this catalyst, in particular, at low temperature around 523 K. Formation of DME was significantly suppressed by using BaZrO3 for the support and also mixing BaZrO3 with Al2O3 for support of Pd-Au bimetal catalyst. Therefore, use of BaZrO3 for the support was effective for increasing CO selectivity and Pd-Au(9 : 1)/BaZrO3-Al2O3(1 : 1) was highly active for CH3OH decomposition into CO and H2, and negligible amount of DME was formed around 523 K.

Keywords
Methanol decomposition, Palladium-gold, Barium zirconate perovskite oxide

1. Introduction

Energy efficiency for effectively used from primary sources is presently as low as ca. 35 %, so more than 60 % of the fuel energy is exhausted as unused heat1). Therefore, most energy conversion is still low efficiency and recovery of unused heat is one of the most important issues for energy conservation, and could also be the most effective methods for reducing CO2 emissions. Large quantities of unused heat are available at around 473-573 K, however this heat has low exergy value and is low quality energy, so development of recovery processes for such low quality heat energy is important for recovery of unused heat.

Methanol decomposition according to the following equation is an endothermic reaction which proceeds at temperatures higher than 423 K from the chemical equilibrium.

\[
\text{CH}_3\text{OH} = \text{CO} + 2\text{H}_2
\]

\[
\Delta H = 95.3 \text{ kJ/mol} \quad \Delta G = -3.2 \text{ kJ/mol at 423 K} \quad (1)
\]

This reaction is simple, however, is more endothermic than the steam reforming reaction as follows2)3):

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} = \text{CO}_2 + 3\text{H}_2
\]

\[
\Delta H = 54.8 \text{ kJ/mol} \quad \Delta G = -26.7 \text{ kJ/mol at 423 K} \quad (2)
\]

In addition, CH3OH is now considered as promising biofuel for automobiles4), through simple oxidation as shown in the Eq. (3),

\[
\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 = \text{CO}_2 + 3\text{H}_2
\]

\[
\Delta H = -674.3 \text{ kJ/mol} \quad \Delta G = -695.1 \text{ kJ/mol at 423 K} \quad (3)
\]

Oxidation of CO and H2 through CH3OH decomposition has higher enthalpy and Gibbs free energy,

\[
\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2
\]

\[
\Delta H = -283.5 \text{ kJ/mol} \quad \Delta G = -246.3 \text{ kJ/mol} \quad (4)
\]

\[
2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}
\]

\[
\Delta H = -486.1 \text{ kJ/mol} \quad \Delta G = -445.6 \text{ kJ/mol} \quad (5)
\]

Total \[
\Delta H = -769.6 \text{ kJ/mol} \quad \Delta G = -691.9 \text{ kJ/mol at 423 K} \quad (6)
\]

Therefore, this reaction is considered suitable for application to automobiles5). In addition, oxidation of CO and H2 generates heat at high temperature with high exergy value and so can be more efficiently recovered.
Consequently, low quality heat energy at around 423 K can be transformed into high quality heat energy through a cycle of oxidation of CO and H\textsubscript{2} formed by CH\textsubscript{3}OH decomposition at low temperature. The chemical equilibrium shows that Gibbs free energy becomes negative at temperatures higher than 423 K, however high conversion through CH\textsubscript{3}OH decomposition is achieved only at temperatures higher than 523 K.

Previous studies of Pd\textsuperscript{6), Cu\textsuperscript{7),8) and Pt\textsuperscript{9),10) catalysts have found that Pd/CeO\textsubscript{2}-La\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} shows high activity and selectivity for CH\textsubscript{3}OH decomposition\textsuperscript{11),12). Similar rare earth oxide effects have been reported by Usami\textsuperscript{13) et al.\textsuperscript{13)−15). However, the activity for CH\textsubscript{3}OH decomposition is still not high in spite of extensive studies\textsuperscript{16),17), in particular, in the low temperature range\textsuperscript{11),12). In addition, few studies have investigated CH\textsubscript{3}OH decomposition compared with the CH\textsubscript{3}OH steam reforming reaction.

The present study investigated Pd-based bimetallic catalyst for active CH\textsubscript{3}OH decomposition catalyst at low temperature and found that Pd-Au supported on Al\textsubscript{2}O\textsubscript{3} has high activity for CH\textsubscript{3}OH decomposition at low temperature as well as fairly high selectivity for dimethyl ether (DME) at 473 K.

2. Experimental

Catalysts were prepared by the conventional impregnation method. Aerosil\textsuperscript{\textregistered} Al\textsubscript{2}O\textsubscript{3} (BET surface area 250 m\textsuperscript{2}/g, Nippon Aerosil Co., Ltd.) was used for the support oxide and suspended into deionized water (250 mL) followed by adding PdCl\textsubscript{2} (Wako Pure Chemical Ind., Ltd.) and HAuCl\textsubscript{4} (Wako Pure Chemical Ind., Ltd.) aqueous solution with 1 mL of 6 M HCl. After evaporation of water to dryness, the powder was dried in a drying oven at 333 K for 6 h and then calcined in air at 673 K for 2 h. BaZrO\textsubscript{3} doped with Y\textsubscript{3+} was prepared by the solid state reaction method and the stoichiometric amount of BaCO\textsubscript{3}, ZrO\textsubscript{2}, and Y\textsubscript{2}O\textsubscript{3} was mixed in an alumina mortar and pestle. The obtained mixture was calcined at 1473 K for 6 h. For mixing with Al\textsubscript{2}O\textsubscript{3} as support oxide, BaZrO\textsubscript{3} powder was first suspended in deionized water and after stirring in water for 1 h, Al\textsubscript{2}O\textsubscript{3} powder was added to the same weight of BaZrO\textsubscript{3} (Al\textsubscript{2}O\textsubscript{3} : BaZrO\textsubscript{3} = 1 : 1) and then aqueous solution of PdCl\textsubscript{2} in diluted nitric acid and HAuCl\textsubscript{4} (Pd : Au = 9 : 1 in weight ratio) was added followed by evaporation to dryness. The obtained powder was dried in air at 333 K for 6 h and then calcined at 673 K for 2 h. The catalyst was pressed into a disc and then crushed followed by sieving with a stainless steel mesh (16-32 mesh). The ratio of metal and composite oxide support were always expressed as the weight ratio in this study.

Methanol decomposition was performed using an atmospheric pressure micro flow reactor. The prepared catalyst (1.0 g) without pretreatment was fixed into the stainless steel reactor with quartz wool. Methanol (Wako Pure Chemical Ind., Ltd., 99.9 % pure) was fed with a micro pump and evaporated in the evaporator arranged ahead of the reactor and heated at 596 K. N\textsubscript{2} gas was used for the balance gas and set at CH\textsubscript{3}OH : N\textsubscript{2} = 1 : 9 in volume with total flow rate of 50 cm\textsuperscript{3}/min. The formed CO, H\textsubscript{2}, CO\textsubscript{2}, and CH\textsubscript{4} were analyzed using gas chromatographs with thermal conductivity detector (TCD) and DME one with hydrogen-flame ionization detector (FID). Conversion of methanol was calculated based on the carbon balance before and after reaction. Yields of H\textsubscript{2} and CO were calculated by the following equations;

\[ \text{H}_2 \text{ yield} = \frac{\text{Formation rate of H}_2}{\text{(Feed rate of CH}_3\text{OH}) \times 2} \]

\[ \text{CO yield} = \frac{\text{Formation rate of CO}}{\text{(Feed rate of CH}_3\text{OH})} \]

3. Results and Discussion

Table 1 summarizes the catalytic activity for CH\textsubscript{3}OH decomposition on various metals or metal oxides supported on Al\textsubscript{2}O\textsubscript{3} at 523 K. Although CH\textsubscript{3}OH decomposition occurred at high temperature around 773 K, little CO or H\textsubscript{2} formation was observed without cata-

| Metal catalyst | CH\textsubscript{3}OH Decomposition on Al\textsubscript{2}O\textsubscript{3} Supported Catalyst at 523 K |
|----------------|----------------------------------------------------------------------------------|
|                | H\textsubscript{2} [%] | CO [%] | CH\textsubscript{3}OHCH\textsubscript{2} [%] | CH\textsubscript{4} [%] | CO\textsubscript{2} [%] | Conversion [%] |
| Pd             | 16.5 | 20.7 | 20.1 | 0 | 0 | 40.8 |
| Ni             | 10.4 | 5.0 | 49.1 | 0 | 0 | 54.1 |
| Pt             | 8.9 | 2.7 | 21.4 | 0 | 0 | 24.1 |
| Cu             | 2.0 | 0 | 3.7 | 0 | 0 | 3.7 |
| Ru             | 1.3 | 0 | 54.6 | 0 | 0 | 54.6 |
| Mn             | 1.2 | 0 | 19.5 | 0 | 0 | 19.5 |
| Au             | 1.0 | 0 | 9.9 | 0 | 0 | 9.9 |
| Fe             | 0.91 | 0 | 62.6 | 0 | 0 | 62.6 |
| Co             | 0.85 | 0 | 73.1 | 0 | 0 | 73.1 |
| No catalyst    | 0.89 | 0 | 0 | 0 | 0 | 1.7 |

Amount of metal loading is 1 wt%. Catalyst 1.0 g, CH\textsubscript{3}OH : N\textsubscript{2} = 1 : 9 volume ratio. Total flow rate: 50 mL/min.

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As shown in Table 1, CO or H$_2$ yield was small on Cu, Ru, Mn, Au, Fe, and Co, whereas high yield of DME was observed. In particular, Fe or Ru catalyzed high yields of DME (> 50%). Therefore, these catalysts are not active for decomposition, however are active for dehydration of CH$_3$OH. In contrast, Pd or Pt shows good activity for H$_2$ formation. Therefore, H$_2$ yield was the highest on Pd/Al$_2$O$_3$ catalyst, despite the low yield of DME, so this study investigated Pd supported on Al$_2$O$_3$ in details. High activity of Pd to CH$_3$OH decomposition was also reported by several groups.$^{10,16}$

Figure 1 shows the temperature dependence of CH$_3$OH decomposition on Pd/Al$_2$O$_3$. H$_2$ and CO formation was observed at 473 K and increased monotonically with higher temperature and reached 100% at 673 K. Formation of DME began at lower temperatures and the yield of DME was as high as ca. 60% at 573 K, however became almost negligible at 673 K, and only CO and H$_2$ were formed at 100% yield. Therefore, Pd/Al$_2$O$_3$ shows high activity for CH$_3$OH decomposition at 623 K, however, the activity is still not high enough at lower temperatures around 473 K.

To further increase CH$_3$OH decomposition activity, the effects of metal additives on Pd/Al$_2$O$_3$ were studied. Figure 2 shows the temperature dependence of Pd-M/Al$_2$O$_3$ (M = Pt, Au, Ni) catalyst on CH$_3$OH decomposition. Addition of these metals or metal oxides was effective for increasing H$_2$ formation rate at 423 K. In particular, Pt or Au increased CH$_3$OH decomposition in the temperature range of 523-573 K. Although H$_2$ yield was almost the same for Pt and Au addition, H$_2$ yield at temperatures greater than 573 K was higher on Pd-Au than Pd-Pt, so further study investigated the Pd-Au bimetallic catalyst.

Figure 3 shows the temperature dependence of CH$_3$OH decomposition on Pd-Au(9 : 1)/Al$_2$O$_3$ catalyst. H$_2$ and CO formation was observed at 473 K and reached 100% at 623 K. DME formation was suppressed by addition of Au, however, the yields of CH$_4$ and CO$_2$ were slightly increased and CO yield was decreased at 673 K compared with the results shown in Fig. 1. Therefore, addition of Au was effective for
decreasing the formation of DME at lower temperatures, however activities for hydrogenation and the water shift reaction were increased.

Effects of Au addition were further studied. Figure 4 shows CO, H₂, and CH₃OH conversion at 523 K as a function of Au amount added. Obviously, yields of CO and H₂ increased with Au amount and the highest H₂ and CO yields were achieved at 30 wt% Au. Further increase in Au addition decreased H₂ and CO yields, which could be reasonably assigned to the low catalytic activity of Au for CH₃OH decomposition as shown in Fig. 4. On the other hand, Au was active to form DME and the DME yield also increased with higher Au addition. The optimum amount for Au addition seems to be 30 wt% of Pd to achieve the highest H₂ and CO yields. Using this catalyst, H₂ yields of 51 % were achieved at 523 K and 95.7 % at 573 K as shown in Fig. 5. However, DME was also formed with high yield (42 %) at 523 K, so suppression of DME formation was still required for low temperature CH₃OH decomposition as a part of the recovery of the wasted heat (see Fig. 5).

The effects of BaZrO₃ with Al₂O₃ support were further studied since BaZrO₃ shows superior proton conductivity so hydrogen spillover effects are expected. Decomposition of CH₃OH may proceed through CH₃ and/or CH₃O surface intermediates, so decomposition of CH₃ might be the rate determining step based on the stability. Therefore, removing hydrogen by hydrogen spillover effects could be effective for prevent DME formation and accelerate CH₃OH decomposition because DME may be formed by reaction between the CH₃ and CH₃O intermediates. Table 2 shows the CH₃OH decomposition activity and product distribution on Pd–Au/BaZrₓ–ₙYₓO₃ or Pd–Au/BaCe₀.₉₅Y₀.₅O₃ catalysts at 523 K. Pd–Au/BaCe₀.₉₅Y₀.₅O₃ was not active for CH₃OH decomposition, however, Pd–Au/BaZrO₃ was active for CH₃OH decomposition based on the small surface area, and the H₂ and O₂ yields were 30.7 % and 30.9 %, respectively. Furthermore, little formation of DME was observed on BaZrO₃ and BaCeO₃ doped with Y, and that BaZrO₃ or BaCeO₃ is effective for preventing DME formation and increasing selectivity for CH₃OH decomposition compared to Al₂O₃ supported catalyst. Therefore, high activity and selectivity for CH₃OH decomposition could be achieved.

![Fig. 4](image1.png)  
Yields of CO, H₂, DME and CH₃OH Conversion at 523 K as a Function of Au Amount Added to Pd

![Fig. 5](image2.png)  
Temperature Dependence of CH₃OH Decomposition on Pd–Au(7 : 3)/Al₂O₃ Catalyst

| Support oxide | H₂ [%] | CO [%] | CH₃OCH₃ [%] | CH₄ [%] | CO₂ [%] | Conversion [%] | BET [m² g⁻¹] |
|---------------|-------|-------|-------------|--------|--------|---------------|-------------|
| BaZrO₃        | 30.7  | 30.9  | 0           | 0      | 0      | 30.9          | 5.9         |
| BaZrₓ₋ₙYₓO₃₋ₙ | 20.2  | 21.8  | 0           | 0      | 0      | 21.8          | 13.7        |
| BaZrₓ₋ₙYₓO₃₋ₙ | 19.5  | 21.4  | 0           | 0      | 0      | 21.4          | 13.8        |
| BaZrₓ₋ₙYₓO₃₋ₙ | 17.4  | 19.2  | 0           | 0      | 0      | 19.2          |             |
| BaZrₓ₋ₙYₓO₃₋ₙ | 8.9   | 5     | 0           | 0      | 0      | 5.0           |             |
| BaZrₓ₋ₙYₓO₃₋ₙ | 10.6  | 6.4   | 0           | 0      | 0      | 6.4           |             |
| BaCeₓ₋ₙYₓO₃₋ₙ | 16.9  | 19.3  | 0           | 0      | 0      | 19.3          | 0.7         |
| BaCeₓ₋ₙYₓO₃₋ₙ | 28.7  | 30.5  | 0           | 0      | 0      | 30.5          | 0.67        |
| BaZrₓ₋ₙCeₓO₃₋ₙ | 38.3  | 38.4  | 22.7        | 0.7    | 0      | 61.8          | 87.2        |
| Al₂O₃         | 52.7  | 53.3  | 0.8         | 0      | 0      | 54.1          | 56.5        |

Pd : Au = 0.9 wt% : 0.1 wt%. Amount of metal loading is 1 wt%. Catalyst 1.0 g, CH₃OH : N₂ = 1 : 9 volume ratio. Total flow rate: 50 mL/min.

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if the surface area of BaZrO₃ was further increased.

Table 2 also shows the effects of Y in the Zr sites of BaZrO₃ on CH₃OH decomposition. Oxygen vacancy was introduced and proton conductivity was increased by doping Y, however H₂ and CO formation rates were decreased, so Y addition to BaZrO₃ was apparently not effective for increasing CH₃OH decomposition activity. Since high temperature calcination is essential for obtaining the single phase of perovskite, the surface area became smaller, so mixing BaZrO₃ with Al₂O₃ was studied for high dispersion of Pd–Au bimetal. X-ray diffraction (XRD) patterns of BaZrO₃/Al₂O₃ mixed oxide before and after reaction are shown in Fig. 6. Obviously, XRD patterns of BaZrO₃/Al₂O₃ were assigned to those from BaZrO₃ and Al₂O₃, and no peak shift or new peaks were observed. Therefore, BaZrO₃ mixed with Al₂O₃ was just a powder mixture before and after reaction. On the other hand, mixing BaZrO₃ with Al₂O₃ was effective for increasing CH₃OH decomposition activity and almost no DME was formed compared with Pd–Au/BaZrO₃ catalyst, as shown in Table 2. Possibly BaZrO₃ has high activity for DME decomposition or low activity for dehydration of CH₃OH. Clearly, mixing BaZrO₃ with Al₂O₃ was effective for high activity and selectivity for CH₃OH decomposition at low temperature.

Figure 7 shows the temperature dependence of CH₃OH decomposition on Pd–Au/BaZrO₃/Al₂O₃ catalyst. Compared with the similar results in Fig. 4, the H₂ and CO yields at lower temperature were clearly much increased and almost 100 % yield of H₂ was achieved at 573 K. Therefore, this catalyst is highly active and selective for CH₃OH decomposition up to 623 K. On the other hand, CO₂ as well as CH₄ formation was observed with increasing temperature, and yields of CH₄ and CO₂ were both about 10 % at 673 K. Therefore, although the yield of CO became slightly smaller than that of H₂, no carbon formation was observed.

Au addition to Pd catalyst was highly effective for increasing CH₃OH decomposition activity, so changes in the surface adsorption species were studied by Fourier transform infrared spectroscopy (FT-IR) to investigate the positive effects of Au addition. Figure 8 shows the FT-IR spectra of the catalyst after CH₃OH adsorption at room temperature, with IR spectra of CH₃OH in the gas phase for comparison. The absorption peaks around 1500-1650 cm⁻¹ were assigned to bending of the CH₃ bond, those around 3000 cm⁻¹ to stretching of CH₂ or CH₃, and those around 3500 cm⁻¹ to bending of the OH bond. C–O bond peaks were also observed around 1100-1200 cm⁻¹. The case of Pd/Al₂O₃, only weak adsorption peaks around 1450-1500 cm⁻¹ were observed and no significant strong absorption bands around 3500 cm⁻¹ and 1600 cm⁻¹ which are typical of the OH group. Therefore, the surface adsorption species of CH₃OH on Pd/Al₂O₃ was CH₃OH, and dissocia-
tive adsorption of CH$_3$OH into CH$_3$ and OH may not have occurred. Similar absorption bands were observed on Pd–Au catalyst, and absorbance of each peak was significantly increased by addition of Au. Therefore, addition of Au may be effective for increasing the amount of CH$_3$OH adsorption and dehydration of surface methoxy species to CH$_2$O or CHO. In spite of the low catalytic activity of Au, the increase in methoxide species on the Pd catalyst was interesting and the details of the reaction mechanism based on the surface adsorption species will be reported in the future.

4. Conclusion

Recovery of waste heat is highly important for energy conservation and reducing CO$_2$ emissions from various process. Since the amount of waste heat is large in the temperature range of 423-523 K, endothermic reactions proceeding in this low temperature range are highly desirable. CH$_3$OH decomposition to CO and H$_2$ occurs around 323 K thermodynamically, however, conversion of CH$_3$OH only proceeds at temperatures higher than 523 K on conventional catalysts. The present study found that Pd–Au/Al$_2$O$_3$ had reasonably high activity for CH$_3$OH decomposition and H$_2$ yield was 16 % and 60 % at 473 K and 523 K, respectively. Furthermore, mixing BaZrO$_3$ with Al$_2$O$_3$ was effective for preventing DME formation, so Pd–Au/BaZrO$_3$–Al$_2$O$_3$ catalyst shows high activity and selectivity for CH$_3$OH decomposition and potential for the recovery of low temperature unused heat. The high CH$_3$OH decomposition activity was hardly changed over 1 h reaction so high stability is also expected for Pd–Au/BaZrO$_3$–Al$_2$O$_3$ catalyst.

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要旨
低温排熱の回収を目的とした担持 Pd–Au 触媒による CH₃OH の分解反応

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473 K 付近の未利用熱の回収を目的に担持 Pd 系触媒でのメタノールから CO および H₂への分解反応を検討した。CH₃OH の水蒸気改質反応に比べ、CH₃OH から CO および H₂への分解反応は大きな吸熱を伴い、低温でも進行することが可能である。本研究では Pd への添加物効果を検討し、Au または Pt の添加は 473 ～ 523 K での CH₃OH から CO および H₂への分解活性の向上に有効であることを見出した。30 wt% Au 添加 Pd は CH₃OH 分解に最も活性が高く、Pd–Au(7 : 3)/Al₂O₃触媒では 523 K の H₂収率は 51 % となった。高い H₂収率は得られるが、この触媒ではジメチルエーテル (DME) 収率も高い。特に、523 K 付近の低温での収率が高い。DME 収率は Pd–Au の担体として BaZrO₃ または BaZrO₃ と Al₂O₃を混合した酸化物を用いることで著しく抑制された。この結果、BaZrO₃を担体とすることで CO 選択率の向上に有効であり、Pd–Au(9 : 1)/BaZrO₃–Al₂O₃(1 : 1) は 523 K 付近で CH₃OH から CO および H₂への分解に活性が高く、DME はほとんど生成しないことが分かった。