

# Gold Based Catalyst Preparation and Reaction Pathway on Partial Oxidation of Methanol to Produce Hydrogen Reaction

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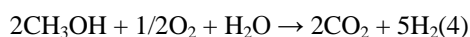
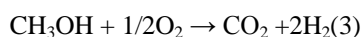
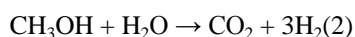
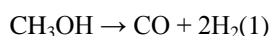
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**Abstract**– Hydrogen production from partial oxidation of methanol (POM) is one of the most promising process for the on-board fuel cell automobile application. Gold supported catalyst will significantly increase H<sub>2</sub> selectivity and decrease the CO formation in POM reaction. In this mini review paper briefly summarizes the catalyst preparation process and possible reaction mechanism which is take place in the POM reaction process.

**Keywords** – Gold catalysts, Reaction mechanism, partial oxidation

## I. INTRODUCTION

Hydrogen is regarded as pure energy source, due to it has high energy efficiency and zero environment pollution, combustion of hydrogen is produce water. Hydrogen can be used directly fuel for the automobile, but challenge is when using hydrogen as a direct fuel for car, people will face safety, storage, refilling and transportation problem. Best solution for that using methanol to produce hydrogen for on-board vehicles, because of methanol has relatively high energy density and high hydrogen to carbon ratio. Hydrogen can be produced from methanol by methanol decomposition[1–4], methanol steam reforming[5–7], methanol partial oxidation[8–13] and oxidative steam reforming of methanol[14–16]. Following are chemical reaction equation for these four reaction:



Partial oxidation of methanol (Eq.3) has several advantages compared to other three reactions. Partial oxidation of methanol is exothermic reaction, which is doesn't require extra energy for the reaction[17], more excitingly air or oxygen can be used as oxidant instead of steam, and also it is main reaction products are hydrogen and carbon dioxide. Methanol decomposition (Eq.1) are not

suggested for fuel cell application, because it is main reaction products include CO, and it is harmful for the expensive platinum anode electrodes in proton exchange membrane fuel cell (PEMFC). CO concentration must be lower than 20 ppm level, otherwise it will rapidly decrease fuel cell efficiency[18-19]. Methanol steam reforming (Eq. 2) and oxidative steam reforming (Eq. 4) are require extra steam generation unit, it needs extra energy to produce steam, and also it will make system complicate and costly.

People have been studied mainly copper[20–22] and palladium[23-24] based catalysts for POM reaction to produce hydrogen, but main problem in this two type of catalysts are produce considerable amount of CO and low stability. Since M. Haruta and his co-workers [25] found that gold supported on TiO<sub>2</sub>,α-Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> catalysts has superior catalytic activity for the CO oxidation at low temperature, gold catalysts attracted more attention in different reaction system. Feg-Wen Chang and his co-workers [26]have studied Au/TiO<sub>2</sub> catalyst for partial oxidation of methanol to produce hydrogen at lower temperature, it shows negligible amount of CO. Also his group further studied different types of supported gold catalysts for selectively produce hydrogen with a target of low emission of CO[10, 11, 27], and they successfully decrease the CO formation in POM reaction. From previously studied relevant literature can be seen, hydrogen production via partial oxidation of methanol over gold based catalyst are effective way to CO free hydrogen generation for fuel cell application in the future.

This review briefly organized gold catalyst preparation for POM and possible reaction mechanism involved in POM are will be discussed. This will helps reader to easy understand of POM reaction to produce hydrogen.

## II. CATALYST PREPARATION

In the beginning gold catalysts assumed as poorly active, because of larger particle size[28]. Since G. C.Bond and P. A. Sermon found that Au/SiO<sub>2</sub> catalyst is active for olefin hydrogenation, because ofsmall gold nanoparticles, people's mind start changing for gold catalysts. In 1989, M. Haruta and his co-workers discovered gold supported

catalyst shows very good catalytic activity towards to CO complete oxidation at low temperature[29]. More and more research focus on preparing highly dispersed gold nanoparticles for different preparation method and optimize the preparation parameter. In the following will give some detailed information for the active gold catalyst preparation.

#### A. Selecting Suitable Catalyst support

Selecting suitable active site for gold catalysts are most important. According to the literature, nature of the support strongly affected on gold dispersion on the surface[30], and state of gold[31]. Also using reducible support rather than the non-reducible support for the oxidation reaction are suggested[25].

#### B. Catalyst preparation method

Recent year most of the gold catalyst have been prepared their catalyst deposition-precipitation[27, 32], co-precipitation[31], impregnation[8] and PVP – stabilized reduction method[33-34]. Among these different preparation method, deposition-precipitation method are favorable for gold catalyst preparation. Because, the catalysts which are prepared by deposition – precipitation method, gives small gold particle size that is main effecting factor for the gold catalyst activity. M. Haruta[28] found that deposition-precipitation method are most effective and easy way to prepare active catalyst for CO oxidation, and this method extensively used in POM reaction gold catalyst preparation as well[27, 35].

#### C. Catalyst preparation parameters

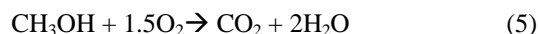
Proper catalyst preparation parameters also main influencing factor for gold catalyst performance. Such as, best control of pH in catalyst preparation, using of suitable precipitation reagent, amount of gold loading to the surface and catalyst calcination temperature are the most effecting parameters. According to the literature, best pH for the gold catalyst preparation is about 8[28, 32], and calcination at lower temperature are suggested[36]. Au/Fe<sub>2</sub>O<sub>3</sub>[31] catalyst preparation process, higher catalytic activity of catalyst using Na<sub>2</sub>CO<sub>3</sub> as reagent rather than the K<sub>2</sub>CO<sub>3</sub>, because catalyst used Na<sub>2</sub>CO<sub>3</sub> precipitant has lower gold particle size (2.3 nm) than the K<sub>2</sub>CO<sub>3</sub> as precipitant (4.5 nm). Most of studied result shows that, gold loading between 1-3 wt.% is effective for gold catalyst, this also matches with gold catalyst for partial oxidation of methanol.

### III. REACTION MECHANISM

In Partial oxidation of methanol reaction, several reaction mechanism are involved, which are complete combustion of methanol, methanol steam reforming, methanol decomposition, water gas shift reaction, reverse water gas shift reaction, CO oxidation and hydrogen combustion reaction. These reactions mainly depend on reaction operation temperature, catalyst and reactant & reaction compositions in the system.

Partial oxidation of methanol reaction strongly depend on temperature. At lower temperature, methanol combustion reaction (Eq. 5) will take place, methanol consume oxygen

occurs highly exothermic reaction. In Au/TiO<sub>2</sub>[26] and Au-Pd/SBA-16-CeO<sub>2</sub>[37] catalysts are shows similar trends.



When increase temperature, the formed water will consumed by steam reforming reaction (Eq. 2), that will increase H<sub>2</sub> selectivity and decrease water selectivity[21, 26].

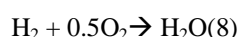
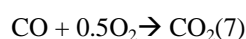
There can also be methanol partial oxidation (Eq. 3) instead of methanol combustion in case of no excess oxygen, which is good for hydrogen generation.

Further increasing temperature, no more O<sub>2</sub> was left and methanol decomposition (Eq. 1) reaction will occur, and it will increase H<sub>2</sub> and CO formation. CO formation will be harmful for platinum anode electrode in fuel cell.

At higher reaction temperature both methanol and oxygen are diminished from the system, now reverse water gas shift reaction (Eq. 6) start to take place over the surface, that will consume H<sub>2</sub> and increase CO formation. This is why most of studied catalysts shows, after optimum reaction temperature, desired reaction products are shows decreasing trend.



This explains the decrease in hydrogen selectivity at higher temperature. Moreover at low temperature low selectivity of hydrogen suggests that surface oxidation of hydrogen happened more selectively over the gold catalysts. When oxygen is excess in the system, CO oxidation (Eq. 7) and H<sub>2</sub> complete combustion reaction (Eq. 8) will occur. Because gold supported catalyst is very active for CO oxidation when presence of oxygen[34] and hydrogen combustion.



Operating POM reaction at mild reaction condition not only have advantages in cost effective manner but also it will helps to eliminate some by products and avoid undesired reaction. CO will form and hydrogen will consume via reverse water gas shift reaction at high temperature. Operating at lower temperature, also increase catalyst stability. Another reason is that high temperature is not favorable for gold catalyst, gold catalyst start sintering at relatively low temperature compared to other catalysts.

### IV. SUMMARY AND OUTLOOK

Selecting suitable support for the catalyst preparation and improving preparation procedure and parameters, and also optimizing reaction condition are the main effecting parameters in this reaction. The studies on gold catalysts are shows better catalytic performance regarding with the CO free rich hydrogen gas compared to the commercial copper zinc based catalyst. However, these catalysts are still need to be improve, specially, catalysts stability of gold based catalyst. It is the main drawbacks of gold based catalyst[12].

Methanol is ideal hydrogen carrier, which can be catalytically convertible to hydrogen. Partial oxidation of methanol over gold based catalyst is promising way to produce hydrogen for on-board vehicles. Based on developed catalysts and studied reaction pathway, it needs to continuous effort on this study, and develop suitable and practical solution for PEMFC engine.

## REFERENCE

- [1] T. Tsoncheva, I. Genova, M. Stoyanova, M.-M. Pohl, R. Nickolov, M. Dimitrov, E. Sarcadi-Priboczki, M. Mihaylov, D. Kovacheva, and K. Hadjiivanov, "Effect of mesoporous silica topology on the formation of active sites in copper supported catalysts for methanol decomposition," *Appl. Catal. B Environ.*, vol. 147, pp. 684–697, Apr. 2014.
- [2] R. Ubago-Pérez, F. Carrasco-Marín, and C. Moreno-Castilla, "Carbon-supported Pt as catalysts for low-temperature methanol decomposition to carbon monoxide and hydrogen," *Appl. Catal. A Gen.*, vol. 275, no. 1–2, pp. 119–126, Nov. 2004.
- [3] J. Xi, Z. Wang, and G. Lu, "Improvement of Cu/Zn-based catalysts by nickel additive in methanol decomposition," *Appl. Catal. A Gen.*, vol. 225, no. 1–2, pp. 77–86, Feb. 2002.
- [4] F. Boccuzzi, a. Chiorino, and M. Manzoli, "FTIR study of methanol decomposition on gold catalyst for fuel cells," *J. Power Sources*, vol. 118, no. 1–2, pp. 304–310, May 2003.
- [5] Y. Ma, G. Guan, C. Shi, A. Zhu, X. Hao, Z. Wang, K. Kusakabe, and A. Abudula, "Low-temperature steam reforming of methanol to produce hydrogen over various metal-doped molybdenum carbide catalysts," *Int. J. Hydrogen Energy*, pp. 1–9, Nov. 2013.
- [6] C. Pojanavaraphan, A. Luengnaruemitchai, and E. Gulari, "Effect of steam content and O<sub>2</sub> pretreatment on the catalytic activities of Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> catalysts for steam reforming of methanol," *J. Ind. Eng. Chem.*, pp. 1–11, Jun. 2013.
- [7] J. Agrell, H. Birgersson, and M. Boutonnet, "Steam reforming of methanol over a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst: a kinetic analysis and strategies for suppression of CO formation," *J. Power Sources*, vol. 106, pp. 249–257, 2002.
- [8] B. Hereijgers and B. Weckhuysen, "Selective Oxidation of Methanol to Hydrogen over Gold Catalysts Promoted by Alkaline- Earth- Metal and Lanthanum Oxides," *ChemSusChem*, pp. 743–748, 2009.
- [9] J. Agrell, K. Hasselbo, K. Jansson, S. G. Järås, and M. Boutonnet, "Production of hydrogen by partial oxidation of methanol over Cu/ZnO catalysts prepared by microemulsion technique," *Appl. Catal. A Gen.*, vol. 211, no. 2, pp. 239–250, Apr. 2001.
- [10] F.-W. Chang, S.-C. Lai, and L. S. Roselin, "Hydrogen production by partial oxidation of methanol over ZnO-promoted Au/Al<sub>2</sub>O<sub>3</sub> catalysts," *J. Mol. Catal. A Chem.*, vol. 282, no. 1–2, pp. 129–135, Mar. 2008.
- [11] F.-W. Chang, T.-C. Ou, L. S. Roselin, W.-S. Chen, S.-C. Lai, and H.-M. Wu, "Production of hydrogen by partial oxidation of methanol over bimetallic Au-Cu/TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> catalysts," *J. Mol. Catal. A Chem.*, vol. 313, no. 1–2, pp. 55–64, Nov. 2009.
- [12] K. L. Hohn and Y.-C. Lin, "Catalytic partial oxidation of methanol and ethanol for hydrogen generation," *ChemSusChem*, vol. 2, no. 10, pp. 927–40, Jan. 2009.
- [13] Y.-J. Huang, K. L. Ng, and H.-Y. Huang, "The effect of gold on the copper-zinc oxides catalyst during the partial oxidation of methanol reaction," *Int. J. Hydrogen Energy*, vol. 36, no. 23, pp. 15203–15211, Nov. 2011.
- [14] S. Velu and K. Suzuki, "Selective production of hydrogen for fuel cells via oxidative steam reforming of methanol over CuZnAl oxide catalysts: effect of substitution of zirconium and cerium on," *Top. Catal.*, vol. 22, no. April, pp. 235–244, 2003.
- [15] R. Pérez-Hernández, G. Mondragón Galicia, D. Mendoza Anaya, J. Palacios, C. Angeles-Chavez, and J. Arenas-Alatorre, "Synthesis and characterization of bimetallic Cu-Ni/ZrO<sub>2</sub> nanocatalysts: H<sub>2</sub> production by oxidative steam reforming of methanol," *Int. J. Hydrogen Energy*, vol. 33, no. 17, pp. 4569–4576, Sep. 2008.
- [16] C. Rameshan, W. Stadlmayr, S. Penner, H. Lorenz, N. Memmel, M. Hävecker, R. Blume, D. Teschner, T. Rocha, D. Zemlyanov, A. Knop-Gericke, R. Schlögl, and B. Klötzer, "Hydrogen production by methanol steam reforming on copper boosted by zinc-assisted water activation," *Angew. Chem. Int. Ed. Engl.*, vol. 51, no. 12, pp. 3002–6, Mar. 2012.
- [17] R. Navarro, M. Pena, C. Merino, and J. Fierro, "Production of hydrogen by partial oxidation of methanol over carbon-supported copper catalysts," *Top. Catal.*, vol. 2004, no. July, 2004.
- [18] H. Oetjen, V. M. Schmidt, U. Stimming, and F. Trila, "Performance data of a proton exchange membrane fuel cell using H<sub>2</sub>/CO as fuel gas," *J. Electrochem. Soc.*, vol. 143, no. 12, pp. 3838–3842, 1996.
- [19] J. Wang, H. Chen, Y. Tian, M. Yao, and Y. Li, "Thermodynamic analysis of hydrogen production for fuel cells from oxidative steam reforming of methanol," *Fuel*, vol. 97, pp. 805–811, Jul. 2012.
- [20] L. Alejo, R. Lago, and M. A. Pefia, "Partial oxidation of methanol to produce hydrogen over Cu-Zn-based catalysts," *Appl. Catal. A Gen.*, vol. 162, pp. 281–297, 1997.
- [21] J. Agrell, "Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>," *J. Catal.*, vol. 219, no. 2, pp. 389–403, Oct. 2003.
- [22] J. Agrell, M. Boutonnet, and J. L. Fierro, "Production of hydrogen from methanol over binary Cu/ZnO catalysts," *Appl. Catal. A Gen.*, vol. 253, no. 1, pp. 213–223, Oct. 2003.
- [23] S. Schuyten, S. Guerrero, J. T. Miller, T. Shibata, and E. E. Wolf, "Characterization and oxidation states of Cu and Pd in Pd-CuO/ZnO/ZrO<sub>2</sub> catalysts for hydrogen production by methanol partial oxidation," *Appl. Catal. A Gen.*, vol. 352, no. 1–2, pp. 133–144, Jan. 2009.
- [24] J. Agrell, G. Germani, S. G. Järås, and M. Boutonnet, "Production of hydrogen by partial oxidation of methanol over ZnO-supported palladium catalysts prepared by microemulsion technique," *Appl. Catal. A Gen.*, vol. 242, no. 2, pp. 233–245, Mar. 2003.
- [25] M. Haruta; S. Tsubota; T. Kobayashi; H. Kageyama; M.J. Genet; B. Dalmon, "Low-Temperature Oxidation of CO over Gold Supported on TiO<sub>2</sub>, α-Fe<sub>2</sub>O<sub>3</sub>," *J. Catal.*, vol. 144, no. 175, pp. 175–192, 1993.
- [26] F.-W. Chang, H.-Y. Yu, L. Selva Roselin, and H.-C. Yang, "Production of hydrogen via partial oxidation of methanol over Au/TiO<sub>2</sub> catalysts," *Appl. Catal. A Gen.*, vol. 290, no. 1–2, pp. 138–147, Aug. 2005.
- [27] F.-W. Chang, L. S. Roselin, and T.-C. Ou, "Hydrogen production by partial oxidation of methanol over bimetallic Au-Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts," *Appl. Catal. A Gen.*, vol. 334, no. 1–2, pp. 147–155, Jan. 2008.
- [28] M. Haruta, "Catalysis of gold nanoparticles deposited on metal oxides," *Cattech*, vol. 6, pp. 102–115, 2002.
- [29] M. Haruta, "Gold catalysts prepared by coprecipitation for low-temperature oxidation of hydrogen and of carbon monoxide," *J. Catal.*, vol. 115, no. 2, pp. 301–309, Feb. 1989.
- [30] C. Pojanavaraphan, A. Luengnaruemitchai, and E. Gulari, "Catalytic activity of Au-Cu/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts in steam reforming of methanol," *Appl. Catal. A Gen.*, vol. 456, pp. 135–143, Apr. 2013.
- [31] L. S. Roselin, L.-M. Liao, Y.-C. Ou, and F.-W. Chang, "Hydrogen Production by Partial Oxidation of Methanol Over Gold Supported on Fe<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>," *J. Nanosci. Nanotechnol.*, vol. 14, no. 9, pp. 7215–7223, Sep. 2014.
- [32] T.-C. Ou, F.-W. Chang, and L. S. Roselin, "Production of hydrogen via partial oxidation of methanol over bimetallic Au-Cu/TiO<sub>2</sub> catalysts," *J. Mol. Catal. A Chem.*, vol. 293, no. 1–2, pp. 8–16, Oct. 2008.
- [33] Q. Chena, L. Luoa, and X. Yangb, "Partial oxidation of methanol on Au-Pd/ceria," *Indian J. Chem.*, vol. 47, no. 3, pp. 1317–1322, 2008.
- [34] W. Jianxin and L. Laitao, "A Comparative Study of Partial Oxidation of Methanol over Zinc Oxide Supported Metallic Catalysts," *Catal. Letters*, vol. 126, no. 3–4, pp. 325–332, Sep. 2008.
- [35] Y.-J. Huang, K. L. Ng, and H.-Y. Huang, "The effect of gold on the copper-zinc oxides catalyst during the partial oxidation of methanol reaction," *Int. J. Hydrogen Energy*, vol. 36, no. 23, pp. 15203–15211, Nov. 2011.
- [36] M. Haruta, "Gold as a novel catalyst in the 21st century: Preparation, working mechanism and applications," *Gold Bull.*, vol. 37, no. 1–2, pp. 27–36, Mar. 2004.
- [37] L. Chen, S. Wang, C. Chen, and N. Zhang, "Catalytic partial oxidation of methanol over Au-Pd bimetallic catalysts: a comparative study of SBA-16, SBA-16-CeO<sub>2</sub>, and CeO<sub>2</sub> as supports," *Transit. Met. Chem.*, vol. 36, no. 4, pp. 387–393, Apr. 2011.