

Combinatorial catalysis concerning PEMFC technology

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Dimethyl ether (DME) or methanol steam reforming catalysis of precious metals loaded on various metal oxides were investigated by combinatorial method. DME steam reforming strongly depends on support metal oxides, however, methanol reforming is independent of support oxides. A newly found methanol steam reforming catalyst, Pd/MnO₂, was mixed with support oxides suitable for DME steam reforming. At high reaction temperature, the catalysts show higher hydrogen yield than Pt/Al₂O₃ which gave the highest hydrogen yield in the series of catalysts. Platinum loaded on carbon added metal oxide to improve its CO tolerance was also investigated by combinatorial method. CO tolerance of each catalyst was evaluated by hydrogen combustion in the presence of CO. IR thermography was effectively employed as a high throughput screening of a series of anode added metal oxide. The addition of niobium oxide, tantalum oxide, titanium or zirconia improves the CO tolerance of Pt/C. Combinatorial addition of niobium oxide and tantalum oxide was more effective to improve the CO-tolerance.

Key words: Combinatorial catalysis, high throughput experiment, PEMFC, DME, anode

1. INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is the most hopeful energy conversion device for mobile use because it can be operated under mild condition. Theoretically, fuel cells can withdraw power from various chemicals; hydrogen is the most probable fuel. The problem of hydrogen for mobile use is difficulty in handling because we need heavy cylinder for transportation if we need high power. Production of hydrogen from liquid chemicals on-site has a merit on transportation.[1-3]

For on-site hydrogen production, methanol and dimethyl ether (DME) are the candidates because they require lower reaction temperature and give less carbonaceous deposition than the steam reforming of methane or other kind of hydrocarbons. Cu-Zn mixed oxide is known as the best catalyst for methanol steam reforming, however, reductive treatment is indispensable before use. The property is not suitable for daily start and stop operation which are often seen in our ordinary life. Precious metal supported on metal oxides could solve this problem since the precious metals maintain metallic state under atmospheric condition. The catalysis of precious metals loaded on metal oxides for steam reforming reactions of methanol and DME are reported.

If we entire methanol as hydrogen source, we need vaporization unit before reaction unit. DME is gas at atmospheric condition and easily becomes liquid at the pressure as low as ~6 atm. We can transport DME as liquid under slightly pressurized condition and use it as gas. DME seems to be better hydrogen source for mobile use. DME steam reforming has been less studied than methanol steam reforming and believed that the catalyst active for methanol steam reforming shows high activity for DME steam reforming since MeOH

forms by the hydrolysis of DME.[4,5] The catalysis of a series of precious metal loaded on various metal oxide was examined for DME and methanol steam reforming. New DME steam reforming catalyst has been found by the database obtained by combinatorial approach.

CO poisoning of anode is another serious problem which should be solved on PEMFC if we use it for mobile use. The hydrogen produced from organic molecules includes certain amount of CO which binds Pt of anode.[1] The Pt covered with CO cannot work for hydrogen splitting any more. PEMFC supplied CO containing fuel produces no power. The alloy formation of Pt-Ru gives high CO tolerance to Pt.[6] It is believed that Ru activates water molecules to react CO bound on Pt, that is so called "bi-functional model." Although the Pt-Ru catalyst shows high CO-tolerance, it requires highly purified hydrogen whose concentration should be less than 100 ppm. Alternative additives should be investigated to improve CO tolerance of Pt. The strong binding of CO to Pt causes by π -back donation from Pt to CO. In order to reduce the donation, platinum should be kept at high oxidation state. Metal oxide addition seems to be effective for that purpose. The addition of metal oxide addition has been less studied than alloy formation since many metal oxides are soluble to strong acidic media. Here we show the investigation results on combinatorial survey of metal oxide addition by combinatorial way for improving CO tolerance of Pt anode. Evaluation of CO-tolerance of anode was carried out not only by conventional cyclic voltammetry but also by IR thermography in gas phase.[7]

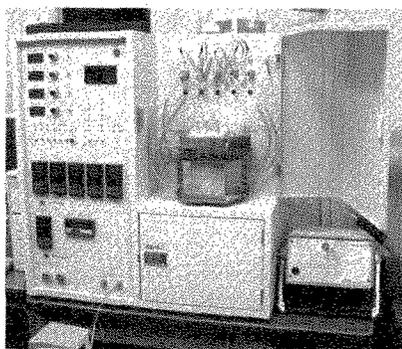
2. EXPERIMENTAL SECTION

2.1 Preparation of catalyst library for steam reforming of methanol or DME

The obtained chemicals were used as received from chemical companies. A catalyst library consisting of precious metals, (Pt, Ir, Pd, Rh, Ru) supported on various metal oxides (La_2O_3 , CeO_2 , TiO_2 , ZrO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , WO_3 , MnO_2 , Al_2O_3 , SiO_2 , SnO_2) was prepared by conventional impregnation method with 5-channel parallel reaction tubes (EYELA ChemiStation PPS-2510). The molecular ratio of precious metal to each metal oxide was 0.01. A typical reaction procedure is as follows; One gram of SiO_2 powder obtained from Merck was delivered to 5 channels. Aqueous solutions of H_2PtCl_6 , IrCl_3 , $\text{Pd}(\text{NO}_3)_2$, $\text{Rh}(\text{NO}_3)_3$, RuCl_3 were impregnated to SiO_2 powder in each tube. The excess amount of water was removed under reduced pressure with stirring and the obtained slurry was dried at 343K for several hours. The dried powders were calcined at 873 K for 5 hours with the ramp rate of 10 K/min. Each powder was put into quartz tube and kept under reduced atmosphere of 10% H_2 in N_2 at 573 K for 2h to assure the metallic phase of precious metals.

2.2 Catalysis measurement

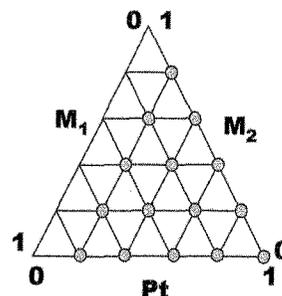
Each catalyst (150 mg) was loaded into a quartz tube reactor (10 mm inner diameter). For DME reforming, a mixture of DME and Ar in the ratio of DME:Ar = 1:99 was passed through water pool via ceramic bubbler at 297.3K in order to supply 3 vol% of water. For MeOH reforming, MeOH and water were separately supplied by passing N_2 through each liquid. The concentration of each chemical was 1% for MeOH and 2% for water. The each mixture was flown onto each catalyst with the flowing rate of 50 mL/min. Each catalyst was up to appropriate temperature. For DME, the reaction was performed at the temperature ranging from 473K to 673K every 50K. For MeOH steam reforming, the reaction was performed at the temperature ranging from 373K to 473K every 20K. The effluent from the reactor was analyzed using a micro GC equipped with two columns; Poraplot Q with He carrier and Molecular Sieve 5A with Ar carrier. The detected chemicals were water, DME, CO_2 by Poraplot Q and hydrogen, methane, CO by Molecular Sieve 5A. The control of temperature and gas composition, and GC was performed by TPD-5R with 5 channel heater manufactured by BEL Japan as shown in Scheme 1. It controls reaction temperature, gas chromatograph and supplies reaction gas for 5 catalysts alternatively.



Scheme 1. Specially designed 5-channel reactor. Reaction temperature, gas composition, and GC are automatically controlled as programmed.

2.3 Preparation of anode with metal oxide

Catalyst libraries were prepared by an automated synthesizer of a JEOL PTW-100. Appropriate amount of ethanolic solutions of H_2PtCl_6 , $\text{Mo}(\text{OEt})_5$, $\text{Ta}(\text{OEt})_5$, $\text{Nb}(\text{OEt})_5$, $\text{Zr}(\text{OEt})_4$, $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_3$, $\text{Ge}(\text{OEt})_4$ were delivered onto carbon support (Valcan XC-72R) at 353 K. After impregnating all solutions, ethanolic solution of potassium ethoxide and formaldehyde were added to reduce platinum ions and to form corresponding metal oxides. The Pt and metal oxides deposited carbon was collected and washed by using a centrifuge, HITACHI himac CT6D. The compositions of prepared catalysts are depicted as phase diagram in Scheme 2. The catalysts were dried at 353 K over night and kept at 483 K in vacuo over night.



Scheme 2. Catalyst composition of Pt/C added M_1O_x and M_2O_y pointed on triangular diagram

2.4 Catalysis measurement

Reaction heat observed at hydrogen oxidation was recorded by IR-thermviewer of a NEC TS7300. A series of catalysts put in Al pans (i.d. 6 mm) was arrayed in a glass cell with Zn-Se window. The gas mixture of 1000 ppm H_2 and 1000 ppm O_2 in N_2 whose flowing rate was 1L/min was flown onto catalyst library for 10 – 30 min. Then the gas composition was changed to pure N_2 for several min. to cool catalysts up to room temperature. The gas mixture of 1000ppm H_2 , 2000ppm O_2 , 1000ppm CO in N_2 was flown onto catalyst library for 20-30 min.

3. RESULTS AND DISCUSSION

3.1 Development of DME steam reforming catalyst based on combinatorial database of DME and MeOH steam reforming

Figure 1a shows the hydrogen concentration in the each effluent on DME steam reforming at 473K. The highest hydrogen concentration of 1.1% was obtained at Pt/ Al_2O_3 . The superior catalysis of Pt/ Al_2O_3 has been already reported by a few research groups. The acidic property of Al_2O_3 accelerates hydrolysis of DME which is believed as rate determining step of the reaction.

The catalysis highly depends on their supports. Al_2O_3 , TiO_2 and ZrO_2 seem to be suitable support for the reaction. Ir and Ru loaded catalysts are less active than Pt, Pd and Rh catalysts. Among Rh loaded catalysts, TiO_2 , ZrO_2 are suitable support and Al_2O_3 and SiO_2 are suitable for Pd. In the case of Pt, the supports described above, TiO_2 , ZrO_2 , Al_2O_3 , SiO_2 are suitable. There seems to be two types of reaction mechanism. First one is the reaction via MeOH formation by hydrolysis following its reforming. Second one is the

direct reforming of DME without formation of MeOH. The reaction over Rh loaded catalyst proceeds without formation of MeOH since Rh loaded catalyst usually shows high activity for steam reforming of hydrocarbons. Pd loaded catalyst is known as less active catalyst for the steam reforming of hydrocarbons than Rh. The reaction over Pd catalysts proceeds by the formation of MeOH. The reaction over Pt loaded catalyst includes two mechanisms.

Figure 1b shows the hydrogen concentration in the each effluent on MeOH steam reforming at 413K. The highest MeOH concentration was obtained at Pd/MnO₂. No apparent trend in support effect and loaded precious metals was observed. The highest activity of Pd/MnO₂ was obtained accidentally on the catalyst.

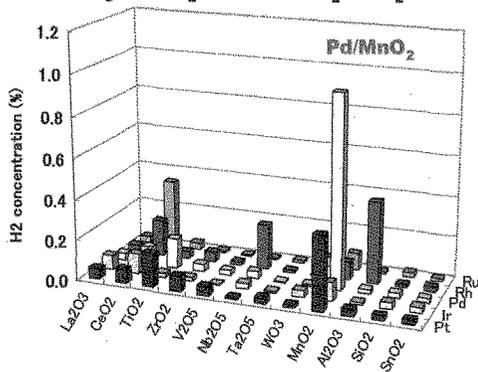
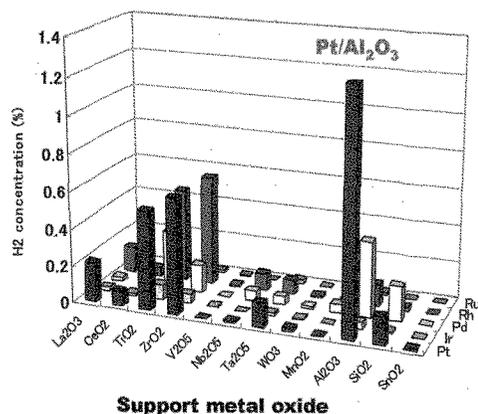
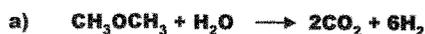
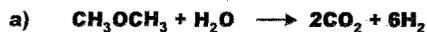
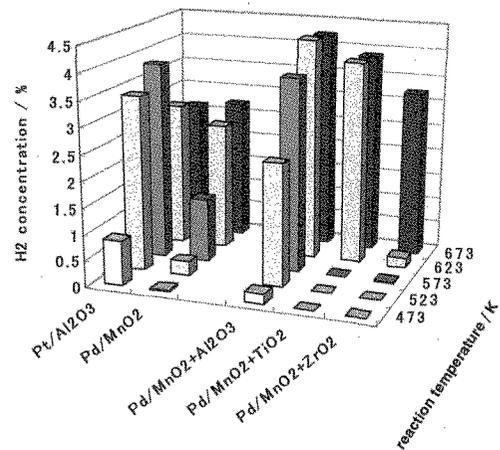


Figure 1. Hydrogen concentration in effluents on a) DME steam reforming over precious metals loaded metal oxides. (DME:H₂O:N₂ = 1:3:96, 1atm, 573 K, SV = 20,000 mL g⁻¹ h⁻¹) b) MeOH steam reforming. (MeOH:H₂O:N₂ = 1:2:97, 1atm, 413 K, SV = 20,000 mL g⁻¹ h⁻¹)

New catalyst for DME steam reforming was developed by combining the suitable support for DME steam reforming and the best catalyst for MeOH steam reforming. Figure 2 shows the hydrogen yield on the reaction over Pd/MnO₂ physically mixed with Al₂O₃, TiO₂, ZrO₂ which are suitable support for DME steam reforming compared with the results of Pt/Al₂O₃ and

Pd/MnO₂ at different temperatures. The ratio of Pd/MnO₂ to each metal oxide is 1:1. Higher hydrogen concentration was observed on these physically mixed systems at high temperature although the hydrogen conversion was lower at Pd/MnO₂+Al₂O₃ than Pt/Al₂O₃ at lower temperature. TiO₂ and ZrO₂ are the suitable supports for hydrogen production without MeOH formation so that higher reaction temperature is required for Pd catalyst to take this reaction route. New DME steam reforming catalyst was successfully obtained by the combination of Pd/MnO₂ suitable for MeOH steam reforming with Al₂O₃ suitable for DME steam reforming on the basis of the results of combinatorial database.

Figure 2. Hydrogen concentrations in DME steam



reforming over Pt/Al₂O₃, Pd/MnO₂, Pd/MnO₂+Al₂O₃, Pd/MnO₂+TiO₂ and Pd/MnO₂+ZrO₂ at reaction temperatures ranging from 473K to 673K.

3.2 CO tolerance evaluation of anode with metal oxide

Addition of metal oxides to Pt/C is expected to reduce the electron donation of Pt to CO since metal oxide reduces electron density of Pt. The problem on the addition of metal oxide is stability in acidic condition because anode contacts to proton exchange membrane which indicates acidic property. The stability of metal oxides should be checked before addition. Table 1 summarized the simple test for the solubility of single metal oxides to 1N H₂SO₄. Nb₂O₅, Ta₂O₅, GeO₂ and TiO₂ were highly stable in acidic media. CeO₂, MoO₃ and ZrO₂ dissolved slightly. CuO, WO₃, In₂O₃ and V₂O₅ almost completely dissolved. Former two classes were tested as the additive metal oxide to Pt/C.

The high throughput screening technology for PEMFC anode has been reported by Mallouk et al.[8] They used the pH indicator to check the electrochemical decomposition of MeOH to H⁺ in solution. The induced pH change was detected as fluorescence of pH indicator. The technology is quite effective for bi-phase reaction, however, its application seems to be difficult for tri-phase reaction because static condition cannot be maintained for the system.

As a new technology for HTS of PEMFC anode, IR thermography was employed. IR thermography can detect reaction heat of two dimensionally arrayed catalysts although it gives no information about reaction product.[9-11] The technology is often used for the

Table 1. Solubility check of metal oxide to 0.5M H₂SO₄ at 353K for 16 hours.

species	initial weight / g	remaining / g	weight loss / %	
CuO	0.153	<0.01	>90	X
WO ₃	0.2463	0.0431	82.5	X
In ₂ O ₃	0.6613	0	100	X
Nb ₂ O ₅	0.9165	0.9146	0.21	OK
Ta ₂ O ₅	0.5190	0.5151	0.75	OK
V ₂ O ₅	0.3526	< 0.01	> 90	X
ZrO ₂	0.7557	0.7033	6.9	?
TiO ₂	0.2396	0.2357	1.63	OK
CeO ₂	0.3995	0.3880	2.8	?

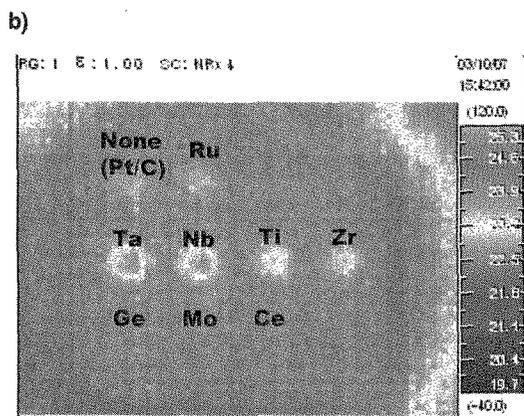
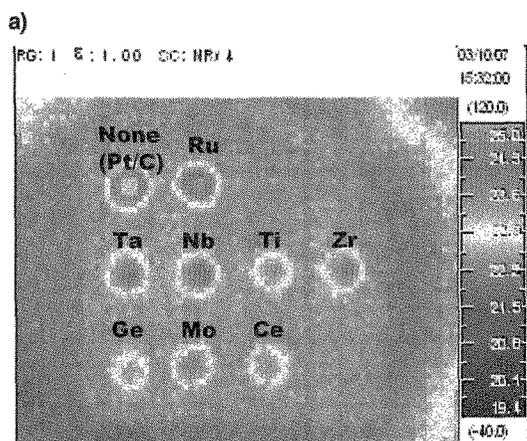


Figure 3. IR thermograph detected reaction heat of hydrogen combustion over Pt/C with metal oxide (Ta, Nb, Ti, Zr, Ge, Mo, Ce).

HTS of combustion catalysts. In order to estimate the activity of each catalyst for hydrogen combustion, detection of reaction heat is enough because there is only one product of water. We checked whether each catalyst can activate hydrogen in the presence of CO by IR thermography.

Figure 3a shows the IR thermograph of hydrogen combustion over Pt/C added various metal oxides. Ru added Pt/C known as the most CO-tolerance anode was arrayed on the top row as the reference. When hydrogen and oxygen containing gas was introduced to

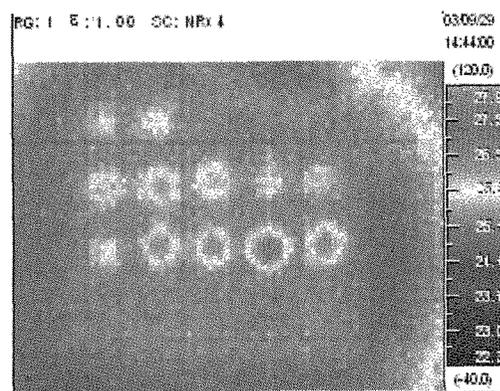
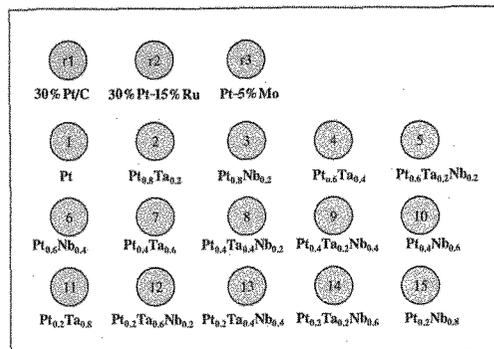


Figure 4. IR thermograph detected the reaction heat of hydrogen oxidation. The reaction gas contains 1000 ppm CO, 1000 ppm H₂ and 2000 ppm O₂.

the cell, reaction heat was observed for all catalysts. This result indicates that all catalysts are active for hydrogen combustion. Each metal oxide addition did not diminish hydrogen activation ability of Pt. Figure 3b shows the result of supplying reaction gas containing H₂, O₂ and CO. The reaction heat of hydrogen combustion was observed on Ta, Nb, Ti, Zr added Pt/Cs. These metal oxides are effective for the improvement of CO tolerance of Pt/C. On the other hand, Ge, Mo and Ce adding Pt/C showed no activity for the reaction. These metal oxides were not effective on the improvement of CO tolerance of Pt/C.

Pt-Ru/C also shows no improvement of CO-tolerance of Pt/C although the Ru addition is known as the most effective method to improve the CO-tolerance. This result indicates that Ru improves the CO-tolerance by different mechanism from that expected for metal oxide additional system. Probably, Ru activates molecular water which attack CO molecule bound on Pt in solution. The mechanism is so called "bi-functional mechanism." The system tested here includes no water to be reacted with CO. This is a plausible reason for Pt-Ru seems not to be effective for the improvement of CO. The metal oxides system improving CO-tolerance have different mechanism of "bi-functional mechanism." It is still speculation, however, the *d*-electron density of Pt was reduced by the metal oxide addition.

The effect of Ta or Nb addition has been reported by our group previously.[12] The addition of these elements negatively shifted the oxidation peak of adsorbed CO, however, the results were no better than

Ru. Multiple additions of metal oxides were tested as a next step.

Fifteen combinations of two metal oxides chosen from Ta, Nb, Ti, Zr, Ge, Mo were added to Pt/C with the ratio among Pt and two metal oxides in Scheme 2. Figure 4 shows the IR thermograph of Ta and Nb adding system when the reaction gas including CO was supplied. $Pt_{0.4}Ta_{0.2}Nb_{0.4}$ system shows higher CO tolerance than single metal oxide of Ta or Nb adding system. The adsorbed CO oxidation over $Pt_{0.4}Ta_{0.2}Nb_{0.4}$ was electrochemically tested; however, very poor CO oxidation peak was obtained. It is due to less CO adsorbed on the catalyst.

4. CONCLUSION

DME steam reforming catalyst was designed based on the knowledge obtained from the database of DME and MeOH steam reforming catalysts. The combination of suitable catalyst for MeOH steam reforming, Pd/MnO₂, and suitable support for DME steam reforming, Al₂O₃ shows higher hydrogen yield than Pt/Al₂O₃ found by usual combinatorial survey at high reaction temperature.

New high throughput screening method of PEMFC anode catalyst was proposed by using IR thermography. The method can evaluate more than 100 catalysts a day. The HTS results in gas phase should be compared with the results obtained by conventional electrochemical measurement.

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