한국수소 및 신에너지학회 논문집(2007.9), 제18권 제3호
Trans. of the Korean Hydrogen and New Energy Society(2007.9), Vol. 18, No. 3, pp. 309~316

수소 제조 촉매 개발을 위한 조합 촉매 기법의 활용

서동진*†, **Eduardo E. Wolf****
*한국과학기술연구원 청정에너지연구센터
**노트르담대학교, 화학공학과

Application of Combinatorial Catalysis Techniques for Hydrogen Generation Catalysts

Dong Jin Suh*† **and Eduardo E. Wolf****
**Clean Energy Research Center, Korea Institute of Science and Technology,*
P.O. Box 131 Cheongryang Seoul 136-791, Korea
***Department of Chemical Engineering, University of Notre Dame,*
Notre Dame IN 46545 U.S.A.

ABSTRACT

조합 및 고속탐색 실험 기법을 촉매 성분의 선정에 활용하였다. 소형 연료전지 작동을 위한 수소 생산에 가장 적합한 것으로 알려진 메탄올 산화 분해용 촉매의 특성을 적외선 화상 및 병렬형 반응 시스템으로 조사하였다. 반응의 모델을 먼저 제시하고 이를 근거로 Cu-Zn-Pd계 촉매를 선정하였다. 먼저 적외선 화상을 이용한 스크리닝을 위해서는 발열 효과라는 촉매 활성의 간접적인 현상을 보여줄 수 있는 적외선 민감 카메라를 이용하여 한 번에 50개의 시료 측정이 가능한 촉매 시료 배열을 설계하였다. 적외선 화상 결과로 높은 활성을 보이는 촉매 시료를 선정한 다음, 병렬형 반응 시스템과 단일 흐름 고정층 반응 시스템으로 선정된 촉매의 활성 특성을 조사 확인하였다. 본 연구에서 제시한 것과 같은 접근 방법으로 지속적으로 얻어진 결과를 반영하여 최적의 활성을 보이는 촉매 성분을 단기간에 찾아내고자 한다.

KEY WORDS : combinatorial catalysis(조합촉매), oxidative decomposition(산화분해), methanol(메탄올), hydrogen(수소), fuel cell(연료전지)

1. Introduction

Combinatorial methods and high throughput experimentation(HTE) have resulted in successful drug discoveries$^{1-3)}$ and materials$^{4-7)}$, and several laboratories in industry and academia have started to apply combinatorial methods to catalytic research$^{7-18)}$. In organometallic catalysis there are less problems to transfer the knowledge of pharmaceutics in methodology and concepts, with respect to heterogeneous catalysis. The application of combinatorial methods to heterogeneous

---

†Corresponding author : djsuh@kist.re.kr

catalysis, however, requires careful consideration not only of material composition, but also of the surface structure. The surface structure of metals supported on porous substrates is difficult to determine a priory and it depends critically on the method of preparation and often on the reaction environment. Hence, to measure the catalytic activity using a combinatorial methodology or high throughput experimentation, it is necessary to devise methodologies that account for such effects. Otherwise, HTE and combinatorial methods can lead to large amounts of useless results if the sensitivity of catalysts to the various factors affecting their surfaces and hence their catalytic activities is not accounted for. The cost of research escalates significantly if a combinatorial approach is taken without accounting for the sensitivity of catalysts to the various factors affecting their surfaces and hence their catalytic activities.

Our approach to combinatorial catalysis is a knowledge-based approach. We start with an exhaustive study of the existing literature that is synthesized into a reaction model that is used to select a selected family of materials to be tested. Fig. 1 schematically shows this inverted pyramid approach that we feel is the most efficient way to utilize combinatorial and HTE methodologies.

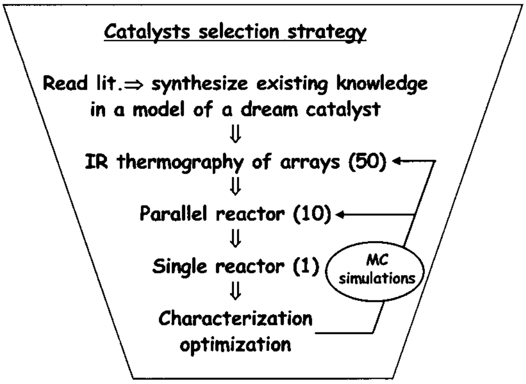

Fig. 1 The proposed inverted pyramid experimental approach

The first level of experimentation is the use of an in situ, spatially resolved technique such as infrared thermography(IRT) to test the activity of an array of eight or nine, and now, up to 50 different materials. The second level of experimentation is to use a parallel reactor that can simultaneously test the activity of ten samples that are selected from the best activities observed in the IRT studies. Finally, the best catalyst is studied in a single flow fixed-bed reactor to get the reaction rate parameters and is characterized to determine its bulk and surface structure. The knowledge gained from these results is then used to formulate a revised model of the surface and the reaction. The revised model is used in a second round of experiments to optimize the catalyst. The final model in this approach will give the best catalyst.

The IRT technique used in our work was first introduced at Notre Dame by Pawlicki and Schmitzl9). Our group used it previously to show the formation of temperature patterns during auto-oscillations occurring during CO oxidation on Rh/SiO$_2$ supported catalysts20,21). Moates et al.22) employed IRT to study an array made of 16 metal supported catalysts that were prepared by a conventional method of impregnating pellets of g-Al$_2$O$_3$ with aqueous solutions of metal salt precursors. Holzwarth et al.23) used infrared thermography to evaluate the catalytic activity of an array with 37 transition metal supported catalysts during the hydrogenation of hexane and the oxidation of isooctane and toluene. The parallel reactor used in the second stage of experimentation was designed and developed by ISRI Inc.24) and tested in our group.

The reaction under study is the oxidative decomposition of methanol that may be the simplest way to generate the necessary hydrogen for portable fuel cells. The oxidative decomposition of methanol offers some obvious advantages over the highly endothermic steam reforming of methanol, a well-established process used for the stationary production of hydrogen, with regard to kinetic aspects. This energetically favorable, exothermic reaction provides a fast response to transients and requires no steam. The Cu- and Pd-based catalysts have been reported to be active for the oxidative decomposition of methanol[25-27]. However, none of them including the traditional catalyst for methanol synthesis Cu/ZnO is robust enough for on-board hydrogen production in a variety of conditions. In this work, we have prepared a series of Cu/Zn/Pd and Cu/Zn/Pd/M catalysts with different compositions and metal combinations by the coprecipitation method and evaluated their reaction characteristics by the selective combinatorial catalysis experimentation.

2. Experimental

2.1 IRT Reactor

The experimental system employed in the IRT studies has been described elsewhere[10,11]. It includes electronic flow controllers to provide gases at specific flow rates, temperature control, the IR-cell reactor and the IR camera(AGA Thermovision 782). A new IR reactor, shown in Fig. 2, has an array containing up to 50 wells and is commercially available from ISRI. In addition of inlets and outlets for the continuous flow of gases, the reactor has heaters that are connected to a temperature controller to maintain the temperature of the reactors constant. The IR camera has an infrared detector and an optical scanner that scans over the whole object constructing an image in one second. The signal collected is displayed on a TV monitor and also recorded in a video tape recorder. During reaction, the temperature of the reactor is increased step by step and the IR intensity is recorded after the image does not change with time. Based on the temperature calibration with blank experiments, the real temperature and the temperature difference with the blank experiment on each spot of the catalysts are obtained. In the IRT experiments, the temperature difference between the catalysts under reaction and the blank experiment is taken as a descriptor of catalytic activity.

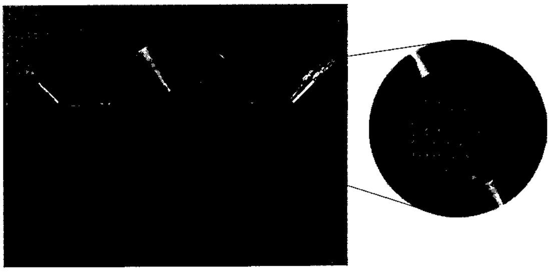

Fig. 2 The IRT reactor with an array of 50 samples

2.2 Parallel Flow Reactor

We also utilize a ten-port micro-reactor manufactured by ISRI(COMBI Reactor^{TM}) that allows one to evaluate the activity of the best catalysts obtained from the IRT studies. The COMBI Reactor shown in Fig. 3 is interfaced on line with a fast gas chromatograph(GC), which provide composition analysis of the effluent from each of the 10 wells. Each well in the COMBI has a capacity of up to 1-2 g of catalyst, thus representing a more scalable result than the one obtained from the catalyst array that only uses a few mg of material. The GC provides sequential analysis of the effluent trapped from each reactor.

The system also has programmable electronic flow controllers to meter various gases to the reactor and a temperature control to maintain the reactor temperature constant. The most active catalyst from the COMBI studies is then studied in detail in a single flow micro-reactor to obtain kinetic results and compare their consistency with the proposed model. The model is then modified accordingly and new formulations/preparations are chosen to optimize the activity of the materials.

2.3 Catalyst Preparation and Reaction

The catalysts were prepared in a parallel preparation system according to the carbonate coprecipitation from aqueous nitrate solutions using sodium carbonate as a precipitating agent. The precipitates were aged with stirring, then filtered, and extensively washed. The resulting precipitates was dried overnight at 383 K and calcined in air at 723 K for 5 h. Prior to reaction, the catalyst was reduced in hydrogen at 573 K for 2 h. The gaseous mixture used for the reaction consisted of methanol vapor and oxygen, diluted nitrogen. The inlet concentration of methanol was managed by using a saturator at the temperature of 273 K. The oxygen/methanol molar ratio in the feed was kept at 0.5. The reaction products were analyzed online by two gas chromatographs connected in series and equipped with thermal conductivity detectors.

3. Results and Discussion

3.1 Model of the Ideal Catalyst

As shown in Fig. 1, we first start with an exhaustive search of the existing literature of the reaction under study to formulate a hypothetical model of the reaction that guides us to search for families of materials that might be active. This approach differs with a more intensive approach for searching every material throughout the periodic table without guidance on materials that have a chance to be active or selected for the reaction under investigation. This model led us to the selection of two groups of materials that have the strongest potential to decompose methanol to hydrogen at low temperatures with the minimum formation of water. The first group contains Cu/ZnO, which selectively produces hydrogen and carbon dioxide. The second group contains Pd, which exhibits very high activity for the decomposition of methanol to hydrogen and carbon monoxide. A series of binary Cu/Zn and ternary Cu/Zn/Pd catalysts were first investigated to determine the optimal compositions and to check the existence of a synergistic effect between the two groups. Next we attempted to obtain further improvement in catalyst performance by incorporation of a fourth component to the ternary catalysts.

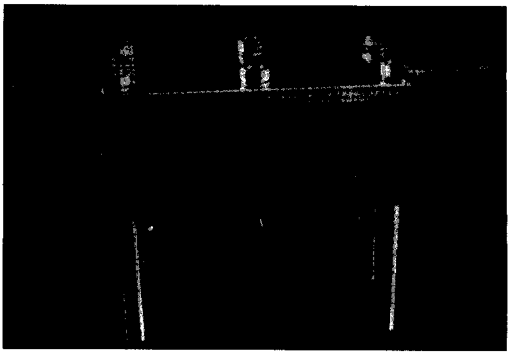

Fig. 3 The parallel flow COMBI reactor

3.2 IRT Reactor

A total of 32 catalysts were examined by IRT in only four experiments. The IRT images of Cu/Zn, Cu/Zn/Pd, and Cu/Zn/Pd/M catalysts were obtained at various temperatures in the IR cell with an array of nine spots(one blank spot). Fig. 4 presents a bar diagram of the temperature difference(DT) obtained from the IRT images of the catalysts with and without reaction as a good indicator of catalytic activity reflecting reaction exothermicity. Fig. 4 shows the effect of the Cu/Zn ratio and Pd addition on the catalytic activity of oxidative methanol decomposition at 423-498 K. The catalytic activity is likely to increase with the increase of the Cu/Zn ratio up to 7/3 or 8/2. It can also be seen that the introduction of Pd improves the catalytic activity significantly. As shown in Fig. 4, the catalyst 7 (Cu/Zn=7/3, 1% Pd) and the catalyst 8(Cu/Zn= 8/2, 1% Pd) were observed to be the most promising catalysts. The IRT results for Cu/Zn/Pd catalysts(not shown) also exhibited no further increase in the catalytic activity with increasing Pd contents over 1%. Hence we decided to keep the Cu/Zn ratio and Pd content at 7/3 or 8/2 and 1%, respectively, to study the quaternary catalysts. From additional IRT results for the quaternary catalysts Cu/Zn/Pd/M(not shown), the potential promoters were found to be Ce and Zr. The addition of Zr showed the highest exothermicity.

3.3 Parallel Flow Reactor

Further work proceeded using the parallel flow COMBI reactor to verify the IRT results under conditions typical of catalytic exploratory results. The results for methanol conversion and selectivity to hydrogen obtained in the parallel flow COMBI reactor for various catalysts selected from IRT results are presented in Fig. 5. The results were in fair accord with the corresponding IRT results. The addition of Pd to Cu/Zn up to 1% increased the conversion of methanol and selectivity to hydrogen. Further improvement in catalyst performance was obtained by incorporation of Ce or Zr into the Cu/Zn/Pd catalysts. The selectivity and conversion exhibit the usual inverse correlation for most catalysts: i.e. the higher the conversion the lower the selectivity. However, the addition of Pd, Ce, and Zr led to increased conversion and selectivity. Although IRT was a quick way to screen which ones were the most promising catalysts in the selected groups of catalysts, it may not give sufficiently accurate results, particularly for complex reaction systems. Some of possible reactions under the reaction conditions studied are exothermic(oxidation and water gas shift reaction) and the others are endothermic(decomposition and steam reforming). It is important to note that the IRT results show the apparent exothermicity of all the reactions involved.

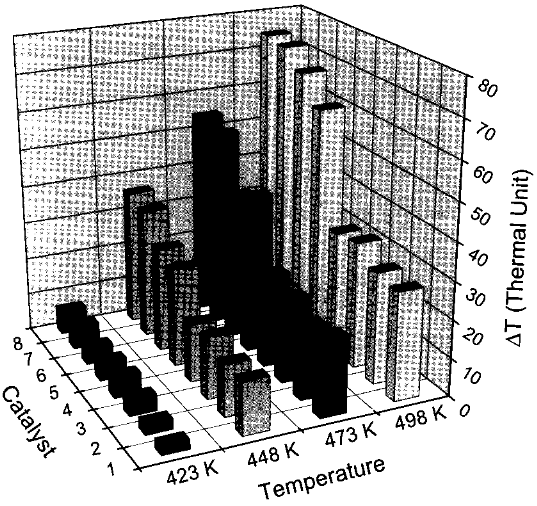

Fig. 4 IRT results for oxidative methanol decomposition over various Cu/Zn and Cu/Zn/Pd catalysts. Reaction conditions: methanol partial pressure 0.036 atm, O_2/methanol=0.5, N_2 balance. Catalysts: 1, Cu/Zn=5/5; 2, Cu/Zn=6/4; 3, Cu/Zn= 7/3; 4, Cu/Zn=8/2; 5, Cu/Zn=5/5, 1% Pd; 6, Cu/Zn=6/4, 1% Pd; 7, Cu/Zn=7/3, 1% Pd; 8, Cu/Zn=8/2, 1% Pd

The quaternary catalyst containing 2% Zr, which showed the highest exothermicity, was actually less active and selective than the other Cu/Zn/Pd/M catalysts. The quaternary 1%Pd-u Zn/Ce7/3/1) catalyst showed 53.6% selectivity at 79.4% conversion being the most active and selective of all the catalysts tested.

3.4 Single Flow Ractor

Finally the most active and selective catalyst was studied in a single flow fixed-bed reactor. The results showed similar conversion-selectivity results to those obtained in the parallel flow COMBI reactor. There are some differences between the two types of reactors in quantitative data probably due to the fact that heat and mass transfer of the fixed-bed plug flow is different from that of the parallel reactor. It should be emphasized that the results presented here were obtained in a fast track experimental program comprising four weeks of experiments. A similar program using a sequential approach would have taken several months. As pointed out in Fig. 1, it is now necessary to characterize some of the most active catalysts to elucidate the main causes for the superior catalytic performance and then to design a new model of the ideal catalyst. It is clearly demonstrated from Table 1, however, that a Ce containing quaternary catalyst is the most active and selective of all the catalysts studied. Further work using multiple characterization techniques will help to optimize the catalysts needed for attaining the objective of this work.

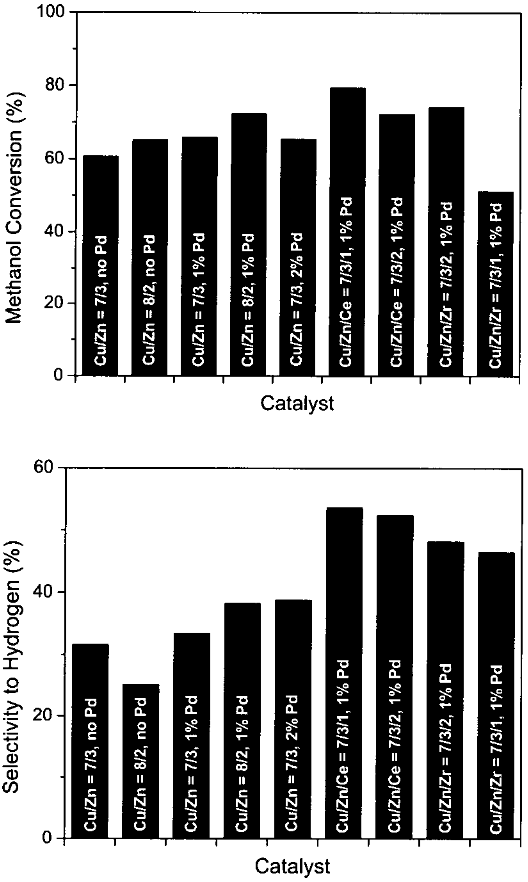

Fig. 5 Conversion and selectivity obtained in the parallel flow COMBI reactor. Reaction conditions: catalyst, 20 mg; total flow rate, 329.6 cc/min; methanol partial pressure, 0.036 atm; O_2/methanol=0.5; N_2 balance

Table 1 Oxidative decomposition of methanol over selected Cu/Zn, Cu/Zn/Pd, and Cu/Zn/Pd/Ce catalysts using a single flow fixed-bed reactor[a]

Catalyst	Temp (K)	Conversion of MeOH (%)[b]	Selectivity to H_2 (%)[b]	Selectivity to CO_2 (%)[b]
Cu/Zn(8/2) no Pd	524	61.1	10.6	41.0
Cu/Zn(8/2) 1% Pd[c]	525	89.9	10.5	42.5
Cu/Zn(8/2) 1% Pd[c]	498	91.4	14.1	47.5

[a] Reaction conditions: catalyst, 50 mg; total flow rate, 164.8 cc/min; methanol partila pressure, 0.036 atm; O_2/methanol= 0.5; N_2 balance

[b] After 2 h of time on stream

[c] Weight % based on oxides

4. Conclusions

1) An inverted pyramidal approach using simple and tested analytical techniques has been demonstrated for the oxidative decomposition of methanol.
2) Addition of Pd to Cu/Zn up to 1% increased the conversion of methanol and selectivity to hydrogen.
3) Addition of Ce or Zr to Cu/Zn/Pd increased the conversion of methanol and selectivity to hydrogen.
4) Further work is needed to characterize and verify the working hypothesis of the selected groups of catalysts.

References

1) E. M. Gordon and J. F. Kerwin, "Combinatorial Chemistry and Molecular Diversity in Drug Discovery", Wiley, New York, 1998.
2) N. K. Terret, "Combinatorial Chemistry", Oxford University, Oxford, 1998.
3) S. R. Wilson and A. W. Czarnik, "Combinatorial Chemistry", Wiley, New York, 1997.
4) X. -D. Xiang, X. Sun, G. Briceno, Y. Lou, K. -A. Wang, and H. Chang, "Combinatorial Approach to Materials Discovery", Science, Vol. 268, 1995, pp. 1738-1740.
5) G. Briceno, H. Chang, X .Sun, P. G. Schultz, and X. -D. Xiang, "Class of Cobalt Oxide Magnetoresistance Materials Discovered with Combinatorial Synthesis", Science, Vol. 270, 1995, pp. 273-275.
6) E. Danielson, J. H. Golden, E. W. McFarland, C. M. Reaves, W. H. Weinberg, and X. D. Wu, "Combinatorial Approach to the Discovery and Optimization of Luminescent Materials", Nature, Vol. 389, 1997, pp. 944-948.
7) E. Danielson, M. Devenney, D. M. Giaquinta, J. H. Golden, R. C. Haushalter, E. W. McFarland, D. M. Poojary, C. M. Reaves, W. H. Weinberg, and X. D. Wu, "A Rare-Earth Phosphor Containing One-Dimensional Chains Identified through Combinatorial Methods", Science, Vol. 279, 1998, pp. 837-839.
8) B. Jandeleit and D. J. Schaefer, T. S. Powers, H. W. Turner, and W. H. Weinberg, "Combinatorial Materials Science and Catalysis", Angew. Chem. Int. Ed., Vol. 38, 1999, pp. 2494.-2532.
9) P. P. Pescarmona, J. C. van der Waal, I. E. Maxwell, and T. Mascmeyer, "Combinatorial Chemistry, High-Speed Screening and Catalysis", Catal. Lett., Vol. 63, 1999, pp. 1-11.
10) D. Wolf, O. V. Buyesvskaya, and M. Baerns, "An Evolutionary Approach in the Combinatorial Selection and Optimization of Catalytic Materials", Appl. Catal. A: Gen., Vol. 200, 2000, pp. 63-77.
11) S. M. Senkan, "High-Throughput Screening of Solid-State Catalyst Libraries", Nature, Vol. 394, 1998, pp. 350-353.
12) C. Hoffmann, A. Wolf, and F. Schüth, "Parallel Synthesis and Testing of Catalysts under Nearly Conventional Testing Conditions", Angew. Chem. Int. Ed., Vol. 38, 1999, pp. 2800-2803.
13) C. M. Snively, G. Oskarsdottir, and J. Lauterbach, "Parallel Analysis of the Reaction Products from Combinatorial Catalyst Libraries", Angew. Chem. Int. Ed., Vol. 40, 2001, pp. 3028-3030.
14) W. Maier, "Combinatorial Chemistry - Challenge and Chance for the Development of New Catalysts and Materials", Angew. Chem. Int. Ed., Vol. 38, 1999, pp. 1216-1218.
15) J. M. Serra, A. Chica, and A. Corma, "Development of a Low Temperature Light

Paraffin Isomerization Catalysts with Improved Resistance to Water and Sulphur by Combinatorial Methods", Appl. Catal. A: Gen., Vol. 239, 2003, pp. 35-42.

16) R. Schlögl, "Combinatorial Chemistry in Heterogeneous Catalysis: A New Scientific Approach or "the King's New Clothes", Angew. Chem. Int. Ed., Vol. 37, 1998, pp. 2333-2336.

17) R. J. Berger, J. Perez-Ramirez, F. Kapteijn, and J. A. Moulijn, "Catalyst Performance Testing: Radial and Axial Dispersion Related to Dilution in Fixed-Bed Laboratory Reactors", Appl. Catal. A: Gen., Vol. 227, 2002, pp. 321-333.

18) J. Holmgren, D. Bem, M. Bricker, R.. Gillespie, G. Lewis, D. Akporiaye, I. Dahl, A. Karlsson, M. Plassen, and R. Wendelbo, "Application of Combinatorial Tools to the Discovery and Commercialization of Microporous Solids: Facts and Fiction", Stud. Surf. Sci. Catal., Vol. 135, 2001, pp. 113-122.

19) P. C. Pawlicki and R. A. Schmitz, "Spatial Effects on Supported Catalysts", Chem. Eng. Prog., Vol. 83, 1987, pp. 40-45.

20) J. Kellow and E. E. Wolf, "Infrared Thermography and FTIR Studies of Catalyst Preparation. Effects on Surface Reaction Dynamics during CO and Ethylene Oxidation on Rh/SiO_2 Catalysts", Chem. Eng. Sci., Vol. 45, 1990, pp. 2597-2602.

21) F. Qin and E. E. Wolf, "Infrared Thermography Studies of Unsteady-State Processes during CO Oxidation on Supported Catalysts", Chem. Eng. Sci., Vol. 49, 1994, pp. 4263-4267.

22) F. C. Moates, M. Somani, J. Annamalai, J. T. Richardson, D. Luss, and R. C. Wilson, Ind. Eng. Chem., Vol. 35, 1996, p. 4801.

23) A. Holzwarth, H. -W. Schmidt, and W. F. Meier, "Detection of Catalytic Activity in Combinatorial Libraries of Heterogeneous Catalysts by IR Thermography", Angew. Chem. Int. Ed., Vol. 37, 1998, pp. 2644-2647.

24) http://www.in-situresearch.com.

25) S. Velu, K. Suzuki and T. Osaki, "Selective Production of Hydrogen by Partial Oxidation of Methanol over Catalysts Derived from CuZnAl-Layered Double Hydroxides", Catal. Lett., Vol. 62, 1999, pp. 159-167.

26) J. Agrell, K. Hallelbo, K. Jasson, S. G. Jaras, 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, 2001, pp. 239-250.

27) M. L. Cubeiro and J. L. G. Fierro, "Selective Production of Hydrogen by Partial Oxidation of Methanol over ZnO-Supported Palladium Catalysts", J. Catal., Vol. 179, 1998, pp. 150-162.