Fuel processing for portable power applications

Jianli Hu[*], Yong Wang, Dave VanderWiel, Cathy Chin, Daniel Palo,
Robert Rozmiarek, Robert Dagle, James Cao, Jamie Holladay, Ed Baker

Pacific Northwest National Laboratory, 902 Battelle Boulevard MSIN K8-93, Richland, WA 99352, USA

Abstract

The present work focuses on fuel processing at a very short contact time (GHSV $= 36,000$–$144,000\,h^{-1}$) and a relatively lower temperature ($<500\,°C$). More than 95% conversion can be achieved by steam reforming of clean fuels, such as isooctane and synthetic diesel. A unique characteristic of the current catalytic system is the flexibility in steaming reforming of different hydrocarbon fuels under different conditions. High efficiency methanol steam reforming catalyst performance has been demonstrated which implies a feasibility in designing a high performance methanol steam reformer with reduced volume for portable device applications.
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1. Introduction

The remarkable recent advances in wireless and portable communications devices (e.g. laptop computers, cellular phones and portable digital assistants) have fueled a need for high energy density portable power sources for consumer use. Similarly, interest in portable power sources has increased in the military and intelligence communities. Currently, portable military electronics are dependent on batteries to supply electrical power for long-duration missions. This poses two major problems which result from the low energy density of current battery systems: excessive weight/bulk, and reduced mission duration.

Compact fuel cell systems that operate on liquid hydrocarbon fuels offer an efficient, lightweight alternative to batteries, thus, allowing for greater portability and longer mission lifetime. For instance, the energy densities of diesel fuel and methanol are each at least an order of magnitude greater than that of lithium-ion batteries. Another option, hydrogen storage (compressed or chemical) provides an energy density not much greater than found in batteries. As shown in Table 1, a hydrocarbon-based fuel cell system operating at just 5% overall efficiency has a higher energy density than a lithium polymer battery and at least equal energy density as a polymer–electrolyte membrane (PEM) fuel cell system operating on stored hydrogen. Clearly, liquid hydrocarbons would be the preferred energy source for a portable power system if a rugged, reliable and lightweight fuel processor were available to convert hydrocarbon fuels to hydrogen. An appropriate fuel processor would efficiently produce hydrogen of sufficient quantity and purity to drive a PEM fuel cell, and would do so within a small volume.

For several years, Battelle has led the development of microprocess technology for various applications and device sizes. These technologies include fuel vaporization [1–4], gas conversion [5–7], fuel processing [2,6–12], heat transfer [1,3,4,13,14], mass transfer [15,16], catalytic combustion [3,4,13,17] and partial oxidation [12]. In each application, the microchannel architecture drastically reduces the heat and mass transfer resistances relative to conventional systems.

Many of these advances are built upon Battelle's aggressive effort to develop catalysts for microreactor applications. Different steam reforming catalysts are developed for hydrogen production from various hydrocarbon fuels. These catalysts were developed for millisecond contact time (GHSV $= 10^4$ to $10^5\,h^{-1}$) applications for use with many different fuels, including methanol, butane, *iso*-octane, diesel, and jet fuel.

Such microprocess and catalyst technology is, thus, a natural fit for portable power systems, where size and weight must be minimized. For instance, the required catalyst volume for a 15 W steam reformer operating at $36,000\,h^{-1}$ GHSV is less than $0.5\,cm^3$. This translates to correspondingly small device footprints, such that the majority of the weight and bulk of the final system is dictated by the related fuel supply rather than the fuel processor (based on multi-day missions).

* Corresponding author. Tel.: +1-509-376-0427; fax: +1-509-376-5106.
E-mail address: jianli.hu@pnl.gov (J. Hu).

Table 1
Comparison of energy densities from various sources

Fuel	LHV[*] (kJ/mol)	Energy density (kW h/kg)	Efficiency required (to match batteries; %)
Methanol	639	5.5	5.5
n-Butane	2650	12.7	2.4
n-Octane	5100	12.4	2.4
H_2 storage	242	0.5–1.0	30–60
Lithium-ion battery	–	0.3 (projected)	–

[*] LHV: lower heating value.

2. Experimental

Development of the portable fuel processor begins with the design, fabrication and testing of individual unit operations. Later, these unit operations are integrated at the bread-board level. This occurs simultaneously with catalyst testing and selection for both the combustor and the steam reformer. The next step, which is beyond the scope of this paper, includes the full integration of all unit operations in a single, rugged device suitable for field testing.

All catalyst preparation, device fabrication, system testing, and product analysis were performed on-site. Proprietary catalyst system typically containing Pd on ZnO was used (patent filed in 2001). The current system is composed of stainless steel process units connected by 3 or 6 mm external diameter stainless steel tubing. Thermocouples and pressure transducers are placed strategically throughout the device, and system data is collected through an on-line data acquisition system.

Catalytic combustion of methanol is used to provide system heat which is necessary for reactant vaporization and preheat as well has for heat of reaction for the endothermic steam reforming of methanol ($\Delta H = +50$ kJ/mol). As illustrated in Fig. 1, methanol (from a syringe pump) and compressed air are fed separately to the vaporizer/preheater, from which the combined vapor stream enters the combustion zone. Hot combustion gases are then used to heat the steam reformer. Downstream of the reformer, the combustion gases then provide heat to the two vaporizers that feed the combustor and the reformer feed stream.
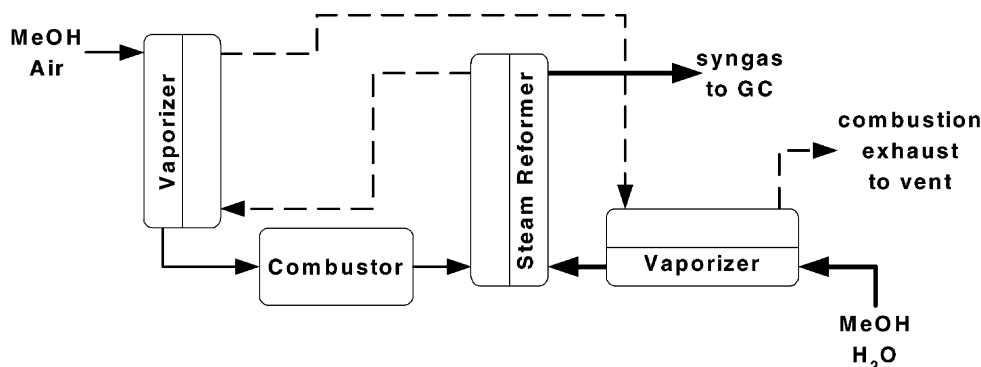
A premixed solution of methanol and water (1:1 ratio by weight) is fed to the system using an HPLC pump. The combined stream first enters the reactant vaporizer, then flows through the steam reformer, where it is converted to H_2, CO_2, and CO. The reformate is chilled, passes through a vapor–liquid separator to remove residual water and methanol, and then flows to the on-line gas chromatograph for analysis.

The gas chromatograph used in our investigation is an Agilent Technologies Micro-GC capable of detecting gases and hydrocarbons as large as C_8. However, in the methanol reforming system, detection of compounds up to C_2 is sufficient. All gases other than H_2, CO_2, CO and CH_4 remain below the detection limit (100 ppm) of the instrument under the system conditions investigated. JP-8 jet fuel has sulfur content of 3000 ppm and boiling range between 80 and 270 °C. Synthetic diesel is sulfur free and has boiling range between 60 and 260 °C.

3. Results and discussion

3.1. Steam reforming of hydrocarbon fuels

Steam reforming catalysts are designed to operate at very high gas hourly space velocity. At a very high GHSV between 36,000 and 144,000 h^{-1} and a relatively low temperature (450–550 °C), greater than 95% conversions can be achieved in steam reforming of clean fuels, such as isooctane and synthetic diesel. A unique characteristic of the current catalyst system is the flexibility in steaming reforming of different hydrocarbon fuels under different conditions (Fig. 2). Compared with other hydrocarbon fuels, methanol steam reforming occurred at much lower temperature (300–350 °C). For the portable power system, lower temperature steam reforming poses great advantages because of less insulating material required which implies the reduced size of the power system.

3.2. Methanol steam reforming with low CO yield

Carbon monoxide is an undesirable product in the methanol steam reforming because it poisons downstream
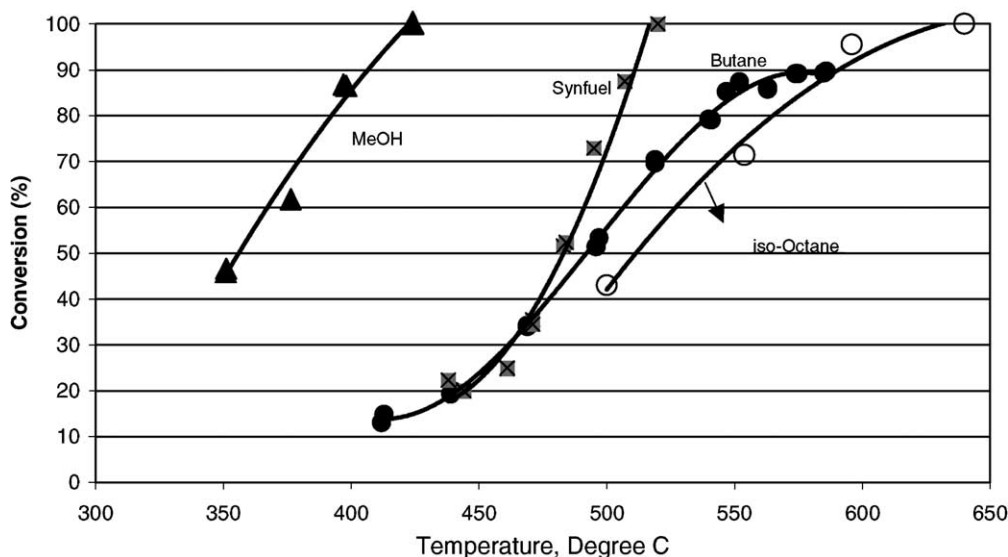

Fig. 1. Bread-boarded fuel processing system for methanol.

Fig. 2. Steam reforming of different hydrocarbon fuels (GHSV = 144,000 h^{-1}, H$_2$O/C = 3:1 and 0.1 MPa).

low temperature fuel cells, such as PEM fuel cells. One of the objectives for catalyst development is to minimize CO production. Compared with unoxygenated hydrocarbons, steam reforming of methanol may undergo different reaction pathways. When using supported noble metal catalysts without water gas shift functionality, methanol decomposition becomes dominant and the product contains high concentrations of CO, and low H$_2$ yield (Fig. 3). In order to minimize CO production, a water gas shift functional catalyst should be incorporated. As shown in Fig. 3, by adding a water gas shift catalyst to the bottom of the methanol decomposition catalyst, H$_2$ yield is enhanced and CO concentration is reduced. It is very interesting that, on a Pd/ZnO catalyst, H$_2$ yield is further enhanced and CO

concentrations as low as 0.7% (in dry gas) are obtained. Originally, this is attributed to better decomposition activity, combined with high water gas shift functionality.

Therefore, the Pd/ZnO catalyst was tested for water gas shift reaction. To our surprise, this catalyst demonstrated very low water gas shift activity. It is postulated that, on this Pd/ZnO catalyst, combined reactions of methanol decomposition and water gas shift reaction are not operative.

3.3. Characteristics of Pd/ZnO Catalyst

It is reported that a Pd–Zn alloy is formed on Pd/ZnO catalysts which functions as an active phase [18,19]. To understand the origination of the active phase, XRD and TPR analyses were conducted to determine if a Pd–Zn alloy structure is necessary to catalyze methanol steam reforming. According to the XRD analysis, during calcination in air, no alloy structure is formed. Results show that alloy structures can be formed during hydrogen reduction at temperatures greater than 350 °C. TPR analysis shows that reduction occurs at 120 °C. Apparently, the reduction takes place at temperatures where alloy formation does not occur. The question remained of whether a Pd/ZnO catalyst reduced at 125 °C exhibits any activity. Two experiments were conducted using the catalyst reduced at 125 and 350 °C. As shown in Fig. 4, the Pd/ZnO catalyst reduced at two different temperatures exhibits the same conversion. However, Pd/ZnO reduced at 125 °C does not contain an alloy structure. These results suggest that the Pd–Zn alloy structure may not be necessary for steam reforming activity. Advocates of Pd–Zn alloy activity may argue that even if no alloy structure is formed at 120 °C, it may still be formed at steam reforming temperatures of 300 °C [19]. Experiments using in situ XRD will be conducted to further investigate the active structure of Pd/ZnO.
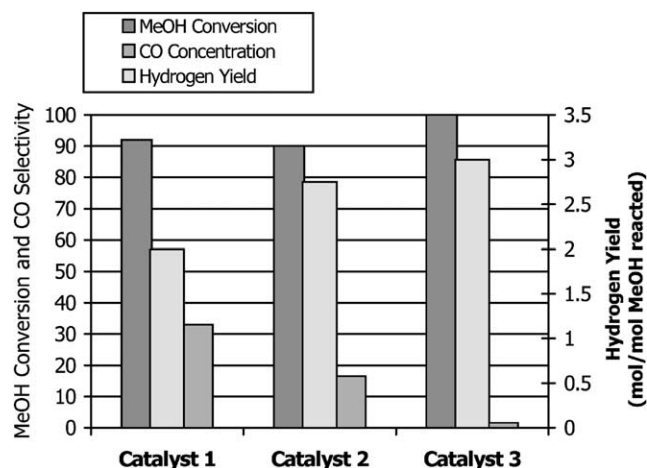

Fig. 3. Different approaches on steam reforming of methanol (catalyst 1: decomposition catalyst, catalyst 2: decomposition+WGS catalyst, catalyst 3: Pd/ZnO-based. Conditions: GHSV = 36,000 h^{-1}, H$_2$O/C = 1.8, 300 °C and 0.1 MPa).
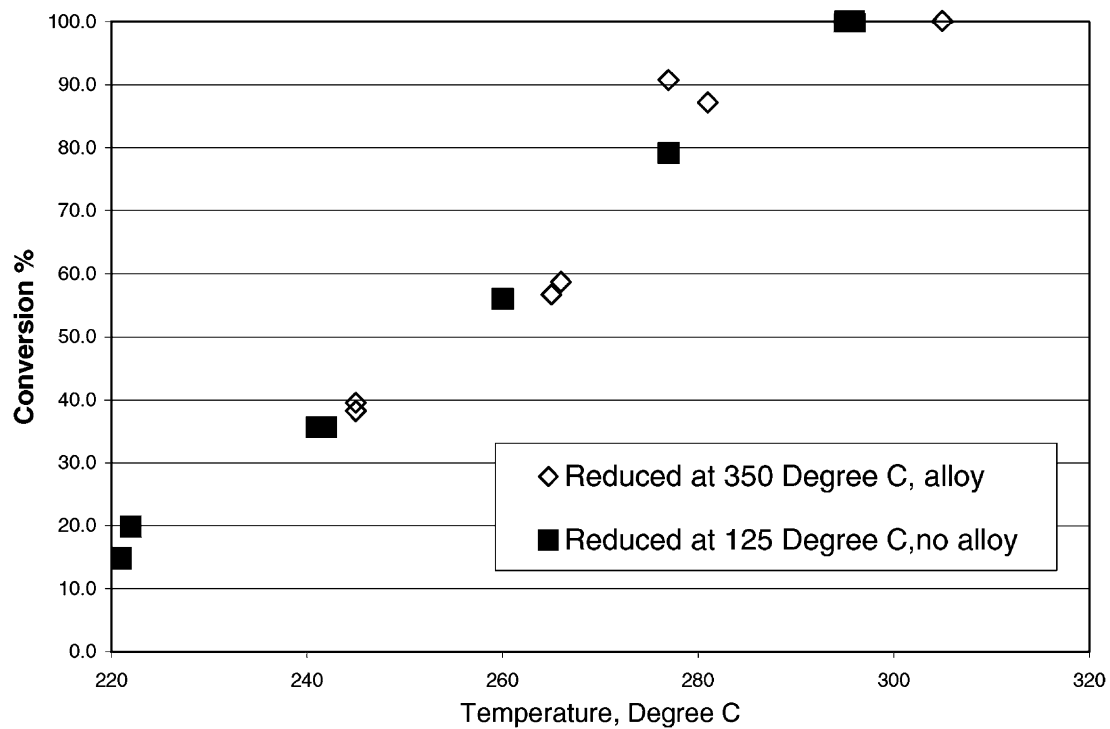
Fig. 4. Effect of reduction temperature on Pd/ZnO catalyst activity in methanol steam reforming (GHSV $= 36{,}000\,h^{-1}$, $H_2O/C = 1.8$ and 0.1 MPa).
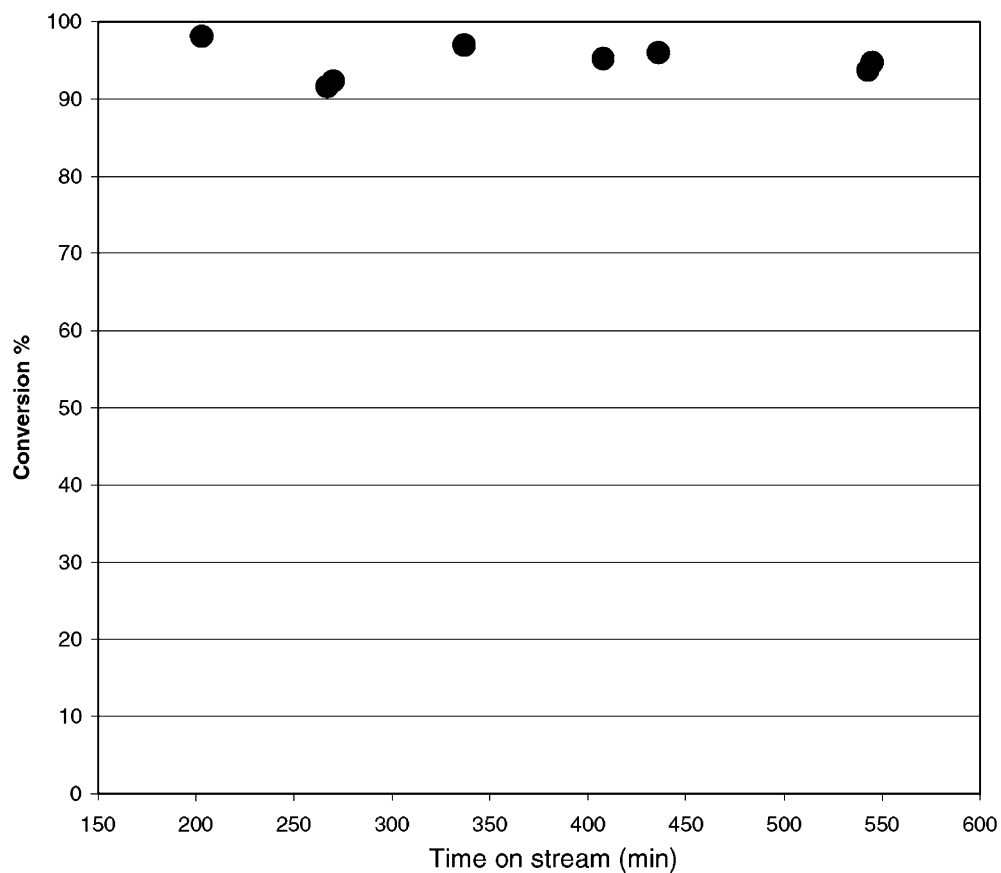
Fig. 5. Steam reforming of synthetic diesel (GHSV $= 144{,}000\,h^{-1}$, $H_2O/C = 3{:}1$ and 0.1 MPa).
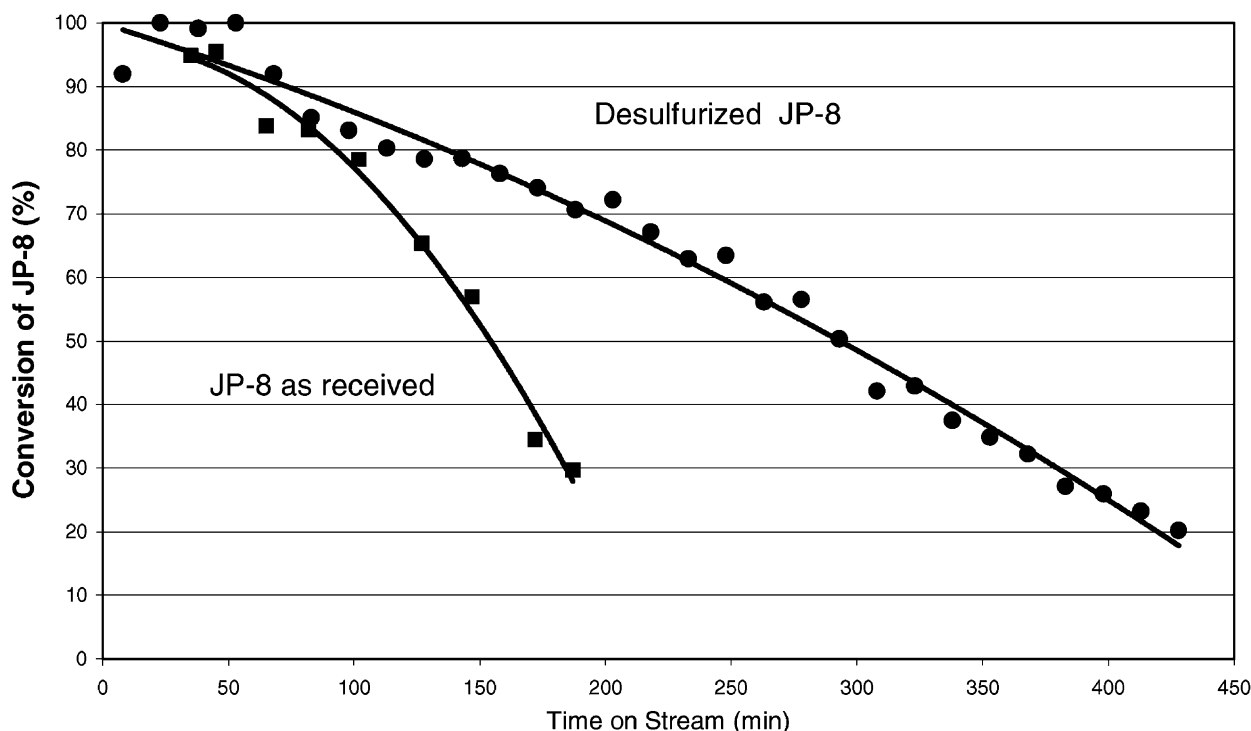
Fig. 6. Steam reforming of as received JP-8 and desulfurized JP-8 (GHSV = 144,000 h^{-1}, H$_2$O/C = 3:1, 650 °C and 0.1 MPa).

3.4. Steam reforming of synthetic diesel and jet fuel

We have been very successful in the development of catalysts for methanol steam reforming and integration of the catalysts into the design of microreactors [20–23]. It is always a challenge to develop steam reforming catalyst applicable for sulfur containing jet fuel, such as JP-8. The sulfur content is 3000 ppm and boiling point range is 80–270 °C. Portable power system will find wide spread applications if JP-8 can be used as fuel. To compare with JP-8, a synthetic diesel fuel, which has similar property as JP-8 but contains no sulfur, was tested in steam reforming. As shown in Fig. 5, at 530 °C and GHSV of 144,000 h^{-1}, conversion as high as 95% has been achieved with essentially no deactivation observed. Fig. 6 shows a comparison of steam reforming activity of the as received JP-8 and desulfurized JP-8. As expected, without desulfurization, sulfur in JP-8 causes significant catalyst deactivation within 3 h. Options for desulfurization have also been considered. The first option is conventional hydrodesulfurization (HDS), which requires operation at high temperatures and pressures. But it is difficult to achieve on-board desulfurization with conventional HDS because of difficulties in operation. Absorption techniques may be a better approach to achieve on-board desulfurization since it does not require high temperature or pressure. The absorbents chosen is zeolite 13X and ZSM-5 which operate at 180 °C and ambient pressure. As shown in Fig. 6, when JP-8 was passed through zeolite-based absorbents prior to steam reforming, the catalyst life is extended to 6 h. These results are promising for a development strategy for microreactor designs. The strategy in designing portable power systems using JP-8 depends development of absorbents that are efficient and can last the period of time required for the application.

4. Conclusions

Fuel processing catalysts suitable for portable power system have been successfully developed. These catalysts are active for steam reforming different fuels at very high GHSV 36,000–144,000 h^{-1} Among hydrocarbon fuels, methanol steam reforming requires relatively low temperature. A Pd/ZnO catalyst used in our research exhibits high activity, low CO concentrations in the reformate and high hydrogen yields. On the Pd/ZnO catalyst, methanol steam reforming does not appear to involve the water gas shift reaction. Characterization of the Pd/ZnO catalyst indicates that alloy structure is formed during high temperature reduction. However, this alloy structure may not be necessary in catalyzing methanol steam reforming.

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