Production of Hydrogen for the Fuel Cells from Methanol over Cu/ZnO/Al₂O₃/ZrO₂ Catalyst

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Abstract We studied on the oxidative steam reforming of methanol(OSRM) with $O_2 ： H_2O ： CH_3OH = 0.3 ： 1 ： 1$ molar ratios over Cu/ZnO/Al₂O₃/ZrO₂ catalyst. The results were compared with those obtained in non-oxidative steam reforming of methanol (SRM), in partial oxidation of methanol (POM) and in decomposition(DEC) of methanol. In OSRM, POM and SRM the catalyst were highly active, CH_3OH conversion is 100% at 240, 260 and 280℃ respectively. In OSRM the catalyst also showed high selectivity, maximum H_2 yield is 292mmol/(kg · s) and CO concentration is below $5 · 10^{-4}$%. Besides the main products, CH_2O and $(CH_3)_2O$ were observed at all temperatures. On the other hand, POM reaction velocity was faster than SRM, but POM produced a few CO at all temperatures, due to CH_3OH decomposition. The production of CO reduced strongly in the presence of water vapor. We studied the interaction between methanol and catalyst by IR spectroscopy. IR spectrum showed the adsorbed methoxy groups, these were converted into formate at high temperature and then decomposed into H_2 and CO in the absence of O_2 or H_2O, but in their presence CO was probably oxidized to CO_2, due to the action of Cu(II).

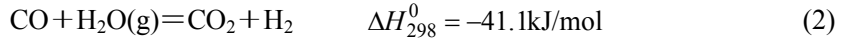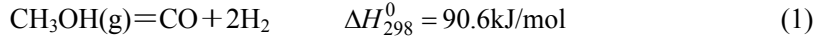**Key words** methanol steam reforming, Cu/ZnO/Al₂O₃/ZrO₂ catalyst, H_2 production

Introduction

The great leader Comrade **Kim Jong Il** said.

"**Scientists and technicians must provide satisfactory solutions to the scientific and technical problems arising in making the national economy Juche-orientated, modern and scientifically-based.**"("**KIM JONG IL** SELECTED WORKS" Vol. 10 P. 194)

Methanol is a suitable liquid source for production of hydrogen in the fuel cell electric engines. A suitable process can produce H_2 in high concentration to obtain high performances of the fuel cells[1]. The highest hydrogen yield may be achieved by the SRM, but the major drawback of SRM is the formation of CO as a by-product, which, even at a low concentration of 10^{-4}%, decreased performance of performance the fuel cell by poisoning in the Pt electrode[2－6].

Hydrogen can be produced from methanol by different reactions. The most simple reaction is endothermic decomposition(DEC, equation (1)) that allow the production of CO and H_2 mixtures of 1 ： 2 molar ratio. These must be further treated with water to convert CO to CO_2 through the water gas shift reaction(WGS, equation (2)).

$$CH_3OH(g) = CO + 2H_2 \qquad \Delta H^0_{298} = 90.6 kJ/mol \qquad (1)$$

$$CO + H_2O(g) = CO_2 + H_2 \qquad \Delta H^0_{298} = -41.1 kJ/mol \qquad (2)$$

For the use in fuel cells, H_2 is generated from methanol, typically through steam reforming of methanol reaction (equation (3)) [7－10]. This is an endothermic reaction and should be performed at around 300℃.

$$CH_3OH(g) + H_2O(g) = CO_2 + 3H_2 \qquad \Delta H^0_{298} = 49.4 kJ/mol \qquad (3)$$

Recently, partial oxidation of methanol (equation (4)), which is an exothermic reaction, has also been suggested as a route for the extraction of H_2 from methanol[11－16].

$$CH_3OH + 1/2O_2 = CO_2 + 2H_2 \qquad \Delta H^0_{298} = -192.2 kJ/mol \qquad (4)$$
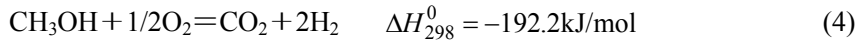
Although CO_2 is being as a product in SRM and POM, the amount of CO_2 produced in these processes is about 50% less as compared with the amount of CO_2 released from the internal combustion engines using gasoline as a fuel. POM, as compared with SRM, leads to a lower H_2 yield. Theoretically the maximum H_2 concentration is 67%, but since the use of pure oxygen is not technically feasible for car traction and air must be used as oxidant, the maximum hydrogen concentration is 41%. Other drawbacks is related to the exothermicity of reaction, high release of heat decreases power efficiency, temperature control of the reaction is difficult and hot spots can occur in the catalyst, leading to reduction of activity [13].

On the other hand, if the catalyst was active for the $CO + O_2$ reaction, residual CO could be reduced to trace amounts. In practice, both SRM and POM produce appreciable CO amount, it strongly depends on the nature of the catalyst and operating conditions [14, 15].

Recently the oxidative steam reforming of methanol (OSRM, equation (5)) reaction based on combination of SRM and POM reactions has been suggested[5, 13, 17－21].

$$CH_3OH(g) + (1-2\delta)H_2O + \delta O_2 = (3-2\delta)H_2 + CO_2 \qquad (5)$$
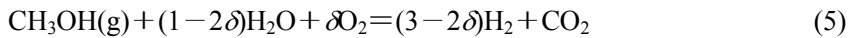
If $\delta = 0.25$, $\Delta H^0_{298} = -71.4 kJ/mol$.

By feeding CH_3OH, H_2O and O_2 (air) in proper amounts, the heat released by POM can balances with progress of SRM and requirement for heating the reactants. In this reaction, if air is used, the maximum H_2 concentration is 65% and it can be suited for rapid startup and power variations by properly varying the methanol/oxygen ratio [5, 13]. Moreover, under the proper conditions, OSRM can produce hydrogen containing very low CO concentration [13, 17, 21].

The OSRM catalysts proposed in the previous literatures [19, 22－32] are mostly based on copper dispersed on metal oxides such as ZnO, Al_2O_3 or ZrO_2 acting as promoter.

The reaction mechanism of OSRM is very complex and not yet defined. In the reacting system, besides SRM and POM, other reaction, such as combustion and decomposition of methanol, can also occur.

We considered the reactions of hydrogen production from the methanol over $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst. Reaction mechanisms based on IR spectrum have also discussed.

Experiment

The catalyst precursor was prepared by co-dropping the solutions of Cu, Zn, Al and Zr nitrates and the solution of sodium carbonate (Na_2CO_3 15%). The resulting slurry was washed with distilled water up to pH 7 and filtered, and then dried at 120℃ for 2h, calcinated at 300℃ for 2h.

Composition of catalyst used in experiment is as follows.

$$Cu : ZnO : Al_2O_3 : ZrO_2 = 40 : 50 : 5 : 5$$

The OSRM test was performed in a fixed-bed glass flow reactor using 1mL of the catalyst (0.6～1.3mm) at 180～300℃ and atmospheric pressure with $O_2 : H_2O : CH_3OH - 0.3 : 1 : 1$ of molar ratio. SRM and POM tests were carried out under the same conditions, but in SRM supplied only H_2O and O_2 in POM, and DEC was tested excluding both O_2 and H_2O.

The catalyst was firstly reduced in a stream of H_2 at 300℃ for 2h and cooled to the reaction temperature. Subsequently, premixed water and methanol with a H_2O/CH_3OH 1.0 molar ratio was fed into the pre-heater by micro pump(liquid flow rate 5mL/h). Gaseous feeds (O_2, air) were adjusted by means of gaseous flow controller.

The reaction products(H_2, CO, CO_2, CH_4, H_2O and CH_3OH) were analyzed on a gas chromatograph("Shimadzu GC-4B") equipped with a Porapak/molecular sieve double packed column.

IR spectra were recorded on a "Shimadzu FT-IR 8161" using a conventional IR cell connected to a vacuum pump and adsorption apparatus. The sample (0.01g) was pressed at 7.5t/cm^2 using a pellet die to form a wafer with a 10mm diameter and placed into in situ IR cell allowing heat under a vacuum.

After the wafer was heated in vacuum for 1h, the wafer was treated at 250℃ for 1h with H_2, and then hydrogen was degassed. The sample was cooled to 200℃ and exposed to methanol vapor (0.2kPa) at 200℃. FT-IR spectra analysis of the sample adsorbed methanol was recorded at room temperature.

Results and Discussion

Fig. 1 shows the methanol conversion according to the temperature in the different processes of H_2 production from methanol over Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalyst.

As shown in Fig. 1, catalytic activity is markedly influenced by temperature and CH_3OH conversion increases rapidly with increasing temperature. In OSRM, POM and SRM tests, conversion of methanol reaches respectively a value of 100% at 240, 260 and 280℃.
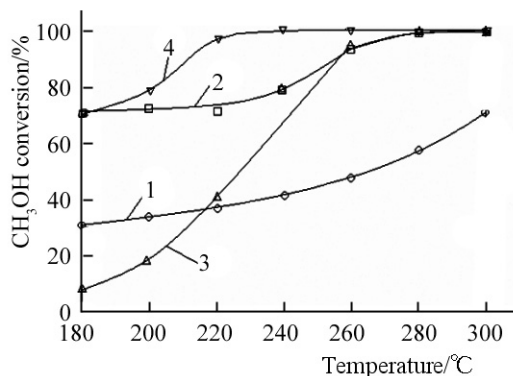

Fig. 1. Methanol conversion according to the temperature
1－DEC, 2－POM, 3－SRM, 4－OSRM

The CH$_3$OH conversion in the presence of both water (SRM) and oxygen (POM) is higher under the condition of DEC. This could be due to an effect of these substances on the oxidation state of Cu.

Previous TPR/TPO measurements [19, 25] suggest that under OSRM conditions Cu(0), Cu(I) and Cu(II) species can be present, depending on temperature and O$_2$ and H$_2$ concentration. Therefore in the zone where O$_2$ concentration is high, copper is in an oxidized state, and methanol oxidation prevails. On the other hand, in the zone where O$_2$ is low and H$_2$ concentration is high, copper is in a reduced form and steam reforming becomes the dominant reaction. This indicates that under OSRM conditions copper is present in both oxidized and reduced states, but the Cu(0) state prevails. By increasing temperature, firstly POM and then SRM reactions are activated. POM can go forward to a small extent due to the limited concentration of O$_2$, and then residual methanol reacts through SRM or DEC.

Methanol total oxidation (6) can occur on CuO-based catalysts.

$$CH_3OH + 3/2O_2 = CO_2 + 2H_2O \qquad (6)$$
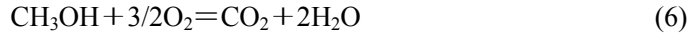
Therefore it can be hypothesized that in OSRM with Cu catalysts methanol combustion occurs rapidly, so oxygen is consumed in the first region of the reactor, and the SRM reaction begins when oxygen has been consumed.

Fig. 2 depicts the selectivity of CO and CO$_2$ according to the temperature in the different processes of H$_2$ production from methanol over Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ catalyst.

In OSRM and SRM reactions CO$_2$ selectivity is higher than in POM and DEC reactions, but CO selectivity is lower. While, in DEC and POM reactions CO is formed in appreciable amounts at over 250℃. It is evident that in DEC test CO is formed by methanol decomposition (1), possibly through intermediate dehydrogenation to formaldehyde (7) and probably the same reaction occurs in POM test.

$$CH_3OH = CH_2O + H_2 \qquad (7)$$
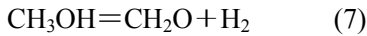
On the other hand in SRM and OSRM tests the formation of CO is reduced below the detection limit. This means that there exists the presence of water vapor. In previous

Fig. 2. Selectivity of CO and CO$_2$ according to the temperature
1−CO(DEC), 2−CO$_2$(DEC), 3−CO(POM), 4−CO$_2$(POM),
5−CO(SRM), 6−CO$_2$(SRM), 7−CO(OSRM),
8−CO$_2$(OSRM)

works [33, 34] on Cu catalysts, this effect is explained by the WGS reaction (2) consuming CO. However, WGS reaction is unable to reduce the CO concentration to very low values as found in our SRM and OSRM. According to some authors [34], it is obvious that this reaction is very limited under the present conditions and probably this reaction is slower than SRM.
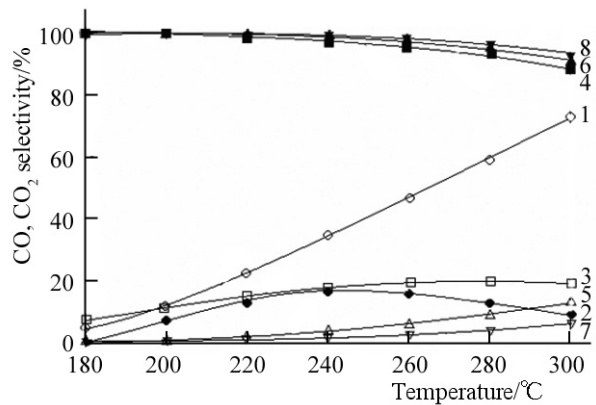
Fig. 3 shows H_2 production rate according to the temperature in the different processes of H_2 production from methanol over $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst.
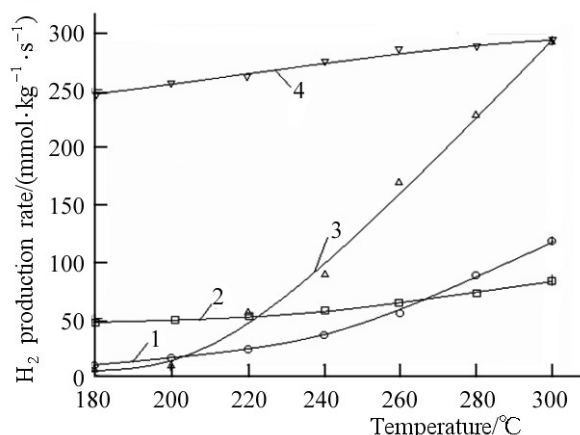

Fig. 3. H_2 production rate according to the temperature
1－DEC, 2－POM, 3－SRM, 4－OSRM

As shown in Fig. 3, in OSRM test H_2 production amounts not only is higher, but also is homogeneously increase at all temperatures than in other tests. H_2 production rate in POM test shows a similar trend but with lower values than in OSRM test. This indicates that OSRM test has the advantage of H_2 production than POM. In SRM test, its values rapidly increase with increasing temperature, due to the CH_3OH conversion with increasing temperature. While, in DEC test H_2 yield is lower, due to this reaction is very slower than other reactions under the present condition.
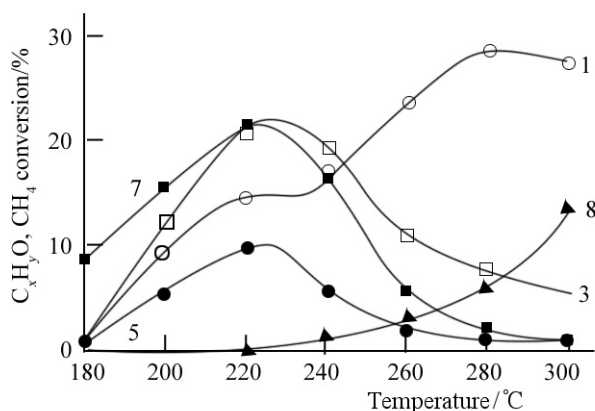
Conversions of methanol to C_xH_yO and CH_4 according to the temperature are shown in Fig. 4, where C_xH_yO means the total amounts $(CH_3)_2O＋CH_2O$.

In OSRM, POM and SRM tests, besides DEC test, C_xH_yO are prevailing at low temperature, showing a maximum at 220～230℃. This is suggesting that at low temperature only dehydration and dehydrogenation occur.

In OSRM test CH_4 is formed in an appreciable amounts (3%) at 300℃. The formation of appreciable amounts of CH_4 can be explained by the higher methanol conversion, in comparison with SRM test. This leads to lower H_2O concentrations under these conditions, therefore the unfavorable effect of steam on CO production

Fig. 4. C_xH_yO and CH_4 conversions according
to the temperature
1－C_xH_yO(DEC), 3－C_xH_yO(POM), 5－C_xH_yO(SRM),
7－C_xH_yO(OSRM), 8－CH_4(OSRM)

is reduced, so that appreciable CO amount can be formed. This is readily converted into CH_4, due to the high H_2 concentration.

Methane as by-product of OSRM can be formed by the reaction (8).

$$CO＋3H_2＝CH_4＋H_2O \tag{8}$$

This reaction can contribute to keep the CO concentration at low level.

On the other hand, in DEC and POM tests CH_4 is negligible, although CO production is high under these conditions. This is probably due to the low H_2 concentrations. Under SRM conditions

methane is also negligible, probably due to very low CO production, as observed above.

The IR spectrum of the adsorbed species arising from the interaction of the methanol at 250℃ with the pre-reduced catalyst(Cu/ZnO/Al$_2$O$_3$/ZrO$_2$ sample) is shown in Fig. 5.

In the low frequency side of the spectrum a complex band with two main maxima at 1 031, 1 088cm^{-1} is observed. In the CH stretching region weak bands with two sharp maximum at 2 953, 2 839cm^{-1} and a weaker broad maximum in the middle (2 889cm^{-1}) are also found, corresponding to a sharp CH$_2$ deformation band at 1 469cm^{-1}. These features can be assigned to adsorbed methoxy groups.

Fig. 5. FT-IR spectra

1－surface species after conduct of the catalyst with CH$_3$OH at 250℃ for 10min, 2－surface evolution after 10min at 350℃

The multiplicity of the band in the region 1 200～900cm^{-1} is due to the presence of two or more kinds of methoxy groups. For example, the C－O stretching of methoxy groups on γ-Al$_2$O$_3$ is founded at 1 095cm^{-1}, and those on ZnO- and ZnO-based systems at 1 060cm^{-1}, and those CuO at 1 055～1 070cm^{-1}, and finally, those on Cu(111) at 1 036cm^{-1} [24].

The sharp strong bands observed at 1 598, 1 381 (shoulder) and 1 376cm^{-1} is the spectrum of the formate ions and these have to be assigned to asymmetric stretching of the O－C－O group (1 598cm^{-1}), the CH deformation mode (1 381cm^{-1}), and to the symmetric O－C－O stretching (1 376 cm^{-1}). Under the same condition of Fig. 5, the gas phase species evolved from the catalyst have been also studied. Actually, a very weak band at 2 040cm^{-1} due to gaseous CO and two weak features near 1 178, 1 103cm^{-1}, likely belonging to dimethyleter gas, can also be detected.

By increasing temperature to 350℃ in the IR cell, the spectra of adsorbed species change as shown in Fig. 5. It is evident that the spectra of both methoxy groups and formate groups decrease progressively in intensity. However, while the bands of formate groups are practically fully disappeared at 350℃, the main band of methoxy groups at 1 100～900cm^{-1} is still present, although much weaker and with the main maximum shifted down to 1 016cm^{-1}.

In parallel the band observed near 1 458cm^{-1} seems to have grown, likely due to the formation of carbonate species. After heat treatment at 350℃ a weak sharp band at 1 690cm^{-1} is evident. It can be assigned to the CO stretching of an adsorbed formaldehyde species.

The IR spectra reported above show that the adsorption of methanol on the catalyst is dissociative. Methoxy groups are formed by adsorbing both on the active sites(which are likely associated to Cu secies) and over inert regions of the catalyst surface, likely mainly associated to alumina. Part
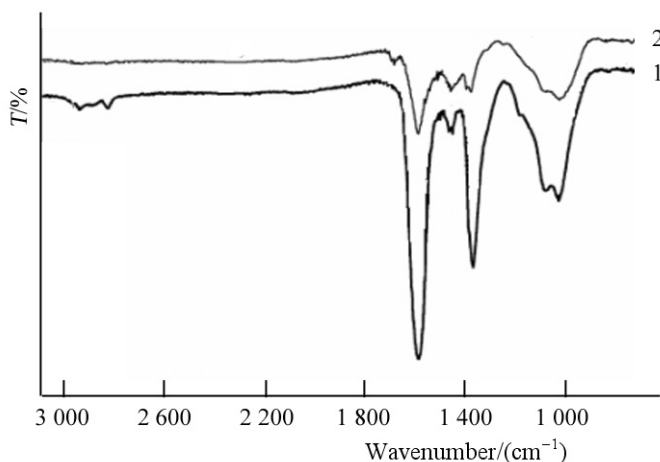
of these methoxy groups, likely those located near or on copper sites, transform easily to formate species, possibly with the intermediacy of dioxymethylene species. At 350 ℃ formate species decompose and, under the conditions of our experiment, mainly give rise to gas phase CO. Dimethyleter is also formed in the gas phase.

It seems quite reasonable to suppose that the mechanisms for DEC, POM and SRM are closely related, and that surface phenomena are similar.

Conclusion

We have studied for the reactions (DEC, POM, SRM, and OSRM) of hydrogen production from methanol over $Cu/ZnO/Al_2O_3/ZrO_2$ catalyst. The conversion of methanol in the presence of both water (SRM) and oxygen (POM) is higher than under the condition of DEC. This could be due to an effect of these substances on the oxidation state of Cu. Moreover, CO is produced in relative low amounts in the presence of water (under SRM conditions), CO_2 being the main product. On the other hand, both CO and CO_2 are produced in noticeable amounts under POM conditions. Under POM conditions, the catalyst is oxidized at least partially. In this case Cu(I) strongly adsorbs CO, while Cu(II) allows its oxidation to CO_2. However, due to the substoichiometric feed in POM test, first O_2 is consumed, and then excess methanol partially decomposes producing CO.

IR spectra show that methoxy groups adsorbed on the active sites(associated to Cu species) transform easily to formate species, and CO is formed, due to their decomposition. The oxidation state of Cu species is influenced by the presence of O_2 and H_2O.

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