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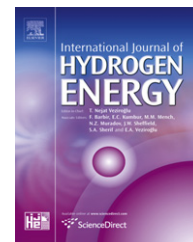
The effect of gold on the copper-zinc oxides catalyst during the partial oxidation of methanol reaction

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A B S T R A C T

Hydrogen production resulting from the partial oxidation of methanol (POM) was investigated using copper-zinc-supported gold catalysts. The influence of oxygen concentration on activity and initiation temperature (T_i) over $Au_{4.3}CZ$ (ca. 4.3 wt.% Au, 32.3 wt.% Cu and 63.4 wt.% Zn) catalysts was compared with CZ (ca. 31.7 wt.% Cu and 68.3 wt.% Zn) catalysts. The $Au_{4.3}CZ$ catalyst was able to react at temperatures lower than 195 °C, while CZ catalyst could not be initiated without pre-activation. In addition, $Au_{4.3}CZ$ performed higher hydrogen selectivity and lower carbon monoxide selectivity than CZ catalyst. The addition of gold might induce a change in the reducibility of copper species and result in the more active species, Cu^0 and Cu^+, on the catalytic surface and, especially, enhance the adsorption of oxygen and methoxy group at low temperature. These adsorbed oxygen atoms could be removed as CO_2, which speed up the rate-determining step of POM. It might influence initiation temperature and catalytic performance, i.e. the POM reaction can be initiated at T_i: 120 °C, with catalytic performance at 95% methanol conversion, 97% hydrogen selectivity, and 5.5% carbon monoxide selectivity at 190 °C over $Au_{4.3}CZ$ without pre-activation.

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1. Introduction

Partial oxidation of methanol (POM), yielding hydrogen, has been widely investigated in the past decade [1–5]. POM reaction that provides a route for converting liquid fuel into hydrogen can be used in mobile fuel-cell systems. Compared to using steam to reform methanol, POM needs no equipping with a steam generation unit. The low reaction temperature of POM can simplify reformer design. In addition, the exothermic property and higher reaction rate at lower temperature can shorten start-up time and reach working temperature more quickly.

Among catalysts used for this process, copper-zinc oxide is the most prominent. It is inexpensive and active under moderate conditions (200–300 °C). However, significant CO generation might limit the application of Cu/ZnO catalyst [1], while high pre-activation temperature (catalyst pre-reduced at ca. 250 °C) for catalyst [1,3,6] results in more complex design and further obstructs the development of a low temperature reformer. Hence, a low temperature reforming process without pre-activation and low CO in hydrogen-rich gas should be a promising solution.

Recent studies show that supported gold catalysts exhibit excellent catalytic activity and could be applied for various purposes [7–12]. Carbon monoxide preferential oxidation (CO PROX) is one of the most widely investigated reactions related to gold-based catalysis. Several advantages of this reaction have been reported, including lowering the reaction

temperature, better selectivity and higher conversion [13–16]. Haruta indicates that the temperature for half conversion of CO in CO PROX reaction over supported gold catalyst was only 9 °C, but it required 61 °C over platinum catalyst [13]. Meanwhile, gold catalyst had higher turnover frequency than platinum catalyst. Venezia et al. [17] found that cerium-supported gold catalyst exhibits a much lower 100% conversion temperature (28 °C) than cerium oxide (450 °C). The possible reason could be due to the weakening of Ce-O by the addition of gold. Boccuzzi et al. [18] also indicated that catalysts interacted with methanol–water–oxygen mixture (1:1:0.2) at 200 °C for a period of time, the H_2/CO ratio of CuO/ZnO is higher than Au/ZnO catalyst while the CO_2/CO ratio of Au/ZnO catalyst is higher than CuO/ZnO catalyst, the gold catalysts play a suitable role for CO abatement.

Bokhoven et al. [19] indicated that in CO PROX reaction, oxygen adsorption is the rate-determining step, suggesting that superoxide oxygen (O_2^-) might be in response to the initiation of the reaction. Nørskov et al. [20] also indicated that oxygen can adsorb onto the site of Au (2 1 1) and produce molecular superoxide oxygen (O_2^-). Oxygen dissociation is still highly controversial, but the molecular superoxide oxygen formed on the catalyst is confirmed by the ESR experiment performed by Iwasawa et al. [14]. Superoxide oxygen should be formed by the adsorption of oxygen on the interface of gold particle and support. Davis and Jacobs [21] deduced that the rate-determining step of steam reforming of methanol may be the decomposition of methoxy species. Boccuzzi et al. [22] indicates that the presence of oxygen can conversion of methoxy species in formate species adsorbed on gold. The formate is a good intermediates for methanol decomposition at low temperature. The amount of CO could be minimized by lowering the reaction temperature. In this study, gold was selected to promote copper-zinc catalyst for lowering the POM initiation temperature (T_i) as well as reaction temperature (T_r) and improving catalytic reactivity. The influence of gold on the reactants and the variation of copper species are also discussed.

2. Material and methods

2.1. Catalyst preparation

Au_xCZ catalysts with various Au loadings were prepared by deposition precipitation following coprecipitation (CP) method. $Cu(NO_3)_2 . 2.5H_2O$ and $Zn(NO_3)_2 . 6H_2O$ solutions (0.5 M) were dropped into 500 mL of deionized water at 70 °C under sonication. Na_2CO_3 was used to maintain the mixture at pH 7. After aging to pH8, the CuZn precipitates were filtrated and washed thoroughly with deionized water, and then dried at 105 °C overnight. Appropriate amount of $HAuCl_4 \cdot 3H_2O$ was dropped into 70 °C, 500 mL deionized water after pulverized CuZn precipitates were added. After aging 1 h, Au_xCuZn precipitates were filtrated and washed thoroughly with 6 L of deionized water, then dried at 105 °C overnight. They were then calcined in air at 400 °C for 2 h. The calcined catalysts were pressed and grounded into 60–80 meshes for catalytic testing. The Au_xZ catalyst was prepared by deposition

precipitation as the procedures to prepare the Au_xCZ catalysts but without calcination.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded by a Rigaku RINT1100 diffractometer using Cu Ka ($\lambda = 0.15406$ nm) radiation. Scanning 2θ angles ranged from 20° to 80° at a rate of $2°$ min^{-1}.

A temperature-programmed reduction (TPR) system equipped with gold-coated TCD and Brooks 5850E mass flow controller were employed for TPR testing. A 55-mg sample was weighed and placed into a U-shaped quartz tube with a 4-mm inner diameter. The samples were pretreated by purging with pure nitrogen for half an hour, then a 10% H_2/N_2 mixture with a flow of 30 mL min^{-1} for another 30 min. The TPR measurements were carried out from room temperature to 500 °C at a rate of 7 °C min^{-1}, and the signal was connected to a signal processor and recorded by computer.

The Cu dispersion measurement was performed following Fujitani and Nakamur [23]. The 55 mg of catalyst was reduced at 240 °C for 30 min and purged with nitrogen for 15 min N_2O was introduced at the rate of 30 mL/min at 300 K for 30 min and purged with nitrogen for 15 min again. A TPR run was then carried out and detected by TCD. The Cu dispersion was calculated by integrating the area followed by multiplying by 2 and divided by the raw TPR area.

In-situ XAS experiments at the Cu K-edge (8979 eV) were performed at the 17C beam line of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The electron storage ring was operated at energy of 1.5 GeV with a stored current of 300 mA in a top-up injection mode. A Si(111) double-crystal monochromator was used to select the energy, with an energy resolution ($\Delta E/E$) of 1.9×10^{-4}. All in-situ X-ray absorption spectra were recorded in transmission mode. The XANES data were analyzed using WinXAS 3.0 software. In in-situ XAS experiment, the fresh oxidized catalyst (10 mg) was mixed with boron nitride (30 mg) and pressed into a sample holder. Even 24% methanol/nitrogen mixture passed over the fresh oxidized copper-zinc catalysts w/wo gold at 150 °C. In addition, some copper-zinc catalysts w/wo gold were pre-reduced in a stream (30 mL/min) of 10 vol% H_2/N_2 at 250 °C for 0.5 h and then reacted with 24% methanol/nitrogen mixture at room temperature.

2.3. Catalytic reaction

Catalytic activity measurements were carried out in a fixed-bed reactor operating at atmospheric pressure. The catalysts were pressed and sieved into 60–80 mesh and 100 mg of catalyst were placed into a quartz tube (inner diameter, 4 mm) stabilized by quartz wool at both ends. A thermal coupler was located in the center of the catalyst bed to control the reaction temperature. Liquid feed (CH_3OH) and gaseous feed (O_2, Ar) were introduced by piston pumps and a Brooks 5850E mass flow controller, respectively. The molar ratio of oxygen to methanol (O/M) was controlled at 0.5. Samples were collected in two sampling loops and sent to the gas chromatograph (a China GC 2000) which was equipped with porapak Q and

molecular sieve 5A columns and two TCDs in parallel for analysis of H_2, CO, CO_2, O_2, CH_3OH, and H_2O.

The catalytic activation of the catalysts was evaluated in terms of their values of the conversion of MeOH (C_{MeOH}), selectivity toward CO formation (S_{CO}), and selectivity of H_2 (S_{H2}). The C_{MeOH} was defined as the number of moles of reacted MeOH divided by the number of moles of MeOH added to the system. The S_{CO} was defined as the number of moles of CO produced, divided by the total number of moles of CO_2 and CO produced. The S_{H2} was defined as the number of moles of H_2 produced, divided by the total number of moles of H_2 and H_2O produced.

3. Results and discussion

3.1. Physiochemical properties of the CuOZnO catalysts with gold

The nominations and metal loadings of various gold-loading copper-zinc catalysts are summarized in Table 1. Most of the gold (around 80%, stoichiometric calculation) was loaded on the CuOZnO or ZnO. Acceptable loss was found, which generally agrees with the literature [24–26]. Fig. 1 shows the diffraction pattern of catalysts. The diffraction peaks of copper-zinc catalyst before calcination were aurichalcite [27] (shown in Fig. 1c). After calcination, all the aurichalcite diffraction peaks disappeared and transformed into ZnO and CuO. Comparing the diffraction pattern of copper-zinc catalysts with various concentrations of gold, Fig. 1e–g, the intensity of the diffraction peaks significantly decreased as the gold content increased. Generally, it was more difficult to distinguish the weaker and broader copper oxide diffraction peak, 38.8°, and zinc oxide, 36.3°, which represent high dispersion and small particle size [27,28]. The result of N_2O chemisorption shows Cu dispersion on gold catalysts was 4% more than on non-gold catalyst (shown in Table 1). Therefore, we suggest that the addition of gold may increase the dispersion of copper oxide in the catalysts and reduce particle size. Furthermore, a gold diffraction peak of (1 1 1) at 38.2° overlapped with copper oxide diffraction peak at 38.8°. Gold (2 0 0) diffraction peak at 44.4° was not found in our samples,
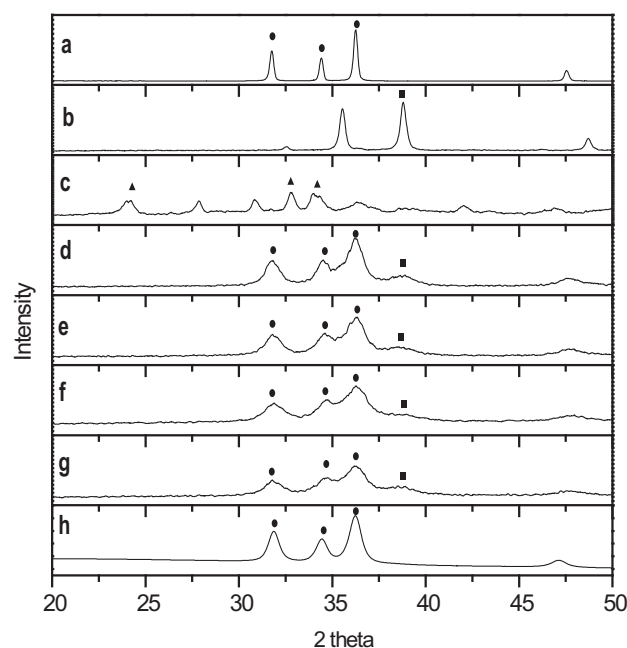
Fig. 1 – Diffractograms of different gold content catalysts. (●)ZnO, (■)CuO, (▲)Aurichalcite. (a)ZnO; (b)CuO; (c)CZ before calcination; (d)CZ; (e)Au$_{0.8}$CZ; (f)Au$_3$CZ; (g)Au$_{4.3}$CZ; (h)Au$_{1.8}$Z.

which implies that the gold particles might have been highly disperse and small in size. TEM images (Fig. 2) of the various gold content catalysts also display that there was no serious sintering during the calcination. Gold particle size was within 2–6 nm after 400 °C calcination.

3.2. Hydrogen temperature programmed reduction

The temperature profile of TPR pattern of copper-zinc catalyst (Fig. 3b) shows one main peak at 205 °C, with a front shoulder at 190 °C and a back shoulder at 215 °C. Petterson et al. indicate that the front shoulder was the reduction of Cu^{2+} to Cu^+ and the main peak was the reduction of Cu^+ to Cu^0 [29]. However, the reduction of copper oxide at the interface with zinc oxide should be considered. Fierro et al. suggest that copper oxides with stronger interaction with zinc oxide are reduced at lower temperature than those copper oxides without any contact with zinc oxide [30]. In Fig. 3a and b, a significantly different reduction temperature of CuO and CuO/ZnO is observed. Therefore, we suggest that the front shoulder and main peak reveal ZnO-assisted reduction of copper oxide, which took place in stepwise fashion. The back shoulder observed in the TPR profile was the reduction of larger sizes of copper oxide, or isolated copper oxide.

After the addition of gold, the reduction profile of CuZnO-based catalyst shifted forward to a lower temperature. The features had no significant change; hence, the reduction pathway should be similar to the CZ catalyst. As the gold content increased from 0% to 4.3%, the main peak shifted from 205 °C to 185 °C. In the meantime, the front shoulder became more distinct and the back shoulder shrunk as gold content

Table 1 – The metallic composition and Cu dispersion of catalysts.

Denominations	Stoichiometric Au loading	Metallic composition[a] (%)			Cu dispersion[b] (%)
		Au	Cu	Zn	
CZ	0	0	31.7	68.3	33.2
Au$_{0.8}$CZ	1	0.8	32.3	66.9	34.4
Au$_3$CZ	3	2.9	31.7	65.4	37.2
Au$_{4.3}$CZ	5	4.3	32.3	63.4	37.3
Au$_{1.8}$Z	2	1.8	–	98.2	–

a The metallic concentration of catalysts were measured by ICP-MS.
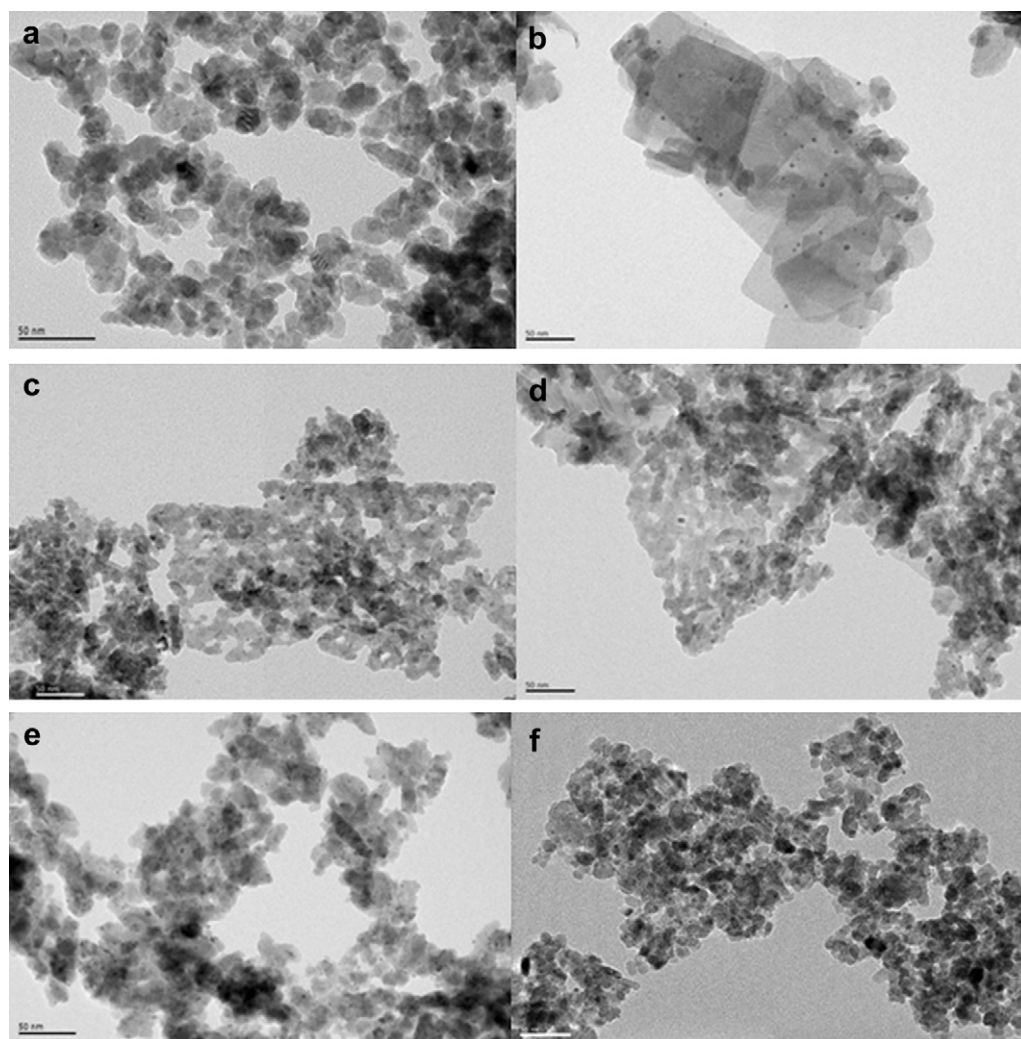b Cu dispersion was determined by N_2O chemisorption method.

Fig. 2 — TEM images of (a) CZ; (b) Au_3CZ-before calcined; (c) $Au_{0.8}CZ$; (d) Au_3CZ; (e) $Au_{4.3}CZ$; (f) $Au_{1.8}Z$.

increased. This phenomenon was owing to the easy reduction of copper oxide particles in contact with the gold particles [31,32], plus with increasing gold content, more copper oxides were influenced. Consequently, the front shoulder and main peak almost merged into one peak and were difficult to distinguish.

The intrinsic reducibility influenced by gold particle should be different from that by ZnO. Nano gold particles have been reported to absorb and then dissociate hydrogen [33]. Definitely, smaller particles with higher surface area can lead to higher absorption amounts. The dissociated hydrogen, it is suggested, spills over to neighboring copper oxide. Hence, increasing gold content can lead to lower reduction temperature, as observed in Fig. 3c—e. We believe that both hydrogen chemisorptions and dissociation effects are in response to observed changes in the reducibility of copper oxide.

3.3. Reactivity of CuOZnO catalyst with gold in the partial oxidation of methanol reaction

The reactivity of the catalysts was tested through POM reaction and is shown in Fig. 4. Methanol conversion can reach 100% at 250 °C over all catalysts, except the $Au_{1.8}Z$ catalyst, but over CZ, lower hydrogen selectivity and higher carbon monoxide selectivity than $Au_{4.3}CZ$ were found. The $Au_{1.8}Z$ catalyst has the lowest carbon monoxide selectivity within these catalysts but the hydrogen selectivity is much lower than other catalysts. The CuO-base catalysts have better catalytic reactivity. The addition of gold enhanced the oxidation of carbon monoxide and the reduction of hydrogen on the CuZn-based catalyst. At lower temperature (ca. 210 °C), both S_{H2} and S_{CO} on $Au_{4.3}CZ$ were still much better than on CZ, except for C_{MeOH}. Generally, CuZn-based catalyst without going through pre-activation treatment (pre-reduction at 250 °C) was difficult to initiate at low temperature (<190 °C). $Au_{4.3}CZ$ which can be initiated at a rather low temperature (ca. 120 °C) and performed 79% of C_{MeOH}, 90% S_{H2} and only 4% S_{CO}. This phenomenon of low POM initiation temperature on the non-preactived $Au_{4.3}CZ$ should be of some concern and investigated in more detail.

To confirm whether the initiation temperature is related to gold content, 0%, 0.8%, 3% and 4.8% of gold-deposited copper-zinc catalysts were compared simultaneously. Table 2 shows the initiation temperature (Ti) in the POM reaction over AuZ
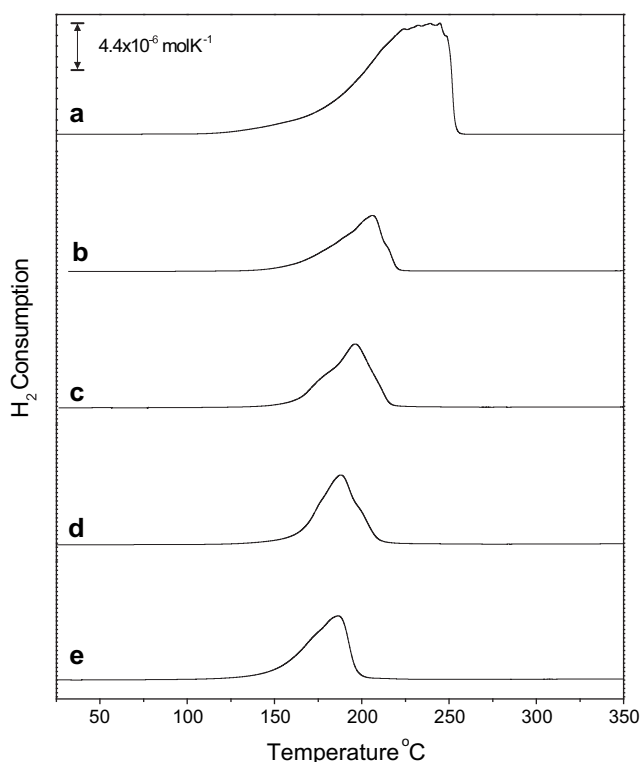
Fig. 3 – Hydrogen temperature-programmed reduction profile of Au$_x$CZ. (a) CuO, (b) CZ, (c) Au$_{0.8}$CZ, (d) Au$_3$CuZ, (e) Au$_{4.3}$CZ.

Table 2 – The initiation temperature and T$_{95}$ of POM reaction.[a]

Sample Name	T$_i$[b]	T$_{95}$[c]
CZ	195	210
Au$_{0.8}$CZ	165	200
Au$_3$CZ	145	200
Au$_{4.3}$CZ	120	190
Au$_{1.8}$Z	150	250

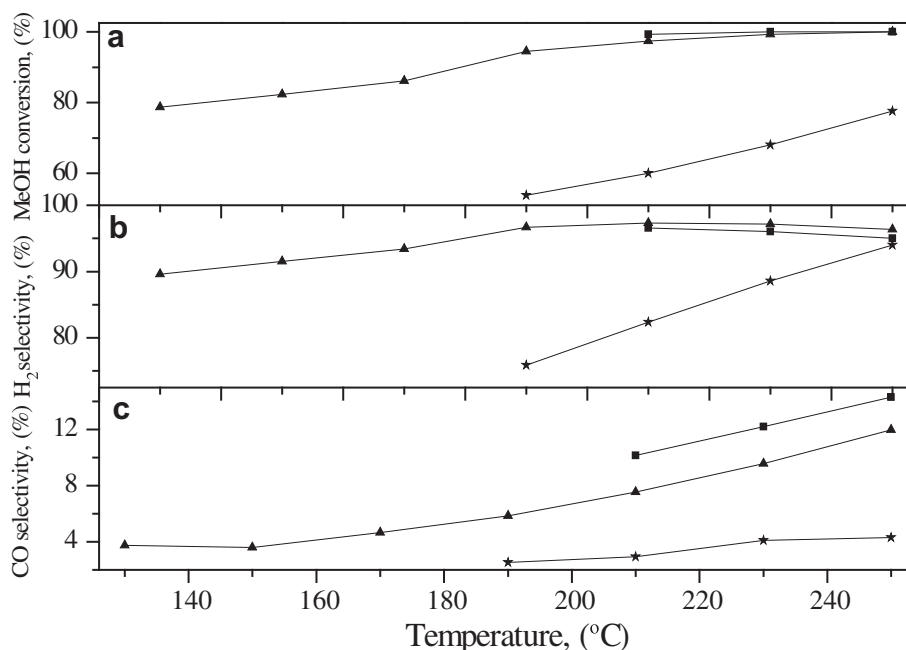a Reaction condition: 100 mg catalysts, O/M = 0.5, GSHV = 60 K, total flow = 100 min^{-1}.
b Temperature start to produce hydrogen.
c Lowest temperature of 95% hydrogen selectivity.

of gold contents. Obviously, the variation of initiation temperature should be related to the addition of gold.

Five various O/M ratios, 0.1, 0.3, 0.5, 0.6 and 0.7, were examined through the POM reaction to find out whether the oxygen concentration would affect the initiation temperature over CZ and Au$_3$CZ. Results are shown in Table 3. Obviously, the T$_i$ of CZ catalyst did not change significantly as O/M ratio changed, but a 75 °C gap was observed on Au$_3$Cu$_{30}$ZnO catalyst. Catalyst with gold is sensitive to oxygen variation; a higher concentration of oxygen can lead to a lower initiation temperature. Regarding gold-contained catalyst, oxygen absorption was found to be a rate-determining step in CO oxidation [14]. This result indicates that accelerating CO oxidation on the catalyst surface may be an important step which affects POM initiation temperature.

Meanwhile, the addition of gold was found to promote hydrogen selectivity. The lowest reaction temperature of 95% S$_{H2}$ (T$_{95}$) were listed in the Table 2. Without the involving of copper, the AuZ presented high T$_{95}$ at 250 °C. The lowest

and CZ catalyst with various gold content. The T$_i$ for Au$_{1.8}$Z catalyst is 150 °C. The initiation temperature decreased from 195 °C to 165, 145 and 120 °C, respectively, at 0, 0.8, 3, and 4.8%

Fig. 4 – (a) Methanol conversion plotted vs. reaction temperature, (b) hydrogen plotted vs. reaction temperature, (c) carbon monoxide selectivity plotted vs. reaction temperature during partial oxidation of methanol for catalysts (■)CZ, (▲)Au4.3CZ, (★) Au$_{1.8}$Z.

Table 3 − The initiation temperature of CZ and Au$_3$CZ at different O/M ratio of POM reaction.[a]

| O/M ratio	T$_i$ of CZ[b]	T$_i$ of Au$_3$CZ[b]
0.1	200	180
0.3	200	160
0.5	195	155
0.6	190	130
0.7	190	105

a Reaction condition: 100 mg catalysts, GSHV = 60 K, total flow = 100 min^{-1}.
b Temperature start to produce hydrogen.

temperature to reach 95% hydrogen selectivity for Au$_{4.3}$CZ was 20 °C lower than that for CZ catalyst. Gold particle increased the selectivity of hydrogen, possibly by consuming the oxygen with preferential oxidation of carbon monoxide to carbon dioxide. To confirm this mechanism, more behaviors of oxygen on the catalyst are discussed.

3.4. The effect of oxygen on the CZ catalyst with gold

The performance of CZ and Au$_{4.3}$CZ catalysts in various O/M ratios (0.1, 0.3, 0.5, 0.6, 0.7) of POM reaction at 200 °C are shown in Fig. 5. Previous study has shown that higher O/M ratio can
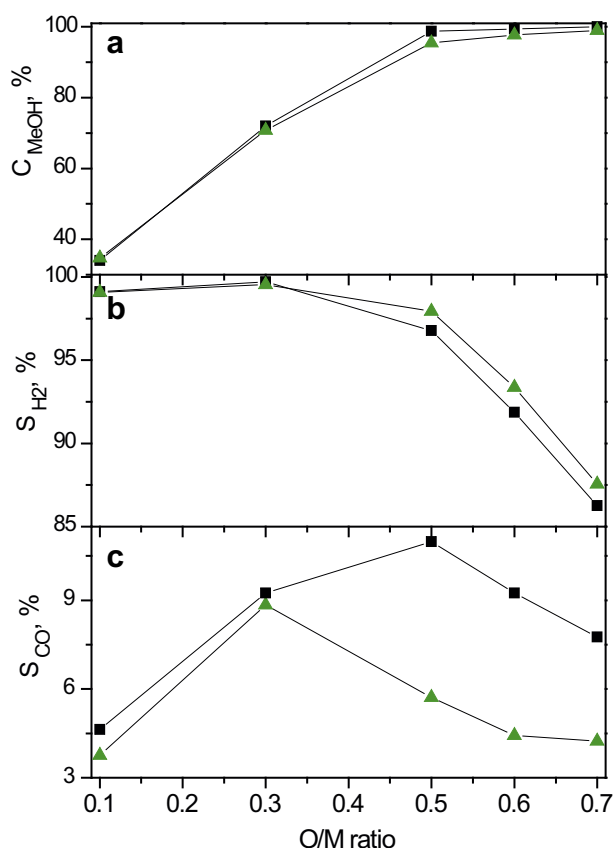
Fig. 5 − The performance of (■) CZ, (▲) Au$_{4.3}$CZ in various O/M ratio of POM reaction at 200 °C (a)Methanol conversion; (b)Hydrogen selectivity; (c)Carbon monoxide selectivity.

initiate the POM reaction at lower temperature. O/M ratio lower than 0.5 showed low methanol conversion, i.e. 34.7% at 0.1 O/M and 70.8% at 0.3 O/M, which was due to the stoichiometric deficiency for the POM process and kinetically insufficient for the decomposition of methanol. When the O/M ratio increased to 0.5 or higher, more than 95% of C$_{MeOH}$ was observed. The increase of O/M ratio can improve methanol conversion, but hydrogen selectivity is influenced by the O/M ratio at the same time. At low O/M ratio, 0.1 and 0.3, high hydrogen selectivity (almost 99%) was observed, but it decreased sharply with increasing O/M ratio. This phenomenon was more severe on CZ than on gold-deposited CZ catalyst, and resulted from the participation of hydrogen combustion.

Adjusting the O/M ratio could also lead to the variation in CO selectivity. Fig. 5c shows that Au$_{4.3}$CZ had lower CO selectivity compared with CZ, representing the capability of gold-deposited CZ catalyst to decrease CO formation. The CO selectivity increased as the O/M ratio rose to 0.3, which is probably due to increased methanol conversion, which subsequently increased the incomplete oxidation of carbon monoxide. Moreover, for the O/M ratio reaching 0.5, the CO selectivity of CZ catalyst continuously increases to 11%. In contrast, Au$_{4.3}$CZ decreases to 5.7%, which is probably due to better oxygen adsorption ability on Au$_{4.3}$CZ, and which performed more completely in the reforming process, producing carbon dioxide instead of carbon monoxide. After increasing the O/M ratios to 0.6 and 0.7, it was observed that S$_{CO}$ decreased from 11% (0.5 O/M) to 7.8% (0.7 O/M) on CZ catalyst. The CO selectivity of Au4.3CZ also decreased from 5.7% (0.5 O/M) to 4.2% (0.7 O/M).

Although the increase of O/M ratio can lower the initiation temperature and suppress CO formation, side reactions and hydrogen combustion cannot be neglected. Hydrogen selectivity decreases from 97.9 to 87.6% and 96.8 to 86.3% on Au$_{4.3}$CZ and CZ, respectively, as O/M ratio increases from 0.5 to 0.7. Nevertheless, gold-deposited CZ catalyst shows better hydrogen selectivity and carbon monoxide selectivity than CZ, confirming that gold is an important active site for CO suppression on CuOZnO-based catalyst in the reforming of methanol at lower temperature.

3.5. The variation of copper species on the CZ catalyst with gold

Copper on the non-preactived CuOZnO-based catalysts should exist in a Cu^{2+} state, which is regarded as non-active state toward reforming [3,34]. Nevertheless, it is reported that Cu^{2+} is active in the combustion of methanol, which is highly exothermic [34,35]. Reitz et al. indicate that the combustion of methanol led to the reduction of a majority of the catalyst because of the severe local heating and depletion of oxygen [35]. To reveal the behavior of copper species on the CZ catalyst with or without gold during the reforming of methanol reaction, the XANES experiment was conducted. The fitted XANES spectra (Fig. 6) show no variation of copper species on the copper-zinc catalyst during the 24% methanol/nitrogen mixture at 150 °C. The main species on the catalyst was copper oxide, the same as the fresh catalyst. However, 62.6% of metallic Cu and 37.5% Cu$_2$O were observed on the
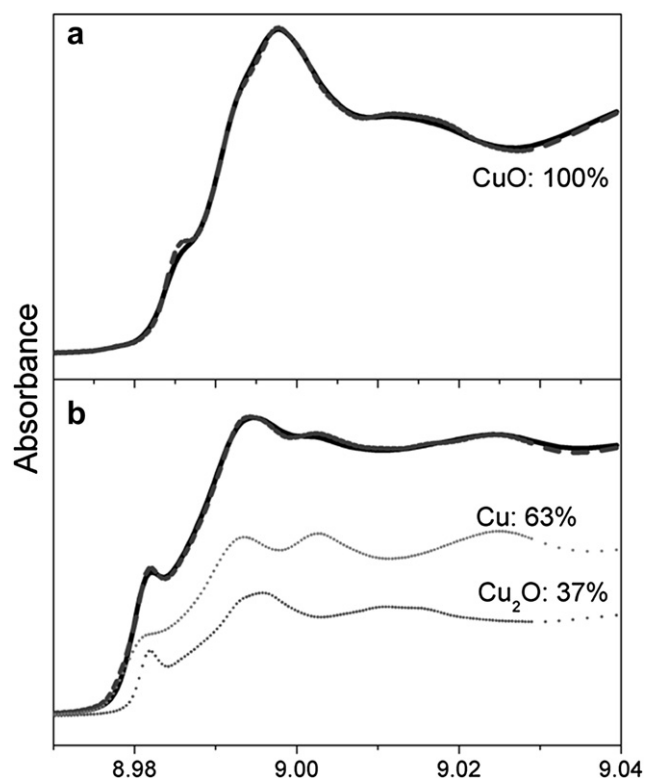
Fig. 6 – The compound fits of in-situ XANES spectra of (a) CZ, (b) $Au_{4.3}CZ$ over DM reaction at 150 °C. Dashed line denotes the best fits of XANES spectra.

Fig. 7 – The compound fits of in-situ XANES spectra of reduced (a) CZ, (b) $Au_{4.3}CZ$ during the 24% methanol/ nitrogen mixture at room temperature. Dashed line denotes the best fits of XANES spectra.

$Au_{4.3}CZ$ sample during the same reaction conditions. The appearance of Cu as the active species represents that methanol can reduce copper oxide into metallic copper on the CuZnO-based catalyst with gold and initiate the reforming reaction at lower temperature.

To find out the effect of methanol, an in-situ XAS experiment of 24% methanol/nitrogen mixture passing over the reduced copper-zinc catalyst with and without gold was conducted at room temperature. With these conditions, methanol was mainly absorbed by the catalyst surface. Comparing the species between CZ and $Au_{4.3}CZ$, higher percentages of Cu_2O and CuO on the $Au_{4.3}CZ$ were observed. Several studies in the literature indicate that the introducing of gold into the catalyst would cause defects in the catalyst (i.e., at the corners, edges, steps) [3,20,34,36]. Those defective sites are effective for the absorption of reactants. Oxygen
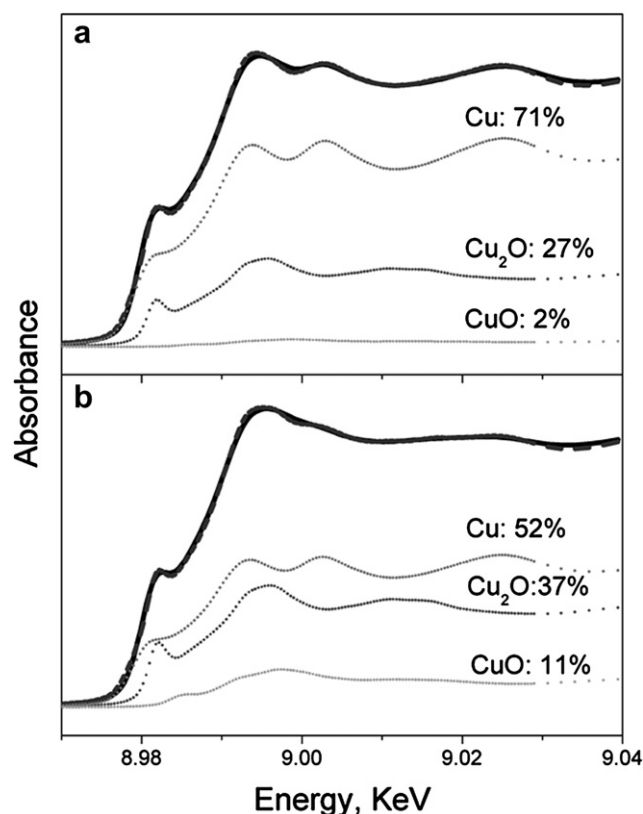
atoms from methanol should have more affinity for adsorbing onto or diffusing into $Au_{4.3}CZ$, and thus inducing the oxidation of metallic copper.

To further discuss how oxygen affects the metallic copper in the presence of gold, an oxidation test was investigated and is described as follows. All the catalysts were reduced by 30 mL/min of 10% H_2/N_2 at 240 °C for 30 min. After reduction, 1% O_2/He was introduced at specific temperatures (i.e., 100, 130, 170 and 210 °C, respectively) for 30 min. Then, 30 mL/min of N_2 was passed through the catalyst bed to purge out residual oxygen. Subsequently, a H_2-TPR was carried out to evaluate the residual concentration of partially reduced copper on the catalyst. The result is shown in Table 4. We can obviously find that gold deposited on copper-zinc catalyst can avoid full oxidation of Cu^0, especially at high oxidation temperatures. This result is astonishing. From the XANES data (Figs. 6 and 7) and Table 3, we know that oxygen atoms can induce the variation of copper species and initiate the reforming of methanol at lower temperature. Moreover, partially reduced Cu^+ or Cu^0 remains on the gold-deposited CZ catalyst, indicating that oxygen should affiliate with the gold particle surface, or interface between gold and support, and thus preventing further oxidation of the copper. Some researchers have also mentioned that the addition of gold suggests increased mobility of surface oxygen in response to the reduction temperature shifting to a lower temperature

Table 4 – The residual concentration of partially reduced copper on the catalyst after oxidation in 1% O_2/He at specific temperature.

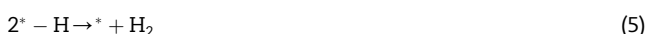| Oxidation Temperature	CZ (%)	$Au_{0.8}CZ$ (%)	Au_3CZ (%)	$Au_{4.3}CZ$ (%)
100 °C	53.3	54.1	54.7	54.8
130 °C	34.6	33.6	35.6	35.7
170 °C	14.1	20.7	20	21.8
210 °C	6	13.5	13.1	13.4

[19,37] and to the enhancement of CO preferential oxidation [20,37]. We believe that these adsorbed oxygen atoms can spill over from the gold to initiate reforming of methanol on the active sites, Cu^0 or Cu^+, at lower temperature.

From the above discussion, the partial oxidation of methanol process on the copper-zinc oxide catalyst with gold may proceed through the following redox mechanism:

(1) $T < 120\ ^\circ C$

$$2^* + O_2 \rightarrow 2^* - O \qquad (1)$$

$$* + CH_3OH \rightarrow *-\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}} OH \qquad (2)$$

(2) $T > 120\ ^\circ C$

$$*-\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}} OH \rightarrow *-CO + 4\ *-H \qquad (3)$$

$$-O + {}^* -CO \rightarrow CO_2 + 2^* \qquad (4)$$

$$2^* - H \rightarrow {}^* + H_2 \qquad (5)$$

* is the active site on the Au_xCZ catalyst. At temperatures lower than $120\ ^\circ C$, most methanol and oxygen is chemisorbed on the active sites of Au_xCZ catalyst. At temperatures $> 120\ ^\circ C$, the preferential oxidation of CO might simultaneously enhance copper oxide to be reduced to active state (Cu^0, Cu^+) (confirmed in Fig. 6), and then initiate the reaction. Bond and Thompson [38] suggest that preferential oxidation of CO on gold-based catalyst can be performed at quite moderate temperature. Accordingly, the dissociation of methanol reaction ((3)) may therefore be regarded as the rate-determining step of the POM reaction on the CuZn-based catalyst. Speeding up the rate-determining step by preferential oxidation of CO (reaction 4) on the CuZn-based catalyst with gold might initiate the POM reaction at low temperature.

4. Conclusions

With the addition of gold, CuZnO catalyst can initiate POM reaction at lower temperature and the initiation temperature can be decreased with increments of gold content. The adsorption and mobility of oxygen on the surface of catalysts should play a critical role in the reaction pathway. Our study supports the conclusion that oxygen atoms from methanol should have more affinity for adsorbing onto or diffusing into gold-deposited CZ catalyst and induce the oxidation of metallic copper at room temperature. In addition, the appearance of partially reduced Cu^+ or, Cu^0 as active species in the POM reaction, suggests that adsorbed oxygen could be removed as CO_2, which would speed up the rate-determining step and simultaneously reduce copper oxide into metallic

copper on the gold-deposited CuZnO-based catalyst, and initiate the reforming reaction at lower temperature.

REFERENCES

[1] Agrell J, Hasselbo K, Jansson K, Järås SG, Boutonnet M. Production of hydrogen by partial oxidation of methanol over Cu/ZnO catalysts prepared by microemulsion technique. Appl Catal A-Gen 2001;211:239–50.
[2] Lin YC, Fan LT, Hohn KL, Bertók B, Friedler F. Catalytic pathways Identification for partial oxidation of methanol on copper-zinc catalysts: CH$_3$OH + 1/2O$_2$ ↔ CO$_2$ + 2H$_2$. Ind Eng Chem Res 2008;48:2523–7.
[3] Alejo L, Lago R, Peña MA, Fierro JLG. Partial oxidation of methanol to produce hydrogen over Cu–-Zn-based catalysts. Appl Catal A-Gen 1997;162:281–97.
[4] Agrell J, Boutonnet M, Fierro JLG. Production of hydrogen from methanol over binary Cu/ZnO catalysts: part II. catalytic activity and reaction pathways. Appl Catal A-Gen 2003;253:213–23.
[5] Tang HY, Erickson P, Yoon HC, Liao CH. Comparison of steam and autothermal reforming of methanol using a packed-bed low-cost copper catalyst. Int J Hydrog Energy 2009;34:7656–65.
[6] Shishido T, Yamamoto Y, Morioka H, Takehira K. Production of hydrogen from methanol over Cu/ZnO and Cu/ZnO/Al$_2$O$_3$ catalysts prepared by homogeneous precipitation: steam reforming and oxidative steam reforming. J Mol Catal A-Chem 2007;268:185–94.
[7] Grisel RJH, Nieuwenhuys BE. A comparative study of the oxidation of CO and CH$_4$ over Au/MO$_x$/Al$_2$O$_3$ catalysts. Catal Today 2001;64:69–81.
[8] Bond GC, Thompson DT. Catalysis by gold catalysis reviews: science and engineering. Catal Rev 1999;41:319–88.
[9] Cameron D, Holliday R, Thompson D. Gold's future role in fuel cell systems. J Power Sources 2003;118:298–303.
[10] Gluhoi AC, Bogdanchikova N, Nieuwenhuys BE. The effect of different types of additives on the catalytic activity of Au/Al$_2$O$_3$ in propene total oxidation: transition metal oxides and ceria. J Catal 2005;229:154–62.
[11] Huang YJ, Ng KL, Huang HY. The OSRM reaction over non-reduced gold promoted copper zinc catalyst. J Chin Inst Eng 2011;34:1–7.
[12] Luengnaruemitchai A, Osuwan S, Gulari E. Selective catalytic oxidation of CO in the presence of H$_2$ over gold catalyst. Int J Hydrog Energy 2004;29:429–35.
[13] Haruta M. Gold as a novel catalyst in the 21st century: preparation, working mechanism and applications. Gold Bull 2004;37:27–36.
[14] Iwasawa Y, Liu H, Kozlov AI, Kozlova AP, Shido T, Asakura K. Active oxygen species and mechanism for low-temperature CO oxidation reaction on a TiO$_2$-supported Au catalyst prepared from Au(PPh$_3$)(NO$_3$) and as-precipitated titanium hydroxide. J Catal 1999;185:252–64.

[15] Caps V, Quinet E, Morfin F, Diehl F, Avenier P, Rousset JL. Hydrogen effect on the preferential oxidation of carbon monoxide over alumina-supported gold nanoparticles. Appl Catal B-Environ 2008;80:195–201.

[16] Pattarasuda Naknam, Apanee Luengnaruemitchai, Sujitra Wongkasemjit. Preferential CO oxidation over Au/ZnO and Au/ZnO-Fe$_2$O$_3$ catalysts prepared by photodeposition. Int J Hydrog Energy 2009;34:9838–46.

[17] Venezia AM, Pantaleo G, Longo A, Carlo GD, Casaletto MP, Liotta LF, et al. Relationship between Structure and CO oxidation activity of ceria-supported gold catalysts. J Phys Chem B 2005;109:2821–7.

[18] Manzoli M, Chiorino A, Boccuzzi F. Decomposition and combined reforming of methanol to hydrogen: a FTIR and QMS study on Cu and Au catalysts supported on ZnO and TiO$_2$. Appl Catal B-Environ 2005;27:201–9.

[19] Bokhoven JA, Louis C, Miller JT, Tromp M, Safonova OV, Glatzel P. Activation of oxygen on gold/alumina catalysts: in situ high-energy-resolution fluorescence and time-resolved X-ray spectroscopy. Angew Chem 2006;118:4767–70.

[20] Nørskov JK, Mavrikakis M, Stoltze P. Making gold less noble. Catal Lett 2000;64:101–6.

[21] Jacobs G, Davis BH. In situ DRIFTS investigation of the steam reforming of methanol over Pt/ceria. Appl Catal A-Gen 2005; 285:43–9.

[22] Manzoli M, Chiorino A, Boccuzzi F. FTIR study of methanol decomposition on gold catalyst for fuel cells. J Power Sources 2003;118:304–10.

[23] Fujitani T, Nakamur J. The effect of ZnO in methanol synthesis catalysts on Cu dispersion and the specific activity. Catal Lett 1998;56:119–24.

[24] Chen YW, Chang LH, Sasirekha N, Wang WJ. Preferential oxidation of CO in H2 stream over Au/MnO$_2$–CeO$_2$ catalysts. Ind Eng Chem Res 2006;45:4927–35.

[25] Schüth F, Wolf A. A systematic study of the synthesis conditions for the preparation of highly active gold catalysts. Appl Catal A-Gen 2002;226:1–13.

[26] Appel LG, Souza KR, Lima AFF, Sousa FF. Preparing Au/ZnO by precipitation–deposition technique. Appl Catal A-Gen 2008;340:133–9.

[27] Shishido T, Yamamoto Y, Morioka H, Takaki K, Takehira K. Active Cu/ZnO and Cu/ZnO/Al$_2$O$_3$ catalysts prepared by homogeneous precipitation method in steam reforming of methanol. Appl Catal A-Gen 2004;263:249–53.

[28] Jones SD, Hagelin-Weaver HE. Steam reforming of methanol over CeO$_2^-$ and ZrO$_2$promoted Cu-ZnO catalysts supported on nanoparticle Al$_2$O$_3$. Appl Catal B-Environ 2009;90:195–204.

[29] Pettersson LJ, Lindström B, Menon PG. Activity and characterization of Cu/Zn, Cu/Cr and Cu/Zr on γ-alumina for methanol reforming for fuel cell vehicles. Appl Catal A-Gen 2002;234:111–25.

[30] Fierro JLG, Jacono ML, Inversi M, Porta P, Cioci F, Lavecchia R. Study of the reducibility of copper in CuO–-ZnO catalysts by temperature-programmed reduction. Appl Catal A-Gen 1996; 137:327–48.

[31] Stephanopoulos MF, Fu Q, Kudriavtseva S, Saltsburg H. Gold–ceria catalysts for low-temperature water-gas shift reaction. Chem Eng J 2003;93:41–53.

[32] Yun-Bao Tu, Jin-Yong Luo, Ming Meng, Wanga Gang, He Jun-Jun. Ultrasonic-assisted synthesis of highly active catalyst Au/MnO$_x$-CeO$_2$ used for the preferential oxidation of CO in H$_2$-rich stream. Int J Hydrog Energy 2009;34:3743–54.

[33] Kartusch C, Bokhoven JA. Hydrogenation over gold catalysts: the interaction of gold with hydrogen. Gold Bull 2009;42: 343–8.

[34] Wolf EE, Schuyten S, Guerrero S, Miller JT, Shibata T. Characterization and oxidation states of Cu and Pd in Pd–CuO/ZnO/ZrO$_2$ catalysts for hydrogen production by methanol partial oxidation. Appl Catal A-Gen 2009;352: 133–44.

[35] Reitz TL, Lee PL, Czaplewski KF, Lang JC, Popp KE, Kung HH. Time-resolved XANES investigation of CuO/ZnO in the oxidative methanol reforming reaction. J Catal 2001;199: 193–201.

[36] Nørskov JK, Lopez N, Janssens TVW, Clausen BS, Xu Y, Mavrikakis M, et al. On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation. J Catal 2004;223:232–5.

[37] Chen Y-W, Sangeetha P, Yang Y- F. Au/FeOx–TiO$_2$ catalysts for the preferential oxidation of CO in a H$_2$ stream. Ind Eng Chem Res 2009;48:10402–7.

[38] Bond GC, Thompson DT. Gold-Catalysed oxidation of carbon monoxide. Gold Bull 2000;33:41–51.