Selective production of hydrogen from partial oxidation of methanol over silver catalysts at low temperatures

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Hydrogen can be effectively and selectively produced from the partial oxidation of methanol over Ag/CeO₂–ZnO catalyst at low temperatures ($T_r < 200$ °C).

Fuel cell technology is promising for efficient conversion of chemical energy into electrical energy with negligible emission of pollutant.¹ There are many types of fuel cell under development. Among them, the proton exchange membrane fuel cell (PEMFC) can operate at the lowest temperature ~ 90 °C and may be applied to mobile cars, cell phones and notebook computers. However, the application is hindered by technical difficulties in storage, transportation and distribution of hydrogen fuel. The difficulties may be eliminated by an on-site catalytic reactor that produces hydrogen from liquid fuels. Methanol is a promising fuel because of its ease of handling, low cost, and abundant feedstock.²

Hydrogen may be produced directly from methanol according to a number of different processes such as steam reforming [SR, eqn. (1)],^{3–4} partial oxidation [POM, eqn. (2)]^{5–9} or oxidative steam reforming (OSR).^{10–11}

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2, \Delta H^0 = +49.4 \text{ kJ mol}^{-1}$$
 (1)

$$CH_3OH + 1/2O_2 \rightarrow 2H_2 + CO_2, \Delta H^0 = -192.2 \text{ kJ mol}^{-1} (2)$$

The endothermic SR is well developed with copper based catalysts at reaction temperatures of $T_r > 230$ °C Comparably, the exothermic POM uses oxygen (air) instead of water as oxidant and does not require an external heat supply.

Recently, the POM reaction has been studied over copper^{5–7} and palladium based^{8,9} catalysts. Nevertheless, a $T_r > 230$ °C is still required and the hydrogen selectivity is still low ($S_{H2} < 70\%$ at $n_{O2}/n_{MeOH} = 0.5$). In our laboratory, Au/ZnO catalyst was used for POM reaction with low CO contamination and high S_{H2} (~95%).¹² But a $T_r > 230$ °C is still needed. It is highly desirable to operate the POM reaction at low temperatures if it is to be coupled to a fuel cell. Herein, we report Ag/CeO₂–ZnO catalyst which not only shows excellent POM performance at low T_r but also exhibits high S_{H2} .

Supported catalysts of Ag/ZnO, Ag/CeO2-ZnO and Ag/CeO2-Al₂O₃ were prepared by the deposition precipitation method.¹² A solution of 0.15 M AgNO₃ (or a mixture solution of 0.15 M AgNO₃ and 0.40 M Ce(NO₃)₃·6H₂O) was precipitated to powders of ZnO $(d \sim 180 \text{ nm}, \text{ from Merk})$ or fumed alumina (from CABOT) suspended in deionized water. Acidity of the suspended solution was adjusted to pH ~ 9.0 with 0.10 M NaOH. After 2 h of stirring at room temperature, the suspension was filtered and washed with deionized water. The resulting precipitate was then dried at 100 °C for 24 h. Another supported catalyst of Ag/CeO2 was prepared by a similar procedure without addition of ZnO or alumina. Supported catalysts of Ag/CeO2-ZnO and Ag/CeO2-Al2O3 were designated as Ag/Ce_xZn and Ag/Ce_xAl (x represents nominal loading of Ce in wt.% of catalysts), respectively. The nominal loading of Ag was 5 wt.% in all of the prepared catalysts. True loadings detected by ICPmass are listed in Table 1. Mixing samples of "Ag/CeO2+ZnO" and "Ag/CeO₂ + quartz" were prepared by physically mixing the Ag/ CeO_2 with ZnO powder or quartz sand at a ratio of 1 : 2. These mixtures were ground into fine powders and then pressure-moulded into granules. They were further crushed, sieved to 60-80 mesh, and reduced for 1 h at 200 °C in a hydrogen flow. The POM activity was tested in a fixed bed reactor (4 mm in id). A reactant gas $(n_{O2}/$

 $n_{\rm MeOH} = 0.5$) of 100 ml min⁻¹ flow with 12.2 mol% CH₃OH (metered by a liquid pump and preheated to about 100 °C), 6.1 mol% O₂ and 81.7 mol% Ar (controlled by mass flow controller) was catalyzed by 0.1 g catalyst. Reaction products were analyzed by a TCD-GC equipped with columns of Porapak Q and Molecular Sieve 5A.

Table 1 also displays POM catalytic performance from the prepared catalysts at 160 °C. H₂, H₂O, CO and CO₂ were major products detected. Dimethyl ether (DME) was an additional by-product found from catalysis over Ag/Ce₂₀Al. The support of silver catalysts significantly affected their C_{MeOH} and S_{H2} in POM. Ag/ZnO showed a higher S_{H2} and S_{CO2} than those of Ag/Ce₂₀Al and Ag/CeO₂. However, Ag/Ce₂₀Zn exhibited the highest methanol conversion ($C_{MeOH} = 92\%$) and S_{H2} (97%) among the studied catalysts. Interestingly, the performance of Ag/CeO₂ increased significantly on physically mixing with ZnO (the mixing catalyst of Ag/CeO₂ + ZnO). In order to exclude a possible dilution effect of ZnO in the Ag/CeO₂ + ZnO, a physical mixture of Ag/CeO₂ and quartz was also tried but showed poor catalytic performance. Evidently, a synergistic effect on C_{MeOH} and S_{H2} exists in Ag/Ce_xZnO.

Fig. 1 demonstrates effect of the Ce loading (*x*) on the catalytic performance of Ag/Ce_xZn catalysts. Both C_{MeOH} and S_{H2} increased with *x*, but they reached a maximum when x = 20. The selectivity of CO₂ ($S_{\text{CO2}} \sim 94\%$) was not affected by the loading of Ce.

Fig. 2 presents the effect of the reaction temperature on the catalytic performance of Ag/Ce₂₀Zn. S_{CO2} decreased on increasing the temperature. This trend may be attributed to the endothermic nature of the reversed water gas shift reaction [RGWSR, eqn. (3)].

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \Delta H^0 = 41 \text{ kJ mol}^{-1}$$
 (3)

 K_{eq} of RGWSR decreases with the temperature and a high S_{CO2} (therefore a low S_{CO}) is therefore expected from the equilibrium at low temperatures. Both C_{MeOH} and S_{H2} in Fig. 2 increased with the reaction temperature and exceeded 98% at 180 °C.

Fig. 3 shows the effect of Ce on the stabilities of Ag/Ce_xZn catalysts. Ag/ZnO catalyst deactivated slowly at the initial stage

Table 1 Physical characterization and catalytic performance of different catalysts at 160 $^\circ\text{C}$

Catalyst	Ag (wt.%)	Ce (wt.%)	$d (nm)^{a}$	ı	C _{MeOH} ^b	S _{H2} ^c	S_{CO2}^{c}	S _{DME} ^d
			Ag	Ce				
Ag/ZnO	4.1	0	30(48)	~	74	83	95	0
Ag/CeO ₂	3.9	~	10	8	69	65	58	0
Ag/Ce ₂₀ Al	5.0	20	11	7	87	17	85	20
Ag/Ce ₂₀ Zn	4.8	18	10(13)	6	92	97	94	0
Ag/CeO ₂ +ZnO	~	~	10	8	78	88	98	0
Ag/CeO ₂ +quartz	~	~	10	8	54	24	89	0
CeO ₂ /ZnO	0	20	~	6	0	0	0	0
^{<i>a</i>} Estimated by XRD using the Scherrer equation and the values in parentheses are used catalysts'. ^{<i>b</i>} $C_{\text{MeOH}} = (n_{\text{MeOH, in}} - n_{\text{MeOH, out}})/n_{\text{MeOH, in}} \times 100\%$. ^{<i>c</i>} $S_{\text{H2}} = n_{\text{H2}}/2(n_{\text{MeOH, in}} - n_{\text{MeOH, out}}) \times 100\%$; $S_{\text{CO2}} = n_{\text{CO2}}/(n_{\text{MeOH, in}} - n_{\text{MeOH, out}}) \times 100\%$; $d_{\text{DME}} = 2n_{\text{DME}}/(n_{\text{MeOH, in}} - n_{\text{MeOH, out}}) \times 100\%$.								

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Fig. 1 Effect of Ce loading on POM Ag/Ce_xZn at 160 °C.



Fig. 2 Effect of reaction temperature on POM over Ag/Ce $_{20}$ Zn.

and drastically after 25 h on stream reaction. Interestingly, the catalytic performance was dramatically enhanced with the addition of a small amount of Ce. Catalysts of $Ag/Ce_{0.6}Zn$ and $Ag/Ce_{20}Zn$ showed no evident deactivation during 30 h. XRD revealed that the particle size of Ag over fresh and used Ag/ZnO catalyst was 30 and 48 nm, respectively (shown in Table 1). The Ag particle size of Ag/Ce_{0.6}ZnO catalyst before and after the reaction was 30 and 29 nm, respectively (not shown in Table 1). Evidently, sintering of Ag particles may be the main cause for the deactivation of Ag/ZnO



Fig. 3 Effect of Ce on stability of Ag/Ce_xZn catalysts at 160 °C.

catalyst. CeO_2 plays an important role in preventing the sintering of Ag particles over Ag/Ce_xZn catalysts.

In conclusion, $Ag/Ce_{20}Zn$ catalyst is an excellent catalyst for selective and effective production of hydrogen from POM at low temperature. A detailed research programme is in progress to clarify the effect of the functions of CeO₂ and ZnO.

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