

Oxidative steam reforming of methanol over CuZnAl(Zr)-oxide catalysts; a new and efficient method for the production of CO-free hydrogen for fuel cells

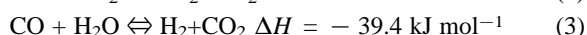
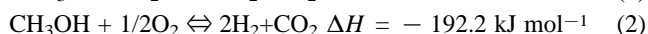
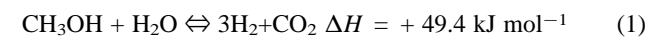
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Steam reforming of methanol in the presence of air over CuZnAl(Zr)-oxide catalysts derived from hydrotalcite-like hydroxycarbonate precursors offers CO-free hydrogen suitable for fuel cells with about 100% methanol conversion at around 230 °C.

Hydrogen is forecast to become a major source of energy in the future.¹ Hydrogen fueled vehicles using fuel cells [e.g. polymer electrolyte membrane fuel cell (PEMFC)] are under development in an effort to reduce CO₂ emissions which accelerate global warming. In addition, fuel cell-powered vehicles, using hydrogen fuel, do not emit any environmental pollutants, such as NO_x, SO_x and hydrocarbons. For use in fuel cells for mobile applications, hydrogen is typically produced through steam reforming of methanol (SRM) [eqn. (1)] over CuZn-based catalysts.² Recently, partial oxidation of methanol (POM) [eqn. (2)] has also been suggested as a route for hydrogen extraction from methanol.³ Unfortunately, both of these reactions produce considerable amounts of CO (> 100 ppm) as a byproduct. For application in PEMFCs, even traces of CO (> 20 ppm) in the reformed gas deteriorates a Pt electrode and the cell performance is dramatically lowered.⁴ Currently, second stage catalytic reactors are being used to remove this CO by the water-gas-shift reaction [eqn. (3)], CO oxidation or methane formation. However, the addition of further steps for fuel gas refinement would lower the total efficiency of the propulsion system. Hence, in order to utilize hydrogen fuel for fuel cells, it is highly desirable to develop a process that can produce hydrogen without CO in the reformed gas.



In the present study, we have performed the SRM reaction in an oxidizing atmosphere (in the presence of air) over a series of novel CuZnAl(Zr)-oxide catalysts obtained by calcining the CuZnAl(Zr)-hydroxycarbonates containing hydrotalcite (HT)/aurichalcite phases, at 450 °C for 5 h. We demonstrate here for the first time that under the reaction conditions employed, a combined steam reforming–partial oxidation of methanol, termed herein after as “oxidative steam reforming of methanol (OSRM)”, reaction takes place to produce CO-free hydrogen with about 100% methanol conversion at 230 °C.

CuZnAl(Zr)-hydroxycarbonate precursors with different Cu:Zn:Al atomic ratios were synthesized by a coprecipitation method at room temperature using a mixture of NaOH and Na₂CO₃ as precipitants.⁵ The (Cu+Zn)/Al(Zr) atomic ratio in the starting solution was varied from 2 to 4. The Cu surface areas (*S*_{Cu}), Cu dispersion (*D*) and the Cu crystallite sizes (*t*_{Cu}) were calculated by the TPR-N₂O passivation experiment as described in the literature.⁶ Catalytic test reactions were performed in a packed-bed micro-reactor (4 mm i.d.) using 90 mg of the catalyst (particle size 0.30–0.355 mm) in the temperature range 180 to 290 °C at atmospheric pressure. Liquid methanol (for the POM reaction) or premixed water and methanol with a H₂O/CH₃OH molar ratio of 1.3 (for the SRM and OSRM reactions) was fed into the pre-heater at a rate of 1.6 or 2.5 cm³ h⁻¹ by means of a micro-feeder. Synthetic air (20.2 vol.% O₂ in N₂) at a rate of 10 to 20 cm³ min⁻¹ and Ar (carrier gas, 43 cm³ min⁻¹) flows were adjusted by means of a mass flow controller. The reaction products were analyzed on-line using two gas chromatographs equipped with TC detectors and porapak Q and molecular sieve 13 X columns. The performance of the catalyst was evaluated after 25 h of on-stream operation.

The physicochemical properties of the catalysts used in the present study are summarized in Table 1. Initially, a systematic study on the POM reaction was performed over a series of CuZnAl-oxide catalysts without Zr (CZAZ-A through CZAZ-D). Among them, the catalyst CZAZ-C exhibited the best performance. Hence, this catalyst was chosen first to be examined for its catalytic performance in the SRM and OSRM reactions. Fig. 1 compares the catalytic performance of the CZAZ-C catalyst in the POM, SRM and OSRM reactions. As will be noted, the methanol conversion is lowest in the SRM reaction at low temperatures and the conversion rate increases rapidly with increasing reaction temperature. The conversion reaches about 100% at around 290 °C where the selectivity of CO is < 5 mol% (CO concentration ≈ 200 ppm). Interestingly, when air was passed through during the SRM reaction, the conversion approaches 100% at a lower temperature of about 230 °C, without any detectable CO in the reformed gas. Because of the high methanol conversion of about 100%, the H₂ production rate in the OSRM reaction increased by a factor of two compared to that obtained from the SRM or POM reactions. It is of great significance that CO only started forming above 260 °C in the SRM reaction, while it started forming above

Table 1 Physicochemical properties of CuZnAl(Zr)-oxide catalysts

Catalyst	Metal composition of the precursors (atomic ratio) ^a				<i>S</i> _{BET} / m ² g ⁻¹	H ₂ consumption ^b / mmol g ⁻¹	<i>S</i> _{Cu} /m ² g ⁻¹	<i>D</i> _{Cu} (%)	<i>t</i> _{Cu} /Å
	Cu	Zn	Al	Zr					
CZAZ-A	0.73	0.88	1.00	0.00	56	3.3	203	38.6	26
CZAZ-B	1.02	1.30	1.00	0.00	71	3.6	181	34.3	29
CZAZ-C	1.42	1.71	1.00	0.00	84	6.0	176	33.4	30
CZAZ-D	1.37	1.80	1.00	0.00	108	4.2	227	43.1	23
CZAZ-E	1.40	1.65	0.45	0.55	82	4.7	232	44.0	23
CZAZ-F	1.38	1.72	0.00	1.00	75	4.3	279	52.9	19

^a Determined by X-ray fluorescence spectroscopy. ^b Hydrogen consumption estimated by the temperature programmed reduction (TPR) experiments.

Table 2 Performance of various CuZnAl(Zr)-oxide catalysts in the oxidative steam reforming of methanol after 25 h of on-stream operation at 230 °C

Catalyst	MeOH conversion		H ₂ production		H ₂ production rate/CH ₃ OH conversion rate	Carbon selectivity (mol%)	
	mol%	Rate/mmol kg ⁻¹ s ⁻¹	rate/mmol kg ⁻¹ s ⁻¹	TOF/10 ³ s ⁻¹		CO	CO ₂
CZAZ-A	37.6	177	378	77	2.1	0.0	100
CZAZ-B	65.4	297	730	166	2.5	0.0	100
CZAZ-C	68.1	348	900	211	2.6	0.0	100
CZAZ-C ^a	100.0	215	542	127	2.5	0.0	100
CZAZ-D	79.6	468	1210	215	2.6	1.2	98.8
CZAZ-E	85.4	630	1626	254	2.6	1.1	98.9
CZAZ-F	90.0	661	1714	295	2.6	0.8	99.2

^a CH₃OH: 8.8 cm³ min⁻¹; H₂O: 11.4 cm³ min⁻¹.

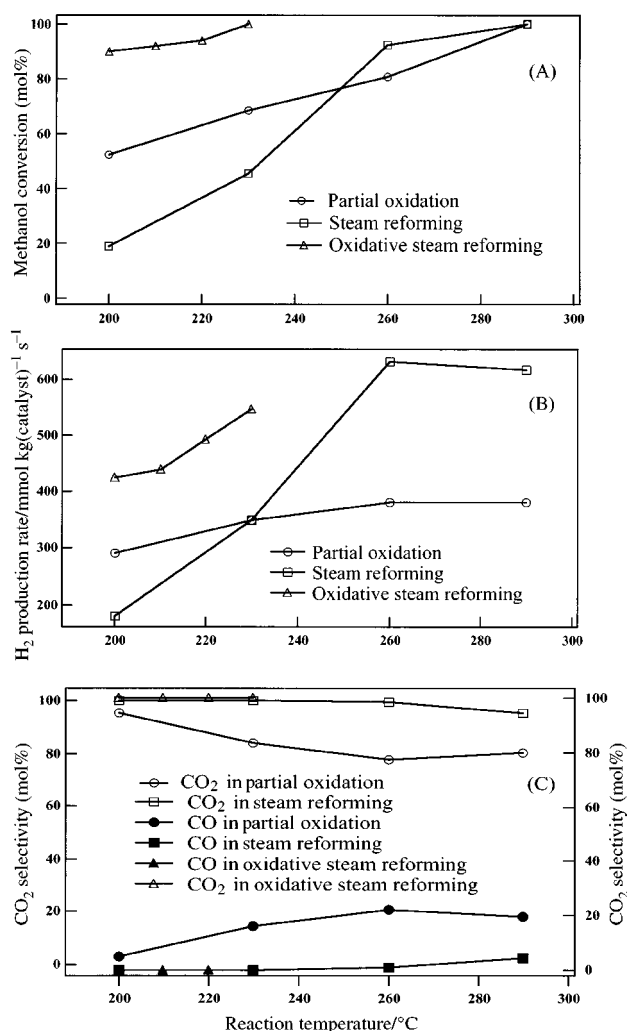
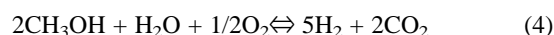


Fig. 1 Effect of temperature on catalytic performance of CZAZ-C catalyst in the partial oxidation, steam reforming, and oxidative steam reforming of methanol; (A) methanol conversion, (B) H₂ production rate, (C) carbon selectivity.

200 °C in the POM reaction. However, in the OSRM reaction, since excess water is present in the feed mixture, the situation is highly favorable for the water-gas-shift reaction [eqn. (3)] to transform CO into CO₂ and H₂.

For the purpose of evaluating the performance of various CuZnAl(Zr)-oxide catalysts in the OSRM reaction, the metha-

nol conversion was reduced by increasing the flow rate of the CH₃OH + H₂O feed mixture to 2.5 cm³ h⁻¹ and the results were collected during 25 h of continuous operation. Table 2 summarizes the catalytic performance of a series of CuZnAl(Zr)-oxide catalysts in the OSRM reaction. It can be seen that the catalytic activity increases with decreasing Al content in the sample. It is also interesting to note from Table 2 that the best catalytic performance was obtained over the catalyst containing Zr instead of Al (CZAZ-F), indicating that Zr is an effective support for CuZn-based oxide catalysts compared to Al in the OSRM reaction. The undesirable byproduct CO is virtually not produced (or only traces are formed) and catalyst deactivation is insignificant over most of the catalysts (except CZAZ-A). Another interesting feature which will be noticed in Table 2 is that a ratio of H₂ production rate/CH₃OH conversion rate of around 2.5 is obtained over all the catalysts. However in the SRM [eqn. (1)] and POM [eqn. (2)] reactions the H₂ production rate/CH₃OH conversion rate ratios would be 3 and 2, respectively. The value of 2.5 obtained for the OSRM reaction suggests that a combined partial oxidation–steam reforming of methanol is taking place under the present experimental conditions. Hence, the overall reaction can be represented by eqn. (4), which is a combination of eqn. (1) and 2. Eqn. (4) satisfies the H₂ production rate/CH₃OH conversion rate ratio of around 2.5 observed in the present investigation.



It is clear from the results presented in the present study that the OSRM reaction over these novel CuZnAl(Zr)-oxide catalysts is a very efficient and convenient method for the production of CO-free hydrogen suitable for fuel cells. Besides producing CO-free hydrogen, the OSRM reaction has an additional benefit in that the reaction is exothermic, thereby minimizing energy consumption. A detailed investigation is in progress into the optimization of the catalyst formulations and the reaction operating parameters to further improve the catalytic performance.

Notes and references

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