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To cite this article: Hsiao-Yu Huang, Shoa-Huai Lee & Yuh-Jeen Huang (2015) Adhesion optimization for catalyst coating on silicon-based reformer, Journal of Adhesion Science and Technology, 29:18, 1937-1950, DOI: [10.1080/01694243.2015.1046755](https://doi.org/10.1080/01694243.2015.1046755)

To link to this article: <http://dx.doi.org/10.1080/01694243.2015.1046755>



Published online: 22 May 2015.



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Adhesion optimization for catalyst coating on silicon-based reformer

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(Received 8 October 2014; final version received 24 April 2015; accepted 27 April 2015)

CMZ (ca. 30.0 wt.% Cu, 20 wt.% Mn, and 50 wt.% Zn) catalyst was chosen for the partial oxidation of methanol (POM) reaction. To enhance adhesion between a silicon-based reactor and catalysts, boehmite and bentonite were used as binders. Changes in conditions such as pH value, ratio of bentonite/boehmite, amount of solid contents per area of substrate, and aging time have crucial effects on adhesion and result in variable performance of catalyst in POM reaction. Regarding optimized adhesion conditions, 13 wt.% weight loss was observed and methanol conversion could be kept at ca. 80–90% of original catalyst performance in a packed-bed reactor. However, poor performance was observed in the micro-channel reactor. The methanol conversion (C_{MeOH}), H_2 selectivity (S_{H_2}), and H_2 yield (Y_{H_2}) achieved 58%, 67%, 5.7×10^{-6} mol/min in micro-channel reformer at 250 °C, respectively.

Keywords: catalyst coating; partial oxidation of methanol (POM); micro-channel reactor; adhesion

Introduction

Fuel cells are the most ideal environmentally friendly technology because they are very efficient at producing pollution-free electricity. However, hydrogen does not occur naturally as a gaseous fuel, and application is hindered by a lack of proper techniques for storage, transportation, and distribution of hydrogen fuel. A compact methanol reformer was developed to safely produce hydrogen via methanol reforming processes, such as POM (partial oxidation of methanol) reaction.[1–5] POM is an exothermic reaction, and hydrogen can be produced at low temperature without an external heat supply. Thus, the process can respond quickly to meet the requirements of fuel cells at any given moment. Although the size of the conventional reformer makes it difficult to apply to modern technologies, such as phones and cameras, several research groups have already focused on building smaller methanol reformers to make further use of its applicability.[6–11]

In the micro-reformer fabrication process, detachment of small particles can easily lead to blocking due to the small dimensions of the micro-channels.[12] As a result, a binder should be added to enhance the adhesion of the catalyst in the micro-channel reactor. Klein [13] mentioned that the best way to get good adhesion between two materials was to form chemical bonds. In a micro-channel system, micro-reactors are usually made of nonporous materials, such as silicon wafer and glass.[14–17] However, coating catalysts onto such substances is difficult. A good binder should provide an

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increased surface area, which means that it will have a high porosity, so that many active centers can be exposed after wet impregnation with a catalytic active species. Among common porous oxides, such as SiO_2 , Al_2O_3 , and TiO_2 , alumina sol was selected in this study as support and binder based on its high surface area.[18] Furthermore, boehmite (AlOOH) sol, which has proven successful as a binder in extruded ceramic processing [19–22], has been indicated as a potential dispersant in alumina suspensions.

Some researchers [9] have used a fill-and-dry coating method coating Cu–ZnO– Al_2O_3 catalyst slurry in the silicon-based micro-reactors and found the maximum H_2 production rate could reach 85 sccm at 300 °C in a methanol feed rate of 9 ml/h. Many factors might affect the capability of the binder. For example, Agrafiotis et al. [23] reported using different precursors to coat alumina onto honeycomb ceramic and found that particles in the form of large agglomerates would exhibit very poor adhesion properties. Reducing the size of the agglomerates down to the order of a few (2–5) microns generally exhibited excellent adhesion to the support. Thus, it is very important to modulate the catalyst/binder mixture, which might affect system performance and catalytic activity. In this study, the characteristics of CMZ (ca. 30.0 wt.% Cu, 20 wt.% Mn, and 50 wt.% Zn) catalyst with binder were compared. Also investigated were the optimum adhesion conditions of a catalytic layer coating on silicon wafer substrate and the performance of catalyst with/without binder in packed-bed reactor or micro-channel reactor.

Material and methods

Preparation of catalytic slurry

The CMZ (ca. 30.0 wt.% Cu, 20 wt.% Mn, and 50 wt.% Zn) catalyst was prepared by co-precipitation method. All precursors, such as copper, zinc, and manganese nitrates, were dissolved and stirred in deionized water at 70 °C. The precipitating agent Na_2CO_3 (2 M) was added to maintain the mixture at pH 7. After aging to pH 8, the resulting precipitate was filtered by deionized water to remove the nitrate. After the precipitate was dried at 105 °C overnight and calcined at 400 °C for 4 h, the fresh catalyst was synthesized. The slurry was prepared by mixing the fresh catalyst with alumina binder [boehmite (Remet), bentonite (Sigma)] at the 5, 15, 25, 35 wt.% of binders to catalysts (B) into deionized water. The catalysts with various weight percentages of binder/catalyst are denoted as CMZ-B5, -B15, -B25, -B35, respectively. Different conditions, such as pH values, ratio of bentonite/boehmite, amount of solid contents per area of substrate, and aging time were investigated in this study.

Pretreatment of silicon wafer

The p-type silicon wafer with 0–100 ohm-cm electrical resistance and 500 μm thickness was used in this study. Before processing the adhesion test, the wafer was pre-treated with a 1:3 mixture of hydrogen peroxide and sulfuric acid for 10 min at 80 °C. Then, a 1:1:5 mixture of hydrogen peroxide, ammonia, and deionized water was used to wash the wafer surface for 10 min at 80 °C. Finally, the wafer was washed with 1:1:6 mixtures of the hydrogen peroxide, hydrochloric acid, and deionized water for 10 min at 80 °C and then rinsed with the deionized water and dried at 80 °C. The wafer was

also treated by O₂ plasma for 60 s to increase the hydrophilicity before the catalyst slurry was deposited.

Characterization

The images of slurries in the micro-channel reactor were performed on a field emission scanning electron microscopy (FESEM) (JEOL, JSM-6330F, 0.5–30 kV). Slurry viscosity was measured using a Brookfield Viscometer (LV DV-I) with the CPE-40 spindle, which can estimate absolute viscosities in the range 0.3–1000 cP.

The adhesive strength of slurries on silicon wafer is estimated by fraction of weight loss (F_L) in an ultrasonic vibration test. The coating method used was drop coating. The slurry was dropped onto the wafer surface and dried at 60 °C overnight. Then, the slurry-coated wafer was calcined at 400 °C for 2 h. After cooling, the wafer was dipped into the ultrasonic vibrator tank under 135 W of power for 30 min. The wafer was dried before weighing, and the weight loss was computed using a balance (METTLER TOLEDO, XP105). Weight loss was calculated as follows:

$$F_L = \frac{W - W_L}{W} \times 100\% \quad (1)$$

where F_L : fraction of weight loss during ultrasonic treatment. W : load amount of catalyst before the treatment. W_L : load after the treatment.

Catalytic activity

Catalysis activity of packed bed

Freshly calcined CMZ catalysts were ground into fine powders, pressure-molded into granules, crushed and sieved with 60–80 mesh, and then pre-activated by reduction in a hydrogen flow for 0.5 h at 270 °C before POM reaction. The catalytic reactions were tested in a packed-bed reactor (4 mm id). Liquid methanol was fed into the pre-heater at a rate of 0.02 ml/min using a liquid pump. Oxygen and argon flows were adjusted using mass flow controllers (Brooks); the total flow was 100 ml/min. Under these conditions, the O₂/CH₃OH molar ratios in the feed were maintained at 0.5. The performance of the reactions over reduced catalysts was measured while raising the temperature from RT.

Reaction products were analyzed by a TCD-GC equipped with columns of Porapak Q (MeOH, CO₂, and H₂O) and Molecular Sieve 5A (CO, O₂, and H₂). H₂, CO₂, CO, H₂O were found as major products in the performed reactions. CH₃OH conversion (C_{MeOH}), H₂ selectivity (S_{H_2}), H₂ yield (Y_{H_2}), and CO selectivity (S_{CO}) are generally defined as:

$$C_{MeOH} = (n_{MeOH,in} - n_{MeOH,out})/n_{MeOH,in} \times 100\% \quad (2)$$

$$S_{H_2} = n_{H_2}/(n_{H_2O} + n_{H_2}) \times 100\% \quad (3)$$

$$S_{CO} = n_{CO}/(n_{CO_2} + n_{CO}) \times 100\% \quad (4)$$

$$Y_{H_2} = n_{H_2}/\text{min} \quad (5)$$

Catalysis activity of micro-channel reactor and catalyst loading

The freshly prepared catalyst solution was injected into the micro-channel reactor by using a fill-and-dry method.[6,7] To avoid the clogging of catalyst particles, two syringes were used separately for air suction and injection of the catalyst slurry in two different sides of the micro-channel reactor. The micro-reactor was dried at 80 °C and calcined at 400 °C for 4 h. A holder was used to conjoin the micro-reactor with the gas inlet and outlet, and then, a gas-tight flow was tested.

A catalytic performance index (X_z) was used by comparing the reaction performance of the coated catalyst with binder to that of the original catalyst without binder in the packed-bed reactor and micro-channel reactor, respectively.

$$X_z = X_b/X_o$$

X : $X = C$ (CH₃OH conversion), S (H₂ selectivity), or Y (H₂ yield)

z : $z = p$ (packed-bed reactor) or m (micro-channel reactor)

b : catalyst with binder

o : catalyst without binder

Results and discussion

Adhesion of slurry on silicon wafer

Good adhesion would prevent losing catalysts by destroying the performance in the micro-channel reactor. The adhesive strength of slurries on silicon wafer was estimated by F_L in an ultrasonic vibration test. However, different conditions, such as binder/catalyst (B), pH values, solid contents per area of substrate, and aging time can affect the adhesion properties of catalysts on silicon substrate. To understand the effects of pH, commercial boehmite sol was coated onto silicon substrate at various pH values (4–9). The weight loss is shown in Figure 1(a). Because boehmite tended to aggregate as the solvent evaporated, the center of slurry produced cracks on the silicon substrate in the range of pH 4–9, with the exception at pH 8, and resulted in very poor weight loss. Optimum weight loss was observed at pH 8. Furthermore, fluidity of the sol is considered a particularly critical parameter for the preparation of crack-free and porous oxide coating.[12] We found that the viscosity of boehmite increased at higher pH (shown in Figure 1(b)). At pH 8, the boehmite-coated silicon substrate had uniform dispersion due to higher viscosity, overcoming slurry aggregation during solution evaporation. However, higher viscosity resulted from gel formation by condensation and dehydration, due to losing the hydroxyl group from the sol. That was because the isoelectric point of boehmite particles was ca. pH 8–9.[24,25] As the pH rose over 8, electrostatic attractive interactions between the particles increased, lowering the zeta potential and leading to coagulation. The OH bonds of boehmite colloidal particles would rapidly be dehydrated and polymerized into the Al–O–Al structure. The loss of OH bonds could break the chemical bond between slurry and silicon substrate, leading to higher weight loss. To overcome this problem, 30% bentonite was added to the boehmite to further raise the viscosity of alumina sol. Bentonite has a useful property in making a sticky coating and was used as an inorganic binder to enhance the adhesion between the catalyst and substrate, such as glass or silicon.[26] Figure 1(b) shows that viscosity of bentonite was independent of the pH values. The viscosity of the boehmite sol increased from 4 cP to 32 cP at pH 8 by adding 30 wt.% bentonite. Figure 1(a) shows that the addition of bentonite into boehmite would vastly improve and enhance the adhesion between boehmite and silicon substrate. Weight loss was reduced to 5–8% at

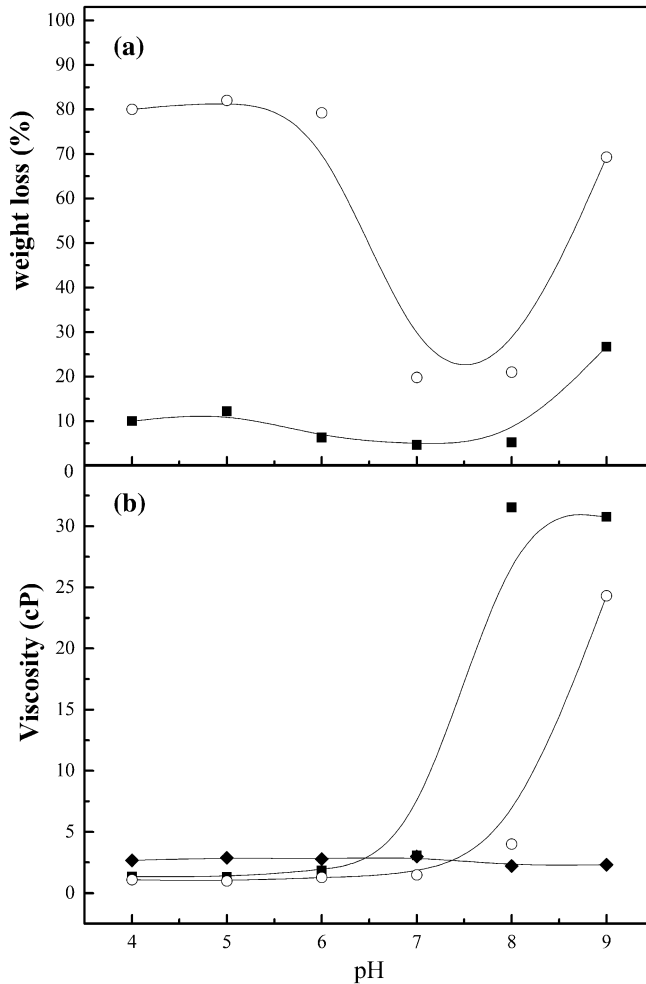


Figure 1. (a) Weight loss patterns of (○) commercial boehmite, and (■) 30 wt.% bentonite in boehmite which adjusted at different pH values coated on silicon substrate. (b) Apparent viscosity of slurries as a function of pH (○) bentonite, (◆) boehmite, (■) 30 wt.% bentonite in boehmite.

pH 6–8 after adding bentonite into boehmite. Due to zinc oxide and copper oxide, it would dissolve at pH less than 7 and 5, respectively.[27] The optimum pH value of bentonite/boehmite sol was kept at 7 to prevent copper oxide and zinc oxide from being dissolved.

The aging time of the alumina sol was supposed to have an effect on the structure of the sol. Variations in weight loss of bentonite in boehmite at different aging times are shown in Figure 2. The figure indicates that the sol had weak adhesion with silicon substrate when the aging time was shorter than 4 h. With increasing aging time, a more polymer-like network with an increasing degree of condensation and hydrolysis was formed. However, an excess degree of condensation or hydrolysis increased the OH group loss, and the sol displayed much weaker adhesion after aging more than 60 h.

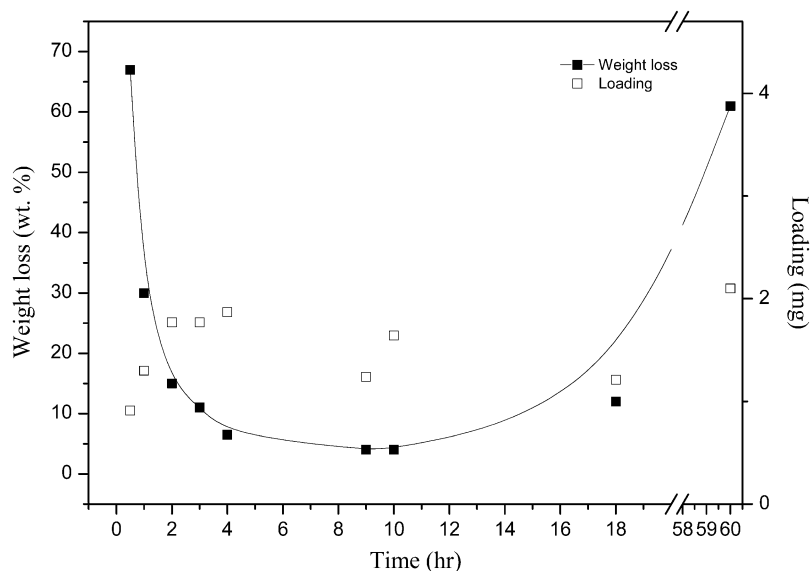


Figure 2. Time stream of the weight loss of bentonite in boehmite at pH 7 (■) weight loss, (□) loading.

The adhesion of catalysts with various percentages of binder (B/C) was tested. Table 1 summarizes the physical properties of CMZ-B x ($x = 0, 5, 15, 25, 35$) catalysts. The ICP-MS result was consistent with stoichiometry of metal weight percentage. After mixing with binder, the Cu, Mn, and Zn ratios were reduced as percentage of binder increased. The specific surface area of CMZ catalyst was similar, from 1.2×10^2 to 1.4×10^2 , after adding boehmite. The TEM images of CMZ-B x catalysts in Figure 3 also show catalyst size from ca. 10–25 nm. By increasing the amount of binder added, thin boehmite fibers (50–200 nm) with an average diameter of ca. 2 nm were formed.

The weight loss tested at various percentages of binder in CMZ catalyst (B/C) is displayed in Figure 4. It shows that more binder content might increase adhesion between slurry and silicon substrate. The optimum ratio for best adhesion was at 50 wt.% of B/C, and the weight loss was less than 10%. But high binder content might affect catalyst performance. Thus, to further improve the adhesion of slurry, a lower

Table 1. Physical properties of fresh CMZ-B x ($x = 0, 5, 15, 25, 35$) catalysts.

Catalysts	Metallic loading (wt.%) ^a				Particle size (nm) ^b		Specific surface area (m ² /g)
	Cu	Mn	Zn	binder	d _{CuO}	d _{ZnO}	
CMZ	30.09	20.06	49.85	–	–	13.4	1.2×10^2
CMZ-B5	29.27	18.38	47.50	3.28	11.25	10.63	1.0×10^2
CMZ-B15	27.42	17.23	45.81	9.54	8.82	12.42	1.2×10^2
CMZ-B25	24.60	16.56	41.04	17.79	–	8.70	1.1×10^2
CMZ-B35	21.58	13.60	35.74	29.09	–	–	1.4×10^2

^aChemical analysis result from ICP-MS.

^bNormal diameter estimated from XRD data using Debye–Scherrer equation.

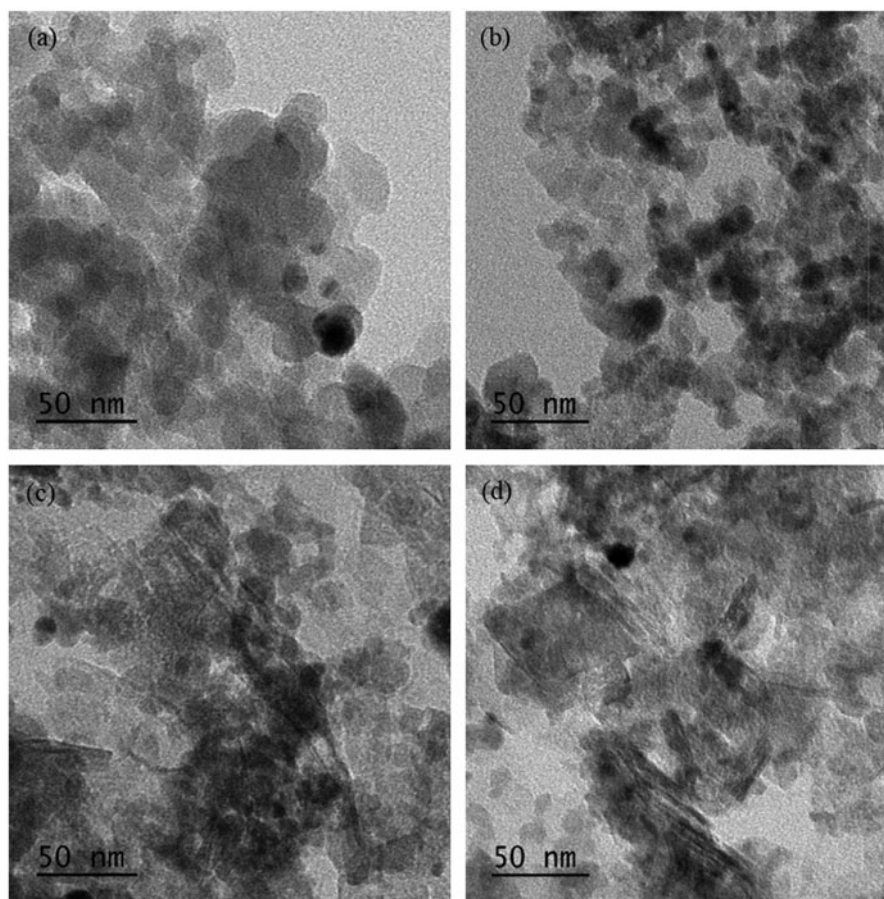


Figure 3. TEM images of (a) CMZ, (b) CMZ-B5, (c) CMZ-B15, and (d) CMZ-B35.

ratio of B/C was necessary. Particle size of the slurry is considered a particularly critical parameter for the preparation of crack-free and porous metallic oxide coating. Reduction in particle size may result in a more densely packed washcoat layer and better coating quality. Agrafiotis et al. [28,29] reported that adhesion characteristics depend strongly on particle size. They found that regardless of the type of the washcoat being deposited, adhesion properties can still be achieved when the characteristic particle diameter has been reduced to below $2\ \mu\text{m}$. Thus, in our study, a catalyst cluster with $0.1\text{--}1\ \mu\text{m}$ in diameter was prepared after ball milling and sieving procedure. In addition, the solid content (catalyst plus binder) per area of silicon substrate was also an important factor for coating. Figure 5 shows that at 15 wt.% of B/C condition, the optimum solid content per area of silicon substrate was controlled at $0.48\ \text{mg}/\text{cm}^2$ and revealed the best adhesion (13% weight loss). When the solid content was less than $0.48\ \text{mg}/\text{cm}^2$ on the silicon substrate, it would result in large voids between the particles and lead to fewer possibilities for good mechanical anchorage or interfacial interaction between them. Additionally, if the solid coating content was more than $0.48\ \text{mg}/\text{cm}^2$ on the silicon substrate, it would result in more particles aggregating

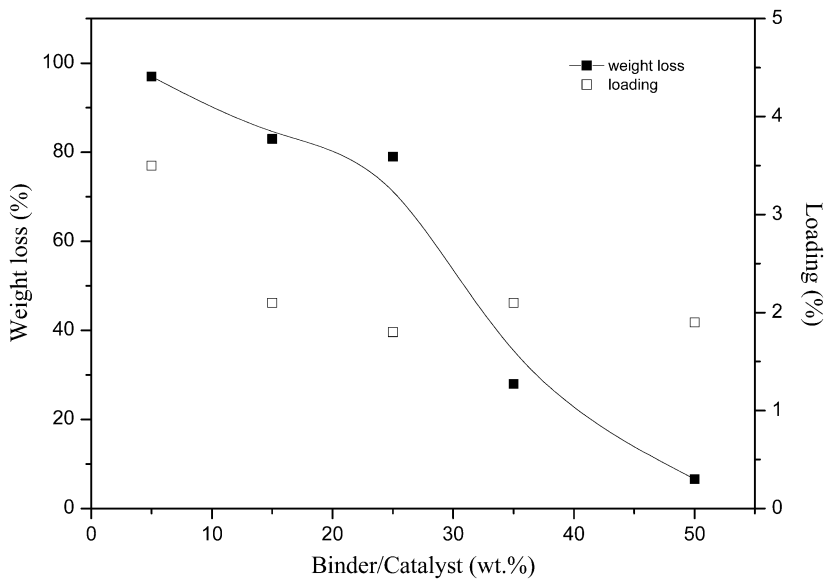


Figure 4. Effect of binder/catalyst ratio on adhesive ability of slurry (binder: 30 wt.% bentonite in boehmite sol at pH 7, catalyst: CMZ) (\square) loading (\blacksquare) weight loss.

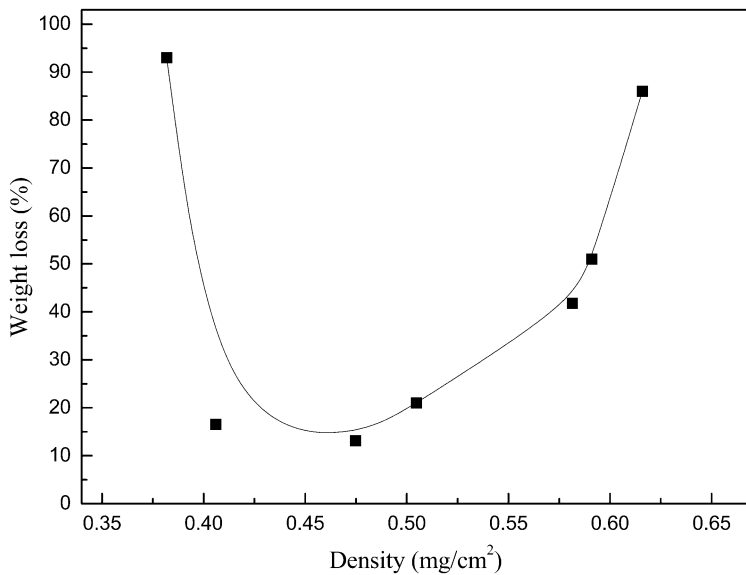


Figure 5. Weight loss pattern of CMZ-B15 at various solid content per area of silicon substrate.

which led to producing cracks during the drying process and reduced adhesion between catalyst and silicon substrate.

Catalysis activity of CMZ-Bx catalysts in the packed-bed reactor

Optimum adhesion conditions of catalyst with binder on the silicon substrate were observed; however, the existence of binder might affect catalyst performance. The temperature profiles of the catalytic performance over CMZ-Bx catalysts are shown in Figure 6. The POM reaction can be initiated over CMZ catalyst at 100 °C after pre-activation, but the initiation temperature would rise with increments in binder. When the percentage of binder was 35%, the initiation temperature was increased to 190 °C. Meanwhile, the C_{MeOH} and S_{H_2} were reduced with increment of binder; i.e., from 98 and 97% to 70 and 80%, respectively, over the catalyst with the binder increasing to 35% at 225 °C.

To realize the effect of binder in the reducibility of the catalyst, the TPR profiles of CMZ-Bx catalysts are also compared in Figure 7. Apparently, CMZ catalyst with no binder exhibited triple peaks in TPR profile at 170, 210, and 230 °C (Figure 7(a)). The

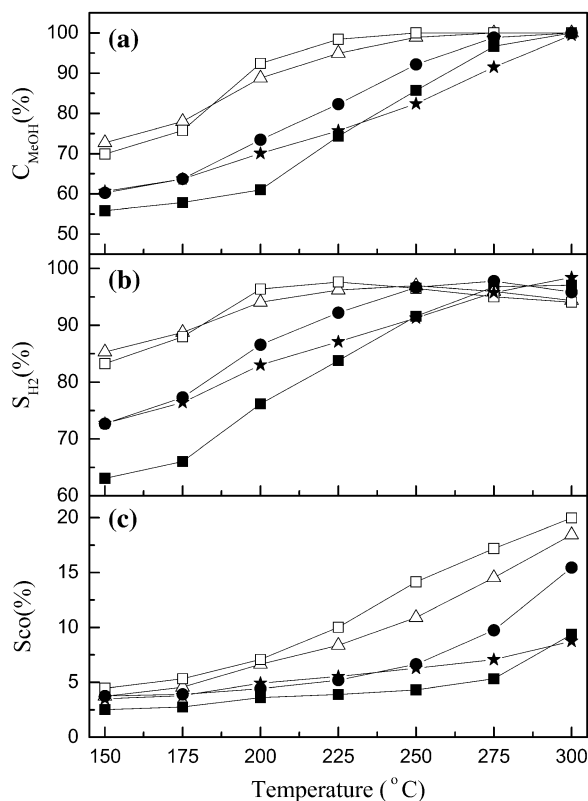


Figure 6. Temperature profiles of catalytic performance (a) conversion of methanol (C_{MeOH}), (b) selectivity of hydrogen (S_{H_2}), (c) selectivity of carbon monoxide (S_{CO}), of the (\square) CMZ, (Δ) CMZ-B5, (\bullet) CMZ-B15, (\star) CMZ-B25, and (\blacksquare) CMZ-B35 in POM reaction in the packed-bed reactor.

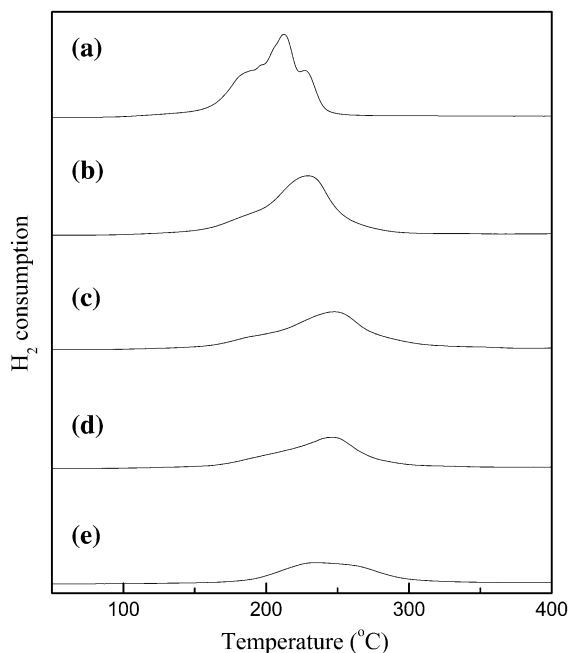


Figure 7. TPR patterns of CMZ catalysts which added different percentages of binder/catalyst (B) (a) CMZ, (b) CMZ-B5, (c) CMZ-B15, (d) CMZ-B25, and (e) CMZ-B35.

first two peaks are attributed to the reduction of isolated CuO and spinel CuMn_2O_4 to metallic copper metal. The last peak at higher temperature could be attributed to the reduction of copper in the interface with support. However, the TPR patterns of CMZ-Bx catalysts, showing a main peak at ca. 250 °C and another broad peak at 170 °C, were obviously different from the CMZ catalyst. In addition, the intensity of peak was reduced by increasing the percentage of binder, which should result from the decrement of copper oxide, manganese oxide, and zinc oxide from adding binder. Moreover, the reduction peak of CMZ-Bx catalysts shifted to a higher temperature. These results reveal that the reducibility of copper oxide would be suppressed with the increment of binder. We supposed that a strong bonding was formed between boehmite and CuO during the calcination process or CMZ catalysts were covered by binder, and therefore, the surface active sites exposed to reactants were reduced, which might result in a worse performance.

The selectivity of hydrogen (S_{H_2}) also decreased with increment of binder. Ogata et al. [30] reported that aluminum oxides were observed after calcining boehmite at temperatures >400 °C. In this study, the X-ray diffraction peak of $\beta\text{-Al}_2\text{O}_3$ at 45° in CMZ-Bx catalysts was found after calcination at 400 °C (shown in Figure 8). The Al_2O_3 binder–CMZ catalyst interactions were anticipated to exert a significant effect upon catalyst performance. Some academic literature [31–33] has revealed that CuO/ZnO/ Al_2O_3 mixed oxides are highly effective in the reverse water–gas shift (RWGS) reaction. This means that addition of Al_2O_3 -based binder (30% bentonite in boehmite) into CMZ catalyst might promote reverse water–gas shift reaction, which might decrease the S_{H_2} .

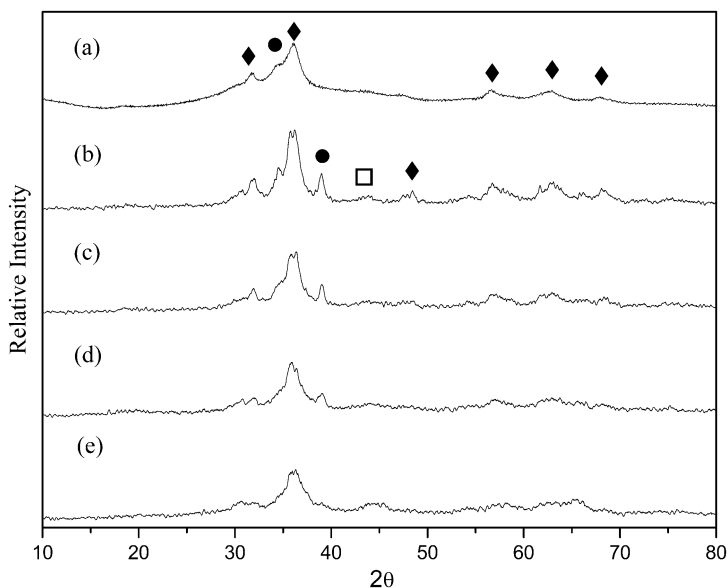


Figure 8. XRD patterns of CMZ catalysts with different percentages of binder/catalyst (B) (a) CMZ, (b) CMZ-B5, (c) CMZ-B15, (d) CMZ-B25, and (e) CMZ-B35 (◆) ZnO, (●) CuO, (□) β - Al_2O_3 .

The micro-reactor test

From previous study, we know that both adhesion and the portion of binder in slurry might affect CMZ performance in the POM reaction. Thus, a catalyst with a diameter of 0.1–1 μm ; solid content per area of silicon substrate at 0.48 mg/cm^2 ; pH 7 of 30% bentonite/boehmite; aging time at 5 h; and 15 wt.% of B/C was selected as the optimum condition for loading into the micro-reactor.

The SEM images of CMZ-B15 coating on the micro-channel reactor are shown in Figure 9. In the cross section, Figure 9(a) indicates that the catalyst layer had few cracks, which might be caused by a sudden shrinking at the initial stage of drying.

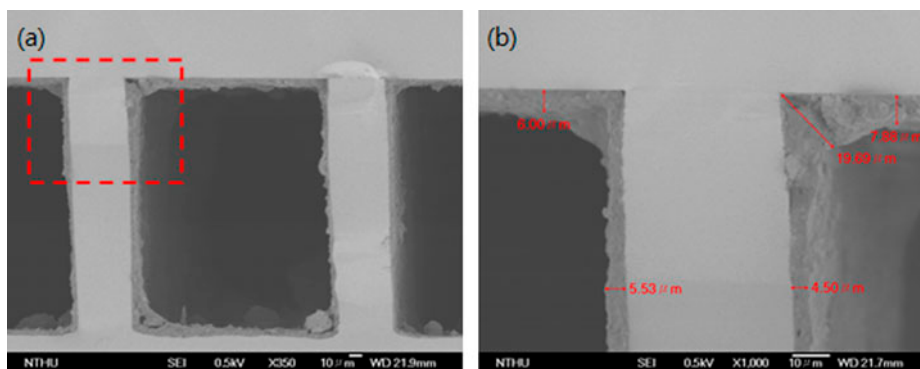


Figure 9. SEM images of (a) CMZ-B15 catalyst coated on the silicon micro-channel and (b) the magnification of image shown in (a).

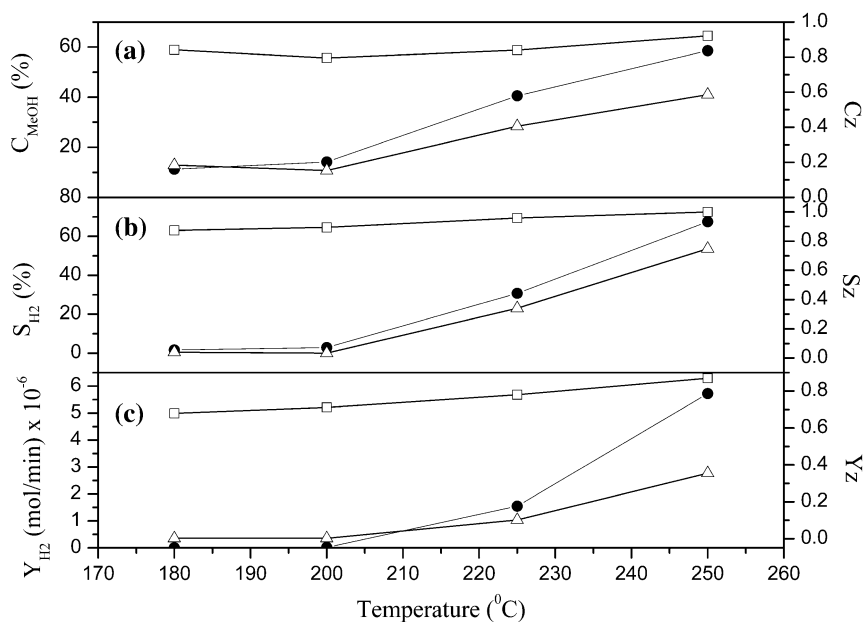


Figure 10. Temperature profiles of (●) catalytic performance (a) conversion of methanol (C_{MeOH}), (b) selectivity of carbon monoxide (S_{CO}), and (c) hydrogen yield (Y_{H_2}) of CMZ-B15 catalyst on micro-channel reactor in POM reaction; and (□, Δ) catalyst performance index [C_Z , S_Z , Y_Z , $z = p$ (□), in the packed-bed reactor (C_p , S_p , Y_p); or $z = m$ (Δ), in the micro-channel reactor (C_m , S_m , Y_m)].

Figure 9(b) shows the thickness of the catalyst layer was ca. 7–19 μm in the edge in the micro-channel cross section. The catalytic performance of CMZ-B15 catalyst on micro-reactor in POM reaction is shown in Figure 10. At 250 $^{\circ}\text{C}$, the C_{MeOH} , S_{H_2} , Y_{H_2} achieved 58%, 67%, 5.7×10^{-6} (mol/min) in micro-channel reactor, respectively. A catalytic performance index shown in Figure 10 was used to compare the reaction performance of the coated catalyst with binder to that of the original catalyst without binder in the packed-bed reactor (C_p , S_p , Y_p) and micro-channel reactor (C_m , S_m , Y_m), respectively. However, the catalyst performance indexes for packed-bed reactor (C_p , S_p , Y_p) are all higher than that for micro-reactor (C_m , S_m , Y_m). This means that the impact of binder for micro-reactor is more critical. In addition, C_p , S_p , and Y_p are more consistent with temperature change, but C_m , S_m , Y_m are very low at low temperature. This means that heat transfer and catalyst loading amounts are much more sensitive factors in the micro-channel reactor system. There are many reasons for this inconsistency, such as different micro-channel reactor designs, the ratio of radius of catalyst cluster to radius of reactor, the catalyst loading method, the amount of catalyst in reactor, and the distribution of catalyst in reactor, all of which complicates the catalyst coating technique in the micro-channel reactor. This should be discussed more in the near future.

Conclusions

The solid content per area of silicon substrate, viscosity, pH, particle size, aging time, ratios of bentonite/boehmite, and binder/catalyst are all important factors for catalyst

coating. However, catalytic activity is suppressed with the increased ratio of binder. Because catalyst particles might be covered with alumina sol, the active sites exposed to reactants are reduced, resulting in poor catalytic performance. Moreover, a higher ratio of the alumina type of binder in catalyst might enhance the RWGS reaction during POM reaction and result in lower S_{H_2} . The optimum adhesion condition for slurry preparation is to maintain the process at 15 wt.% of B/C, 0.48 mg/cm² solid content per area of silicon substrate, 30 wt.% bentonite/boehmite at pH 7, ca. 5 h of aging time, and a catalyst particle diameter of 0.1–1 μ m. The weight loss was 13 wt.%. The catalyst performance index for conversion in packed-bed reactor is ca. 0.8–0.9 and very consistent at all reaction temperatures; however, for micro-channel reactor, it is worse, especially at low temperature. The C_{MeOH} , S_{H_2} , Y_{H_2} achieved were at 58%, 67%, 5.7×10^{-6} (mol/min) on micro-channel reactor at 250 °C, respectively.

Acknowledgements

The authors are grateful for the financial support of this work from the Ministry of Science and Technology of Taiwan (Project Number: MOST 104-3113-E-007-002-).

Disclosure statement

No potential conflict of interest was reported by the authors.

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