

Process intensification by micro-channel reactor for steam reforming of methanol

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Abstract

Catalyst coating in micro-channel reactor for steam reforming of methanol (SRM) is advantageous compared to micro-packed reactor as one part of fuel processor in the application of fuel cell for portable application. In the present study, the performance and pressure drop of catalyst coated and catalyst packed in micro-channel reactor with commercial catalyst in both cases were compared for steam reforming of methanol. The different sols (alumina, zirconia and mixed sol of alumina and zirconia) as a binder for the catalyst have been used to compare the stability and performance. Though the initial performance exhibited by using different sols was same at 290 °C, the performance decay of 20% was observed after 6 days of continuous operation in the case of using zirconia as binder. This may be due to relatively unstable catalyst coating and nonuniform dispersion of catalyst particles on the ZrO₂ binder. Among the different sols, mixed sol of alumina and zirconia comparatively showed better stability and performance. Though the pressure drop in packed catalyst in micro-channel reactor was higher compared to that in catalyst coated micro-channel reactor, the almost complete conversion of methanol in SRM reaction was achieved with packed catalyst in micro-channel reactor at lower temperature.

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Keywords: Catalyst coating; Steam reforming of methanol; Fuel cell; Micro-channel reactor

1. Introduction

Micro-channel reactor with catalyst coating in steam reforming of methanol is a promising candidate for portable electronics to get the compactness in the structure of fuel processor and the advantages with respect to transient behavior, hydrodynamics, heat and mass transfer characteristics.

The main feature of micro-structured reactors is the high surface-area-to-volume ratio in comparison to conventional chemical reactors. Heat-transfer coefficient in this micro-channel reactor is also significantly higher than that for traditional heat exchangers. In addition to heat transport, mass transport is also considerably improved in micro-structured reactors. The flows in the micro-channels are mostly laminar, directed, and highly symmetric. Process parameters such as pressure, temperature, residence time, and flow rate are more

easily controlled in reactions that take place in small volumes. Micro-structured reactors also give opportunities for new production concepts. Depending on demand, more micro-structured reactors or such subunits could be connected in parallel so that the required intermediate products and end-products can be produced in their required amounts [1]. There are two ways of loading catalyst inside the micro-channels. One way is the coating method where catalyst is coated uniformly inside micro-channels with a thickness of micrometer range (Fig. 1a) with the help of some binders. In another method, catalysts of moderate size particles are packed inside the micro-channels. There should be filter type elements in the inlet and outlet points of the micro-channels in order to trap inside the micro-channels so that catalyst should not loss with the produced gas or due to back pressure (Fig. 1b).

The first wall-coated reactor for steam reforming of methanol was used by de Wild and Verhaak [2]. They made the wash-coated plate-fin type heat exchanger. The wash-coated heat exchanger showed better performance as compared to packed beds. The problem in micro-channel reactors lies in low durability of the catalyst. There is limited literature concerning the durability of the catalyst where catalyst deactivation at faster

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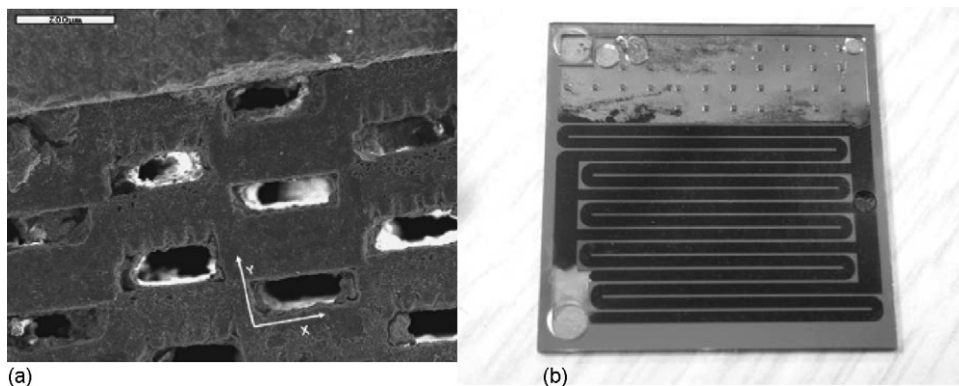


Fig. 1. (a) Catalyst coated ceramic micro-reactors (adopted from Ref. [20]) and (b) catalyst packed micro-reactor (adopted from Ref. [21]).

rate has been reported [2,3]. More catalyst loading and increase in porosity inside the coating are required to increase of the durability of catalyst. There are four types of catalyst used in the literature for SRM reaction associated with catalyst coated micro-channel reactor: $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$, $\text{CuO}/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Cu}/\text{CeO}_2/\text{Al}_2\text{O}_3$ and Pd/ZnO . In the micro-channel reactor, $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst coating was used by Bravo et al. [4], Park et al. [5], Kawamura et al. [6] and Lim et al. [7]. The other types of catalyst like $\text{CuO}/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{Cu}/\text{CeO}_2/\text{Al}_2\text{O}_3$ and Pd/ZnO were used by Zapf et al. [8], Men et al. [9,10] and Pfeifer et al. [11,12]. For $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst, all the groups except Kawamura et al. [6] used commercial catalyst and the coating was made with the slurry of catalyst powder and alumina/zirconia sol. Before coating of the catalyst, the micro-channel sheet was undercoated with the alumina/zirconia sol in order to enhance the adhesion between catalyst powders and the substrate structure. For $\text{CuO}/\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Cu}/\text{CeO}_2/\text{Al}_2\text{O}_3$ catalyst, Zapf et al. [8] and Men et al. [9,10] used the alumina binder prepared by mixing of γ -alumina powder, water, PVA (binder) and acetic acid. Lim et al. [7] used zirconia sols for coating. The preparation of alumina/zirconia sol in all above cases involved nitric acid as a catalyst and this sol may produce non-continuous surface layer on the thermally treated micro-structured metal foils [13]. The reason for the bad adhesion of these coatings probably is the high condensation rate in the sol, leading to a granular fine structure of the gel film. Therefore, there is a need of change of preparation of sol which gives continuous and stable coating at high temperature.

There are mainly three types of coating procedure of catalyst on micro-channels or walls [14]. (1) One method involved the preparation of catalyst by conventional one (or use of commercial catalyst), then making very fine powder by milling followed by making catalyst slurry with different types of binders (alumina/zirconia sol, hydroxyethyl cellulose, hydroxyl propyl cellulose, etc.). The prepared slurry was coated on the undercoated channels/walls by dipping or spray method. The undercoating was made with washcoating of prepared Al_2O_3 or ZrO_2 sol, anodic oxidation (if the substrate is aluminium), making alumina binder with PVA, electrophoretic deposition and chemical vapor deposition (CVD). Among them sol-gel coating was used widely. (2) In another method of coating of catalyst, one comparatively thick layer of support material (like

Al_2O_3 or ZnO or ZrO_2) was coated on the substrate by the above mentioned method followed by wet impregnation of the metal solution in nitrate form or other form. (3) Another method is electroless plating [3]. In this method, a copper based catalyst was prepared on an aluminium plate by the electroless plating, which consisted of displacement plating of zinc, an intermediate plating of metal (iron, nickel, cobalt or tin) and chemical plating of copper. There is also a potentiality of coating of Pd based catalyst based on this method.

Lim et al. [7] showed the high performance with $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ reforming catalyst (ICI 33-5) coating bonded by zirconia. Though zirconia brings the catalyst thermally stable, the pro-longed operation may cause the coating unstable, especially as the preparation method was conventional one (this may lead to high condensation rate leading to formation of particles). The high stability and better performance for Cu based catalyst with $\text{Al}_2\text{O}_3 + \text{ZrO}_2$ support due to well-dispersed copper on large surface of $\text{Al}_2\text{O}_3 + \text{ZrO}_2$ has been reported by Agrell et al. [15] and Chao et al. [16].

With a view to the current status of this type of reactor, the main aim of the present paper is to study the compact methanol steam reformer with high performance and better durability of the system. Three different sols (alumina, zirconia and mixed sol of alumina plus zirconia) have been used for the coating purpose. Another aim of this paper is to compare the performance and pressure drop in between the micro-packed reactor and catalyst coated micro-channel reactor.

1.1. Experimental set-up

Fig. 2 shows the experimental set-up. It mainly consists of liquid feed pump (KdScientific), compact reactor unit comprising vaporizer plate followed by reactor plate, PID temperature controller and facilities for hydrogen flow. The feed rate of the liquid mixture was fixed at 0.01 ml/min except during the pressure-drop measurement in the coated and packed catalyst in the micro-channel reactor where the feed rate was varied from 0.005 to 0.03 ml/min. The water and methanol ratio in the feed was 2:1 as it is generally recommended for getting low concentration of CO. The reactor was heated through electrical heater. Micro-channeled plate made of stainless steel has been used as a reactor considering its high resistivity against corrosion. The

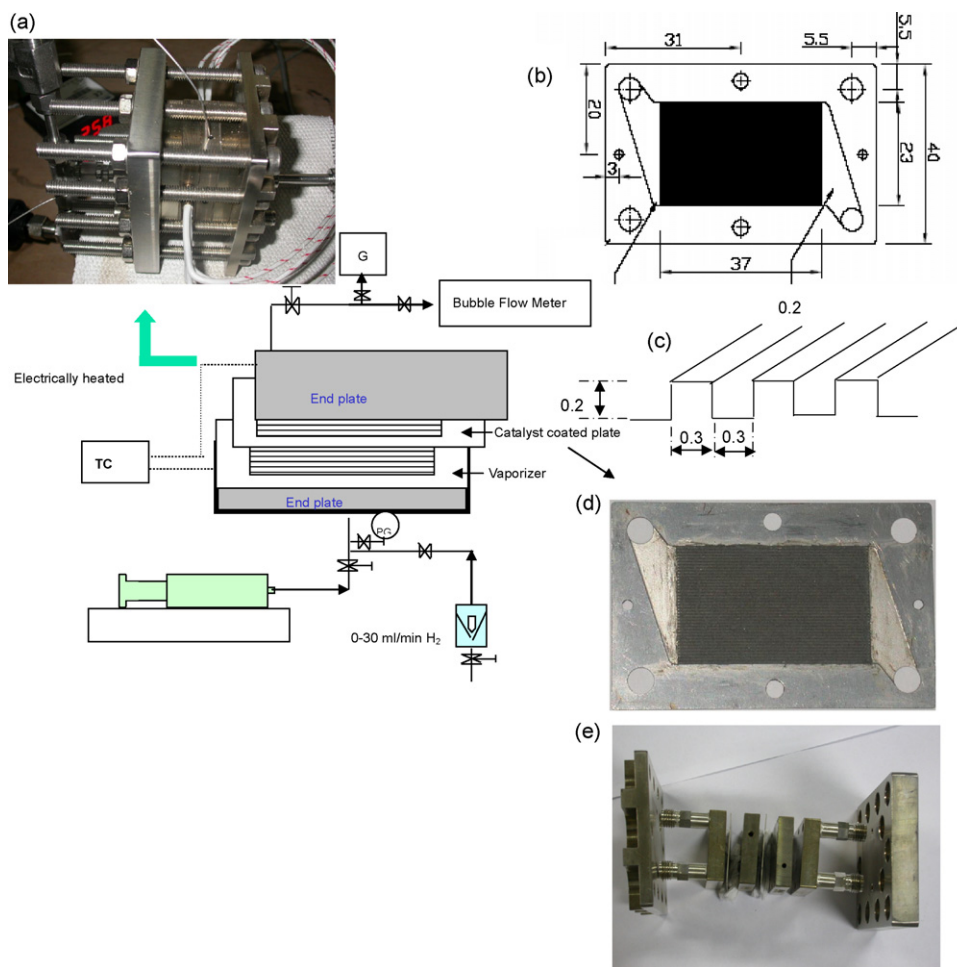
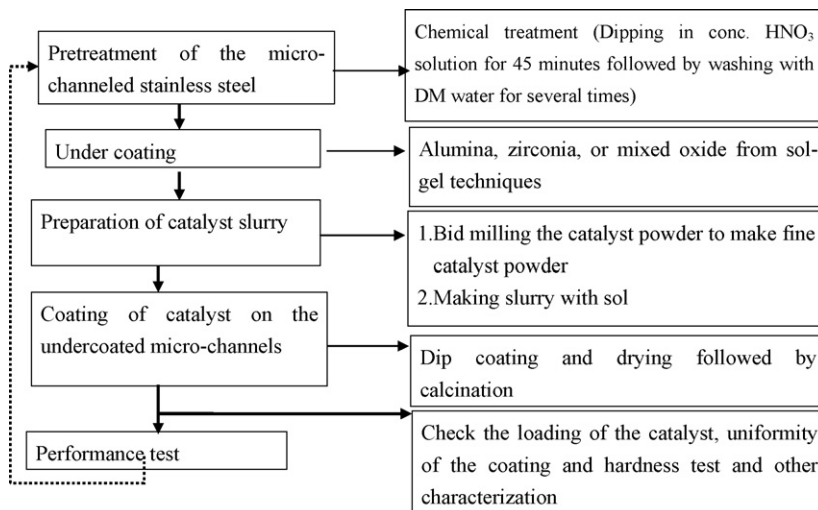


Fig. 2. Experimental set-up. (a) Schematic diagram with the photo of reactor unit, (b) dimension of micro-channeled plate, (c) dimension of the micro-channels, (d) catalyst coated micro-channels and (e) reactor assembly.

dimension of the plate has been given in Fig. 2b (dimensions are in mm). The plate is 62 mm in length and 40 mm in width and each channel is 37 mm in length and total width of 40 channels and 38 fins is 23 mm. The dimension of each channel and fin are provided in Fig. 2c. The channels are created by wet etching

method. The width of each channel and each fin is 300 μm and the depth of the channel is 200 μm. The coating procedure is explained in Scheme 1. The etched channel was pretreated with conc. HNO₃ for removal of chloride ion followed by heat treatment at 500 °C for 1 h and undercoating with the prepared sol.



Scheme 1. Different steps of coating on micro-channeled plate.

The undercoating was made to increase the adhesive strength between the catalyst and the micro-channel wall. The different sols (alumina, zirconia and mixed (alumina and zirconia 1:1 molar ratio) sol) were prepared for that purpose. The undercoating was performed by dipping in 20 wt.% of the prepared sol. After that, it was kept for drying at room temperature followed by in an oven at 80 °C for 5 h. Finally it was calcined at 500 °C for 2 h in order to decompose and eliminate carbon species present in the sol and to achieve high surface area [13]. The different prepared sols were also used for the coating of the commercial catalyst on the micro-channel plate. Catalyst was coated on the micro-channels using dip-coating method by making slurry with the prepared sol and bid-milled catalyst powder after the pretreatment. Initially hydrogen was passed at low flow rate (10 ml/min) for 1 h at 200 °C in order to activate the catalyst. The reactor was heated with two heating plates heated by four cartridge heaters. The temperature of the reactor was regulated by PID controller connected with the cartridge heaters. Three thermocouples of type K, one in the heating plate, one in the outlet of the micro-channelled reactor plate and the last one near the inlet of reactant were fixed in order to monitor the temperature at different parts of the system. The produced gas stream was directed through a cold trap to remove liquid components and then passed to an on-line gas chromatograph for analysis of H₂, CO and CO₂ or to bubble flow meter for measuring flow. The gas chromatograph (Acme 6000M) was equipped with a Carbosphere column and a TCD detector using helium as the carrier gas. The pressure drop across the system was measured through manometer connected in the inlet point and outlet point of the reactor.

1.2. Preparation of sols and catalyst coating

The precursors for alumina and zirconia were aluminium secondary butoxide (Fluka) and zirconium(IV) propoxide (Aldrich), respectively, for the preparation of alumina, zirconia and mixture of alumina and zirconia. The procedure described by Haas-Santo et al. [13] and Zeng [17] was followed for the method of preparation of the sol. During the preparation of sol, the hydrolysis of the alkoxides, which is very fast leading to fine particles in the sol, is protected through the addition of acetylacetone as stabilizer. The acetylacetone was added in the molar ratio of unity with that of alkoxide. Ethyl alcohol was used as

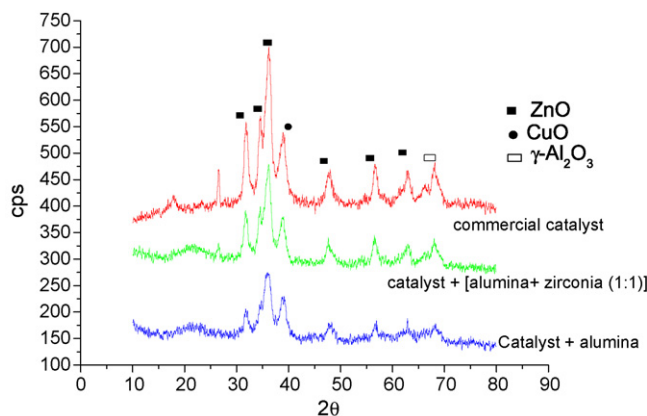


Fig. 3. XRD patterns with commercial catalyst and catalyst slurry with different sol (calcination at 300 °C).

the solvent. The water added was in the molar ratio of 2:1 with respect to alkoxide. The final pH of the solution was maintained at 4.5 by adding nitric acid. The final concentration of the resulting sol was 20 wt.% which produced uniform coating on the stainless steel plate. The viscosity and density of the resulting sol were 3.5 mPa s and 900 kg/m³, respectively. The viscosity and density were measured by Brookfield viscometer (DV-I+ digital viscometer) and specific gravity bottle, respectively. The thickness of the undercoated layer was 5 μm.

Commercial catalyst (Cu/ZnO/Al₂O₃-MDC-3; Sud-Chemie) was used to test the performance of the wall-coated micro-channel reactor. Catalyst size is one of the factors to get uniform coating in the micro-channels. Catalyst was bid milled for 10 h at 3000 rpm to get very fine size of particles. The particle size after ball-milling was found to be 1 μm which was suitable for wash-coating. The particle size and thickness of the catalyst layer were measured by SEM. Then catalyst slurry was prepared by adding the fine catalyst powder to the prepared sol in the weight ratio of 85:15 of catalyst and metal oxide (sol), respectively. The sol did not affect the catalyst chemically which was confirmed from XRD pattern (Fig. 3). This figure only shows the change to smaller crystallite size with the sol compared to that with the original catalyst. Dip coating was used for coating of the catalyst on the micro-channels. A uniform and robust catalyst layer was obtained (Fig. 4a). The amount of coated catalyst on one plate

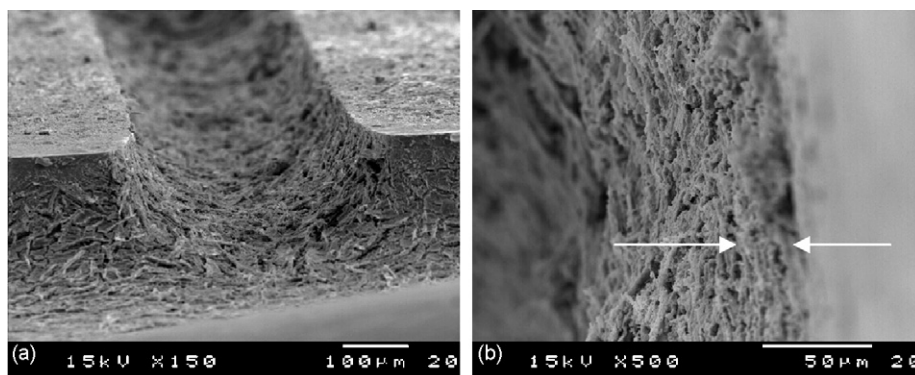


Fig. 4. (a) SEM imaging of catalyst coated micro-channels and (b) thickness of the catalyst coated layer.

is 45 mg (measured by weight difference) and the thickness of the catalyst layer is 25 μm (Fig. 4b).

2. Results

2.1. Catalyst performance with different prepared sols

The catalyst coated micro-channelled plate was dried at room temperature followed by drying at 80 °C for 5 h. Then it was calcined at 300 °C for 2 h. The calcined catalyst coated micro-channelled sheet was housed with the heater and end plate for the performance test (Fig. 2e). Fig. 5 shows that the developed micro reactor exhibited good performance. In the performance test, methanol conversion of 99.3% at 290 °C was obtained (Fig. 5) at the liquid feed rate of 0.01 ml/min (which corresponds to 1.245 h^{-1} as WHSV) with 0.7% CO in the resulting gas with mixed sol (alumina + zirconia) as undercoating and catalyst binder. The production rate of hydrogen was 0.025 mol/h for one micro-channelled plate. Assuming 60% efficiency of fuel cell and 80% utilization of H_2 , the maximum estimated electric power is 0.8 W by the produced hydrogen from micro reformer. Fig. 5 also shows the effect of temperature on methanol conversion and the composition of the produced gases at constant feed rate (0.01 ml/min). As temperature was increased, methanol conversion also increased with the enlarged amount of CO produced with comparatively less amount of H_2 production.

The performance with pure alumina and zirconia sols as undercoating and catalyst binder had also carried out. Alumina and zirconia mixed sol comparatively produced stable coating as the catalyst loss after 6 days operation was only 15 wt.% while comparing the stability and durability of the catalyst coating in continuously operated system for 6 days with different sol as a binder with respect to undercoating and making catalyst slurry. Though the catalyst performance with different sols (Al_2O_3 , ZrO_2 and $\text{Al}_2\text{O}_3 + \text{ZrO}_2$) was almost same initially (especially at higher temperature; Fig. 6), it decreased by 20% with ZrO_2 sol as a catalyst binder. This may be attributed mainly from unstable coating with ZrO_2 sol which results of 40 wt.% loss of catalyst after 6 days operation in addition to catalyst deactivation. The ease of textural control and thermal stability of alumina when

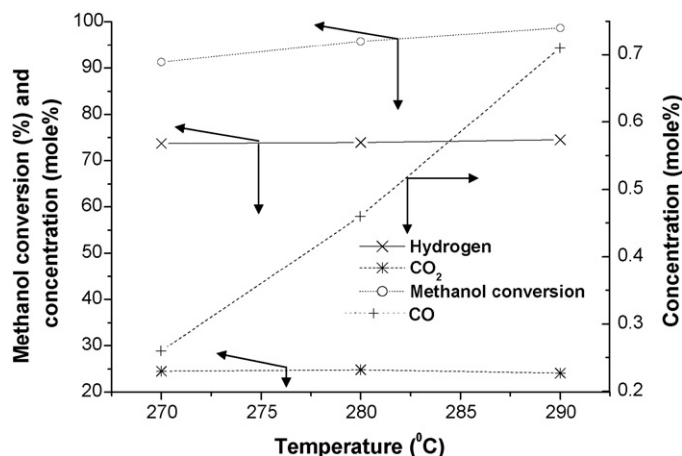


Fig. 5. Composition of reformat vs. temperature (290 °C).

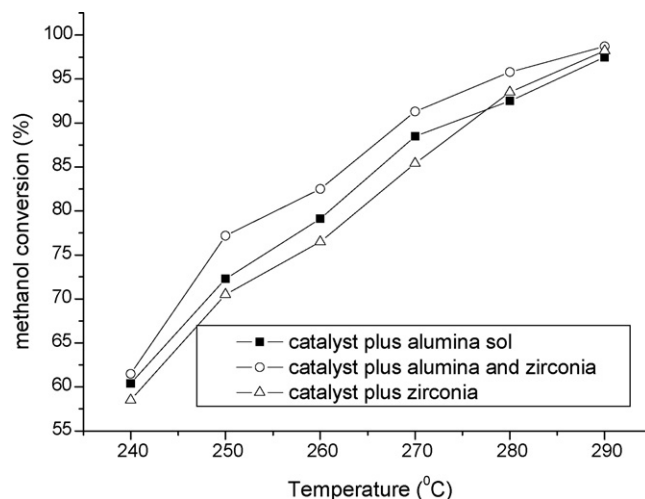


Fig. 6. Methanol conversion at different temperature with different types of catalyst binder (i.e. alumina, zirconia and alumina plus zirconia sol) (feed rate of liquid mixture = 0.01 ml/min).

it was mixed with zirconia may be the other reason for relatively higher performance with alumina and zirconia sol plus catalyst. The thermal stability with mixed sol of alumina and zirconia can be explained by the occurrence of Zr–O–Al phases by migration of zirconium ions to the subsurface layers of the support [18]. Highly dispersed catalyst particles on the highly disordered or amorphous states of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ sol exhibited better performance on long term basis. Though ZrO_2 generally brings the catalyst thermally more stable, the relatively unstable coating with zirconia sol can be explained by the development of crystalline structure which starts at 300 °C and shows tetragonal structure at the calcinations temperature of 500 °C, whereas alumina leads to increase the crystallization temperature of the zirconia and hence to stabilize their structure as coating (Fig. 7).

The temperature shock was applied in the catalyst coated micro-channel reactor after continuous operation for 6 days (i.e. after 146 h) at 290 °C. The temperature cycle was operated in a difference of 1 h from 200 to 330 °C in which it was kept constant at 300 °C for 30 min (Fig. 8). The catalyst-coated reactor

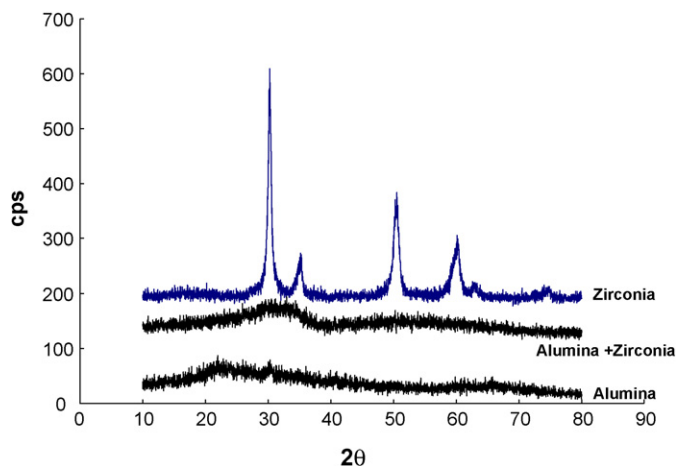


Fig. 7. XRD pattern of different prepared sol showing the crystallinity of zirconia at the calcination temperature of 500 °C.

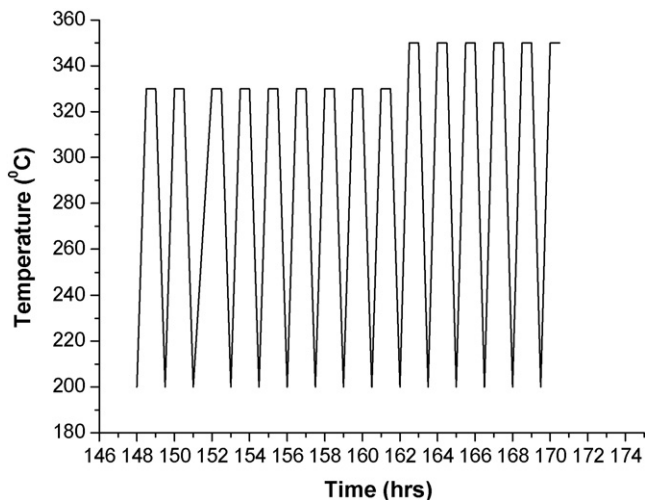


Fig. 8. Temperature cycling after 6 days continuous operation at 290 °C.

exhibited almost constant performance for nine cycles, but the CO concentration increased gradually which was an indication of starting of catalyst deactivation slowly. After that, the temperature range was changed from 200–330 to 200–350 °C in the cycle. The decay behavior was observed instantaneously and by operating more cycles, the catalyst became more deactivated leading to the decrease of methanol conversion and increase of CO concentration in the dry reformat gas (Fig. 9). This may be due to the possibility of sintering the catalyst due to large temperature fluctuation and operating at high temperature. Cu/ZnO/Al₂O₃ catalyst is very temperature sensitive especially if it operates at high temperature (>300 °C). At the temperature higher than 300 °C, there is possibility of sintering of the active phase (Cu) which is responsible for deactivation of the catalyst very fast.

2.2. Comparison of catalyst coated reactor and packed bed reactor

The performance test was also carried out with packing same amount of catalyst (45 mg) on the channels. During the reaction,

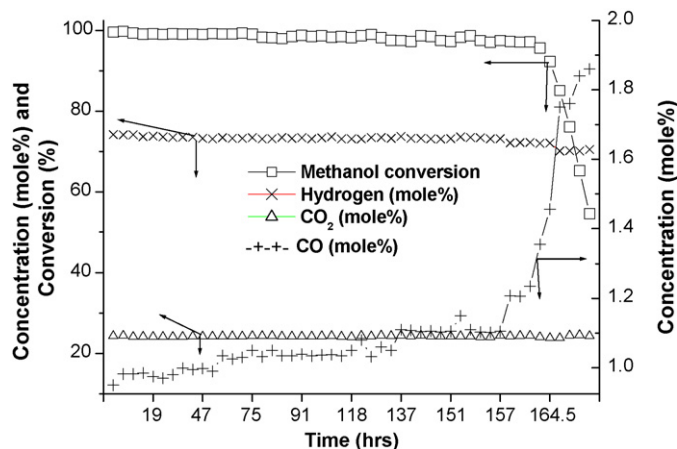


Fig. 9. Methanol conversion and composition of dry reformat gas during the constant temperature operation at 290 °C and temperature cycling.

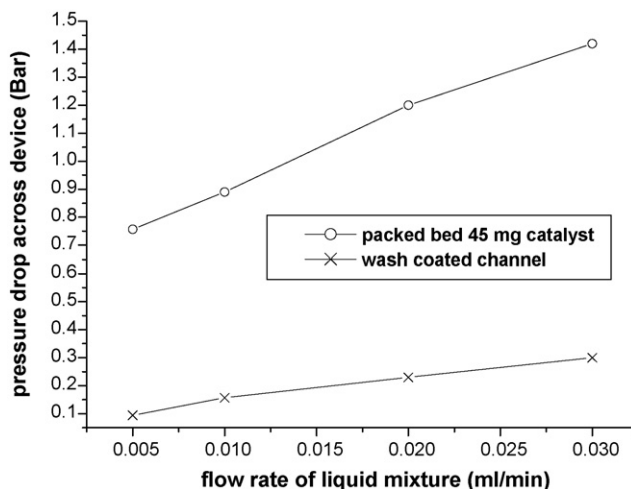


Fig. 10. Pressure drop characteristics in catalyst coated micro-channels and micro-packed bed reactors (temperature = 270 °C).

the catalyst particles were displaced to the outlet of the micro-channelled plate. For a given catalyst loading, the pressure drop in wall-coated micro-channels is six times lower than that in packed-bed reactors (Fig. 10). This may be due to the existence of frictional losses around the packed particulates in addition to skin friction while the losses in catalyst-coated micro-channels would be primarily skin frictional losses. The almost complete conversion was achieved with wall coated micro-channel reactor at 290 °C whereas for micro-channel reactor with catalyst packed, that was 270 °C (Fig. 11). The relatively inferior performance with wall coated micro-channel reactors may be associated with the effectiveness of the catalyst particles since the addition of alumina + zirconia sol to the catalyst leads to the reduction of the effective surface area exposed to reactants, whereas the effective surface area exposed to reactants is unchanged for the micro-packed micro-channel reactor [19]. The effective amount of catalyst also decreases when the catalyst was mixed with sol for coating purposes. This results relatively low amount of catalyst loading inside the micro-channels.

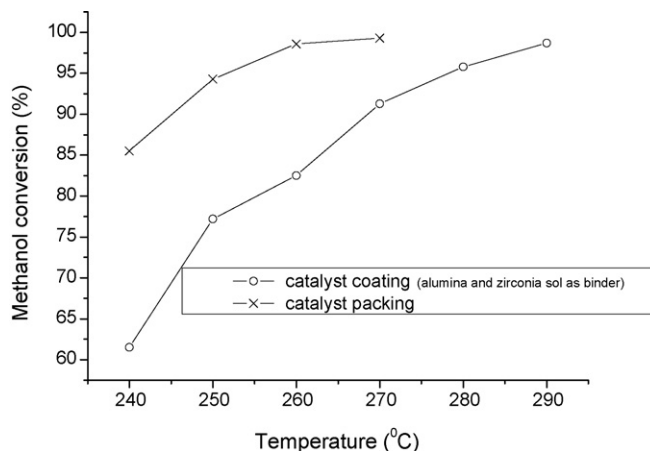


Fig. 11. Comparison of performance with catalyst (micro-packed bed) and catalyst plus sol (catalyst coated micro-channels).

Consequently it exhibited lower performance compared to that in micro-packed bed reactor operating at the same temperature.

3. Conclusions

A successful coating of catalyst was made on micro-channeled stainless steel plate. Different types of sols were used for the purpose of coating of the catalyst. Mixed sols ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) showed relatively stable coating in comparison to other sols (Al_2O_3 and ZrO_2). The durability of the catalyst coating was tested by continuous 6 days operation.

Though the performance with the three different prepared sol plus catalyst was initially same, the performance with ZrO_2 sol plus catalyst was decreased after 6 days operation by 20%. The comparison of catalytic activity and pressure drop was carried out between packed catalyst in micro-channel reactor and catalyst coated micro-channel reactor. Though the superiority with catalyst coated micro-channel reactor was observed in terms of pressure drop across system compared to that in micro-packed reactor, the catalyst performance was at higher side with micro-packed reactor.

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References

- [1] K. Jahnisch, V. Hessel, H. Lowe, M. Baerns, Chemistry in microstructured reactors, *Angew Chem. Int. Ed.* 43 (2004) 406–446.
- [2] P.J. de Wild, M.J.F.M. Verhaak, Catalytic production of hydrogen from methanol, *Catal. Today* 60 (2000) 3–10.
- [3] C. Fukuhara, H. Ohkura, Y. Kamata, Y. Murakami, A. Igarashi, Catalytic properties of plate-type copper-based catalysts, for steam reforming of methanol, on an aluminum plate prepared by electroless plating, *Appl. Catal. A: Gen.* 273 (2004) 125–132.
- [4] J. Bravo, A. Karim, T. Conant, G.P. Lopez, A. Datye, Wall coating of a $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ methanol steam reforming catalyst for micro-channel reformers, *Chem. Eng. J.* 101 (2004) 113–121.
- [5] G.-G. Park, D.J. Seo, S.-H. Park, Y.-G. Yoon, C.-S. Kim, W.-L. Yoon, Development of microchannel methanol steam reformer, *Chem. Eng. J.* 101 (2004) 87–92.
- [6] Y. Kawamura, N. Ogura, T. Yamamoto, A. Igarashi, A miniaturized methanol reformer with Si-based microreactor for a small PEMFC, *Chem. Eng. Sci.* 61 (2006) 1088–1097.
- [7] M.S. Lim, M.R. Kim, J. Noh, S.I. Woo, A plate-type reactor coated with zirconia-sol and catalyst mixture for methanol steam-reforming, *J. Power Sources* 140 (2005) 66–71.
- [8] R. Zapf, C. Becker-Willinger, K. Berresheim, H. Bolz, H. Gnaser, V. Hessel, G. Kolb, P. Lob, A.-K. Pannwitt, A. Ziogas, Detailed characterization of various porous alumina-based catalyst coatings within microchannels and their testing for methanol steam reforming. Part A, *Trans. IChemE* 81 (2003) 721–729.
- [9] Y. Men, H. Gnaser, R. Zapf, V. Hessel, C. Ziegler, Parallel screening of $\text{Cu}/\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts for steam reforming of methanol in a 10-channel micro-structured reactor, *Catal. Commun.* 5 (2004) 671–675.
- [10] Y. Men, H. Gnaser, R. Zapf, V. Hessel, C. Ziegler, G. Kolb, Steam reforming of methanol over $\text{Cu}/\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts in a microchannel reactor, *Appl. Catal. A: Gen.* 277 (2004) 83–90.
- [11] P. Pfeifer, K. Schubert, M.A. Liauw, G. Emig, Electrically heated microreactors for methanol steam reforming. Part A, *Trans. IChemE* 81 (2003) 711–720.
- [12] P. Pfeifer, K. Schubert, M.A. Liauw, G. Emig, PdZn catalysts prepared by washcoating microstructured reactors, *Appl. Catal. A: Gen.* 270 (2004) 165–175.
- [13] K. Haas-Santo, M. Fichtner, K. Schubert, Preparation of microstructure compatible porous supports by sol–gel synthesis for catalyst coatings, *Appl. Catal. A: Gen.* 220 (2001) 79–92.
- [14] A. Kundu, Y.G. Shul, D.H. Kim, Methanol reforming processes, in: T.S. Zhao, K.D. Kreuer, T.V. Nguyen (Eds.), *Advances in Fuel Cells Book Series*, vol. 1, no. 7, Elsevier Publications, 2007, pp. 417–470.
- [15] J. Agrell, H. Birgersson, M. Boutonnet, I. Melian-Cabrera, R.M. Navarro, J.L.G. Fierro, Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO_2 and Al_2O_3 , *J. Catal.* 219 (2003) 389–403.
- [16] W. Cao, G. Chen, S. Li, Q. Yuan, Methanol-steam reforming over a $\text{ZnO}-\text{Cr}_2\text{O}_3/\text{CeO}_2-\text{ZrO}_2/\text{Al}_2\text{O}_3$ catalyst, *Chem. Eng. J.* 119 (2006) 93–98.
- [17] Q. Zeng, Fabrication of Al_2O_3 -coated carbon fiber-reinforced Al-matrix composites, *J. Appl. Polym. Sci.* 70 (1998) 177–183.
- [18] S. Damyanova, P. Grange, B. Delmon, Surface characterization of zirconia-coated alumina and silica carriers, *J. Catal.* 168 (1997) 421–430.
- [19] O.J. Kwon, S.-M. Hwang, J.-G. Ahn, J.J. Kim, Silicon-based miniaturized-reformer for portable fuel cell applications, *J. Power Sources* 156 (2006) 253–259.
- [20] T. Conant, A. Karim, S. Rogers, S. Samms, G. Randolph, A. Datye, Wall coating behavior of catalyst slurries in non-porous ceramic microstructures, *Chem. Eng. Sci.* 61 (2006) 5678–5685.
- [21] A. Kundu, J.H. Jang, H.R. Lee, S.-H. Kim, J.H. Gil, C.R. Jung, Y.S. Oh, MEMS-based micro-fuel processor for application in a cell phone, *J. Power Sources* 162 (2006) 572–578.