

Development of microchannel methanol steam reformer

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Abstract

Microchannels were patterned on the metal sheets and fabricated to make a reformer and vaporizer unit. Three types of patterned sheets were prepared to construct a base structure. The aspect ratio of microchannels can be regulated by changing the number of microchannel sheets. Catalyst was deposited inside the microchannel of a reformer unit. Electric heaters provide heat for the endothermic reaction and the vaporization of liquid fuel. A vaporizer and a reformer unit were connected serially to make a proto-type microreactor. The dimensions of the reformer and vaporizer unit excluding fittings were about 70 mm × 40 mm × 30 mm, respectively. The steam reforming of methanol was conducted with the microreactor. The performance of the microreactor was investigated at various operating conditions. The developed fuel processor generates enough hydrogen for power output of 15 We.

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1. Introduction

Small polymer electrolyte membrane fuel cells (PEMFCs) can be an attractive power source for portable electronic devices. In order to apply fuel cell systems to portable devices, it is essential to develop a small and lightweight hydrogen supplier. Candidates for the hydrogen supplying units involve metal hydrides, chemical hydrides and hydrocarbon fuel reformer. Because of advantages such as high energy density and instant recharge of liquid fuel, a fuel processor can be a competitive hydrogen supplying unit for this type of fuel cells.

Methanol is an attractive fuel because of its low reforming temperatures, good miscibility with water and low content of sulfur compounds. In general, a fuel processor for PEMFCs consists of a fuel vaporizer, reformer, carbon monoxide reducer and catalytic combustor. Microchannel technologies can miniaturize and integrate this complicated system. Recently, microchannel fuel processors have been developed by several investigations [1–6]. Holladay et al. developed an integrated methanol fuel reformer system which was composed of two vaporizers/preheaters, a reformer, catalytic combustor, and heat exchanger [1]. They used 316 stainless steel as a substrate for the fabrication of integrated system. Kawamura et al. developed a micro fuel processor

which consisted of vaporizer and reformer [3]. They used micro-patterned silicon wafers to fabricate sub unit. Tasic et al. evaluated an integrated fuel processor consisted of a ceramic steam reformer and catalytic chemical combustor [4]. The objective of this study is to develop a micro fuel processor which consisted of a vaporizer and reformer. Microchannels were patterned on the stainless steel sheets and fabricated to make a reformer and vaporizer unit. Catalyst was deposited inside the microchannel of the reformer unit. Electric heaters provided heat for the endothermic reaction and the vaporization of liquid fuel. A vaporizer and a reformer unit were connected serially to make a proto-type microreactor. The steam reforming of methanol was conducted with the microreactor. The maximum throughput of the fuel processor was determined.

2. Experimental

2.1. Fabrication of microchannel vaporizer and reformer

A stainless steel sheet was used to fabricate the components of a microchannel reactor and vaporizer. Microchannels were patterned on the metal sheets using a wet chemical etching. Three types of patterned sheets were prepared to construct a base structure. Fig. 1 shows individual parts of a base structure. The thickness of metal sheet was 200 μm.

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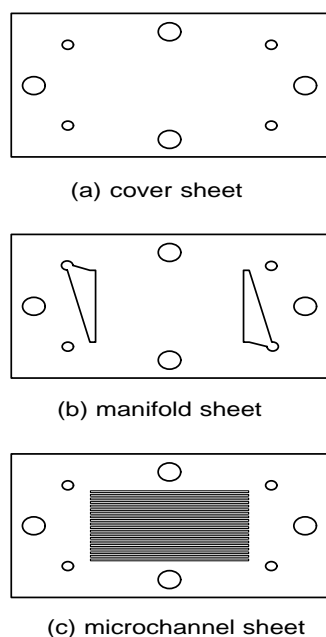


Fig. 1. Individual pattern of metal sheets: (a) cover sheet; (b) manifold sheet; and (c) microchannel sheet.

A cover sheet has four holes which act as a flow path. A manifold sheet has two holes for flow path and two triangular manifolds for enhancing the uniform distribution of flow through each microchannel. A microchannel sheet has four holes for flow path and 20 parallel channels of a rectangular shape on it. The microchannels are 500 μm wide, 200 μm in deep and 33 mm long. The aspect ratio of channels can be regulated by changing the number of microchannel sheets. To enhance the flow distribution among microchannels, the number of manifold sheets was determined by measuring the pressure drop of the assembled structure for a given dimension of microchannels. The configuration of a base structure consists of two cover sheets, three manifold sheets and three microchannel sheets. In this configuration, the depth of microchannels was 600 μm . A representative configuration of stacking is illustrated in Fig. 2.

A commercial Cu/ZnO/Al₂O₃ catalyst was used for steam reforming of methanol. The catalyst slurry for reformer was made of ICI Syntex 33-5 catalyst, 20 wt.% Alumina sol (NYACOL[®] AL20DW colloidal alumina, PQ Corporation), distilled water and 2-propanol. Alumina sol was used as a binder with solid contents 15 wt.%. A cover sheet and three microchannel sheets were stacked into single structure to prepare the substrate for catalyst coating. In order to enhance the adhesion between catalyst powders and the substrate structure, alumina-sol was undercoated on the surface of microchannel and dried at 60 °C. In the microchannel coating, the surface tension of solvent is very important. So, we added small amounts of 2-propanol to reduce the surface tension. Then, the catalyst slurry was well stirred for 2 h. The suspension of powdered catalysts and alumina-sol was coated on the preformed alumina layer. After drying in air, catalyst

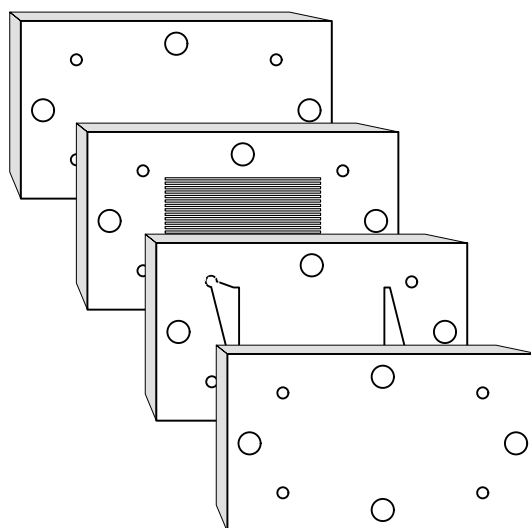


Fig. 2. Representative configuration of base structure.

coated metal structure was calcined at 350–400 °C. The other part of reformer structure which consisted of three manifold sheets and a cover sheet laid upon a coated structure and assembled. The microchannel vaporizer has the same configuration as that of reformer. Both the reactor and vaporizer units were composed of three base structures and two end-plates for housing. The assembling method of patterned metal sheets and end plates was similar with that of Rouge et al. [7]. The dimensions of the reformer and vaporizer unit excluding fittings were about 70 mm \times 40 mm \times 30 mm, respectively. Fig. 3 shows the assembled unit of reformer. Both sides of end-plates have two holes for rod-type electric heaters, respectively.

2.2. Experimental set-up

Fig. 4 shows the schematic diagram of experimental set-up. Rod-type heaters were inserted into end-plates to supply heat for a vaporization and endothermic reaction. The reduction of catalyst was performed by flowing H₂/N₂ stream at 280 °C. The hydrogen concentration of gas mixtures was 10% for the reduction. After 2 h of reduction, Steam reforming of methanol was conducted in the temperature range of 200 to 260 °C. The temperature of vaporizer maintained at 120 °C using electric heaters and a controller. A syringe pump supplied the mixture of methanol and water to the vaporizer. The vaporized fuel was reacted inside a reformer and converted into a hydrogen rich stream. The liquid components in the produced stream were separated using a cold trap maintained at 5 °C. The flow rate of reformed gas was measured by a soap-bubble meter. The composition of dry reformed gas was analyzed by a gas chromatograph (Agilent 6890N). The temperature of reformer unit was varied to measure the activity of catalyst. The flow rate and composition of feed mixture were varied to investigate the optimum reaction condition.

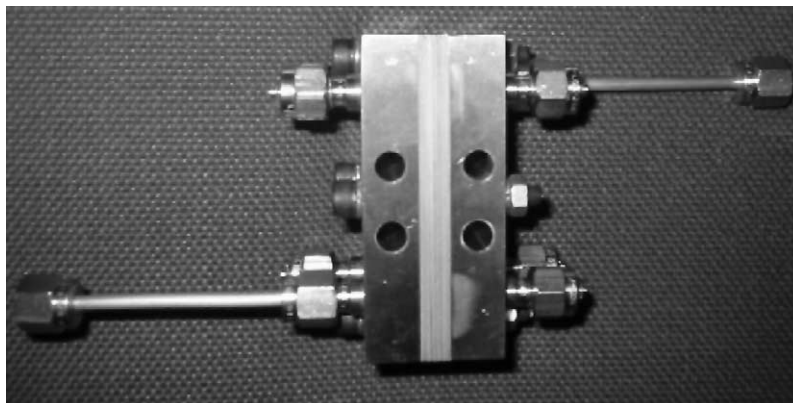


Fig. 3. Photograph of the assembled reformer.

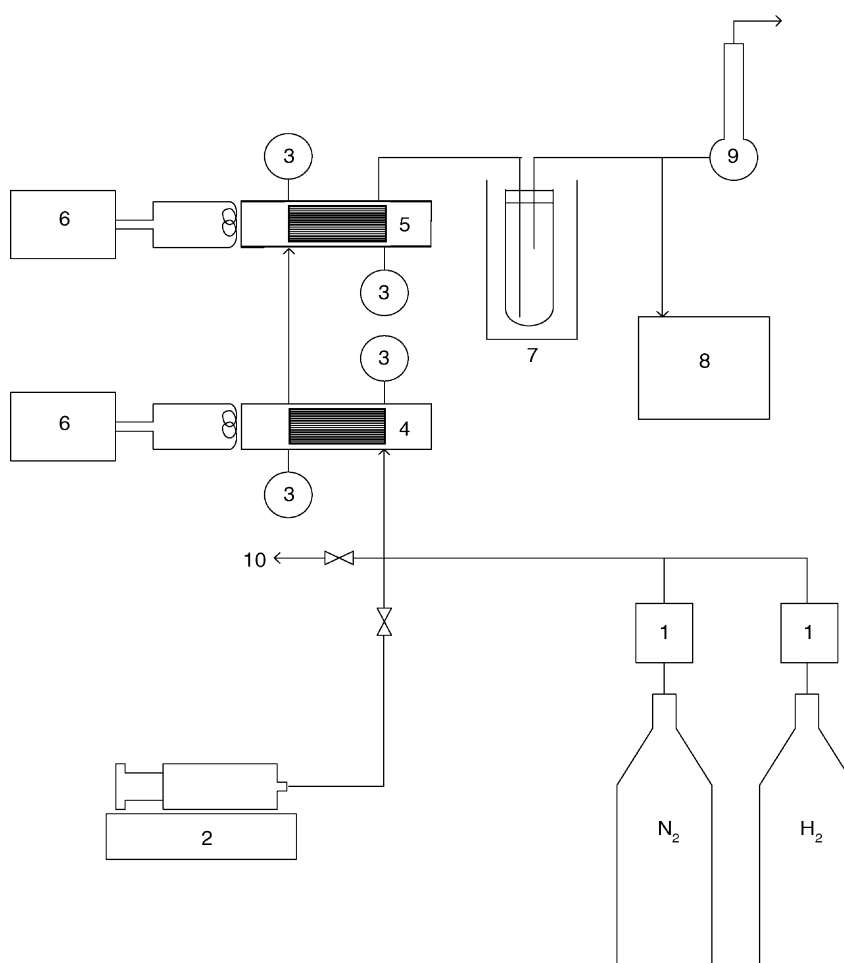


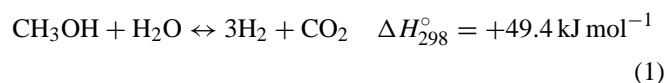
Fig. 4. Schematic diagram of experimental set-up. (1) Flow meter; (2) syringe pump; (3) thermocouples; (4) fuel vaporizer; (5) reformer; (6) electric heater and controller; (7) cold trap; (8) gas chromatography; (9) soap-bubble meter; (10) purge line.

3. Results and discussion

3.1. Effect of temperature on a composition of produced gas

Methanol and steam can be converted into a hydrogen-rich stream in the presence of Cu/ZnO/Al₂O₃ catalyst during

the reforming process. The three main reactions for this combination of reactants and products can be written by the following equations [8–10].





Eq. (1) is the algebraic summation of Eqs. (2) and (3). Eq. (2) represents methanol decomposition. Eq. (3) represents a water-gas shift reaction. The major products of this process are H_2 and CO_2 . The minor quantities of CO are also produced [11]. For the application of PEMFCs, the composition of produced gas requires high concentration of H_2 and low concentration of CO . The composition of produced gas at different temperatures is shown in Fig. 5. The concentrations of H_2 increased from 72 to 75 vol.% as the reaction temperature decreased from 260 to 200 °C. The steam to carbon ratio (moles of water/moles of methanol) of feed mixtures did not show much influence on the concentration of H_2 and CO_2 . The concentration of CO increased from 0.17 to 1.6 vol.% as the reforming temperatures increased from 200 to 260 °C. The concentration of CO also increased as the steam to carbon ratio decreased. The slight raise of CO concentration is due to a reverse water-gas shift reaction. For a given temperature, CO concentration can be reduced by changing the steam to carbon ratio. The forward reaction of Eq. (3) is more favorable at the condition of a high content of water in reactant and low temperature. For the application of fuel cells, even a trace of CO (>10 ppm) in the produced gas can lower the performance of PEMFCs significantly. An additional CO -clean up unit is required to reduce CO concentration.

3.2. Effect of temperature on a production rate of H_2

Fig. 6 illustrates the effect of reaction temperature on a production rate of H_2 . The production rate of H_2 was in-

creased with increasing reaction temperature and decreasing steam to carbon ratio. The increase of H_2 production rate is due to the increased activity of catalyst at higher temperature. Steam to carbon ratio showed little effect on methanol conversion in the range of experiments. However, the increase of steam to carbon ratio means the decrease of methanol feed rate at a constant feed rate of liquid fuel. Therefore the H_2 production rate decreased at higher steam to carbon ratio. The highest production rate was achieved at 260 °C and steam to carbon ratio of 1.1 for a constant feed flow rate of 6 cm^3/h . The production rate of H_2 was 0.252 mole/h at this operating condition. Assuming 60% efficiency of fuel cell and 80% utilization of H_2 , the estimated electric power corresponded to 8 We.

3.3. Effect of feed flow rate on a methanol conversion and production rate of H_2

The effect of feed flow rate on a methanol conversion was investigated to determine the maximum throughput of the developed microchannel steam reformer. The steam to carbon ratio was kept constant at 1.1 (moles of water/moles of methanol) to achieve the highest production rate of H_2 . As shown in Fig. 7, methanol conversions were decreased as the reaction temperature decreased. Therefore, a higher temperature is desirable to get higher methanol conversions. However, the forward reaction of Eq. (3) is exothermic and more favorable at a lower temperature. The hydrogen selectivity slightly decreased because of a reverse water-gas shift reaction at higher temperatures. Considering the effect of reaction temperature, there is a trade-off relationship between methanol conversion and H_2 selectivity. The H_2 production rate was increased with increasing feed flow rate.

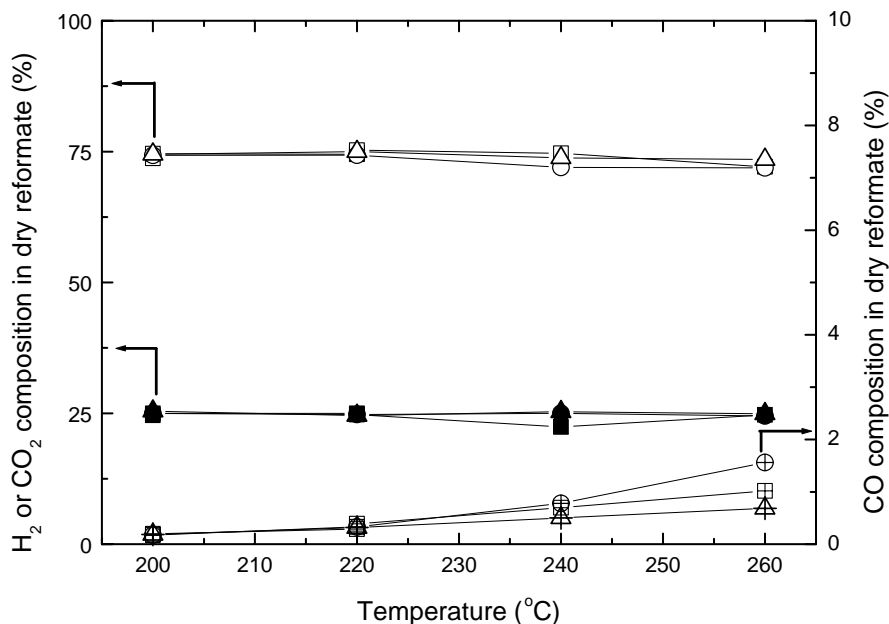


Fig. 5. Composition of dry reformat as a function of reaction temperature. Feed flow rate of methanol and water mixture = 6 cm^3/h , H_2 , open symbols; CO_2 , solid symbols; CO , crossed symbols. Experimental data: (○) S/C = 1.1; (□) S/C = 1.5; (△) S/C = 2.0.

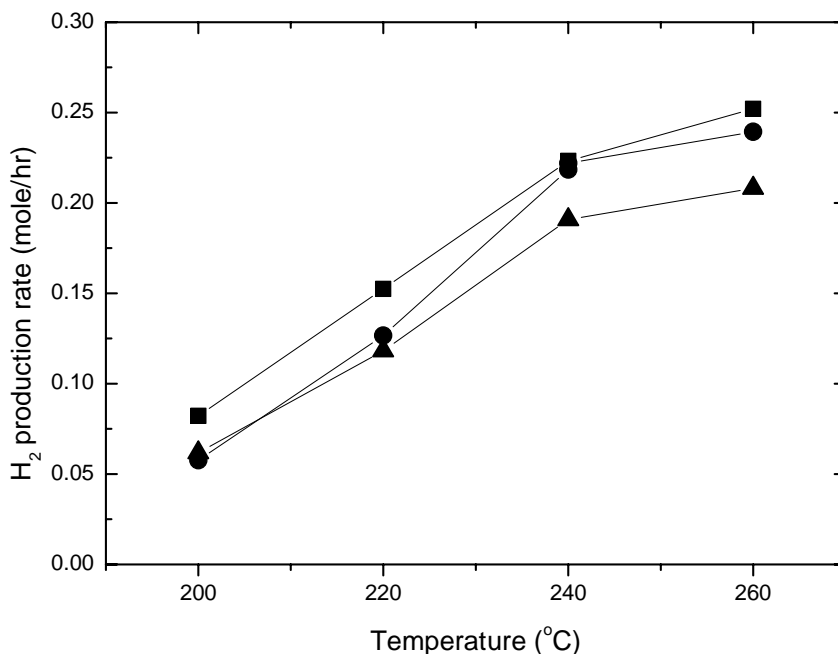


Fig. 6. H₂ production rate as a function of reaction temperature. Feed flow rate of methanol and water mixture = 6 cm³/h. Experimental data: (■) S/C = 1.1; (●) S/C = 1.5; (▲) S/C = 2.0.

The methanol conversion increased as the feed flow rate decreased until the feed flow rate of 6 cm³/h. However, the methanol conversion slightly decreased with decreasing a feed flow rate in the range of 3–6 cm³/h. A lack of uniformity in the flow distribution reduced the methanol conversion at a feed flow rate of 3 cm³/h. When the temper-

ature was 260 °C, the maximum flow rate of feed may be restricted to 12 cm³/h in order to maintain 90% conversion at least. In this operating condition, the production rate of H₂ was 0.498 mole/h and the estimated power output was 15 We. The base case performance and operating conditions were presented in Table 1.

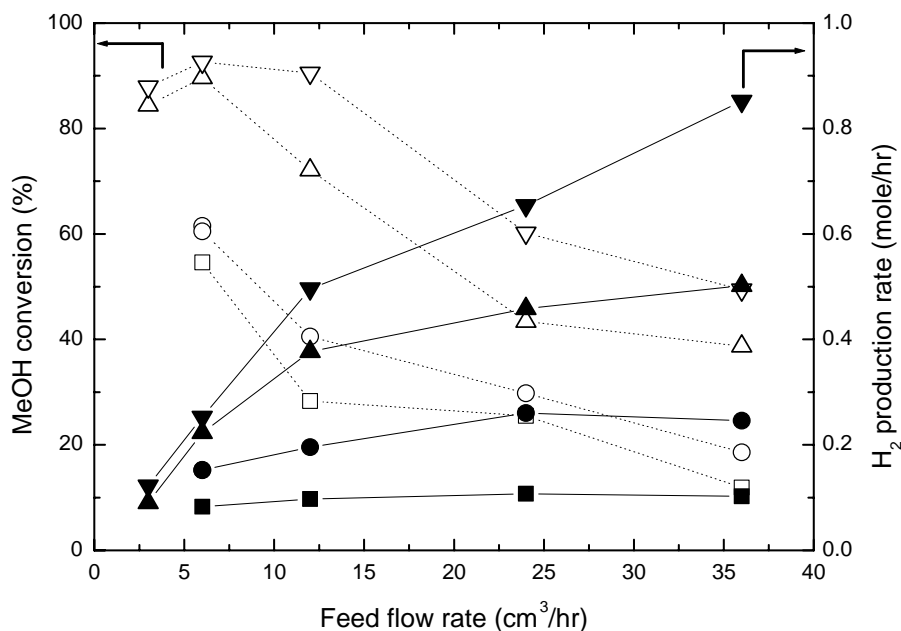


Fig. 7. Performance of reactor/vaporizer as a function of feed flow rate S/C = 1.1. Methanol conversion (%): open symbols; hydrogen production rate (mol/h): solid symbols. Experimental data: (□) 200 °C; (○) 220 °C; (△) 240 °C; (▽) 260 °C.

Table 1
Base case performance and operating conditions of developed reformer

| | |
|--|--|
| Vaporizer temperature | 120 °C |
| Reformer temperature | 260 °C |
| Pressure | 1 atm |
| Steam to carbon ratio, S/C | 1.1 |
| Feed flow rate | 12 (cm ³ /h) |
| Methanol conversion | >90% |
| Gas composition, dry basis | 73.4% H ₂ 25% CO ₂ 1.6% CO |
| H ₂ production rate | 0.498 (mol/h) 186 sccm 33 Wt |
| Estimated electric power assumptions: fuel cell efficiency = 60%, H ₂ utilization = 80% | 15 We |

4. Conclusion

The developed micro fuel processor consisted of a vaporizer and reformer unit. The dimensions of both units are almost same (70 mm × 40 mm × 30 mm). Rod-type electric heaters were suitable to control the temperature of each unit, respectively. The performance of the microreactor was investigated at various operating conditions. The developed fuel processor generates enough hydrogen for power output of 15 We. Further investigations are required for the fabrication of catalytic combustor, CO-cleanup unit and thermal integration of the total system.

Acknowledgements

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References

- [1] J.D. Holladay, E.O. Jones, M. Phelps, J. Hu, *J. Power Sources* 108 (2002) 21.
- [2] N. Ogura, Y. Kawamura, A. Igarashi, in: *Proceedings of 2002 Fuel Cell Seminar, Palm springs, CA, 18–21 November, 2002*, p. 243.
- [3] Y. Kawamura, N. Ogura, T. Katsumata, A. Igarashi, in: *Proceedings of 2002 Fuel Cell Seminar, Palm springs, CA, 18–21 November, 2002*, p. 699.
- [4] S. Tasic, D. Gervasio, R. Koripella, S.P. Rogers, S. Samms, J. Hallmark, in: *Proceedings of 2002 Fuel Cell Seminar, Palm springs, CA, 18–21 November, 2002*, p. 725.
- [5] M. Schuessler, M. Portscher, U. Limbeck, *Catal. Today* 2941 (2003) 1.
- [6] J.D. Holladay, E.O. Jones, M. Phelps, J. Hu, *J. Power Sources* 108 (2002) 21.
- [7] A. Rouge, B. Spoetzl, K. Gebauer, R. Schenk, A. Renken, *Chem. Eng. Sci.* 56 (2001) 1419.
- [8] B.A. Pepply, J.C. Amphlett, L.M. Kearns, R.F. Mann, *Appl. Catal. A Gen.* 179 (1999) 21.
- [9] S.P. Asprey, B.W. Wojciechowski, B.A. Pepply, *Appl. Catal. A Gen.* 179 (1999) 51.
- [10] X. Jhang, P. Shi, *J. Mol. Catal. A Chem.* 3782 (2002) 1.
- [11] J.A. Christiansen, *J. Am. Chem. Soc.* 43 (1921) 1670.