

Hydrogen Production from Carbon Dioxide Reforming of Methane over Ni/Zeolite Catalysts: Effect of an Upscale Synthesis

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Abstract: The effect of an upscale synthesis of K-H zeolite has been investigated on carbon dioxide reforming of methane. The up-scaled synthesis using a one-step sol-gel process by microwave heating technique from alumatrane and silatrane has been performed in triple and quadruple as much as the size of regular synthesis with a fixed composition of SiO_2 : $0.1\text{Al}_2\text{O}_3$: $3\text{K}_2\text{O}$: $410\text{H}_2\text{O}$. 8% Ni loading catalysts were prepared by the method of incipient wetness impregnation. Activity testing has been performed with packed bed reactor equipped with a gas chromatograph at a reaction temperature of 700°C under atmospheric pressure and the reactant molar ratio of CH_4 : CO_2 of 1. The results revealed that the up-scaling in K-H zeolite synthesis significantly affected on the methane conversion and slightly changed H_2 selectivity.

Keywords: CO_2 Reforming of Methane, K-H Zeolite, Ni Supported Catalyst, H_2 Production.

Introduction

Hydrogen is a potential alternative to be used as a cleaner energy resource. Production of hydrogen from carbon dioxide reforming of methane becomes more attractive way to utilize CO_2 , which is the greenhouse gas and by-product of many industrial processes. One important problem obstructing this process is catalyst deactivation due to carbon deposition and metal sintering, which result in the active metal site losses. Therefore, the better activity and stability of catalysts are necessary to be improved. Zeolite becomes one of the attractive supports for carbon dioxide reforming of methane. Its high surface area is expected to provide the better metal dispersion and enhance the activity. Moreover, the basicity of zeolite would possibly decrease carbon deposition. Thus, the method of zeolite synthesis has become one of the increasing interests. Conventionally, zeolite synthesis is performed by

Hydrothermal crystallization using alkaline conditions with an amorphous aluminosilicate gel as a starting material [1,2] or by hydrothermal conversion in alkaline or neutral solution [3]. By the combination of hydrothermal crystallization and microwave heating technique, smaller and more

uniform particles can be obtained in shorter time [4]. Therefore, this combination technique has also been used to yield crystalline products in many studies. Based on the previous studies [5], silatrane and alumatrane can be successfully utilized as precursors for the aluminosilicate gel using potassium hydroxide as a hydrolytic agent. However, the regular synthesis yields the insufficient amount of zeolite needed in both activity testing and characterizations. Thus, in this present work, an attempt has been made on scaling up the K-H zeolite synthesis from silatrane and alumatrane. The effect of upscaling on the activities of hydrogen production was investigated.

Experimental

Silatrane and lumatrane were synthesized using the procedure of Wongkasemjit *et. al.* [6,7]. Moreover, the one-step sol-gel process with microwave heating technique for K-H synthesis was performed by using the method of Sathupunya *et al.* [8] with some modifications. The gel solutions were scaled up from single batch scale to quadruple batch scale in accordance with the adjustment of gelling time. The amount of all starting materials were tripled and quadrupled, respectively, in order to achieve the same gel composition of SiO_2 : $0.1\text{Al}_2\text{O}_3$: $3\text{K}_2\text{O}$: $410\text{H}_2\text{O}$. Ni-based catalysts were prepared by incipient wetness impregnation using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the metal precursors. 8% Ni was loaded on K-H zeolites synthesized at different batch scales. Afterwards, the catalysts were dried at 110°C overnight and calcined in air at 500°C for 5 hours for complete decomposition of precursors.

The fresh catalysts (0.1 g) were packed in the quartz tube reactor and reduced under hydrogen atmosphere at 600°C for 1 hour. After that, the reduced catalysts were flushed under a stream of helium at the reaction temperature for 20 min. Then, the methane and carbon dioxide (molar ratio of CH_4 : CO_2 = 1:1) were introduced to the reactor at 700°C at atmospheric pressure. Space velocity of total gas mixture (GHSV) was $30000 \text{ mL h}^{-1} \text{ g}^{-1}$. The concentrations of input reactants and products were analyzed using a Hewlett Packard 5890 Series II equipped with Carbosphere column.

The crystal structure of K-H zeolite was identified by using X-Ray Diffraction (XRD), performed on the Rigaku X-ray diffractometer system with a Rint 200 wide-angle goniometer, Cu-K α radiation, 30 mA and 40 kV. Scand speed of 5° (2Θ /min with a scan step of 0.002° (2Θ)) was applied during a continuous run in the 10° to 60° (2Θ) range. Phase identification was carried out using the reference database (JCPDS-files) supplied with the equipment.

Results and Discussion

Initially, the single scaled batch was synthesized only 0.1 g of K-H zeolite was obtained which was not enough to perform both catalytic activity measurement and characterizations. Therefore, an attempt to obtain more yield of synthesized K-H zeolite was made by up scaling from single batch scale to triple and quadruple batch scale, respectively. Furthermore, the effect of up scaling batch on the activities was investigated. From Fig. 1, the XRD results show that the crystalline K-H zeolites were obtained from both triple and quadruple batch scale.

As shown in Figs. 2 and 3, two experiments show different outcomes on CH_4 and CO_2 conversions. For the Ni supported K-H synthesized from quadruple batch scale, the conversions of CH_4 and CO_2 were higher than that on Ni supported K-H zeolite synthesized from triple batch scale. The conversions of CH_4 and CO_2 on the quadruple batch scale were quite constant with increasing time on stream. However, the conversion of CH_4 on the triple batch scale little decreased with time on stream.

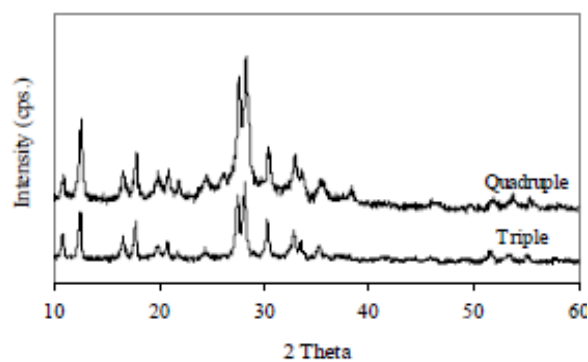


Fig. 1 XRD patterns of K-H zeolites at different batch scale.

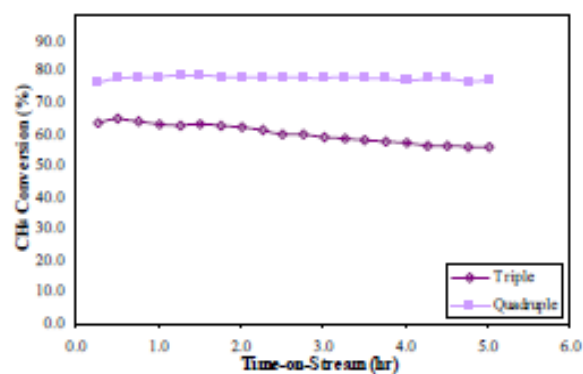


Fig. 2 Conversion of CH₄ with difference batch scale.

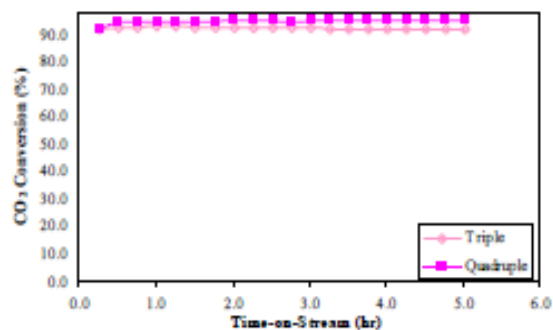


Fig. 3 Conversion of CO₂ with difference batch scale.

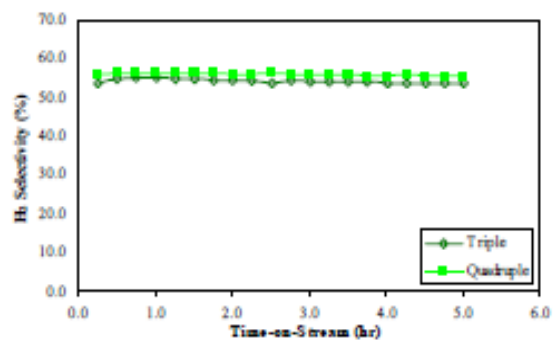


Fig. 4 Selectivity of H₂ with difference batch scale.

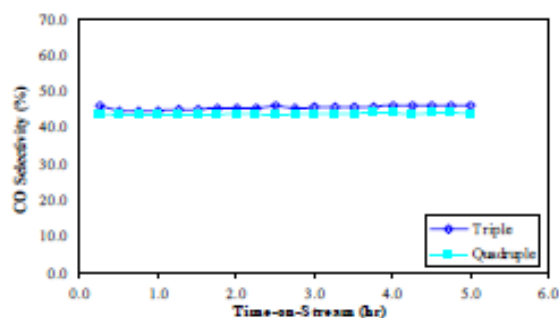


Fig. 5 Selectivity of CO with difference batch scale.

Moreover, it was obviously seen that both scales did not exhibit the significant difference in the selectivities of H_2 and CO concerned. Nevertheless, the catalysts prepared from both batch scales provided higher selectivity on H_2 than on CO as shown in Figs. 4 and 5.

For the production of H_2 and CO, it was found that the Ni supported K-H zeolite synthesized from both triple and quadruple batch scales did not show much difference in the production of CO. At the same time, the production of H_2 on the catalyst prepared from quadruple batch scale was higher than on the one prepared from the triple batch scale shown in Figs. 6 and 7

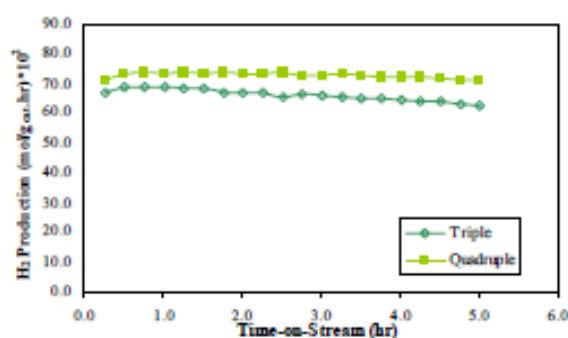


Fig. 6 Production of H_2 with difference batch scale.

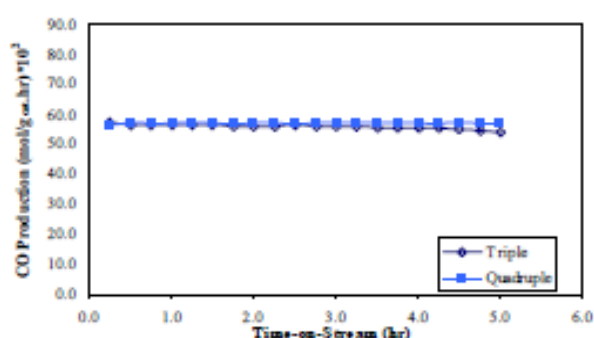


Fig. 7 Production of CO with difference batch scale.

Conclusions

From this preliminary study, the result indicated the Ni supported K-H synthesized catalysts at different batch scale did not offer much differences in terms of the selectivities of H_2 and CO, the conversion of CO_2 , and the production of CO. However, the difference on methane conversion is surprising, possibly due to the inappropriate of gelling time. More investigations for appropriate synthesis conditions are needed and will be further performed.

Acknowledgements

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