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Effect of support materials upon platinum catalyst prepared on the wall surface of silicon microchannel

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ABSTRACT

Effect of oxide support prepared over the wall surface of silicon microchannel on the activity and selectivity of platinum catalyst was studied by the dehydrogenation of cyclohexane. Baking of the silicon chip affected the catalytic activity by changing the thickness of surface silica layer. Several kind of oxide layer was prepared over the optimum silica layer at the silicon microchannel wall. Alumina layer prepared by sol–gel method using distilled water for the hydrolysis (sol–gel–aqueous method) gave optimum performance of platinum catalyst. Mist decomposition method can provide efficient platinum catalyst, however, the activity was not as stable as the ordinary impregnation method.

1. Introduction

Use of the micro-structured chemical system attracts considerable attention in recent years [1]. Microchannel reactors are said to have distinct advantages in comparison to conventional reactors such as: high heat and mass transfer rate, constant reaction temperature (isothermal) and higher safety [2]. In recent reviews, selection and preparation of catalytic microreactors attract considerable attentions [3,4]. Due to small sizes of the microchannels, the preparation of catalyst becomes very important factor to design efficient catalytic reactor. Surface coating method is preferable rather than packed bed type configuration in view point of high pressure drop [3]. Chip-like micro-structured reactors with a thin-film catalytic coating is also reviewed for its high integrity and resulting high thermal response [4]. For the high temperature use, metallic materials are used including planar silicon chips [5].

In our previous studies [6,7], small particles of catalyst were successfully supported on a planar yttria stabilized zirconia (YSZ) as an electrode catalyst for solid oxide fuel cell by mist decomposition technique. The method is to generate mist of aqueous solution of catalyst precursor with ultrasonic oscillator and the mist was directly deposited on the heated surface of the base plate. This method was applied to prepare platinum catalyst over a silicon microchannel reactor wall, where importance of surface preptreatment for catalyst support was pointed out [8]. This study aims to analyse the effects of support materials for supported platinum catalyst on the surface of structured silicon chip for the microreactors.

2. Experimental

2.1. Preparation of microchannel structure on a silicon chip

A preparation procedure of microchannel is summarized in Fig. 1. A planar silicon wafer (5 in.) was cut into 1/4 size chip. The chip was washed with acetone under ultrasonic and dried at a room temperature. (1) The chip was then baked in the air at 1173 K to form thin SiO_2 protecting layer for TMAH(tetra-methyl ammonium hydroxide) treatment in the following step. Microchannel was then prepared over the surface by photolithography method. (2) Photo resist was coated on the surface by spin coating method. (3) A mask pattern was placed over spin coated photo resist. It was then exposed to UV light and (4) mask pattern was copied over photo resist. (5) HF treatment then transcribed the pattern into SiO_2 layer. (6) After removing photo resist polymer from the surface. (7) Deep channel was prepared with TMAH treatment. (8) Thus prepared deep channel was again baked in the air at 1173 K for designated time to control the thickness of the silica layer which will be used as a support layer of the catalysts.

2.2. Preparation of catalyst layer on the microchannel wall

Oxide support layer and platinum catalyst were then prepared inside the channel. Fig. 2 shows the cut model of the reactor. (1) Oxide support materials are prepared by sol–gel method on the surface of silica layer. Surface of the chip was protected by label paper except for the channel structure. The oxide sol was spin

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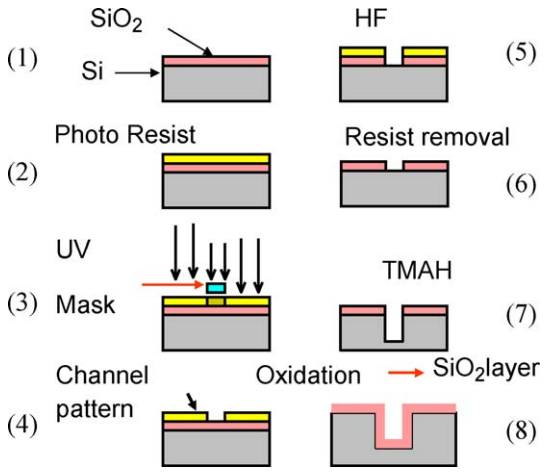

Fig. 1. Preparation of microchannel structure.

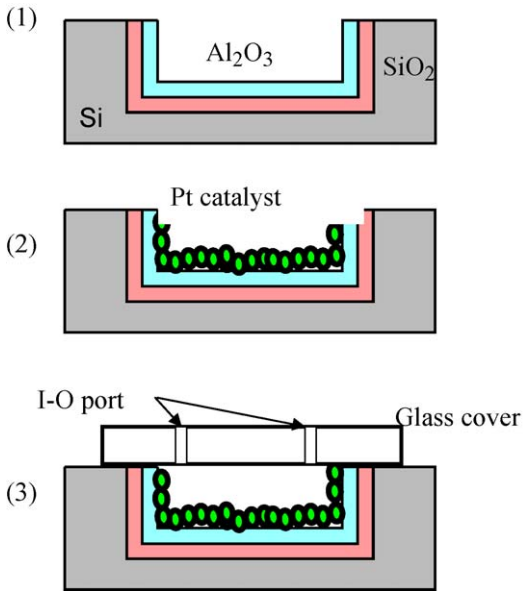

Fig. 2. Preparation of supported wall catalyst.

coated on the surface of the chip. After the label paper was removed, the chip was dried and calcined at 1073 K for 1 h. Two methods were used to prepare alumina sol. (1) Sol–gel–aqueous method: aluminium isopropoxide was hydrated with distilled water for 24 h and kept for another 24 h after HNO_3 was added. (2) Sol–gel–alcoholic method: aluminium isopropoxide was hydrated with mixture of distilled water, acetyl acetone, ethanol, and HNO_3 for 6 h. (3) Then platinum catalyst was prepared over the oxide layer by ultrasonic mist decomposition method. (4) The channel was finally covered with Pyrex glass using electrostatic method under 1000 V at 673 K after preparation of catalyst. Inlet and outlet port of gaseous reaction mixture made of stainless steel were placed on the top of Pyrex cover glass with ceramic glue. The catalytic channel was 13.5 mm of width and 25.5 mm of length and 200 μm of depth.

2.3. Preparation of platinum catalyst by the mist decomposition method [3,4]

The apparatus for mist decomposition method is shown in Fig. 3. Aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (0.012 mol/l) was set in the reservoir and mist of the solution was generated with ultrasonic transducer. The mist was introduced onto the chip

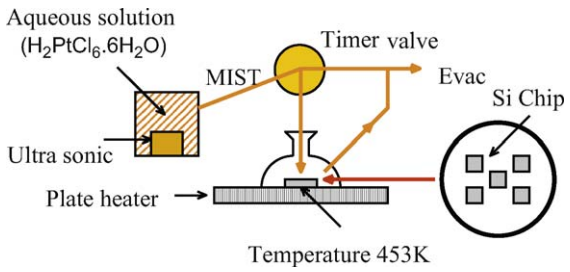

Fig. 3. Apparatus for mist decomposition method.

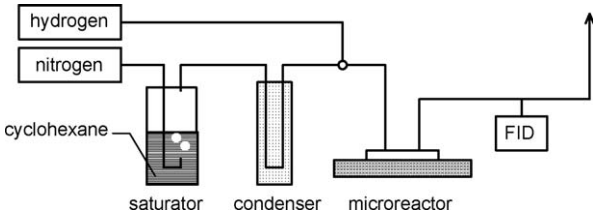

Fig. 4. Reaction apparatus for dehydrogenation of cyclohexane.

heated on the plate heater at 453 K under the flow of air (2.5×10^{-3} m^3/s) using the evacuation pump placed at the end of the flow line. In order to avoid recombination of the droplets on the surface, a periodic operation using timer valve was conducted such as 10 s spray and 30 s dry for total 3600 s operation time. As a comparison, impregnated catalysts were also prepared by adding the solution onto the channel by micro-syringe and dried on the plate heater.

2.4. Reaction apparatus

As a test reaction, dehydrogenation reaction of cyclohexane was conducted. Fig. 4 shows schematic diagram of reaction apparatus. The microreactor chip was placed on the planar electric heater. The catalyst was reduced under flow of hydrogen at 773 K and then the reaction was started with feeding the mixed gas of cyclohexane (4.08×10^{-8} mol/s) and nitrogen (1.84×10^{-4} mol/s) at 723 K as a standard reaction condition. The concentration of cyclohexane was adjusted by controlling the temperature of saturator. The products were analysed by gas chromatography.

3. Results and discussion

3.1. Effect of silica support layer

In our previous study on the dehydrogenation of propane, the oxidation treatment of the chip surface showed important role on

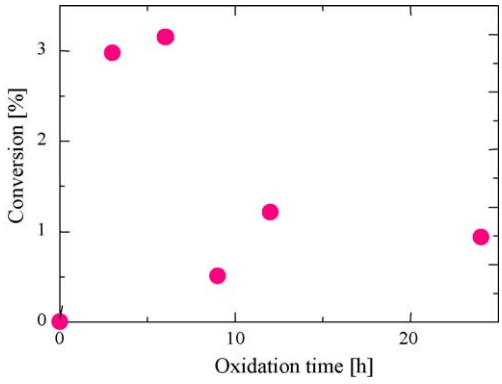

Fig. 5. Effect of pretreatment time of Si surface on the conversion of cyclohexane.

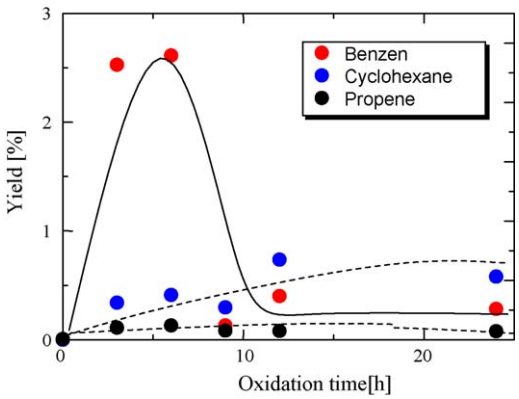

Fig. 6. Effect of pretreatment time of Si surface on the product distribution of cyclohexane dehydrogenation.

the catalytic activity of platinum. The baking time which controls the depth of SiO_2 layer on the Si-chip surface gave maximum activity for 6 h baking at 1273 K. The baking condition corresponds 0.13 μm thickness of silica layer [8]. In this study, the effect of baking time prior to platinum catalyst preparation was also tested from 0 to 24 h at 1273 K. Platinum catalyst was then prepared by mist decomposition method and the amount of supported platinum per microchannel was about 0.01 mg. Although initial deactivation was observed on all the samples for 2 h, stable activity was obtained after 2 h. Fig. 5 shows the effect of baking (oxidation treatment) time on the conversion of cyclohexane at the steady state activity. A maximum conversion was observed at around 4–6 h. This agrees the previous results on the dehydrogenation of propane which suggests the thickness of support silica layer plays important role for dehydrogenation reactions [8]. In this reaction not only benzene but also cyclohexene and propene were observed as products. The yield of each products is shown in Fig. 6. All through the reported cases in this paper, the yield of propene was very small and can be neglected. The high yield of benzene was mainly observed on the 4 and 6 h samples but decreased steeply after 9 h. While cyclohexene gradually increased with treatment time and the yield of cyclohexene was twice as much as that of benzene over 24 h-sample. These showed that the thickness of silica support layer not only affected on the catalytic activity but also on the product selectivity.

3.2. Screening of support oxide layer

Above results showed similar tendency to dehydrogenation of propane but the conversion level was not so high. Therefore screening of support material was conducted. Support oxide was

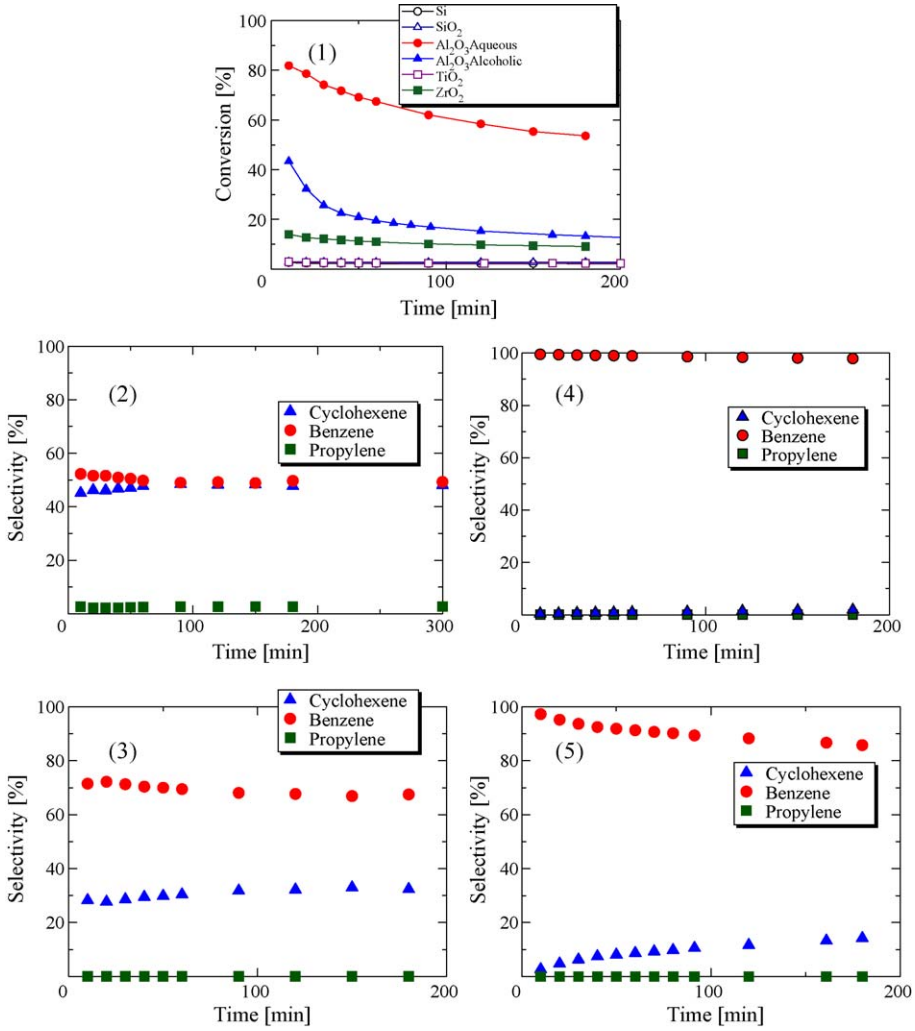

Fig. 7. Effect of support materials layered on the silicon channel wall. (1) Conversion of various supports, selectivity over, (2) Pt/Si, (3) $Pt/SiO_2/Si$, (4) $Pt/Al_2O_3/SiO_2/Si$ prepared by sol–gel–aq. method and (5) $Pt/Al_2O_3/SiO_2/Si$ prepared by sol–gel–alc. method.

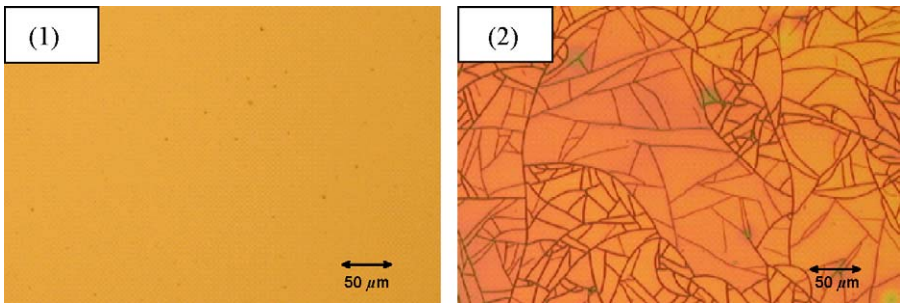

Fig. 8. SEM images of (1) alumina layer prepared by sol–gel–aq. method and (2) alumina layer prepared by sol–gel–alc. method.

prepared over microchannel baked at 1273 K for 6 h by sol–gel–aqueous method unless otherwise noted. In the screening test, Pt loading was increased compared to the previous section in order to point up the differences in conversion and selectivity. Thus Pt catalyst was prepared by impregnation method and total amount of supported platinum per microchannel was 0.05 mg. The time course of conversion is shown in Fig. 7-1. Some catalysts showed initial deactivation. The conversions of untreated Si surface and SiO_2 (baked at 6 h) were very small and agreed with the results of the previous section. TiO_2 and ZrO_2 showed enhancement effect to some extent and Al_2O_3 supports showed the highest activity. It is worth noting that variation of preparation method (i.e. sol–gel–aqueous and sol–gel–alcoholic) of alumina resulted in great difference of conversion. The selectivity of representative catalysts is shown in Fig. 7-2 to -5. Selectivity of Pt/Si is shown in Fig. 7-2. The selectivity to benzene and to cyclohexene was almost the same, while selectivity to benzene was twice as much as that to cyclohexene on the $Pt/SiO_2/Si$ which is shown in Fig. 7-3. The selectivity over alumina prepared by sol–gel–aqueous method is shown in Fig. 7-4. The selectivity to benzene was stable and almost 100% while conversion changed from 80% to 55% as shown in Fig. 7-1. The selectivity over alumina prepared by sol–gel–alcoholic method is shown in Fig. 7-5. At the initial stage, complete conversion to benzene was observed, however, selectivity to benzene decreased with reaction time and that to cyclohexene gradually increased with time. Final selectivity to cyclohexene was about 15%.

The surface morphologies of these two alumina surfaces were compared in Fig. 8. Alumina surface prepared by sol–gel–aqueous method showed smooth mirror like surface, while that prepared by sol–gel–alcoholic method showed mirror surface with full of small cracks. These crack structure or exposed interface between silica layer and alumina layer might cause the unstable activity and selectivity.

Senkan et al., studied high throughput testing of platinum catalyst with dehydrogenation of cyclohexane using microreactor [9]. They found continuous decrease of activity for 24 h and concluded that the deactivation was caused by coke formation. They also pointed out the deactivation could be controlled by optimizing co-catalysts. Assuming the same deactivation mechanism, the enhanced acidity at the SiO_2–Al_2O_3 interface in case of sol–gel–alcoholic method, might cause the increase of coke formation.

3.3. Mist decomposition method for Pt catalyst preparation

As support oxide was selected as alumina layer prepared by sol–gel–aqueous method, platinum catalyst was prepared by mist decomposition method and activity was tested. Preparation time varied from 1 to 3 h. The amount of supported platinum was proportional to the mist exposure time and increased as 0.01, 0.02 and 0.03 mg. The time course of conversion is shown in Fig. 9. The initial activity of standard sample (1 h) was very high but the activity decreased with reaction time to reach 10% of conversion. Considering that the amount of supported platinum was 20% of impregnation method, the efficiency of platinum at the fresh state could be very high. When preparation time was increased to 2 h, initial activity was much higher and higher than that of impregnation method as shown in Fig. 7. The platinum content of this sample is almost a half of that prepared by impregnation method. The decrease of activity was also slower than the standard sample and gave 40% of conversion at 180 min of reaction. However extending the preparation time to 3 h caused apparent decrease of initial activity. The conversion as low as 10% was kept constant during the reaction (180 min). As is not shown in the figure, behaviour of selectivity of standard (1 h) sample was similar to that of shown in Fig. 7-5 and selectivity to benzene gradually decreased. On the other hand, that of 2 h sample was similar to that shown in Fig. 7-4 and stable selectivity to benzene was observed. For the 3 h-sample, selectivity to benzene was 60–80% while that to cyclohexene was 20–40%.

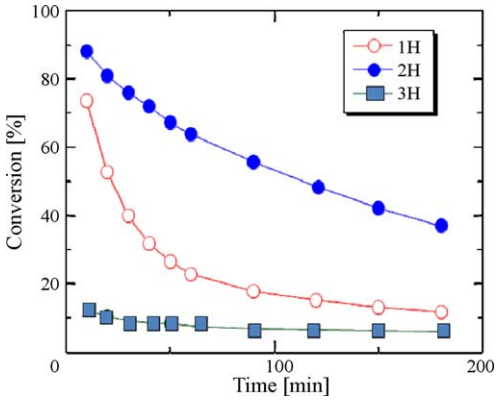

Fig. 9. Effect of spray time on the catalytic activity of Pt/Al_2O_3 (sol–gel–aq.)/SiO_2 catalyst prepared by mist decomposition method.

In conclusion, mist decomposition method can produce efficient catalyst compared to the ordinary impregnation method but the catalytic activity was not stable. Preparation time of mist decomposition affected activity and selectivity.

Ahmed and Chowdhury pointed out that the activity was affected by the orientation of adsorbed benzene, which depends on the dispersion of metal [10]. In our case, mist decomposition conditions may affect the dispersion of the platinum particles which will give optimum performances. As the surface characterization is not completed yet, further studies are needed for the effects of preparation conditions of mist decomposition method.

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