Introduction
Fuel cells which convert chemical energy directly into electrical energy with high efficiency and low pollutants have considered as represent a commercially renewable energy device. Development of fuel processing for fuel cell system has focused largely on hydrogen or synthesis gas production from hydrocarbons and alcohols, and the conversion of fuels to hydrogen is performed by one of four major techniques (i.e., as steam reforming, partial oxidation, auto-thermal reforming, and carbon dioxide reforming) [1]. Among the technologies, steam reforming is the most prevalent technology of hydrogen production and steam methane reforming produces a hydrogen-rich gas that is typically on the order of 70 to 75% hydrogen on a dry mass basis. Although, much recent research has reported that the development of variable catalysts for the technology, the catalyst deactivation has regarded as a major drawback of technical advancement [2]. Therefore, the objective of this research was to investigate the activities of a nickel-based catalyst supported by mixed oxide including calcium, titanium, and aluminum.

Materials and Methods
Nickel-based catalysts containing titanium were prepared with a fixed 10 wt.% nickel loading, and varying amounts of calcium titanate, 11 to 50 wt.% of the support. The activities and stabilities of the catalysts for methane steam reforming were evaluated and compared with those of a commercial product. Steam reforming was performed in reactors made of quartz and Inconel materials. A continuous flow fixed-bed reaction was operated with steam to carbon ratios of 1.0 to 3.0, at 750 to 850 °C and atmospheric pressure for 10 to 100 hours. The inlet and outlet gases were analyzed by a gas chromatograph equipped with TCD- and FID-detectors. Various characterizations were investigated to assess the relationship between the chemical-physical properties of the catalysts and their activities.

Results and Discussion
With increasing the calcium titanate (CaTiO₃) content, the activities of methane conversion and hydrogen selectivity of the nickel-based catalysts showed no tendency to increase while, Ni/Al₂O₃(20)-Al₂O₃(80) catalyst represented the highest activity in the reaction. Compared with the commercial catalyst, FCR-4 from Süd-Chemie, and the nickel-based catalysts showed similar performances for the steam reforming of methane.

In order to investigate catalytic stability, the nickel-based catalyst containing 20 wt.% calcium titanate (Ni/Al₂O₃(20)-Al₂O₃(80)) and a reference catalyst, Ni/Al₂O₃, were applied to the methane steam reforming through time-on-stream 100 hours with a low steam to carbon ratio of 1.0. While Ni/Al₂O₃ exhibited 9.9% deactivation in the stability test, Ni/Al₂O₃(20)-Al₂O₃(80) represented 1.5% deactivation in the same. The spent catalysts in the stability test were performed by thermo-gravimetric analysis under air flow (Figure 1). As a result, the carbon deposition amount on Ni/Al₂O₃ was about twice that on Ni/Al₂O₃(20)-Al₂O₃(80). This suggested that the nickel-based catalysts containing calcium titanate might have preventing ability to deactivation derived from coking during the reaction.

The methane reforming activity was observed at nickel-based catalyst containing 20 wt.% CaTiO₃ comparing to reference catalysts. The nickel-based catalyst containing calcium titanate represented the superior stability for long-term reactions in this research. Consequently, the addition of calcium titanate to nickel-alumina effectively inhibits their deactivation through carbon deposition.

Figure 1. Thermo-gravimetric analysis (TGA) of samples after stability testing. (under air flow with 10 °C/min heating)

References