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Sol-Gel Method for Preparation of LiLaNiO/γ-Al_2O_3 Catalyst over Monoliths used in POM Reaction

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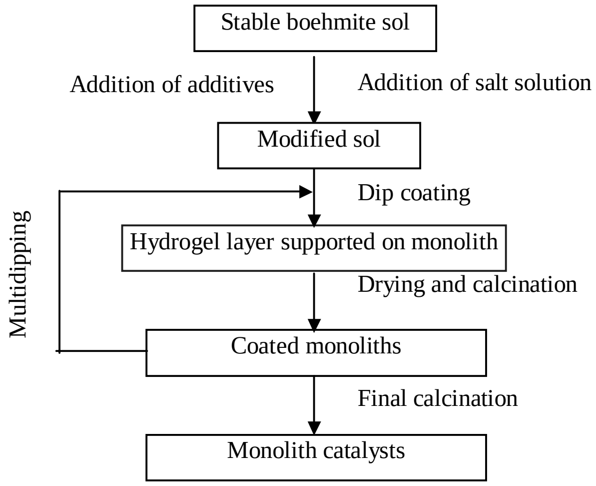
Abstract: A new method for preparing LiLaNiO/γ-Al_2O_3 monolithic catalyst was described and discussed. The catalyst, which was supported over the monolith, was evaluated in a POM to syngas process. Relative stable catalytic properties during the 120 hours operation at atmospheric pressure were found for the catalyst. Under the high space velocity of 9.0×10^4l/(kg·h)(CH_4), the conversion of methane came to 95.5%, and the selectivity of carbon monoxide was not below 96.0% at 1123K when ratio of the feedstock (CH_4/O_2) was equal to 2.0.

Keywords: Monolith, LiLaNiO/γ-Al_2O_3 catalyst, POM, syngas.

Partial oxidation of methane (POM) has several advantages over the traditional industrial method of steam reforming, such as much higher space velocity, reduced capital and operation cost and optimized the ratio of the products (H_2/CO). Many investigators are interested in the POM reaction over monolith now[1-3]. Monolith is a kind of ceramic-like metal oxide material. It has relative high surface to volume ratio compared to commercial pellets, low pressure drop during the reaction process[2], low thermal coefficient of expansion, good thermal shock resistance and so on. Contact times of the catalytic reaction in monolithic reactor can reach as short as microseconds at atmospheric pressure. So it is very suitable for the high temperature and high space velocity catalytic processes (such as POM). However, although monolith (cordierite or alumina-silica-titania) is somewhat porous and rough-textured, it has a relatively low surface area with respect to catalyst support requirements[3]. Accordingly, a suitable refractory metal oxide layer with high surface area is needed to serve as a support upon which finely dispersed catalytic metal may be distended. Most of the investigators prefer to use the washcoating method to prepare a monolith catalyst, but it would cause the increasing of the size of metal particles during the calcination processes, and the active components of the catalyst could not be dispersed uniformly on the support surface. Here, we reported a sol-gel method for the deposition of a thin layer of LiLaNiO/γ-Al_2O_3 over the monoliths, the as prepared catalysts were stably operated for partial oxidation of methane to syngas at high space velocity.

The catalyst was prepared as follows. PURAL SB powders (Condea GmbH, Germany) were used in the preparation of boehmite sol, and the preparation procedure was described in detail elsewhere[4]. When the stable boehmite sol was obtained, binder and plasticizer as additives were added to adjust the viscosity of the sol, and the sol was stirred for some time until it became stable and homogeneous again. $Ni(NO_3)_2$, $LiNO_3$ and $La(NO_3)_3$ solutions were then added respectively to the boehmite sol. After stirring for certain time with strict control of the pH value of the system, a stable homogeneous composite sol was obtained. Monoliths were dipped into the modified sol for several minutes till a gel layer was covered on, then they were dried at low temperature for 24 hours and calcined at 823K for 4 hours. The above dip and calcination procedures were repeated for several times until enough active components for the catalytic reaction were supported on the monoliths. The coated monoliths, which were calcined at needed temperature for several hours would be used in the catalytic reactions. NiO loading of the catalysts was about 10wt% (compared with γ-Al_2O_3).

Figure 1 Preparation procedure of LiLaNiO/γ-Al_2O_3 monolithic catalyst by sol-gel method



POM reaction was carried out in a fixed-bed quartz reactor. The monoliths were cylindrical shapes with a diameter of 7mm and a length of 10mm. The annular space between the catalyst and the quartz tube was sealed with a high temperature alumina-silica-cloth to minimized bypass of the reactant gases around the annular space between the catalyst sample and the quartz tube. The reaction was performed at atmospheric pressure, 1123K, and the feedstock ratio (CH_4/O_2) was kept constant at 2.0.

The monolith catalysts were evaluated for POM reaction at different space velocities of CH_4 (from 3.0 to 18.0 x10^4l/(kg·h)), and the results were shown in **Figure 2**. The conversion of methane was higher than 93%, the selectivity of carbon monoxide reached about 95% at the $GHSV_{CH4}$ = 1.8x10^5l/kg·h, the results were comparable to that using corresponding catalyst but without the monolith support[5].

Figure 2. Influence of space velocity on the performance of Ni-monolith catalyst for POM to syngas, (CH_4/O_2=2:1, 1123K)

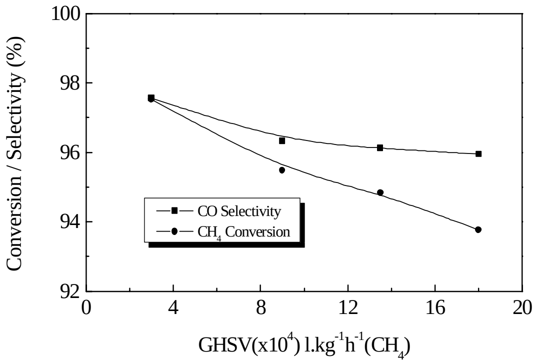
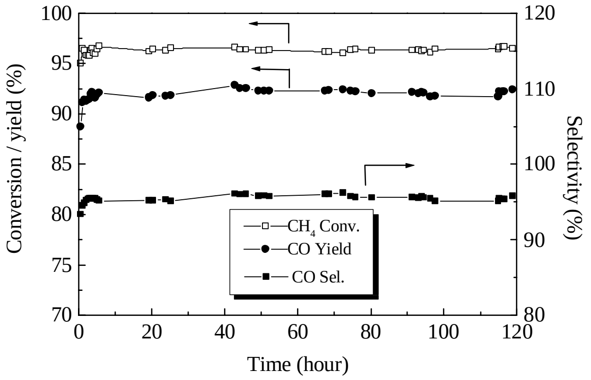


Figure 3. Reaction performance of LiLaNiO/γ-Al_2O_3 monolith catalyst as a function of time (CH_4/O_2=2:1, GHSV=9.0 x10^4l/kg·h, 1123K)



Although the Ni-based catalyst has similar conversion and selectivity to the precious metals catalysts under similar conditions, but it usually deactivates slowly during the reaction process due to the volatilization and metal loss. Schmidt[7] has observed that after the 22 hours performance, the conversion and selectivity of a Ni-monolith catalyst decreased by ~2%, and less than 0.1wt% Ni remained on the front of the catalyst. Other workers also have reported the unstable activity of Ni catalysts as well[7]. Therefore most of the investigators preferred the precious metals to the transitional metals as the POM catalysts. In order to examine the deactivity of our Ni-based monolith catalysts, we operated the reaction for 120 hours at $GHSV_{CH4}$ =

9.0×10^4 l/kg·h, and the results were shown in **Figure 3**. It shows that the catalysts are stable. The methane conversion, the selectivity of carbon monoxide and the yield of the carbon monoxide kept higher than 95.5%, 96% and 92% respectively during the 120h performance. That indicated the LiLaNiO/γ-Al_2O_3 monolithic catalyst, which was prepared through the new method is relatively stable.

We think there might be two reasons for such results: First, the addition of Li and La give the catalyst better stability during the reaction, which is already studied in our previous work[8]. Second, sol-gel based method prepared catalyst has stronger interaction with the support, which prohibited the loss of active elements during reaction[9]. The study about the interaction of the support with metal particle and the study of the loss of active components are in process.

The above results demonstrated that it was suitable to prepare the monolith supported LiLaNiO/γ-Al_2O_3 catalyst by sol-gel method. The as-prepared catalyst can be stably operated for partial oxidation of methane to syngas at ultra-high space velocity.

Acknowledgments

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