HIGH PRESSURE CO_2 REFORMING OF CH_4 OVER NI/MGO CATALYST DERIVED FROM NANO-MgO

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Introduction

There has been a general interest in recent in the more efficient use of natural gas (methane) and in the decrease of carbon dioxide in the atmosphere. The production of synthesis gas by CH_4/CO_2 reforming is one of the attractive routes for the utilization of CH_4 and CO_2. The product mixture of this reaction from a stoichiometric (1:1) feed has a high CO/H_2 ratio that is suitable for methanol and F-T synthesis, because low CO/H_2 ratios favor methanation and suppress chain growth [1]. Great efforts have been focused on the development of catalysts that shows high activity and stability.

Generally, CH_4 is preserved at high pressures in natural gas fields, and most F-T synthesis and methanol synthesis from CO/H_2 are performed at high pressures in the GTL (gas to liquid) process. Hence, from an economical point of view, the CH_4/CO_2 reforming should be carried out at high pressures in such a process [2]. In addition, in terms of the utilization of synthesis gas, the compressed synthesis gas is more convenient. It has been proposed that researchers must appreciate that the key problem is catalyst life at high pressures because customers need H_2 at >1.0 MPa and compression of large volumes of product gas is not very acceptable [3]. As it is well known that higher pressures favor coking and deactivation of catalysts in the CH_4/CO_2 reforming to synthesis gas, researches of the reforming reaction at high pressures are required. However, most of the researches were performed at atmospheric pressure, and only a few studies were conducted at high pressures [2-8]. To date no high stable Ni-based catalysts are reported in the dry reforming of methane at high pressures. Our searches have shown that Ni/MgO-AN catalyst (Ni-loading: 8.8%wt), the support of nano-MgO (named as MgO-AN) prepared by thermal processing of an alcogel of $Mg(OH)_2$, was extremely stable at 973-1123 K for CH_4/CO_2 reforming at atmospheric pressure [9]. In this paper, we have explored the catalytic performance of Ni/MgO-AN at high pressures CH_4/CO_2 reforming.

Experimental

Catalyst preparation and characterization. Magnesia support was prepared by sol-gel method with $MgCl_2{\cdot}6H_2O$ (A.R., Beijing Yili Chemical Reagent Co.) and $NH_3{\cdot}H_2O$ (A.R., Beijing Yili Chemical Reagent Co.). Obtained $Mg(OH)_2$ hydrogel was changed to alcogel by washing with ethanol and then calcined at 650 ºC in flowing N_2 for 5 h, named as MgO-AN (S_{BET} = 59.3 m^2/g). Catalyst of Ni/MgO-AN (Ni-loading: 8.8%wt, S_{BET} = 48.1 m^2/g) was prepared by wet impregnation of an aqueous solution of $Ni(NO)_3{\cdot}6H_2O$ (A.R., Beijing Yili Chemical Reagent Co.) onto MgO-AN support [9]. The obtained paste was dried at 120 ºC overnight and then calcined at 650 ºC for 5 h in air. Temperature programmed oxidation (TPO) experiments of carbon species formed on catalysts were performed on a thermogravimetric analyzer (SETARAM TGA 92) in flowing air. TEM measurements were performed on a H-800 electron microscope.

Catalyst tests and product analysis. A catalytic activity test of CH_4/CO_2 reforming was carried out in a fixed-bed continuous-flow reaction system. The reactor was made of a quartz tube (7 mm i.d.) tightly fixed in a stainless steal tube. A Viton O-ring pressed by a locking nut was used to prevent the gas from leaking into the ringed gap so as to eliminate the influence of the metal wall. The reaction temperature was measured by a thermal couple, which was protected with a quartz tube (6 mm o.d.) with a dead end. The flow rate of CH_4/CO_2 = 1/1 (Huayua gas chemical & technology Ltd. Co., Beijing) was controlled by a mass flow controller (Brooks 5850E) and the pressure of the reaction system was controlled by a back-pressure regulator (Type 806, Badger Co.). The outlet gas was cooled to remove H_2O and sampled by a six-port valve and analyzed by an on-line gas chromatograph (Varian 3400 GC, Ar carrier and 2 m TDX-01 column) with a TCD detector. The catalyst bed contains 40 mg Ni/MgO-AN that was diluted with 100 mg inactive α-Al_2O_3 (Homemade by calcining the commercial Al_2O_3 to 1350 ºC). Before the reaction, the catalyst was reduced with a flowing 5.0% H_2/N_2 at 1123 K for 1 h. Blank reaction tests showed that CH_4 conversion is less than 2.0% under the current reaction conditions within 50 h.

Results and Discussion

Figure 1 shows the dependence of CH_4 conversion and CO yield on the time on stream for 8.8%Ni/MgO-AN catalyst with GHSV=1.6×10^4 ml/h·g_{cat} under 1.5 MPa at 1023 K. Results indicate that activity of the catalyst decreases with increasing the reaction time-on-steam (TOS) up to 10 h, but no further decline is observed thereafter when the reaction was continued to TOS = 50 h. Both CH_4 conversion and CO yield can reach a constant value, 23.5% and 29.6% respectively. The CH_4 conversion and CO yield can be estimated to be 39.5% and 49.5% on the basis of thermodynamic calculation in CO_2 reforming CH_4 (CH_4/CO_2 = 1/1, total pressure 1.5 MPa, reaction temperature 1023K) at equilibrium.

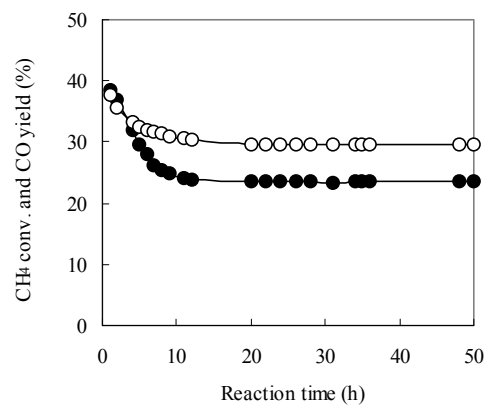

Figure 1. Stability test for 8.8%Ni/MgO-AN at 1.5MPa 1.6×10^4 ml/h·g_{cat} 1023K CH_4/CO_2=1/1. —○— CO yield —●— CH_4 conversion

Pressure and space velocity dependences studies were conducted at pressures varying from 1.0 to 2.0 MPa and at space velocity from 1.2×10^4 to 2.0×10^4 ml/h·g_{cat}. Results show that the stability in these different reaction conditions is the same with the behavior depicted in Figure 1. **Figure 2 and 3** show the effect of pressure and space velocity on CH_4 conversion and CO yield. These results show CH_4 conversion and CO yield decreased with increasing the reaction pressure as well as with increasing the reactant space velocity as expected from thermodynamics analysis. The effect of space velocity on activity implied that the reaction system had eliminated the contribution of mass-transport control.

It has been recognized that carbon deposition is the main cause of the deactivation of supported nickel catalysts in the reforming of CH_4 with CO_2 [10]. TPO measurements (**Figure 4**) show that the amount of carbon deposition on the used catalyst increases slowly with reaction time up to a constant value within 50 h. After 10 h on stream the loading of carbon deposition does not increase any more

with reaction time. The increasing tendency of carbon deposition is inverse proportion with the decreasing tendency of the CH_4 conversion and CO yield during the initial period. Although carbon was deposited on the catalyst, the activities became unchanged thereafter after 10 h on stream. The results imply that the carbon deposition did not block all active sites [5].

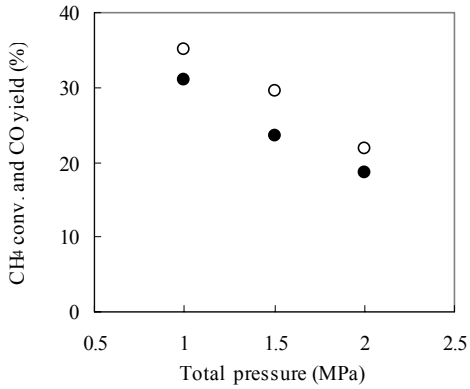

Figure 2. Dependence of activity on total pressure over 8.8%Ni/MgO-AN at 1.6×10^4 ml/h·g_{cat} 1023K CH_4/CO_2=1/1 TOS=50h. —○— CO yield —●— CH_4 conversion

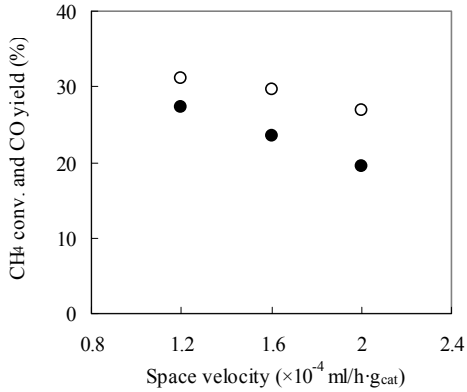

Figure 3. Dependence of activity on space velocity over 8.8%Ni/MgO-AN at 1.5MPa 1023K CH_4/CO_2=1/1 TOS=50h. —○— CO yield —●— CH_4 conversion

The sinter of nickel is another cause of deactivating catalysts in the CH_4/CO_2 reforming [10]. The TEM image of reduced catalyst shows that the metal nickel was dispersed on the magnesia supports uniformly (**Figure 5A**). In the TEM observation of used catalyst, larger nickel particle are found on the surface of catalyst **(Figure 5B)**. At the same time, TEM measurements revealed that the carbon deposits were of the filamentous types that can be removed by reaction with CO_2. The TEM image shows that the filamentous carbon grows from the larger nickel particle and some small nickel crystal stand on the tip and the middle of the filamentous carbon.

From the stable activity and unchanged amount of carbon deposition after 10 h on stream, it can be concluded that the catalyst deactivation was closely related with the amount of carbon deposits on the catalyst. The stable catalysis of Ni/MgO-AN catalyst seems to be associated with its ability to avoid formation of graphitic carbons and to maintain a dynamic equilibrium of the filamentous carbons with the reactant and product molecules at the catalyst surface.

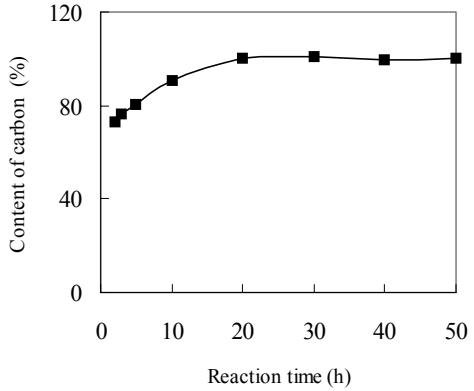

Figure 4. Dependence of the amount of carbon deposition on reaction time over 8.8%Ni/MgO-AN at 1.5MPa 1.6×10^4 ml/h·g_{cat} 1023K CH_4/CO_2=1/1. —○— CO yield —●— CH_4 conversion

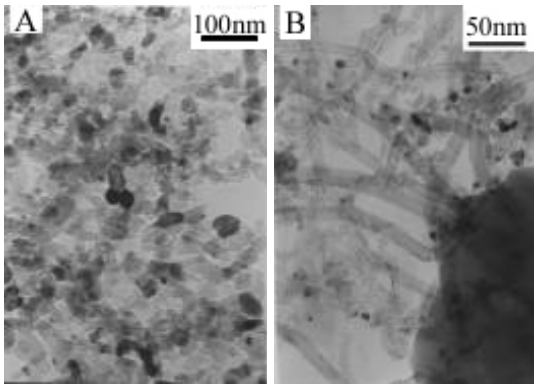

Figure 5. TEM images of fresh and used 8.8%Ni/MgO-AN
A. Reduced on flowing 5.0% H_2/N_2 for 1h at 1123K
B. After 50h on stream at 1.5MPa 1.6×10^4 ml/h·g_{cat} 1023K

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