Flyash as Support for Ni Catalysts in Carbon Dioxide Reforming of Methane

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(Received January 13, 1999; CL-990035)

A series of Ni catalysts supported on flyash treated by various chemical methods was tested for carbon dioxide reforming of methane. Ni catalyst on the flyash treated with CaO (Ni/Ash-CaO) shows high conversion and stability, being close to those of the well-reported Ni/Al_2O_3 and Ni/SiO_2 catalysts with conversions approaching thermodynamic equilibrium levels.

Carbon dioxide reforming of methane producing low H_2/CO ratio has several advantages over steam reforming and partial oxidation of methane.[1] This reaction also has very important environmental implications because both methane and carbon dioxide are greenhouse gases. In recent years, extensive research has been done on the catalytic reforming of methane with carbon dioxide to produce synthesis gas. Metals such as Ni, Pd, Pt, Ru, Rh, and Ir have proved to be effective catalytic components for this reaction. However, no industrial application has established to date. One of the major problems is the deactivation of catalyst caused by carbon deposition.[1-4] Noble metals are found to be much less sensitive to coking than nickel. Economical considerations for industrial application still stimulate developments of non-noble metal catalysts of high activity and long-term stability. It has been reported that Ni/MgO[5-6] or Ni/La_2O_3[7-8] catalysts have high activity and good stability for CO_2 reforming of methane, but Ni/MgO has to be activated at quite high temperatures (above 800 °C) prior to the catalytic reaction. La_2O_3 is not suitable as catalyst support in commercial scale because of its high cost. Flyash is a waste solid from power plants. More than 150 millions tons of flyash are generated each year in the world. Cost-effective disposal and utilisation of flyash have attracted continuing interest. Formed at temperatures above 1000 °C, flyash is mainly consisted of aluminosilicate and highly thermostable. Thus, it could be a potential catalyst support. In this communication we report the preliminary studies on Ni/flyash catalysts which show high activity and good stability for CO_2 reforming of methane.

Raw flyash was obtained from Tarong Power Station of Queensland, Australia. The results of XRF measurements indicate that the sample is mainly consisted of aluminosilicate (97.2%) with a small amount of other components such as Fe_2O_3 (0.7%), TiO_2 (1.5%), MgO (0.2%) and K_2O (0.4%). The sample was treated by different chemical methods before catalyst preparation. Two portions of the sample were dispersed into 0.5 N NH_3 and 2 N HNO_3, respectively, at room temperature for 24 h under stirring. They are labelled as Ni/Ash-NH_3 and Ni/Ash-HNO_3. One portion of the sample was dispersed into a saturated $Ca(OH)_2$ solution and another portion was mixed with CaO at a ratio of ash:CaO = 95:5 and the mixture was also dispersed into water. The last two slurries were kept at 150 °C for 24 h, then filtrated, washed and dried, named as Ni/Ash-$Ca(OH)_2$ and Ni/Ash-CaO, respectively. Nickel was loaded onto the ash, four treated ash samples, and two commercial oxides, SiO_2 and γ-Al_2O_3 by a wetness impregnation method using $Ni(NO_3)_2 \cdot 6H_2O$. Ni loading of 5 wt% was maintained for all catalysts. The catalysts were calcined in air for 4 h at 500 °C and reduced *in situ* at 500 °C for 3 h prior to catalytic tests. Catalysts were tested in a flow quartz reactor equipped with a gas chromatograph (Shimadzu GC 17-A) at temperatures ranging from 500-800 °C, with a constant feed composition of 30:30 ml/min of CH_4: CO_2.

Figure 1 shows CO_2 conversions over various Ni/Ash systems, Ni/Al_2O_3 and Ni/SiO_2 catalysts at different temperatures. As expected the CO_2 conversion increases with temperature for all catalysts except for Ni/Ash-HNO_3, which has no catalytic activity for this reaction even at 800 °C. Interestingly, it is found that the catalytic activity of Ni/Ash catalysts is related to the chemical treatment of the flyash: treatments with bases (NH_3, and CaO) result in active catalysts. The larger amount of base (CaO) was used, the better the activity of the resultant catalyst. Ni/Ash-CaO catalyst demonstrates higher activity in terms of CO_2 conversion, being much closer to that of Ni/SiO_2 catalyst. CO_2 conversions over Ni/SiO_2 and Ni/Ash-CaO catalysts are approaching the thermodynamic equilibrium values.

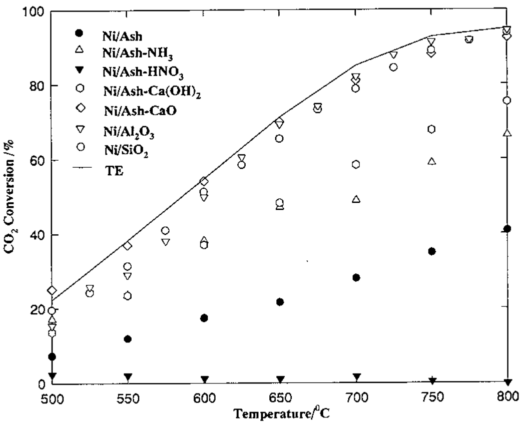

Figure 1. CO_2 conversions over Ni catalysts supported on various flyash. CH_4:CO_2=1:1, P_{tot} = 1 atm, M/F=0.2 g s ml^{-1}.

There is no new crystal phase observed from X-ray diffraction patterns after the treatments. The extent of reaction during chemical treatments are limited to the surface of the flyash particles. However, the catalytic activity of the final Ni/Ash catalyst is very sensitive to the change on the surface of flyash particles. The surface became certainly more basic by treatment with base (NH_3 or CaO) leading to enhanced adsorption of acidic reactant CO_2. All catalysts supported on flyash treated with a base showed higher CO_2 conversion than that of Ni on the as-received flyash. This is not unexpected as it has been found that acid treatment of supported Ni catalysts decreased the catalytic activity[9] while addition of basic promoters[10-12] generally enhanced the conversion of CO_2 in reforming of methane with CO_2. Among all flyash supports BET surface areas of base-treated flyash was found to be larger.

Another possible reason for the improvement of catalytic performance may be that the surface nature of the base-treated flyash particles enhances the dispersion of active component Ni. Besides, the size of the metal particles, defects in the metal phase, etc. may also vary accordingly. XRD measurements showed that the nickel crystallite size on Ni/Ash-NH_3 and Ni/Ash-CaO are smaller than those on Ni/Ash, which confirms that base treatment increased the nickel dispersion on support. Detailed study on these aspects is in process.

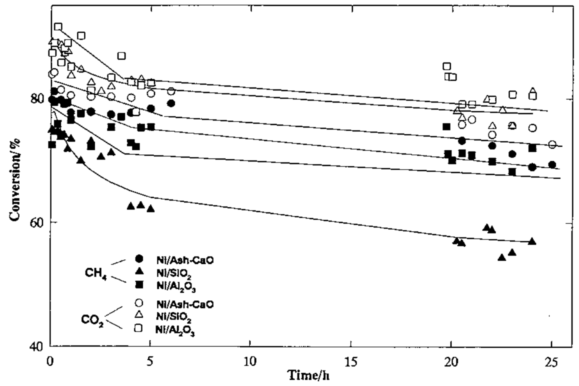

Figure 2. Stability of Ni/Ash-CaO, Ni/SiO_2 and Ni/Al_2O_3 catalysts at 700 ^{0}C. $CH_4:CO_2=1:1$, $P_{tot} = 1$ atm, M/F = 0.2 g s ml^{-1}.

The stability of Ni/Ash-CaO, Ni/SiO_2 and Ni/Al_2O_3 catalysts at 700 °C was investigated (Figure 2). It is seen that CO_2 conversions are generally higher than CH_4 conversions. This can be ascribed to the reverse water-shift reaction. The conversions over Ni/Ash-CaO and Ni/Al_2O_3 catalysts decrease slightly faster at the first 3 h, probably due to the accumulation of carbon deposits, and then the deactivation rates are slowed down whereas Ni/SiO_2 catalyst shows a continuous deactivation. After 24 h performance, CH_4 and CO_2 conversions over Ni/Ash-CaO catalyst decreased from the initial 79% and 84% to 69% and 75%, respectively. Whereas for Ni/SiO_2, CH_4 and CO_2 conversions are reduced from 75% and 89% to 57% and 81%, respectively. These results suggest that Ni/Ash-CaO catalyst exhibits not only high activity but also a better stability. The stability of Ni/Ash-CaO is possibly due to the fundamental component of aluminosilicate in flyash. Aluminosilicate can prevent the formation of nickel aluminate and nickel silicate during calcination as normally occurring in Ni/Al_2O_3 and Ni/SiO_2 systems. Nickel aluminate and nickel silicate have been found to be inactive in reforming of methane reaction with carbon dioxide because they are difficult to be reduced to Ni metal. Some researchers showed that Ni supported on zeolites gave much higher catalytic activity and a long term stability at 800 °C for this reaction.[13,14] Addition of CaO produced a protective layer of calcium aluminate and calcium silicate which also prevented the possible nickel sintering as well as carbon deposition.[15] The formation of calcium aluminate and calcium silicate is the possible reason for the stability of the Ni/ash-CaO catalyst. For other two catalysts, it is found that Ni/Al_2O_3 showed less extent of Ni sintering than Ni/SiO_2, which accounts for the less deactivation of Ni/Al_2O_3.

In summary, the present research reveals that flyash is a potential support material for Ni catalysts for carbon dioxide reforming of methane to synthesis gas. The treatment of flyash with a base, prior to Ni loading can greatly improve the catalytic activity and stability of the resultant catalysts. Such treatments can enhance adsorption of CO_2 and influence the state of nickel. Moreover, the formation of calcium aluminate and calcium silicate due to treatment with CaO, prevents the carbon deposition and nickel crystallite sintering, thus resulting in less deactivation. This preliminary study shows some promising results of flyash as a catalyst support for the CO_2 reforming of methane. Further investigation is desirable to test the long term stability of flyash supported catalysts.

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