Reforming of Methane and Coalbed Methane over Nanocomposite Ni/ZrO_2

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Introduction

One of the most attractive chemical approaches for the utilization of CO_2 and methane resources, e.g. coalbed gases, could be the catalytic CO_2 reforming of methane (CRM) to produce syngas (a mixture of H_2 and CO). CO_2 molecules in this CRM reaction function as a clean oxidant for the methane molecules. We have discovered recently that nanocomposite Ni/ZrO_2 catalysts, which consists of comparably sized Ni-metal (10-15 nm) and zirconia (7-25 nm) nanocrystals, are highly active and extremely stable for the CRM reaction at 700-800°C with a stoichiometric CO_2/CH_4 = 1.0 mixture [1,2]. However, in some other resources, the molecular CO_2/CH_4 ratio can be below the stoichiometry of the CRM reaction. A simple and convenient technological solution for the utilization of such resources is to add water (steam) as a compensation since catalytic steam reforming of methane (SRM) produces the same kind of products. In the present work, we demonstrate first that the nanocomposite Ni/ZrO_2-AN catalyst [1,2] also exhibits superior catalytic performance than the conventional oxide-supported Ni catalysts (Ni/ZrO_2-CP and Ni/Al_2O_3) for the SRM reaction. Our further study on combined steam and CO_2 reforming of methane (CSCRM) over the nanocomposite Ni/ZrO_2-AN catalyst will show that the extremely stable nanocomposite catalyst could make the CCSRM viable for producing syngas with flexible H_2/CO ratios.

Experimental

Preparation and catalytic testing of Ni/ZrO_2 catalyst Conventional 12.9 wt% Ni/ZrO_2-CP (the BET surface area: 18 m^2/g, reducibility of Ni: 98.5% and Ni-dispersion: 5.8) and nanocomposite 12.1 wt% Ni/ZrO_2-AN (the BET surface area: 38 m^2/g, reducibility of Ni: 95.2% and Ni-dispersion: 9.4) catalysts were prepared according to our previous methods [1-4]. Z107 (13.0 wt% Ni/Al_2O_3-C) sample is a commercial catalyst for the industrial SRM reaction. The catalytic reaction was conducted at 800°C, measured by a thermal couple in a quartz-well inserted into the catalyst bed, in a vertical fixed-bed U-shape quartz reactor (i.d.10mm) under atmospheric pressure as described previously [1-4]. A specially designed chamber was placed ahead of the reactor inlet and used to make the stoichiometric mixture of CH_4 and steam (H_2O/CH_4=1.0). This chamber was heated to 300°C to ensure no condensation of the water reactant. For the combined steam and CO_2 reforming reaction, CO_2 is also mixed with other reactants in the chamber. Unless otherwise specified, the space velocity by the methane reactant was $GHSV_{CH4} = 1.2\times10^4$ ml/(h·g_{cat}). Before the reaction, the catalyst was reduced in situ with H_2 (40ml/min) at 700°C for 3 h. Products from the reactor were analyzed on line by a gas chromatograph (SQ206) equipped with TCD and a carbon molecular sieve (80~100 mesh) column.

Results and Discussion

Figure 1 shows the TEM micrograms of the reduced Ni/ZrO_2-AN and Ni/ZrO_2-CP samples. It is remarkable that the structure of nanocoposite Ni/ZrO_2-AN catalyst is distinctive compared with the conventional Ni/ZrO_2-CP catalyst.

The catalytic data of SRM reaction at conditions of P=0.1MPa, T=800°C, $GHSV_{CH4}$ = 12,000 ml/(h·g_{cat}), H_2O/CH_4=1.0 are given in **Figure 2** by plotting CH_4 conversion against the reaction time on-stream over the different catalysts.

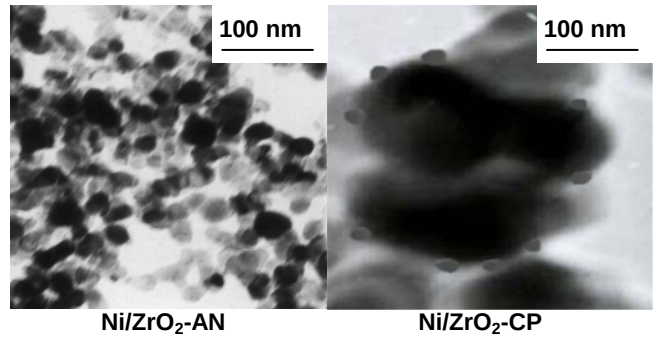

Fig. 1. TEM micrograms of the reduced Ni/ZrO_2 catalysts

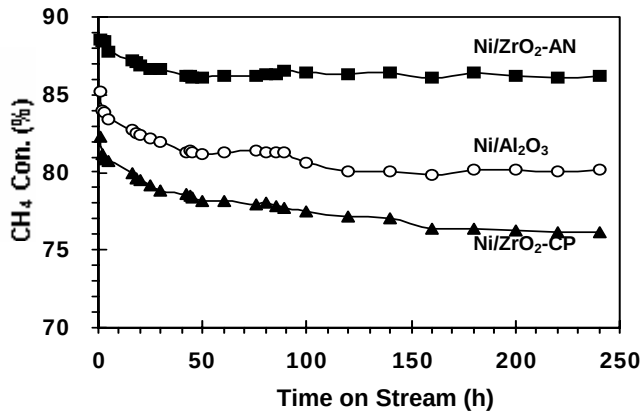

Fig. 2. Catalytic activity and stability during SRM process (P=0.1MPa, T=800°C $GHSV_{CH4}$=12,000 ml/(h·g_{cat}), H_2O/CH_4=1.0

Although all the three catalysts showed high and stable catalytic activities in the SRM process for 240 hrs reaction time on stream with CH_4 conversions of 87-88%, 81-84% and 76-83% respectively which are close to the thermodynamic equilibrium values (90%) at 800°C, the nanocomposite Ni/ZrO_2-AN catalyst is apparently more active as well as more stable than the commercial Z107 and the conversional Ni/ZrO_2-CP catalyst at this space velocity.

To further demonstrate the catalyst stability at methane conversion far below its thermodynamic equilibrium value, all the catalysts were tested with stepwise increasing the space velocity of methane from $GHSV_{CH4}$ = 12, 000 to 96, 000 ml/(h·g_{cat}) and the results are showed in **Figure 3**. The data for the first 150 hrs reaction time on stream, which were the same as those at reaction TOS=150~200 hrs, were not shown in **Figure 3**.

It is evident that the nanocomposite Ni/ZrO_2-AN catalyst showed extremely stable catalysis for the SRM reaction since the observed catalytic methane conversions were stable every time after changing the reaction GHSVs from $GHSV_{CH4}$ = 12, 000 to 96, 000 ml/(h·g_{cat}), and surprisingly, the conversion at every specific GHSV was kept constant after switching between several different GHSVs during 400 hrs reaction time on stream; In contrast, the conventional Ni/ZrO_2-CP and commercial Z107 catalyst began deactivating at high space velocity of $GHSV_{CH4}$ = 48, 000 ml/(h·g_{cat}) and this deactivation is severely irreversible and by the end of 400 hrs they almost had no activity.

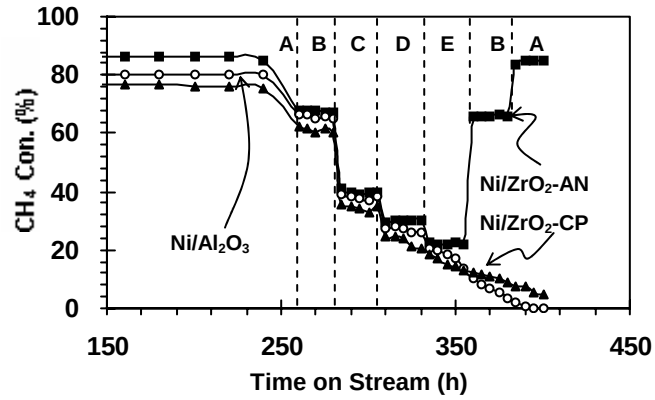

Fig. 3. Catalytic stability test at different methane space velocities of $GHSV_{CH4}$ = 12,000(A), 24,000(B), 36,000(C), 48,000(D), and 96,000(E) ml/(h·g_{cat}) (P=0.1MPa, T=800°C, H_2O/CH_4=1.0)

It should be mentioned that we operated SRM reaction with rather lower H_2O/CH_4 molar ratio=1.0 and high space velocity as compared with most SRM process conducted under an H_2O/CH_4 molar ratio between 2.0-5.0 [6] to avoid the deactivation caused by sever carbon deposition under an H_2O/CH_4 molar ratio below 2.0 at atmospheric pressure [7]. However, with high H_2O/CH_4 molar ratios (>2.0), the following drawbacks exist: (a) the equilibrium of water-gas shift reaction ($H_2O + CO = H_2 + CO_2$) will become favorable, as a result, the H_2/CO_2 mole ratio in product will be high, which is not preferable for the downstream process such as methanol and Fischer-Tropsch synthesis; (b) an enormous amount of energy will be consumed in the production of steam thus the energy efficiency and process economy will decrease. Therefore, the development of nanocomposite Ni/ZrO_2-AN catalyst with high activity and stability under low H_2O/CH_4 molar ratio is promising for commercial utilization in the future SRM process.

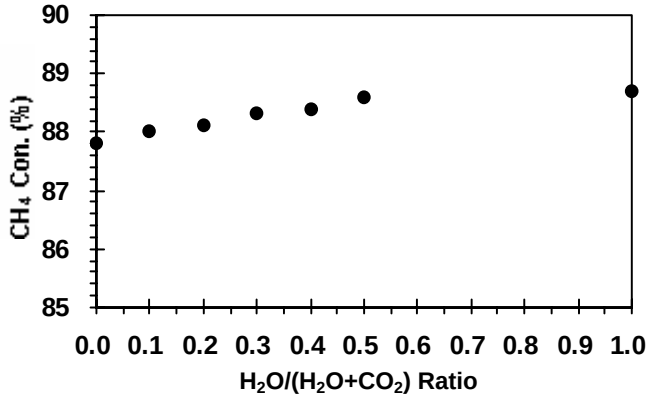

Fig. 4. Effect of the feed $H_2O/(H_2O+CO_2)$ ratio on methane conversion (P=0.1MPa, T=800°C, $GHSV_{CH4}$=12,000 ml/(h·g_{cat}), (H_2O+CO_2/CH_4=1.0)

We further applied the nanocomposite Ni/ZrO_2-AN catalyst in the CSCRM reaction since its remarkable catalytic activity and stability both in CRM [1-4] and SRM reactions. **Figure 4** shows the effect of the feed $H_2O/(H_2O+CO_2)$ ratio on methane conversion. With different H_2O/CO_2 ratios, the CH_4 conversion was stable and maintained between 87.8%-88.8%. **Figure 5** shows the effect of the feed $H_2O/(H_2O+CO_2)$ ratio on the H_2/CO ratios of the products. It is clear that, with the increase of steam content in the feed, the H_2/CO ratios of the products increased from 1.0~3.0. Thus on the nanocomposite Ni/ZrO_2-AN catalyst, we could achieve syngas with flexible H_2/CO ratios of 1.0~3.0 by CSCRM reaction for different downstream synthesis, and could eliminate carbon formation which is a serious problem in the methane CO_2 reforming process [7].

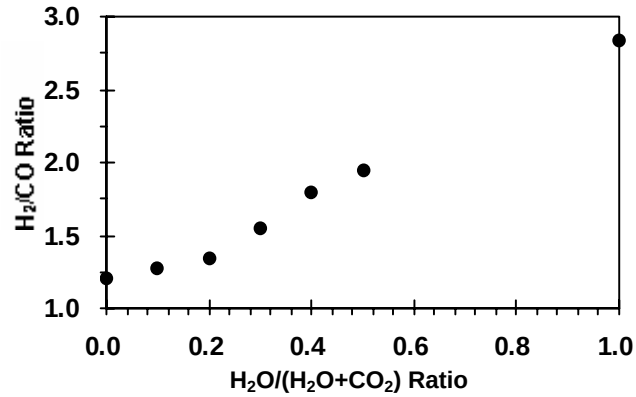

Fig. 5. Effect of the feed $H_2O/(H_2O+CO_2)$ ratio on H_2/CO ratio (P=0.1MPa, T=800°C, $GHSV_{CH4}$=12,000 ml/(h·g_{cat}) $(H_2O+CO_2)/CH_4$=1.0)

Conclusions

This work proves that the nanocomposite Ni/ZrO_2-AN catalyst is highly active and extremely stable for both the steam reforming and the combined steam and CO_2 reforming of methane. In comparison with commercial Ni/Al_2O_3 catalyst, the nanocomposite Ni/ZrO_2-AN catalyst allows the use of a much higher space velocity of the reaction feed and a stoichiometric H_2O/CH_4 and $H_2O/(H_2O+CO_2)$ ratios, which could meet requirements for the commercial utilization of different methane and CO_2 resources.

References

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