Carbon as an Intermediate during the Carbon Dioxide Reforming of Methane over Zirconia-Supported High Nickel Loading Catalysts

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Ni/ZrO_2 catalysts with more than 10wt % Ni loading give a birth of a large amount of carbon deposition, but the carbon plays as an intermediate to react with CO_2, which is contributed to both high activity and good stability towards carbon dioxide reforming of methane.

In recent years, a renewable study on catalytic conversion of CO_2 or CH_4 is becoming an attractive and challenging subject since these are regarded as major greenhouse gases.[1-3] Zirconia supported noble metals catalysts have been found to have an advantage over other conventional supports such as Al_2O_3, SiO_2 and TiO_2 in terms of less deactivation in the dry reforming.[4] ZrO_2 is unique because there is a very low concentration of Lewis acid sites on the surface, which will decrease coke formation caused by the support, therefore the operation ability is possibly increased at high temperature. On Ni/ZrO_2, it was unfortunately found that the reaction could not be performed when increasing nickel loading to more than 10% due to a serious plug of the reactor by coke.[5] This communication reports new achievements on Ni/ZrO_2 especially with high nickel loading for the dry reforming without catalyst deactivation under dilution conditions for both the feed and catalyst. The present results show that 13% Ni/ZrO_2 catalyst exhibits high activities for the CH_4 and CO_2 conversions as well as the availability for a long term operation in the dry reforming with the help of a large fraction of the deposited carbon on the catalyst surface. This can be explained by that the deposited carbon shows a high reactivity to carbon dioxide, therefore acts as an intermediate, and its amount remains constant during the reaction involving the deposited carbon necessarily.

Supported nickel catalysts were prepared by impregnation of zirconia with the solution of nickel nitrate, drying at 373 K overnight, and calcination at 773 K for 4 h. Activity tests were carried out under atmospheric pressure using 0.05 g catalyst sieved 0.7 - 1 mm, which was mixed with 0.25 g quartz sand particles. The catalyst was reduced in 5% H_2-N_2 (in vol.) at 973 K for 2 h prior to reaction test. The deposited carbon was measured by thermogravimetric analysis (TGA) coupled with temperature programmed surface reaction technique (TPSR) in 20% CH_4-20% CO_2-He at a heating rate of 5 K min^{-1} after the catalyst was reduced in 5% H_2-N_2 at 973 K for 1 h.

A series of Ni/ZrO_2 catalysts covered by a wide range of nickel loading, 2.5-23wt %, are tested by the carbon dioxide reforming of methane at temperatures 773, 873, 973, 1023, 1073 and 1123 K, respectively. Among these catalysts, the 13% Ni/ZrO_2 catalyst exhibits the highest activity for conversions of methane, $X(CH_4)$, and carbon dioxide, $X(CO_2)$, as well as the highest yield for productions of hydrogen and carbon monoxide. Like a general trend, $X(CH_4)$ and $X(CO_2)$ increase with a rise of reaction temperature. $X(CH_4)$ at 1023 K is > 75%, and increases to > 90% at 1123 K. Especially, nearly 100% of CO_2 conversion at 1123 K is measured for the highest nickel loading catalyst. The selectivities for H_2 and CO increase as increasing the reaction temperature, and reach to nearly 100% at 1123 K, which consequently results in an increase of the H_2/CO to about 1. These results indicate that Ni/ZrO_2 catalyst shows as high activity and selectivity as that reported in the literature.[5,6]

Furthermore, we used the 13% Ni/ZrO_2 catalyst to perform a long-term test at 1023 K. The change of methane conversion, $X(CH_4)$, as a function of reaction time is displayed in Figure 1. It clearly shows that $X(CH_4)$ is almost stable during the reaction for 30 h, which indicates that no significant deactivation of the catalyst is occurring. It is noted that the rate measured within the first hour is close to the level at its steady state. This phenomenon is quite different from that on nickel catalysts using other supports such as Al_2O_3, CaO, and La_2O_3 as reported by Zhang and Verykios,[6] wherein the reaction took at least more than 4 h to reach a steady state. Our present finding suggests that these new catalytic sites, which are quickly formed on the Ni/ZrO_2 catalyst surface upon exposure to the reactants, are active and stable towards the reaction of CH_4 and CO_2.

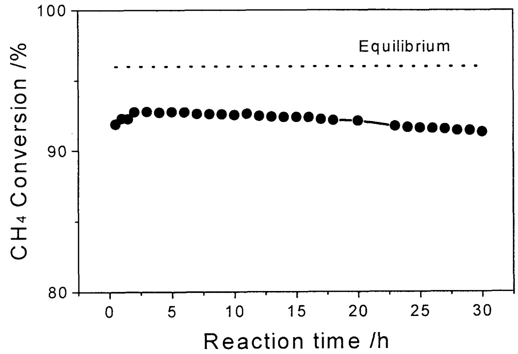

Figure 1. Conversion of methane as a function of time on stream over 13% Ni/ZrO_2 catalyst.
Reaction conditions: P = 0.1 MPa, $CH_4/CO_2/N_2$ = 1/1/3, 1023 K, M/F = 60,000 g s m^{-3}, 0.05 g catalyst.

In order to understand why the high nickel loading catalyst shows good stability and high activity, the catalyst is further studied using TGA and characterized by means of other techniques such as XRD, SEM, XPS and XANES. The catalyst was *in situ* reduced before TGA. XRD and XPS results show that the supported nickel oxide is reduced to metallic nickel. Figure 2 shows the carbon formation and removal on 13% Ni/ZrO_2 catalyst. In the first TPSR run, carbon deposition on the catalyst proceeds at a very rapid rate 0.84 mmol $(g_{cat}\ min)^{-1}$ to give rise to a sharp slop, and reaches its saturation (W_{carbon}/W_{cat} = 0.285) at below 973 K. When the catalyst is subsequently hold at 973 K, the rate for the carbon deposition is calculated as 0.17 μmol (g_{cat} min)$^{-1}$, which is much less than that formed in the heating process. This means that the amount of the deposited carbon remains nearly constant and the rate of carbon formation is dynamically equilibrated with that of carbon removal. Compared with that on Ni/ZrO_2 catalyst, an ignorable amount of deposited carbon is measured on ZrO_2, which indicates that on Ni/ZrO_2 catalyst the initial carbon deposition in a large volume occurs mainly on the metallic nickel sites instead of the support. In addition, the deposited carbon can be completely removed by the subsequent reaction with CO_2, which reveals that the carbon is rather reactive to CO_2. Meantime, the metallic nickel can be oxidized to nickel oxide when prolonging the CO_2-treating time as detected by XANES. These results suggest that the oxygen species from CO_2 decomposition exhibit a very high activity to the oxidation of both the reduced nickel sites and deposited carbon.

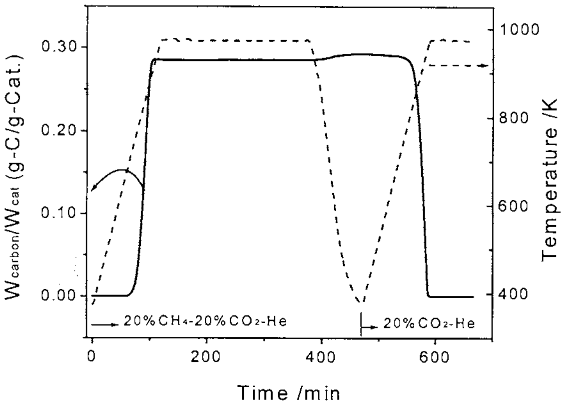

Figure 2. TGA profile of carbon formation and removal on 13% Ni/ZrO_2 catalyst.

Test conditions: P = 0.1 MPa, M/F = 60,000 g s m^{-3}, 0.05 g catalyst, 5 K min^{-1}, $CH_4/CO_2/He$ = 1/1/3 for the first TPSR run and CO_2/He = 1/4 for the second TPSR run.

For the sake of clarifying the role of the deposited carbon in the reaction, a good correlation between normalized activity of methane conversion and the C/Ni ratio is set up as shown in Figure 3. Generally, the higher the ratio of the deposited carbon to nickel is, the higher the normalized activity is, which implies that the ability for the formation of the initial carbon is closely related to the reaction activity. As reported in the previous work,[2] two types of carbon species could be formed on nickel based catalysts, and were identified by temperature programmed hydrogenation or oxidation. One is active and its amount has been revealed to correlate with reaction activity, therefore is regarded as an active reaction intermediate. The other is inert and its amount increases with increasing the reaction time. So that, the correlation presented in Figure 3 illuminates that the initially deposited carbon, at least part of it, can be ascribed to an active reaction intermediate to participate in the reaction. This proposal is strongly supported by our SEM results. It is observed that the diameter of the carbon filament grew up following the reaction time, which should be accompanied by a reduction in its length since the carbon weight remains constant as measured by TGA. This suggests that the oxidation of the carbon by CO_2 via the reverse Boudouard reaction can occur on the top of carbon filaments to produce CO.

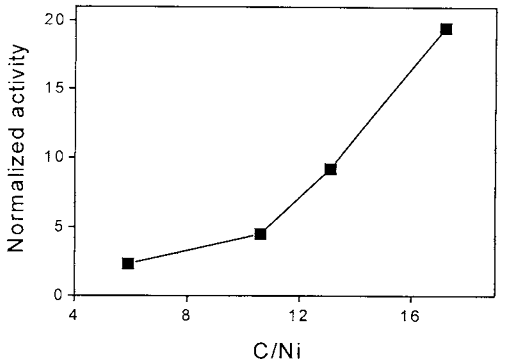

Figure 3. Correlation of the molar ratio of carbon deposited on catalyst to nickel loading (C/Ni) with normalized activity of methane conversion. The amount of deposited carbon is obtained from TGA via the first TPSR run of Figure 2. Normalized activity is defined as conversion rate of methane molecule per Ni molecule, CH_4 (s Ni)$^{-1}$.

Reaction conditions: P = 0.1 MPa, $CH_4/CO_2/N_2$ = 1/1/3, 973 K, M/F = 60,000 g s m^{-3}, 0.05 g catalyst.

Furthermore, carbon formation from methane decomposition was also examined. It is observed that the amount of the deposited carbon (W_{carbon}/W_{cat} > 0.9 on 13% Ni/ZrO_2) is much larger than that formed from reactant gases. The high rate 2.08 mmol (g_{cat} min)$^{-1}$ measured for the carbon deposition demonstrates that the metallic nickel is rather active to methane decomposition. These results suggest that during the CO_2 and CH_4 reaction most of the initially formed carbon may be produced from methane decomposition, and such kind of carbon subsequently plays a role as one of the active reaction intermediates. It is clear that the rates of the carbon formation and removal remain in a dynamic equilibrium as proceeding the reaction. Accordingly, the removable property of the deposited carbon by reaction with oxygen species from CO_2 decomposition certainly contributes to good stability of Ni/ZrO_2 catalyst in the carbon dioxide reforming of methane.

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