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# Problem of coke formation on $Ni/ZrO_2$ catalysts during the carbon dioxide reforming of methane

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## ABSTRACT

The suitability of zirconia-based nickel catalysts for the $CO_2$ reforming reaction has been investigated with emphasis on the stability of the catalysts under conditions favourable towards carbon formation. It has been found that between 720°C-780°C catalysts having lower loadings of nickel (< 2wt%) are more stable than those with higher nickel contents at stoichiometric $CO_2/CH_4$ ratios. Two forms of deposited carbon were observed for the less stable catalysts, whereas more stable catalysts had only one form of deposited carbon.

## 1. INTRODUCTION

$CO_2$ reforming is the reaction of methane with carbon dioxide to give synthesis gas (1):

$$CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2 \qquad (1)$$

The main problem with $CO_2$ reforming is the ease with which carbon deposition occurs on the catalyst under stoichiometric conditions($CO_2/CH_4$=1). Carbon deposition is known to occur mainly via reactions (2) and (3):

$$2CO \rightleftharpoons C + CO_2 \qquad (2)$$

$$CH_4 \rightleftharpoons C + 2H_2 \qquad (3)$$

Earlier studies showed $Pt/ZrO_2$ catalysts to be stable in comparison to $Ni/ZrO_2$ catalysts. The latter formed coke under $CO_2$ reforming conditions (1). It has been shown previously that zirconia-containing catalysts with high loadings of nickel (ca. 90 wt%) are active for the gasification of carbon formed by CO disproportionation at low temperatures (ca 300°C). (2,3). These results indicate that carbon formed on Ni based catalysts can be removed which makes the material a suitable candidate to replace Pt based catalysts. In the present paper we report first results on the formation and removal of coke formed during $CO_2/CH_4$ reactions.

## 2. EXPERIMENTAL

### 2.1 Catalyst Preparation and Characterisation

A range of $Ni/ZrO_2$ catalysts with varying Ni loadings was prepared. Monoclinic zirconia used as support, (RC100), was supplied by Daichi Kigenso , Japan. It was calcined at 650°C for 15 hours in a stream of flowing air (30 ml/min). One catalyst was also prepared from support

calcined at 850°C . The catalysts were prepared by incipient wetness impregnation of calcined $ZrO_2$ grains (0.3-0.6 mm) with an aqueous solution of nickel nitrate. The resultant materials were dried for 8 hours at 120°C and then calcined once again at 650°C for 15 hours in flowing air..

The nickel loading (wt%) was determined by XRF measurements using a Philips PW1480 spectrometer.Values for the surface areas of the catalysts were obtained using a Micromeretics ASAP 2400 system. Combined thermogravimetric analysis/differential scanning calorimetry analysis on catalyst samples were carried out subsequent to catalytic testing using a Polymer Laboratories Thermal Science, STA 1500 system. Experiments in air or $N_2$ flows were carried out using a gas flow rate of 30 $cm^3$ $min^{-1}$. In each case approximately 17mg of the used catalyst was analysed with a linear heating rate of 5°C/min. The specific metal surface areas were determined by means of $H_2$ chemisorption at room temperature (22°C) using a volumetric adsorption/desorption system. Prior to these measurements, each sample was reduced for two hours at 450°C. The straight line portions of the isotherms obtained were extrapolated to zero pressure to obtain an estimate of the metal surface area ( and hence the dispersion).

## 2.2 Catalyst Testing

The catalyst testing was carried out in a fixed bed continuous flow reactor made from a 4 mm i.d. quartz tube. Catalyst testing was generally carried out by either cycling the catalyst through a range of temperatures or by ramping it to a fixed temperature and maintaining it at that temperature. Prior to testing all the catalysts were reduced in a 95%/5% $N_2/H_2$ flow at a temperature of 600°C for one hour. The total flow through the fixed bed was 170 ml/min. In initial experiments the typical composition of the gas stream was such that $CH_4/CO_2/He$ = 1/3.7/4.9. In later experiments with more stable catalysts the $CO_2/CH_4$ ratio was adjusted downwards, keeping the He flow the same. A flow of $N_2$ of 5.1 ml/min was also added to the gas stream to act as an internal standard. The amount of catalyst used in all cases was 0.3g, this resulted in a bed depth in all cases of approximately 1cm. The educts were analysed by gas chromatography (Varian 3700) using a Carbosieve S column.

**Table 1** Characteristics of the catalysts examined

| Sample ID | Ni Loading (XRF) /wt% | Specific Surface Area /$m^2$ $g^{-1}$ | Specific Ni Area /$m^2$ Ni (g cat)$^{-1}$ | Dispersion / % |
|---|---|---|---|---|
| 6% $Ni/ZrO_2$ | 6.15 | 19 | | |
| 4%$Ni/ZrO_2$ | 4.1 | 24 | | |
| 2.1%$Ni/ZrO_2$ | 2.14 | 21 | 1.59 | 11.4 |
| 1.7% $Ni/ZrO_2$ (650)*(850)** | 1.71 | 17 | 1.31 | 11.6 |
| 1.9% $Ni/ZrO_2$ (850)*(850)** | 1.95 | 18 | 0.84 | 6.6 |
| 1.1% $Ni/ZrO_2$ | 1.14 | 26 | 0.89 | 12.2 |
| $ZrO_2$ (650) | - | 29 | - | - |
| $ZrO_2$ (850) | - | 13 | - | - |

*support calcination temperature **calcination temperature of metal impregnated support

## 3. Results and Discussion

Fig. 1 shows the $CO_2$ conversion for a $CO_2/CH_4$ ratio of 4 for three different catalysts. Initial testing was carried out at a $CO_2/CH_4$ ratio of 4, because the tendency to form coke was

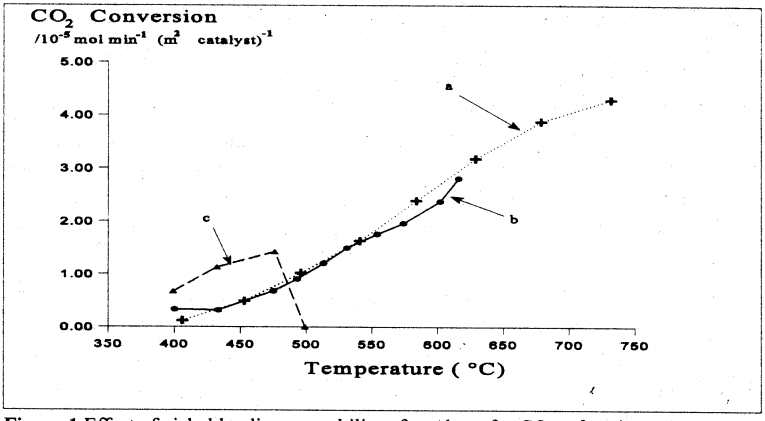


**Figure 1** Effect of nickel loading on stability of catalysts for $CO_2$ reforming $CO_2/CH_4$= 4. (a) 1.1% $Ni/ZrO_2$ (b) 4% $Ni/ZrO_2$ (c) 6% $Ni/ZrO_2$. Graph shows deactivation of 6% $Ni/ZrO_2$

reported to be low in excess $CO_2$ (4). Although the catalyst with the highest loading (curve c, 6% $Ni/ZrO_2$) was the most active at the lowest temperature, this material deactivated at T≤ 470°C. In parallel a rapid increase in the pressure drop across the catalyst bed occurred. TEM photographs of the used catalyst showed carbon filaments extending from the nickel particles, similar to those reported to be formed on nickel catalysts during steam reforming (5,6).

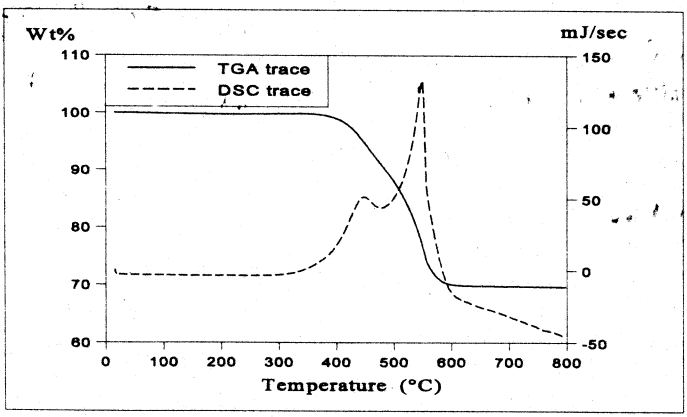


**Figure 2** TGA/DSC analysis of deactivated 6% $Ni/ZrO_2$ (see Fig. 1). Weight loss and exothermic peaks indicate combustion of carbon in air.

Fig. 2 shows the TGA/DSC trace obtained in flowing air for the used (deactivated) 6% $Ni/ZrO_2$ catalyst. The extensive weight loss and the exothermicity is indicative of loss of carbon from the catalyst at temperatures above 350°C. The 4% $Ni/ZrO_2$ catalyst also gave a weight loss

(12 wt%) on heating in air. However, the used 1.1% $Ni/ZrO_2$ material did not show any weight loss or exothermic peak on DSC analysis but rather exhibited a slight weight gain on treatment in air, which is speculated to be due to oxidation of $Ni^0$. The DSC trace of the used 6% $Ni/ZrO_2$ (Fig. 2) showed two exothermic peaks, and this seems to be characteristic of samples having a greater amount of carbon (or, alternatively, of samples having a higher loading of nickel). These two peaks indicate that there are two different types of carbon on the surface. Catalysts containing lower loadings of nickel, however, have only one exothermic peak and this corresponds to the lower temperature peak shown in Fig. 2. The higher temperature peak may be a more stable form of carbon which might be associated with the loss of activity observed, possibly because its formation is irreversible under these conditions.

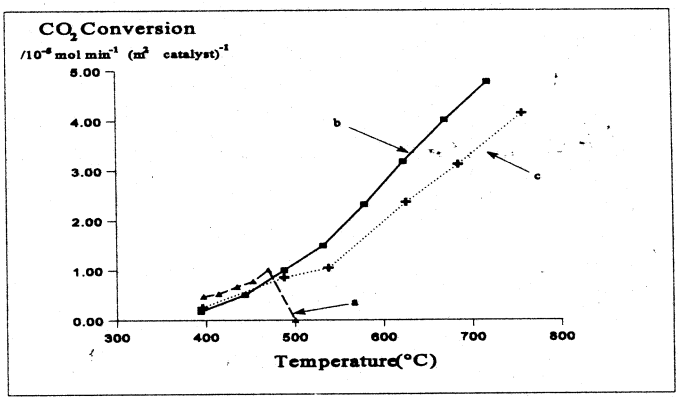


**Figure 3** $CO_2$ conversion against temperature for (a) 4% $Ni/ZrO_2$ at $CO_2/CH_4$=2, (b) 1.1% $Ni/ZrO_2$ $CO_2/CH_4$=2, and for , (c) 1.1% $Ni/ZrO_2$ $CO_2/CH_4$=1,

Fig. 3 (curves a and b) shows results obtained with a lower $CO_2/CH_4$ ratio of two. It can be seen that the higher nickel loaded catalyst (4% $Ni/ZrO_2$) also lost activity under these conditions. The catalyst with the lowest loading of nickel (1.1% $Ni/ZrO_2$) was stable under these conditions and showed no weight loss on TGA/DSC analysis. Fig. 3 (curve c) gives the results for the 1.1% $Ni/ZrO_2$ catalyst obtained with a $CO_2/CH_4$ ratio of unity. The TGA/DSC experiment on this sample showed that there was some carbon deposition (2% weight loss) .

In a different experiment the 4% $Ni/ZrO_2$ catalyst was heated to 730°C in helium flow before the $CO_2$ and $CH_4$ were introduced ($CO_2/CH_4$ =1). In this case, only minor deactivation was observed (see Fig. 4). Note that this in contrast to the situation when the same sample deactivated very rapidly (Fig. 3). When the sample was heated in the reaction mixture, it had completely deactivated prior to reaching the desired temperature. While the catalyst was relatively stable for 20 hours on stream (fig 4), an increase in the pressure drop across the catalyst bed indicated carbon deposition. This leads us to conclude that carbon formation is significantly more pronounced at low temperatures than above 720°C.

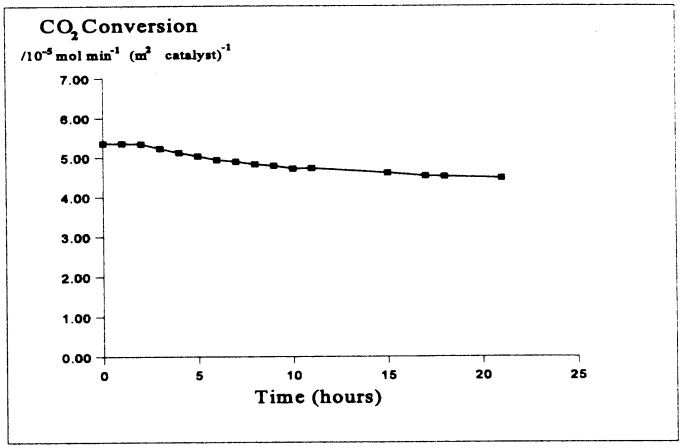


**Figure 4** Stability of 4% $Ni/ZrO_2$ in $CO_2/CH_4$ = 1 feed streams with variation on heating procedure: 4%$Ni/ZrO_2$ heated to 730°C in He, $CO_2/CH_4$ feed then switched on

Figs. 5, 6, and 7 show DSC traces obtained in a flow of air for a series of $Ni/ZrO_2$ catalysts. Fig 5 shows the effect of nickel loading on the type of carbon deposited. The catalysts had been used for $CO_2$ reforming under different conditions, but the severity of the conditions increase for the lower loadings of catalysts. In general, we see two types of carbon on the catalyst in the temperature ranges 450-480°C and 580-600°C. The amount of the high temperature carbon peak seems to increase with the nickel loading. The trace for the 6% $Ni/ZrO_2$ (after deactivation at 470°C in a $CO_2/CH_4$ = 4 flow) is the same as in Fig. 2. There are clearly two types of carbon deposited on the catalyst, with the carbon burning off at the higher temperature seeming to predominate. This form of carbon is less evident on a 4% $Ni/ZrO_2$ catalyst (after 50 hours reaction at 601°C, $CO_2/CH_4$ =4). There is no evidence of any carbon formation on the 1.1% $Ni/ZrO_2$ catalyst after a cycle and reaction at 623°C for 20 hours ($CO_2/CH_4$ =2).

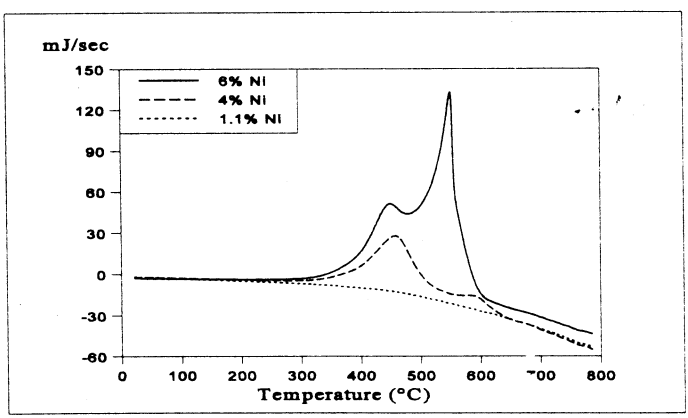


**Figure 5** DSC analysis of used $Ni/ZrO_2$ catalysts having different loadings of nickel. 6% $Ni/ZrO_2$ after deactivation ($CO_2/CH_4$= 4) (see fig. 1) , 4% $Ni/ZrO_2$ after 50h reaction at 601°C ($CO_2/CH_4$= 4), 1.1% $Ni/ZrO_2$ after cycle and 20 hours reaction at 623°C ($CO_2/CH_4$=2)

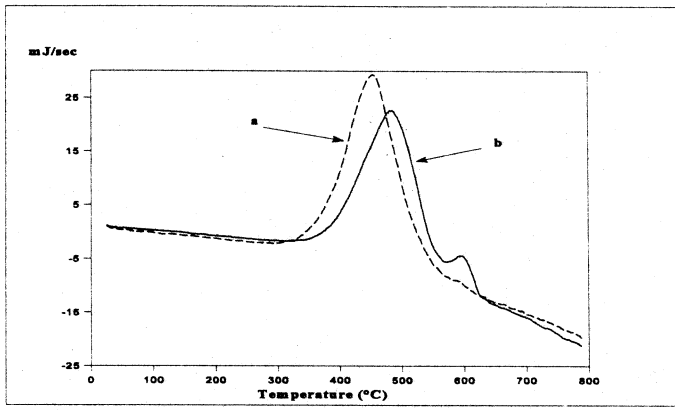


**Figure 6** DSC analysis of (a) 1.7% $Ni/ZrO_2(650)(850)$ and (b) 1.9% $Ni/ZrO_2(850)(850)$ after life tests for 50 hours at 620°C, $CO_2/CH_4$=1. Conversions during the life tests are equivalent.

Fig. 6 shows equivalent results for two catalysts with very similar Ni contents, the first (curve a) having been prepared from a sample of zirconia calcined at 650°C and the second (curve b) having been prepared from a sample calcined at 850°C.

Both catalysts were first tested at 620°C for 50 hours at a $CO_2/CH_4$ ratio of unity and gave equal and constant conversions at this temperature. Again we observed two forms of carbon for 1.9% Ni, with support $ZrO_2$ calcined at 850°C, but only one form in the case of 1.7% $Ni/ZrO_2$ (support calcined at 650°C). This may be connected with the loss of support surface area, as the surface area of the $ZrO_2$ decreases from 29 to 13 $m^2\ g^{-1}$ for this increase in calcination temperature. The higher calcination temperature might also lead to a reduced level of interaction between the support and the metal phase and hence it can be speculated that the high temperature carbon is absent when Ni has a better chance of interacting with $ZrO_2$ or since the particle size seem similar ( Table 1).

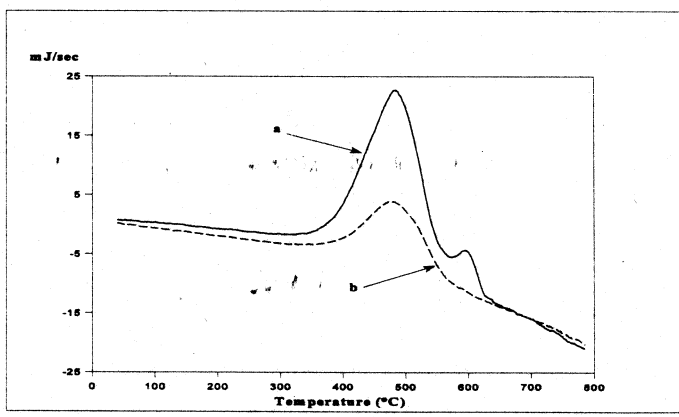


**Figure 7** DSC analysis of 1.9% $Ni/ZrO_2$ after reaction for 50 hours at (a) 620°C and (b) 769°C

Fig. 7 shows the results of a DSC experiment for the 1.9% $Ni/ZrO_2$(850°C) catalyst operated at a higher temperature (769°C). There was less carbon (3 wt%) deposited at 769°C than at the lower operating temperature (8% at 620°C). This supports the conclusion reached above that there is less carbon deposition for $Ni/ZrO_2$ catalysts operated above 720°C.

Further work is required to determine the nature of the different forms of carbon formed on $Ni/ZrO_2$ catalysts during $CO_2$ reforming.

**Conclusions**

$CO_2$ reforming of methane over $Ni/ZrO_2$ catalysts results in carbon deposition for $CO_2/CH_4$ ratios of unity. The stability of the catalysts under carbon forming conditions may be optimised by using catalysts containing low loadings of nickel. Two forms of carbon are observed by DSC analysis on used catalysts having higher loadings of nickel, but only one form is observed with lower loadings of nickel. If the support is calcined at higher temperatures, then catalysts of low loadings also exhibit two types of carbon when tested at 620°C. This may suggest that an interaction between nickel and zirconia contributes to stability. The more stable form of carbon is not observed if the catalyst has been only operated at higher temperatures (769°C).

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