HIGH SURFACE AREA SILICON CARBIDE AS CATALYST SUPPORT

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INTRODUCTION

A novel method has been developed by which activated carbon is converted into high surface area silicon carbide [1]. It comprises the catalytic conversion of nickel loaded activated carbon by reacting it with hydrogen and silicon tetrachloride. Nickel catalyzes both the gasification and the SiC formation, eq. 1 and 2, respectively.

$$C(s) + 2H_2(g) \rightleftarrows CH_4(g) \tag{1}$$

$$SiCl_4(g) + CH_4(g) \rightleftarrows SiC(s) + 4HCl(g) \tag{2}$$
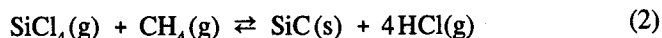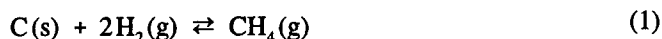
Application of a fluidized bed CVD reactor enables the manufacture of large amounts of SiC granulates with surface areas ranging from 30 to 80 m^2/g [2]. This report deals with the application of high surface area SiC in the carbon dioxide reforming of methane, eq 3.

$$CO_2(g) + CH_4(g) \rightleftarrows 2CO(g) + 2H_2(g) \tag{3}$$
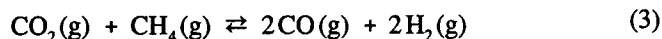
The advantage of utilizing SiC over conventional support lays in its high thermal stability, thermal shock resistance, and heat conductivity [3]. The tendency for coke formation in the CO_2 reforming is higher compared to that in steam reforming which calls for the application of noble metal based catalysts (Rh, Ru, Pt) [4].

EXPERIMENTAL

The high surface area silicon carbide is synthesized in a fluidized bed CVD reactor by reacting H_2 and $SiCl_4$ (45 mol% and 5 mol% in argon) with Norit activated carbon (Elorit, peat-based, steam activated, 655 m^2/g) which had been loaded with 5wt% nickel via pore volume impregnation with nickel nitrate. 30% of the carbon is converted into SiC. The residual carbon has been removed by oxidation in flowing air at 1023 K for 4 hours. The textural properties of the resulting porous SiC were; surface area: 30 m^2/g, pore volume (N_2 adsorption): 0.2 ml/g.

α-Al_2O_3 (Norton, 30 m^2/g) is applied as a reference support material. The noble metal catalysts were prepared by pore volume impregnation of the chloride salts of the desired metal to arrive at 1w% metal loading. The CO_2 reforming experiments have been carried out in fixed bed reactors (ID: 6 mm) using a gas mixture of CH_4, CO_2, and Ar with a flow of 10, 10 and 150 ml/min., respectively. The catalysts amount varied between 10 and 100 mg and were mixed with nonporous SiC to ensure good heat transfer through the bed. The product gases were analyzed with a Hewlett-Packard gas chromatograph.

RESULTS and DISCUSSION

The objective of this research is to determine the stability of SiC based catalysts in a high temperature gas-phase reaction. The total stability of this catalyst system is categorized in three parts: (1) sintering of the SiC, (2) sintering of the active phase, and (3) catalytic activity.

Sintering of high surface area SiC

It is shown that the high surface area SiC retains a major part (>80%) of its surface area, which means that SiC does not sinter under the applied reforming conditions. Although CO_2 reforming is referred to as "dry" reforming, some steam (~2%) is present under reaction conditions, due to the water-gas shift reaction. Previous reports showed that the presence of steam at elevated temperatures causes extensive oxidation and sintering of SiC [2,3] leading to low surface area SiO_2. From the absence of this SiO_2 as identified by X-ray diffraction it can be concluded that the SiC structure is stable after exposure to reforming conditions for 80 hours.

Sintering of the active phase

The metal dispersion after synthesis and ageing under reforming conditions are displayed in table 1.

Table 1. Metal dispersion of reforming catalysts. After synthesis and spent catalysts (80 hours at 1170 K under reforming conditions)

	Ru		Rh	
	Al_2O_3	SiC	Al_2O_3	SiC
$D_{initial}$ (%)	4.4	5	46	20
D_{spent} (%)	0.4	0.1	2	0.8

D ≡ (surface metal atoms)/(total metal atoms)

Similar dispersion of Ru are obtained after synthesis on SiC

and Al_2O_3. The alumina base Rh catalyst displays a higher initial dispersion compared to its SiC based counterpart. Aging at reforming conditions causes severe sintering of the active phase in both cases. The highest residual dispersion was found for Rh on Al_2O_3, *viz.* 2%.

Catalytic activity

Fig. 1 displays the activity of a 1w% Pt/SiC catalyst at 1170 K. The activity of the catalyst increases in the first 10 hours of reforming and remains fairly constant after that period. The activity of the bare SiC support is shown in Fig. 2; for comparison HF treated SiC is included as well. These results show that the activity of bare high surface area SiC increases approximately linearly as a function of time on stream. The CH_4 conversion after 30 hours at 1170 K amounts to 0.4. The HF treated SiC displays negligible activity.
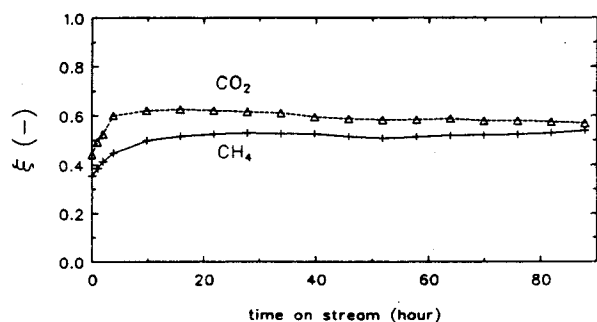

Fig. 1. Activity of 1w% Pt/SiC versus time on stream at 1170 K, $CO_2/CH_4 = 1$, W/F = 2.5 g_{cat}/mol_{CH4}
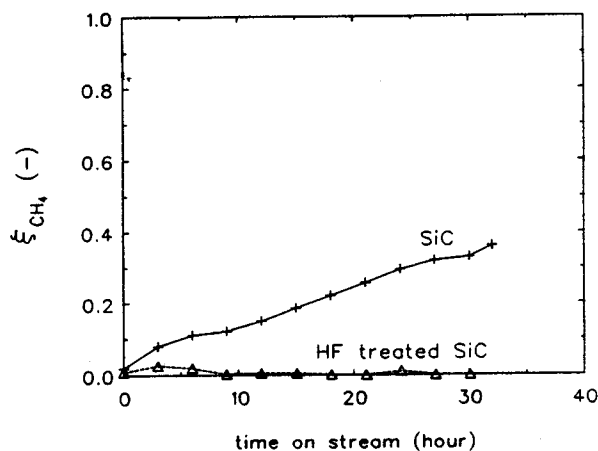
Fig. 2. Activity of SiC and HF treated SiC versus time on stream at 1170 K, $CO_2/CH_4 = 1$, W/F = 4.2 g_{cat}/mol_{CH4}

The activation of both Pt/SiC and bare SiC during reforming

is probably caused by the catalytic activity of the nickel used to synthesize the SiC. Major part of this nickel is initially present as nickel silicide. During reforming this phase might decompose into a silicon phase and metallic nickel, which accounts for the activity enhancement. The activity of this nickel containing SiC support does not influence these catalytic data, because the activity of the noble metal catalysts is much higher than that of the support alone.

Reference experiments with Rh and Ru both on SiC and Al_2O_3 showed that Rh on Al_2O_3 has the highest activity. The activities of Rh on SiC and Ru on Al_2O_3 were moderate, whereas Ru and Pt both on SiC showed similar, but relatively low activities.

CONCLUSIONS

High surface area SiC is stable at reforming conditions at a CO_2/CH_4 ratio of 1. No sintering, oxidation, or change in SiC crystallinity occurs after 80 hours reforming at 1170 K. Comparison of Al_2O_3 and SiC based catalysts shows that the extent of sintering of rhodium is similar on SiC and Al_2O_3. The decrease in dispersion of ruthenium is fractionally larger on SiC than on Al_2O_3. The synthesis nickel in the SiC activates at reforming conditions. Removal of the nickel phase can be achieved by washing with a HF solution. No significant influence of the support on activity is found for the Al_2O_3 and SiC based catalysts. Optimization in Rh and Ru dispersion on SiC might lead to comparable CO_2 reforming catalysts with higher heat conductivity and thermal shock resistance than Al_2O_3 based ones.

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REFERENCES

1. R. Moene, F.W. Tazelaar, J. Schoonman, M. Makkee, and J.A. Moulijn, Proceedings of Carbon '94, Spanish Carbon Group, Granada, Spain, p. 532.
2. R. Moene, L.F. Kramer, J. Schoonman, M. Makkee, and J.A. Moulijn, Proceedings of the 6th Int. Symp. Scientific bases for the preparation of heterogeneous catalysts, Louvain-la-Neuve, 1994, p. 379.
3. R. Moene, M. Makkee, and J.A. Moulijn, Proceedings Advanced catalytic materials, MRS Fall meeting 1994, Boston, to be published.
4. Rostrup-Nielsen and Bak-Hansen, J. Catal., 144 (1993) 38.