

## DESIGN OF STABLE CATALYSTS FOR METHANE - CARBON DIOXIDE REFORMING

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### ABSTRACT

Pt-ZrO<sub>2</sub> is an active and stable catalyst for methane- carbon dioxide reforming reaction. The reaction between CO<sub>2</sub> and CH<sub>4</sub> to yield synthesis gas might proceed via two different pathways. At high temperatures (>1075K) CO<sub>2</sub> can be dissociated on Pt to CO and adsorbed oxygen. Methane can be dissociated to H<sub>2</sub> and carbon at temperatures above 775K. Recombination of the adsorbed oxygen and carbon yields a second CO molecule. At low temperatures i.r. studies of CO<sub>2</sub> adsorption on Pt-ZrO<sub>2</sub>, showed that CO was formed and in addition carbonates were formed on the support. A linear relationship between the activity and the Pt-ZrO<sub>2</sub> perimeter length indicates that the support might be important for activating carbon dioxide and subsequent reaction with carbon.

### 1. INTRODUCTION

Carbon dioxide reforming of methane to produce synthesis gas, (CO<sub>2</sub>+CH<sub>4</sub> = 2CO+2H<sub>2</sub>; ΔH°<sub>298K</sub> = 261.0 kJ/mol) has attracted substantial interest recently (K. Seshan *et al.* 1994, A.T. Ashcroft, *et al.* 1991, J.T. Richardson *et al.* 1990). The reaction route is well suited to produce CO rich syngas or very pure carbon monoxide for the synthesis of bulk chemicals such as acetic acid [4], dimethyl ether and alcohols *via* the oxoalcohols synthesis [5]. The reaction contains similar elementary reaction steps as in steam reforming (H<sub>2</sub>O+CH<sub>4</sub> = CO+3H<sub>2</sub>; ΔH°<sub>298K</sub> = +206.2 kJ/mol) [6], but the absence of water and the higher C/H ratio in the reactant feed favors coke formation [7]. Coke forms readily *via* methane decomposition (CH<sub>4</sub> = C+2H<sub>2</sub>; ΔH°<sub>298K</sub> = +74.9 kJ/mol) and CO disproportionation (2CO = C +CO<sub>2</sub>; ΔH°<sub>298K</sub> = -172.4 kJ/mol).

Both nickel and platinum based catalysts are active for the CO<sub>2</sub>-reforming reaction. The disadvantage of nickel based catalysts is their tendency to form coke and deactivate rapidly [6]. We have shown earlier that Pt/ZrO<sub>2</sub> is a stable (by virtue of low rate of coke formation) and active catalyst for CO<sub>2</sub>, CH<sub>4</sub> reforming [8]. In this contribution we address the characteristics of Pt/ZrO<sub>2</sub> catalysts that influence its catalytic behaviour in order to be able understand the mechanism of the catalysed reaction and help in to optimising catalyst.

## 2. EXPERIMENTAL

ZrO<sub>2</sub> (RC100, Daichi Kigenso, Japan) used in this study contained only the monoclinic phase. The oxide was pressed into pellets and crushed to 0.3-0.6mm grains. These grains were then calcined at 1125K for 15 hours in a stream of dry flowing air (30 ml/min). The catalysts were typically prepared by impregnation of the calcined supports with aqueous 0.1 molar solution of H<sub>2</sub>PtCl<sub>6</sub>. Subsequently, the catalyst precursors were dried at 395K for 8 hours and calcined at 925K for 15 hours in flowing air (30 ml/min).

Catalyst testing was performed in fixed bed (300 mg) continuous flow reactors (using a GC to analyze the products). The feed had a composition of CH<sub>4</sub>/CO<sub>2</sub>/He = 1:1:2 and was passed over the catalyst with a space velocity of 28000 h<sup>-1</sup> (GHSV). Prior to testing, the catalysts were typically reduced *in situ* with 5% H<sub>2</sub> in N<sub>2</sub> for one hour at 1125K. Coke formed on the catalyst was determined by combustion in oxygen and measuring the amount of carbon oxides generated [8,9].

The reaction on the catalyst surface was followed by *in situ* i.r. spectroscopy using a Bruker IFS88 FTIR spectrometer for the characterisation of sorbed species and mass spectroscopy for the analysis of gas phase. The state of Pt was further investigated by *in situ* X-ray absorption spectroscopy (Daresbury, UK, beamline 9.1, transmission mode, Si(220) monochromator, Pt-L<sub>III</sub> edge). Details of catalyst characterisation techniques are reported elsewhere [8,9].

## 3. RESULTS

The characteristics of the catalysts used in this study are shown in Table 1. In all the cases the support is a monoclinic ZrO<sub>2</sub> (Gimex, RC100). For the preparation of the catalysts wet

Table 1 Physicochemical properties of Pt/ZrO<sub>2</sub> catalysts investigated

code	BET area (m <sup>2</sup> .g <sup>-1</sup> )	Pt loading (wt%)	H/Pt	Pt dispersion* (%)	Accessible Pt atoms (10 <sup>18</sup> )	Pt atoms at Pt - ZrO <sub>2</sub> boundary (10 <sup>18</sup> )
1	17	2.0	0.60	60	11	2.4
2	18	1.0	0.82	80	7.4	2.3
3	18	0.5	1.12	100	4.6	2.3
4	17	0.5 <sup>†</sup>	0.33	30	1.5	0.2
5	16	0.4	1.25	100	3.7	2.5
6	16	0.3	1.30	100	2.7	2.0
7	17	0.2	1.35	100	1.8	1.4
8	16	0.1	1.50	100	0.9	0.7

\* catalysts were reduced at 675K. <sup>†</sup>catalyst calcined at 1125K, all others at 925K

impregnation of H<sub>2</sub>PtCl<sub>6</sub> on ZrO<sub>2</sub> precalcined at 1125K was used. Pt dispersions were determined by hydrogen chemisorption. Pt at the interface between Pt particle and ZrO<sub>2</sub> was calculated using Pt particle size determined from hydrogen chemisorption and EXAFS measurements and assuming spherical shape for Pt particles.

For the series of Pt/ZrO<sub>2</sub> catalysts shown in Table 1, we see from *Figure 1* that the catalyst activity initially increases with the amount of accessible Pt atoms but reaches a plateau even when the amount of accessible Pt is still increasing. Diffusional limitations were excluded by appropriate measurements and, also thermodynamic limitation was excluded. This indicates that not all Pt atoms contribute equally active for the activity of the catalyst. However, the catalyst activity seems to

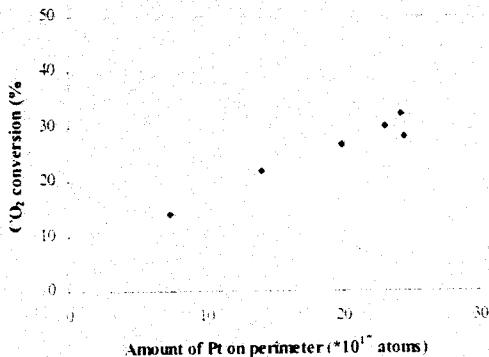


Figure 2 Dependence of catalyst activity at 875K on the amount of Pt on the Pt-ZrO<sub>2</sub> perimeter of Pt/ZrO<sub>2</sub> catalysts

Figure 3 shows the i.r. spectra of CO<sub>2</sub> adsorption on a Pt/ZrO<sub>2</sub> catalyst (sample 3, Table 1). The spectra indicate the formation of carbonate type species on the support (1540-1365 cm<sup>-1</sup>) and linearly bound CO (2035cm<sup>-1</sup>) on Pt metal. Catalysts which did not show this carbonate formation, such as Pt/SiO<sub>2</sub>, were almost inactive for CO<sub>2</sub>/CH<sub>4</sub> reforming. Dissociation of CO<sub>2</sub> (to CO and adsorbed oxygen) on Pt was also seen using transient experiments.

Pulse transients using methane showed that methane decomposed over Pt giving gas phase hydrogen and leaving carbon on Pt. Subsequent admission of oxygen in pulses indicated that the carbon deposited by methane decomposition could be removed quantitatively by oxidation. Pulsing of carbon dioxide could also oxidize this carbon quantitatively and give gas phase CO. These reaction cycles could be repeated on the catalyst.

#### 4. DISCUSSIONS

The presence of CO on Pt (seen by the i.r. bands at 2053 cm<sup>-1</sup>, and carbon dioxide transients) indicates the dissociation of CO<sub>2</sub>. This indicates rapid dissociative adsorption of CO<sub>2</sub> into CO and atomic oxygen over Pt. However, XANES measurements under these reaction conditions did not indicate oxidation of Pt by the decomposition of carbon dioxide. This is to be expected because Pt-O is not stable at these higher temperatures (>800K) and therefore the oxygen would be liberated to the gas phase leaving Pt in a metallic state.

We have seen from methane transient experiments that it dissociates over Pt leaving carbon behind and generating hydrogen in the gas phase. If carbon dioxide dissociation occurs in a concerted

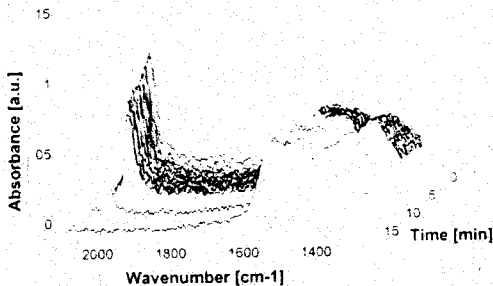


Figure 3 Time resolved IR spectra during CO<sub>2</sub> adsorption on Pt/ZrO<sub>2</sub>. T=775K, pCO<sub>2</sub>=0.25, total flow 30ml/min<sup>-1</sup>

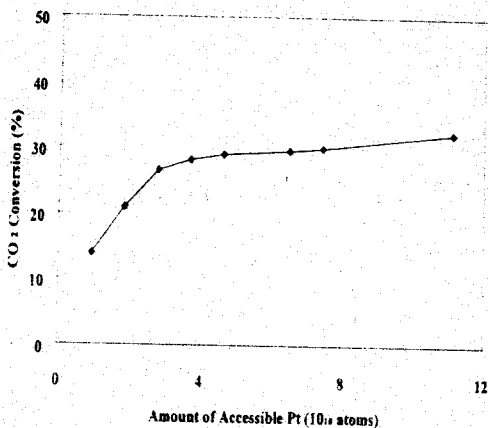


Figure 1 Influence of the Pt-loading on the activity of Pt/ZrO<sub>2</sub> catalysts for CO<sub>2</sub>/CH<sub>4</sub> reforming at 875K  
CO<sub>2</sub>/CH<sub>4</sub>/He/N<sub>2</sub> = 42/42/75/10, 300mg catalyst

fashion with methane decomposition the carbon left behind can react with adsorbed oxygen (which is not stable over Pt under reaction conditions) from CO<sub>2</sub> and generate CO. Steady state and non steady state kinetic measurements suggest that methane carbon dioxide reforming proceeds in sequential steps combining dissociation and surface reaction of methane and adsorbed oxygen species.

The linear relationship between perimeter length and activity of Pt/ZrO<sub>2</sub> indicates the importance of the support for catalytic activity. We believe that the activation of CO<sub>2</sub> occurs on the support at the Pt-ZrO<sub>2</sub> perimeter (as carbonates) which is followed by the reaction of the

activated carbonate with methane to give H<sub>2</sub> and CO. We propose that the activated carbonate is the source for the oxygen which reacts with the carbon formed, from methane, on Pt. The idea of carbon dioxide activation on the support is also substantiated by the experiments with Pt-black. This catalyst showed a significant lower activity (two orders of magnitude) than Pt/ZrO<sub>2</sub> because Pt-black does not have the possibility of activation the CO<sub>2</sub> on the support. This implies that the perimeter is involved in the rate determining step of the reaction, possibly by combining carbon, formed from methane on the metal, and oxygen, formed from the carbonates on the support.

## 5. CONCLUSIONS

Methane reforming with carbon dioxide over Pt/ZrO<sub>2</sub> proceeds in a complex sequence of reaction steps involving decomposition of methane on the Pt to CH<sub>x</sub> (average value of x=2) and H<sub>2</sub>. In the second set of reactions CO<sub>2</sub> reduction occurs via initial formation of a carbonate type species at the metal-support boundary. The reaction between the surface bound carbon (from methane dissociation) and the carbonate (from CO<sub>2</sub> activation) yields carbon monoxide via a formate intermediate. A stable catalyst can only be achieved if the two sets of reactions are balanced.

The support and the active metal play an important role in ensuring catalyst stability. For a noble metal such as Pt, which itself has a low tendency to form coke, the minimization of the concentration of acid sites on the support is most critical. ZrO<sub>2</sub> is unique in that respect as it combines strong anchoring of the Pt metal particle and very low concentrations of (Lewis) acid sites (important for minimizing carbon formation on the support). A 0.5wt%Pt/ZrO<sub>2</sub> catalyst shows very good stability and proved to be well suited for upscaling [10].

## 6. ACKNOWLEDGMENTS

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