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The role of the oxidic support on the deactivation of Pt catalysts during the CO₂ reforming of methane

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Abstract

Pt supported on γ -Al₂O₃, TiO₂ and ZrO₂ are active catalysts for the CO₂ reforming of methane to synthesis gas. The stability of the catalysts increased in the order Pt/ γ -Al₂O₃ < Pt/TiO₂ < Pt/ZrO₂. For all catalysts, the decrease in activity with time on stream is caused by carbon formation, which blocks the active metal sites for reaction. With Pt/TiO₂ and Pt/ZrO₂, deactivation started immediately after the start of the reaction, while the Pt/ γ -Al₂O₃ catalyst showed an induction period during which carbon was accumulated without affecting the catalytic activity.

Keywords: Pt catalysts; Catalyst deactivation; Methane/CO₂ reforming

1. Introduction

Methane/CO₂ reforming is an important route to produce CO rich synthesis gas or very pure carbon monoxide [1,2]. The highly endothermic reaction yields equimolar amounts of CO and hydrogen. Under usual reaction conditions the catalysts deactivate severely due to coke formation [3] via the exothermic CO disproportionation ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$; $\Delta H_{298\text{K}}^0 = -172.4$ kJ/mol) and the moderately endothermic methane decomposition ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$; $\Delta H_{298\text{K}}^0 = +74.9$ kJ/mol). Reduction of the deactivation was achieved either by adding water or oxygen to the feed gas stream, i.e., to couple methane–CO₂ reforming with methane steam reforming [4] or partial oxidation of CH₄ [4]. Alternatively, the amount of coke may be

minimized by using catalysts which show a relatively slow rate of methane decomposition and/or CO disproportionation. In this respect, noble metal catalysts were reported to be promising [4–7].

We reported previously that Pt supported on ZrO₂ is active, selective and stable for the CO₂/CH₄ reforming and that the extent of coke formation [8] was minimal. In order to test to what extent this is unique to Pt/ZrO₂, the catalytic properties of Pt catalysts supported on γ -Al₂O₃, TiO₂ and ZrO₂ are compared in the present study.

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by the incipient wetness technique. For this purpose, a solution

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of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in water (0.01 g Pt per ml) was used. The support was first calcined for 15 h at 1125 K (heating rate 3 K/min) in flowing air (30 ml/min (NTP)). The support was isostatically pressed into pellets at 4000 bar for 5 min. The pellets were crushed and sieved to give grains having diameters between 0.3 and 0.6 mm. The grains were impregnated with the H_2PtCl_6 solution to yield a catalyst with 0.5 wt.-% Pt. The water was removed by heating the catalyst at 365 K for 2 h in a rotating evaporator followed by drying over night at 395 K in static air. Subsequently, the impregnated grains were calcined at 925 K for 15 h (heating rate 3 K/min). The Pt content of the catalyst was determined by atomic absorption spectroscopy. The following supports were used: $\gamma\text{-Al}_2\text{O}_3$ (000-3AQ, AKZO), TiO_2 (P-25, Degussa, mixture of anatase and rutile) and ZrO_2 (RC-100, Gimex, monoclinic).

2.2. Catalyst testing

Typically 500 mg of catalyst were loaded into a tubular quartz reactor (inner diameter 5 mm) which was placed in an oven. The catalyst grains were kept in place by quartz wool plugs. A thermocouple was placed on top of the catalyst bed to measure the catalyst temperature. The oven temperature was controlled by a Eurotherm temperature controller. The catalysts were reduced in situ with 5% H_2 in N_2 for 1 h at 1125 K. After reduction, the temperature was lowered in Ar to the reaction temperature (875 K) and the catalyst was subsequently exposed to the feed gas mixture (25% CH_4 , 25% CO_2 , 5% N_2 and 45% Ar for a total flow of 283 ml min^{-1}). The reaction products were analyzed in a gas chromatograph (Varian GC3300), equipped with two 3 m carbosieve columns and a TCD.

2.3. Analysis of the carbon deposited on used catalysts

The amount of carbon on used catalysts was determined by oxidation to CO_2 using oxygen.

Prior to the analysis, the used sample (200 mg) was heated in He to 925 K (heating ramp 30 K./min) to remove any adsorbed CO_2 . Subsequently, oxygen pulses (525 μl) were added to the He stream. The oxygen content of the outlet was monitored with a mass spectrometer. Pulsing was continued until changes in the oxygen signal were no longer observed. The amount of carbon oxidized was calculated from the oxygen uptake.

2.4. Dispersion measurements

The dispersion of Pt was determined by pulse hydrogen chemisorption. The catalysts were reduced ex situ at 1125 K. Subsequently, the catalysts were again reduced at 675 K in the pulse chemisorption apparatus. The samples were then flushed for 1 h in Ar at 675 K and cooled down to 273 K. At this temperature, 52 μl pulses of 6% H_2/Ar were passed over the sample and the concentration of H_2 at the reactor outlet was determined by a TCD. The dispersion was calculated from the extent of H_2 uptake assuming a Pt/H ratio of one.

3. Results

The physicochemical properties of the catalysts are summarized in Table 1. The catalysts have similar metal dispersions.

Fig. 1 shows the activities of the different catalysts at 875 K as function of time on stream. The activities of the catalysts were initially similar. However, the Pt/ $\gamma\text{-Al}_2\text{O}_3$ deactivated almost completely within 10 h. Pt/ TiO_2 deacti-

Table 1
Physicochemical properties of the investigated Pt catalysts

Catalyst	Metal loading (wt.-%)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pt dispersion * (%)
$\gamma\text{-Al}_2\text{O}_3$	0.5 ± 0.2	112	35
TiO_2	0.5 ± 0.2	5	25
ZrO_2	0.5 ± 0.1	16	33

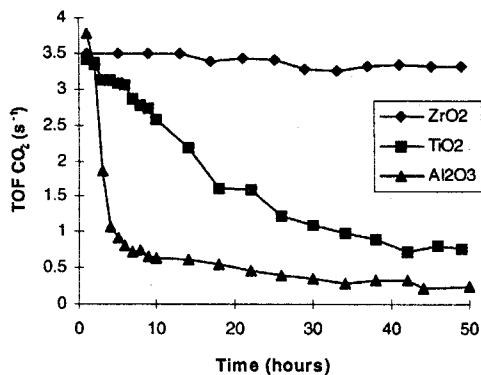


Fig. 1. Stability tests of different supported Pt catalysts for CO_2/CH_4 reforming at 875 K.

vated with 80% within 50 h on stream whereas the Pt/ ZrO_2 showed only a 5% deactivation within 50 h on stream.

After use at 875 K for 25 h, the Pt dispersions of the different catalysts were again determined with and without the carbon removed from the surface by oxidation in 5% O_2/He at 675 K. The results of these dispersion measurements are compiled in Table 2. The coked samples showed low hydrogen uptake values, while those of the oxidized and reduced samples (e.g., after carbon removal) were identical to those of the fresh samples.

Because the original dispersion was restored after burning the coke accumulated, we conclude that the dispersion of the catalyst is unaffected by use. Thus, we conclude that it is not the loss in metal dispersion that causes the deactivation during use, but the coverage of Pt by coke. In order to probe for the rate of coke

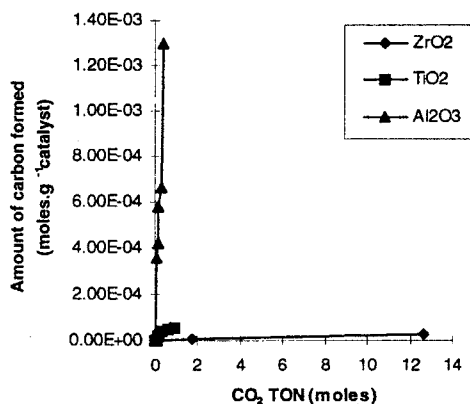


Fig. 2. Amounts of carbon formed as a function of the total amount of CO_2 converted for different Pt catalysts during CO_2/CH_4 reforming at 875 K.

formation in comparison to the rate of the reforming reaction, the reaction was stopped after various times on stream (i.e., after 0.5, 1, 2, 5, 10, 25 h for Pt/ $\gamma\text{-Al}_2\text{O}_3$; 2, 5, 10, 25, 50 h for Pt/ TiO_2 and 25, 180 h for Pt/ ZrO_2) and the amount of carbon was determined.

In Fig. 2, the amount of carbon deposited on the catalyst as function of the number of feed molecules converted (i.e., the turn over number, TON) is shown. The graph indicates that Pt/ $\gamma\text{-Al}_2\text{O}_3$ formed more coke than Pt/ TiO_2 and Pt/ ZrO_2 . In Fig. 3, the reaction rates for the three catalysts (i.e., the number of molecules converted per accessible Pt site per s) are plotted versus the amount of carbon formed. The Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst showed an induction period during which the catalyst maintained high activity despite the carbon accumulation. Subse-

Table 2
Dispersions of the different Pt catalysts, fresh, used and after regeneration

Catalyst	Treatment	Apparent dispersion (%)	CO_2 conversion (%)
Pt/ $\gamma\text{-Al}_2\text{O}_3$	Fresh catalyst	35	32
Pt/ $\gamma\text{-Al}_2\text{O}_3$	Used at 875 K for 25 h	9	3
Pt/ $\gamma\text{-Al}_2\text{O}_3$	Used at 875 K for 25 h, after carbon burn off	35	
Pt/ TiO_2	Fresh catalyst	25	20
Pt/ TiO_2	Used at 875 K for 25 h	0.5	8
Pt/ TiO_2	Used at 875 K for 25 h, after carbon burn off	25	
Pt/ ZrO_2	Fresh catalyst	33	30
Pt/ ZrO_2	Used at 875 K for 25 h	7	29
Pt/ ZrO_2	Used at 875 K for 25 h, after carbon burn off	32	

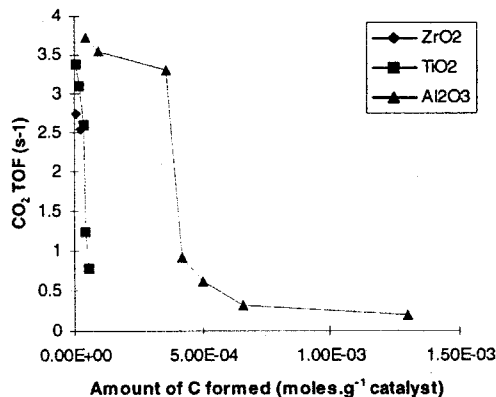


Fig. 3. Activity of Pt catalysts as a function of the amount of carbon formed during CO₂/CH₄ reforming at 875 K.

quently, the catalyst deactivated quickly. Pt/TiO₂ and Pt/ZrO₂ did not show such an induction period.

4. Discussion

All three catalysts deactivated with time on stream. Because hydrogen chemisorption showed a marked decrease of the accessible metal surface area after use, the deactivation is concluded to be caused by blocking of a fraction of the metal surface or by sintering. The fact that the catalysts could be completely regenerated by means of oxidation suggests that it is primarily coke that blocks the metal surface. There was no indication of a change in the size of the metal crystallites.

The concentrations of coke formed on the three catalysts is very different after 25 h of reaction. Pt/ZrO₂ and Pt/TiO₂ showed low concentrations of coke, 7.7×10^{-6} and 4.6×10^{-5} mol carbon per g catalyst, respectively, while the concentration of coke deposited on the Pt/ γ -Al₂O₃ sample is significantly higher, i.e., 6.6×10^{-4} mol carbon per g catalyst. The way the coke and the available metal surface change the rate of methane/CO₂ reforming during the experiments is quite different for the three tested catalysts. For Pt/ZrO₂ and Pt/TiO₂, the TOF strongly decreased with increasing amounts of carbon deposited while a more complex deacti-

vation pattern was found for Pt/ γ -Al₂O₃. In the latter case, the initial build up of coke is not accompanied by a decrease in activity. However, after a certain period, the deactivation sets in and proceeds more rapidly compared to the other two samples. A separate experiment in which the γ -alumina carrier was exposed to the reaction gas mixture at 875 K for 25 h showed clearly that the amount of coke formed was nearly identical with that on Pt/ γ -Al₂O₃. This indicates that the coke is primarily formed on the carrier material. The reason for the different deactivation behavior for the Pt catalysts is then speculated to be related to the fact that the surface of the Pt crystallites of Al₂O₃ differs from that on partially reduced supports like TiO₂. In both cases, coke formation is concluded to occur primarily on the support. The coke formed on the support covers, with time on stream, the metal particle. In the latter case of Pt/TiO₂, it is well established that small oxidic crystallites decorate the metal particles [9,10] and may so allow the oxide catalyzed reaction to occur close to the metal, which in turns lets coking start immediately to affect adversely the reaction on the metal.

5. Conclusions

The results show that the activity of the catalysts for the methane/CO₂ reforming is determined by the availability of Pt. The deactivation is primarily caused by coke deposition on the Pt crystals. The deactivation is concluded to originate from the catalyst support and the individual deactivation behavior depends subtly on the microstructural arrangement of the metal particle on the support.

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