

Carbon Deposition during Carbon Dioxide Reforming of Methane—Comparison between Pt/Al₂O₃ and Pt/ZrO₂

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The relation between coke formation and the deactivation of supported Pt catalysts during CO₂ reforming of methane at temperatures above 1070 K such as used in the commercial process was studied. Temperature-programmed oxidation and temperature-programmed reaction with CO₂ were applied to Pt catalysts (Pt/Al₂O₃ and Pt/ZrO₂) which were exposed to CH₄/CO₂ (reforming reaction conditions) or CH₄/He (facile coke formation) to identify the carbon species. The activity decrease for Pt/Al₂O₃ was rather slow and minor at high temperature (≥ 1070 K), while it was fast and almost complete during a comparative experiment at low temperature (875 K). Coke deposited on the supported Pt particles was oxidized by CO₂, but coke on the Al₂O₃ support was not removed at 1070 K. At this temperature the decay in activity with time on stream corresponded solely to the amount of coke accumulated on Pt particles. This indicates the main reaction between CO₂ and CH₄ on all Pt atoms without significant participation of the support. The activity is concluded to decrease gradually due to coverage of Pt by coke induced by CH₄ decomposition (initial phase of deactivation observed at high temperature). After a while only the perimeter of Pt particles remains as site of activity. There, the activity is speculated to be stable because of the higher reactivity of CO₂ at the metal-support boundary. Gradually, the coke on the support (Al₂O₃) increases to an extent that it blocks the reaction also at that location. In contrast to the situation with Pt/Al₂O₃, coke was not observed on Pt/ZrO₂ even after exposure to reforming gas (CH₄/CO₂) for 12 h. The combination of three factors is concluded to cause the high catalytic stability of Pt/ZrO₂ in CO₂/methane reforming: (i) coke on Pt (supported on ZrO₂) is more reactive toward CO₂ than coke on Pt (supported on Al₂O₃) under reforming reaction conditions; (ii) methane decomposition is slower on Pt/ZrO₂ than on Pt/Al₂O₃; and (iii) coke is hardly formed on the ZrO₂ support. © 2001 Academic Press

INTRODUCTION

CO₂ reforming of methane is attractive to generate synthesis gas with a H₂/CO ratio of unity. This ratio can be adjusted by combining CO₂ reforming with steam reforming from 1 to 3. Note that gas fields sometimes contain CO₂ (≥ 25 vol%), which may be an incentive to apply in part CO₂ reforming rather than separating methane and CO₂ (1). Typically, supported Ni or noble metals are reported as potential catalysts for the reaction (1–13). Catalyst deactivation, however, is a serious challenge and must be overcome by an effective catalyst. Two potential causes of deactivation exist, i.e., coke deposition (1, 2, 4–13) and sintering of the metal particles (2, 4, 10, 11). Most authors agree, however, that coke formation is the main cause of deactivation.

Coke originates mainly from two reactions, i.e., methane decomposition (CH₄ → C + 2H₂) and carbon monoxide disproportionation (2CO → C + CO₂). The former is endothermic and favored at higher temperatures and under lower pressures, while the latter is exothermic and favored at lower temperatures and higher pressures.

Pt/ZrO₂ has been found to be stable for more than 500 h during reaction at 900 K (12, 14). On the other hand, Pt/Al₂O₃ and Pt/TiO₂ deactivate rapidly under the same conditions. It has been shown earlier that the stability of supported Pt Catalysts depends strongly on the nature of the support and its ability to form carbonates (14–17). The reaction is thought to proceed at the interface of Pt and ZrO₂ (14, 15), demonstrating that a bifunctional mechanism is operative on Pt/ZrO₂ at relatively low temperatures (875 K). The reaction sequence involves dissociation of methane on Pt to molecular hydrogen and partially dehydrogenated methane (CH_x: $0 \leq x \leq 3$) as a surface species. This CH_x species is oxidized by CO₂ chemisorbed on the support. Unbalanced rates of these processes result in coking and deactivation (14–17). Although carbon is generated under these conditions both on Pt and on the support, deactivation appears to be solely related to the carbon on

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the Pt atoms in the vicinity of the perimeter near the support (17). While these elementary steps are well confirmed, the marked differences between different supports and the variations in stability as a function of temperature remain quantitatively unexplained.

Pt/ZrO₂ and Pt/Al₂O₃ have been chosen for the present study as these materials represent the most significant differences with respect to the catalytic stability, the former being very stable and the latter deactivating rapidly. These two materials are, thus, suitable model catalysts for developing a better understanding of the nature of coking in methane CO₂ reforming. The purpose of the present communication is to address mechanistic details of coking and its relation to catalyst performance at temperatures typically used for commercial operation (≥ 1070 K). Temperature-programmed oxidation (TPO), temperature-programmed desorption (TPD) of CO₂, and temperature-programmed reaction (TPRn) with CO₂ are used to characterize the reactivity of the coke on supported Pt catalysts which were exposed to CH₄/CO₂ (CO₂ reforming of methane) or CH₄/He (methane as the source of coking).

METHODS

Catalyst Preparation

Pt/ZrO₂ and Pt/Al₂O₃ were prepared by the wet impregnation technique. For this, H₂PtCl₆ · 6H₂O in water (10 mg Pt per ml), ZrO₂ (RC-100, Gimex, Japan), and Al₂O₃ (000-3AQ, AKZO, The Netherlands) were used. The ZrO₂ powder was pressed at 4000 bar for 5 min, while Al₂O₃ was obtained by extruding the gel. The pellets were crushed and sieved to particles with diameter between 0.3 and 0.6 mm. The grains were calcined for 15 h at 1125 K (heating rate 3 K min⁻¹) in flowing air (30 ml min⁻¹) and subsequently impregnated with Pt (0.5 wt%). The catalysts were dried at 365 K for 2 h in a rotating evaporator and were followed by drying overnight at 395 K in static air. The impregnated grains were calcined (heating rate 3 K min⁻¹) for 15 h at 925 K in flowing air (30 ml min⁻¹). The Pt content of catalysts was determined by atomic absorption spectroscopy. The dispersions of Pt for PtAl₂O₃ and Pt/ZrO₂ were 80 and 100%, respectively (17), after the catalysts were reduced at 775 K.

Reforming Reaction

Typically, 300 mg of catalyst was loaded into a tubular quartz reactor (inner diameter 5 mm), which was placed in a furnace (200 mg of Pt/ZrO₂ was used for measurement at 1125 K). The catalyst grains were kept in the middle by plugs of quartz wool at both sides. A quartz-sleeved thermocouple was placed on the top of catalyst to measure the catalyst temperature. The furnace temperature was controlled by a Eurotherm temperature controller. After the

catalyst was reduced *in situ* with H₂/N₂ (5/95 (v/v)) for 1 h at 1125 K, the temperature was lowered in flowing Ar to the reaction temperature and the reactant gas (25% CH₄, 25% CO₂, 5% N₂, and 45% Ar with a total flow of 170 ml min⁻¹) was fed to the reactor. The reaction products were analyzed by a gas chromatograph (Varian 3400) equipped with a 3m-carbosieve column and a TCD.

Temperature-Programmed Oxidation (TPO) and Temperature-Programmed Reaction (TPRn) with CO₂

TPO and TPRn with CO₂ were performed in an Altamira AMI-2000 apparatus. One hundred milligram of catalysts was loaded into a tubular quartz reactor and a thermocouple was placed at the top of the catalyst layer. The catalyst was reduced with H₂ for 1 h at 1120 K. After reduction, the temperature was lowered to 1070 K in flowing He and the feed gas mixture (CH₄/CO₂ (1/1) or CH₄/He (1/1) with a total flow of 28 ml min⁻¹) was fed to the reactor for required time. Then, the catalyst was kept in He for 30 min at the temperature and cooled to 340 K.

For the TPO experiment, the sample was subsequently exposed to a flow of O₂/He (5/95 with a total flow of 30 ml min⁻¹) at 340 K and subsequently heated up to 1273 K (heating rate 10 K min⁻¹). CO ($m/e = 28$) and CO₂ ($m/e = 44$) originating from the deposited carbon were measured with a mass spectrometer and these were also checked quantitatively by GC (HP-5880).

TPO was also measured for unsupported metallic Pt. For this purpose, [Pt(NH₃)₄]²⁺(OH)₂ (15.2 mg) was loaded to the reactor and calcined for 5 h at 923 K (heating rate 3 K min⁻¹) in O₂/He (5/95 with total flow of 30 ml min⁻¹) and subsequently reduced with H₂ at 1120 K and treated in the same way as described above.

For TPRn with CO₂, CO₂/He (10/90 with a total flow of 30 ml min⁻¹) was fed instead of O₂/He in the above experiment. After the temperature reached 1273 K, it was kept for 10 min under CO₂ atmosphere. Only CO ($m/e = 28$) was analyzed. The contribution of CO fragment due to carrier gas CO₂ (11.4%) was subtracted.

Temperature-Programmed Desorption (TDP) of CO₂

For this purpose the same apparatus as for TPO was used. Prior to adsorption, the catalyst was reduced with H₂ at 1120 K. Subsequently, the catalyst was degassed in He and cooled to 325 K. At this temperature CO₂ (50 ml min⁻¹) was fed to the reactor for 1 h. After degassing at 325 K the desorption sequence was started (He flow 30 ml min⁻¹, heating rate 10 K min⁻¹). The evolving gases were monitored by means of a TCD (GC, HP-5880).

Scanning Electron Microscopy (SEM)

SEM picture for unsupported metallic Pt was measured by HITACHI S-800 after the reduction.

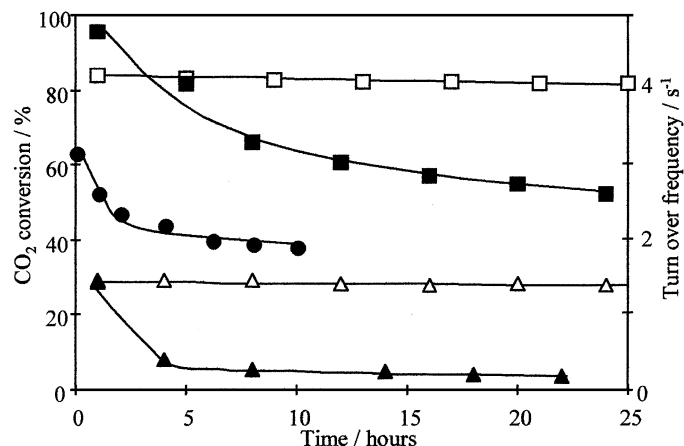


FIG. 1. Stability tests for supported Pt catalysts at different temperatures with $\text{CO}_2/\text{CH}_4/\text{Ar} + \text{N}_2 = 42/42/85/\text{ml min}^{-1}$. $\square$, Pt/ZrO₂ (0.2 g) at 1125 K; $\blacksquare$, Pt/Al₂O₃ (0.3 g) at 1125 K; $\bullet$, Pt/Al₂O₃ (0.3 g) at 1070 K; $\triangle$, Pt/ZrO₂ (0.3 g) at 875 K; $\blacktriangle$, Pt/Al₂O₃ (0.3 g) at 875 K. (TOF was calculated based on the dispersions shown in the text. TOF values for $\square$ and $\triangle$ have been multiplied by 0.8 and 1.3, respectively, in order to use the same scale.)

RESULTS

Figure 1 shows the CO_2 conversion ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$) over Pt/Al₂O₃ and Pt/ZrO₂ as a function of time on stream at different reaction temperatures. The results are reproduced from Refs. 14 and 15. Since the equilibrium CO_2 conversions at 1125, 1070, and 875 K are 98, 96, and 61%, respectively, the contribution of reverse reaction on catalytic activity and stability would be minimized. Note that Pt/ZrO₂ maintains stable activity for 500 h at all temperatures, while Pt/Al₂O₃ deactivates almost completely during the low-temperature (875 K) experiments, but only partly during the high-temperature (≥ 1070 K) experiments.

Temperature-Programmed Oxidation

TPO profiles of the carbon on Pt/Al₂O₃ and Pt/ZrO₂ after exposure to CH_4/CO_2 for 1, 12, and 24 h are shown in Fig. 2. Figure 2b is the expansion of Fig. 2a between 573 and 1173 K. The intensity for CO ($m/e = 28$) was 11.4% compared to that for CO_2 ($m/e = 44$) for all TPO experiments corresponding perfectly to fragmentation of CO_2 . Thus, all coke was converted to CO_2 . Two peaks (small shoulder at 750 K and main peak at ≥ 840 K) were observed for Pt/Al₂O₃. Both peaks increased with time of exposure. With Pt/ZrO₂ evolution of CO_2 was not observed even after 12 h exposure.

Most authors propose that coke causing catalyst deactivation originates from CH_4 (6, 18, 19). Using thermogravimetry, van Keulen *et al.* demonstrated that for supported Pt catalysts carbon was not formed via CO disproportionation, but via CH_4 decomposition despite the fact that the Boudouard reaction ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) is thermodynamically fea-

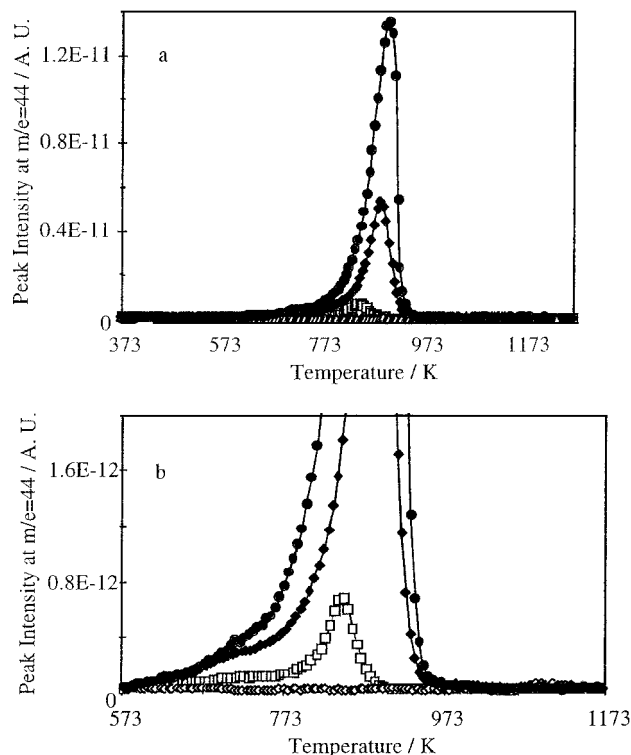


FIG. 2. Temperature-programmed oxidation (TPO) profiles for supported Pt catalysts after exposure to CH_4/CO_2 at 1070 K (Fig. 2b is an expansion of Fig. 2a). $\diamond$, Pt/ZrO₂ for 12 h; $\square$, Pt/Al₂O₃ for 1 h; $\blacklozenge$, Pt/Al₂O₃ for 12 h; $\bullet$, Pt/Al₂O₃ for 24 h.

sible under reaction conditions (19). In order to explore coking under the more severe conditions of the present study, Pt/Al₂O₃ and Pt/ZrO₂ were exposed to CH_4/He for 10 min at 1070 K and carbon deposition was analyzed subsequently by TPO (see Fig. 3). Two peaks (shoulder at 750 K and main peak at >840 K) were observed for Pt/Al₂O₃ and the peak temperatures coincided approximately with those

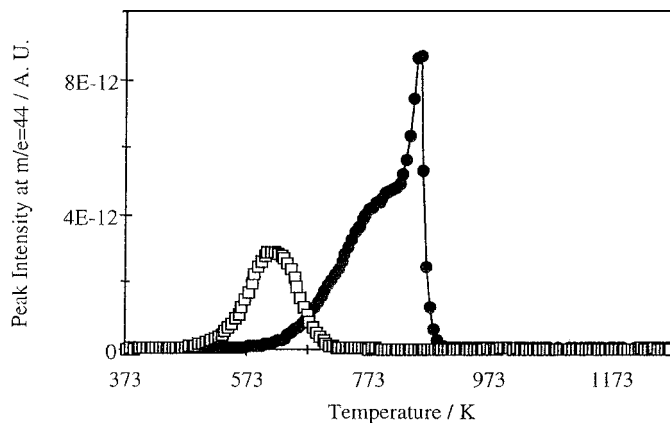


FIG. 3. Temperature-programmed oxidation (TPO) profiles for supported Pt catalysts after exposure to CH_4/He at 1070 K for 10 min. $\square$, Pt/ZrO₂; $\bullet$, Pt/Al₂O₃.

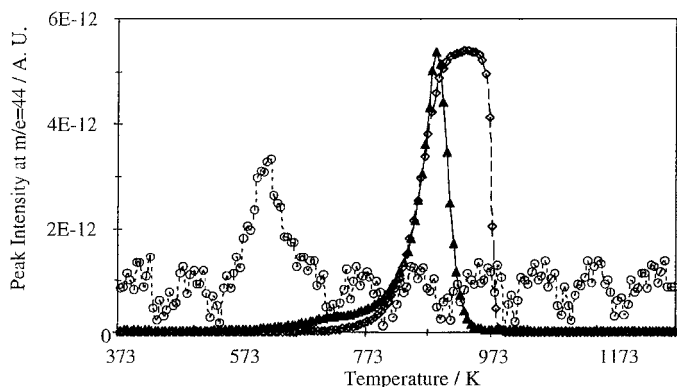


FIG. 4. Temperature-programmed oxidation (TPO) profiles after exposure at 1070 K for (○) unsupported metallic Pt ($\times 50$) (CH₄/He for 1 h), (▲) Pt/Al₂O₃ (CH₄/CO₂ for 12 h), and (◇) Al₂O₃ ($\times 0.1$) (CH₄/CO₂ for 12 h).

after exposure to CH₄/CO₂, while a single peak (615 K) was observed for Pt/ZrO₂. The peak temperature for Pt/ZrO₂ was about 140 K lower than that for Pt/Al₂O₃. It should be emphasized that the amount of coke was almost the same when Pt/Al₂O₃ was exposed to CH₄/He for 10 min, or when exposed to CH₄/CO₂ for 24 h. This is in agreement with the conclusion that CH₄ decomposition is the source of coking (19).

To analyze the origin of the TPO peaks, the TPO profile for Pt/Al₂O₃ after exposure to CH₄/CO₂ for 12 h is compared with those for unsupported metallic Pt after exposure to CH₄/He for 1 h and Al₂O₃ after exposure to CH₄/CO₂ for 12 h (see Fig. 4). For unsupported metallic Pt and Al₂O₃ only one peak was seen and the temperatures were about 620 and 930 K, respectively. The peak area for Al₂O₃ was 20 times larger than that for Pt/Al₂O₃ after feeding the same gas (CH₄/CO₂) for 12 h. Similarly, the TPO profile for Pt/ZrO₂ after exposure to CH₄/He for 10 min is compared with that for unsupported metallic Pt after exposure to CH₄/He for 1 h and ZrO₂ after exposure to CH₄/He for

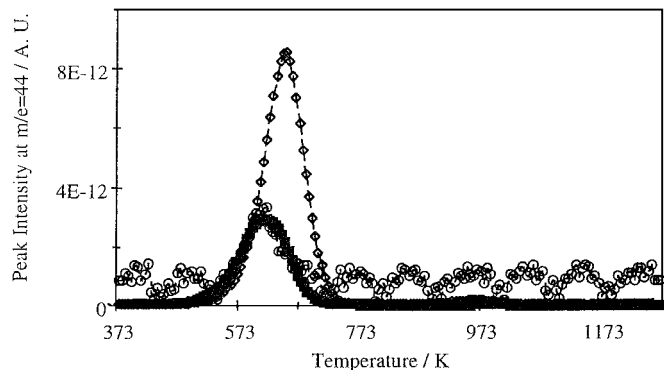


FIG. 5. Temperature-programmed oxidation (TPO) profiles for (○) unsupported metallic Pt ($\times 50$) (for 1 h), (■) Pt/ZrO₂ (for 10 min), and (◇) ZrO₂ (for 12 h) after exposure to CH₄/He at 1070 K.

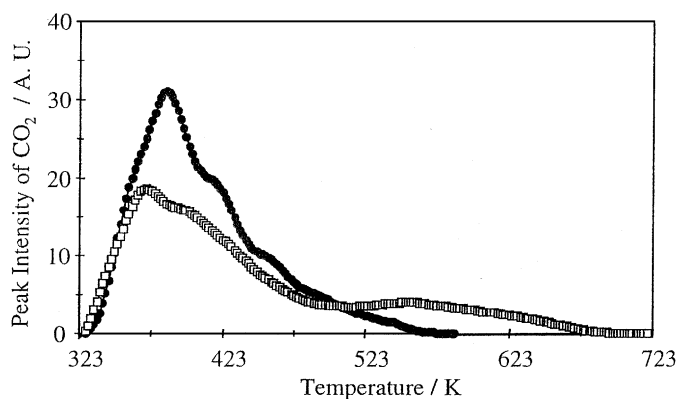


FIG. 6. Temperature-programmed desorption (TPD) profiles of CO₂ for supported Pt catalysts. ●, Pt/Al₂O₃; ○, Pt/ZrO₂.

12 h (see Fig. 5). For ZrO₂ a single peak was observed and the temperature maximum of the CO₂ desorption peak was (655 K) was 40 K higher than that for Pt/ZrO₂.

Temperature-Programmed Desorption of CO₂

In order to prove if carbonate on the support contributes to the TPO profiles, TPD of CO₂ was measured for Pt/Al₂O₃ and Pt/ZrO₂ and the results are shown in Fig. 6. Carbonate on Pt/Al₂O₃ and Pt/ZrO₂ desorbed below 573 and 723 K, respectively. This indicates that carbonate is not present on the catalyst after degassing at 1070 K and does not contribute to the TPO profiles.

Temperature-Programmed Reaction with CO₂

Figure 7 shows TPRn profiles with CO₂ for Pt/Al₂O₃ and Pt/ZrO₂ freshly reduced and treated in CH₄/He for 5 or 10 min. After considering the contribution of the CO₂ fragmentation to CO ($m/e = 28$), the results suggest that CO is not evolved during the experiments with the freshly reduced catalysts. This rules out the possibility of any significant contribution of the CO₂ dissociation ($2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2$) during TPRn with CO₂. *In situ* IR experiment had earlier shown decomposition of CO₂ to CO for a very short time on stream (14–16). During the current TPRn experiments the concentration of CO was too small to be detected. For coked Pt/Al₂O₃ catalyst (Fig. 7a) peaks were observed below and above the reaction temperature at which the kinetic measurements were made (1070 K). For Pt/ZrO₂ (Fig. 7b) two peaks appeared below 1070 K, one of those peaks occurring 70 K lower than that on Pt/Al₂O₃. This indicates that part of the coke on Pt/Al₂O₃ and all of the coke on Pt/ZrO₂ could be removed (by CO₂) at the temperature at which the reforming reaction was carried out. For Pt/Al₂O₃ significantly larger amounts of coke were produced after 5 min exposure than on Pt/ZrO₂, and most of the coke was formed in the initial 5 min, the amount increased rather slowly after that period. The peaks

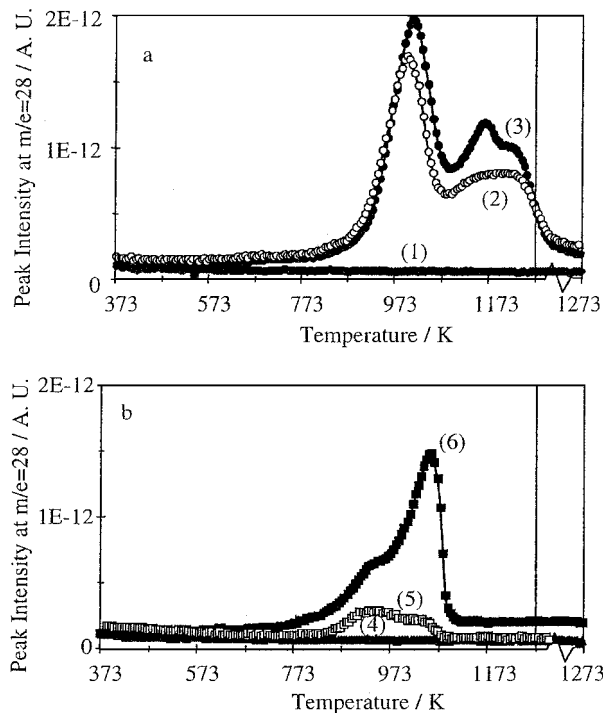


FIG. 7. Temperature-programmed reaction (TPRn) with CO₂ profiles for (a) Pt/Al₂O₃ and (b) Pt/ZrO₂, freshly reduced and exposed to CH₄/He at 1070 K. During TPRn, the temperature was increased up to 1273 K and kept at this temperature for 10 min in CO₂. (1), (4), Reduced in H₂; (2), (5), treated in CH₄/He for 5 min; (3), (6), treated in CH₄/He for 10 min.

for Pt/ZrO₂ increased sharply from 5 to 10 min exposure. The peak at lower temperature was more significant in 5 min, but the latter increased much more than the former after 10 min exposure (Fig. 7b). In order to check the possibility that some of coke remained on the catalyst after TPRn with CO₂, TPO was carried out subsequently (see Fig. 8). The absence of peaks in Fig. 8 indicates that all coke

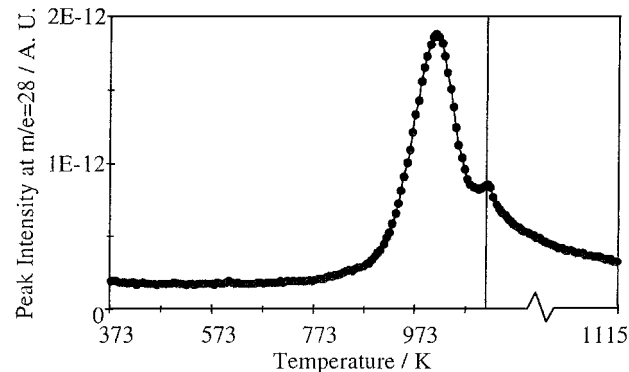


FIG. 9. Temperature-programmed reaction (TPRn) with CO₂ profile for Pt/Al₂O₃ after exposure to CH₄/He at 1070 K for 10 min. During TPRn, the temperature was increased up to 1115 K and kept at this temperature for 25 min in CO₂.

on the catalyst was removed by reaction with CO₂ up to 1273 K.

In order to assign the peaks of TPRn with CO₂ on Pt/Al₂O₃ (treated in CH₄/He for 10 min), the temperature was increased only up to 1115 K during TPRn. The catalyst was kept in CO₂ at this temperature for 25 min and subsequently TPO was measured. The resulting profiles of TPRn with CO₂ and TPO are shown in Figs. 9 and 10, respectively. For comparison, a TPO profile without TPRn with CO₂ is also shown. It can be seen from Fig. 9 that, even after the temperature reached a steady value, the peak intensity decreased continuously, indicating further removal of coke with time on stream. This indicates that part of the strongly adsorbed carbon was removed at 1115 K. Figure 10 shows that the low-temperature peak disappeared completely and almost half amount of coke reacting in the high temperature peak was removed by reaction with CO₂ up to 1115 K.

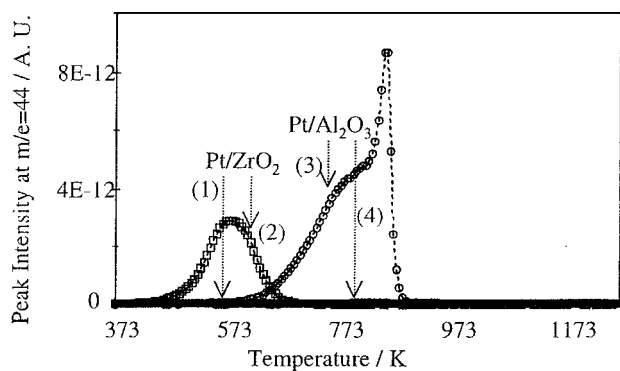


FIG. 8. Temperature-programmed oxidation (TPO) profiles for supported Pt catalysts, coked or after TPRn with CO₂ to 1273 K (all catalysts were treated in CH₄/He for 10 min at 1070 K). (1) Pt/ZrO₂ after TPRn; (2) Pt/ZrO₂ coked; (3) Pt/Al₂O₃ coked; (4) Pt/Al₂O₃ after TPRn.

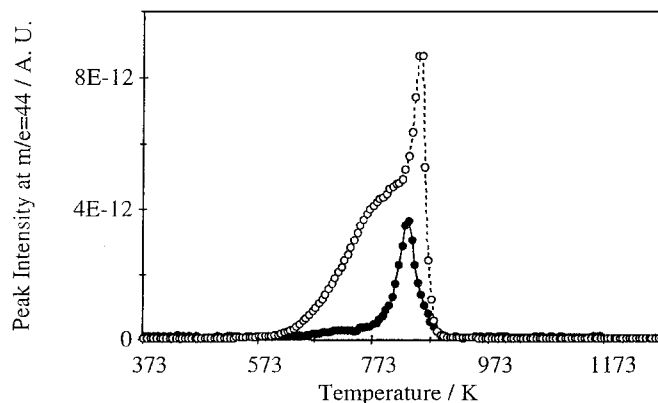


FIG. 10. Temperature-programmed oxidation (TPO) profiles for Pt/Al₂O₃ (both catalysts were treated in CH₄/He at 1070 K for 10 min). ○, Coked; ●, after TPRn to 1115 K.

DISCUSSION

Peak Assignment of TPO and TPRn with CO₂ Profiles

During TPO two peaks were observed on Pt/Al₂O₃ (750 and ≥ 840 K) and a single peak was observed on unsupported metallic Pt (620 K) or Al₂O₃ (930 K) (see Fig. 4). In this context, Barbier *et al.* (20) identified two types of coke by TPO after cyclopentane reforming over Pt/Al₂O₃. The more reactive carbon has been attributed to coke on Pt and the less reactive to coke on the support. Note that two kinds of coke were also observed on Pt/Al₂O₃ used at 875 K for the CO₂ reforming of methane (17). Since coke is more easily removed from metallic Pt than from Al₂O₃ (see Fig. 4), the low-temperature peak is assigned to coke on Pt and the high-temperature peak to coke on the support. From the intensities of the peaks we conclude that most of the coke for Pt/Al₂O₃ was located on the support. Its concentration increased with reaction time.

TPO (Fig. 10) was carried out to check if residual coke remained on the catalyst after TPRn with CO₂ to 1115 K (Figs. 7a, 9). The results also support the conclusion that coke on Pt is more easily combusted than that on Al₂O₃. The resulting single peak (TPO, Fig. 10) corresponds to the high-temperature peak of TPRn with CO₂ (Fig. 7a)

and to the high-temperature peak of TPO for coke on Al₂O₃ (Fig. 4). The low-temperature peak of the TPRn with CO₂ (Fig. 7a) therefore corresponds to coke on Pt particles and the high-temperature peak to coke on the Al₂O₃ support.

In contrast to Pt/Al₂O₃, the combustion characteristics of coke on Pt/ZrO₂ (TPO, Figs. 3 and 5), unsupported metallic Pt, and ZrO₂ were almost identical. However, the amount of CO₂ desorbing from ZrO₂ during TPO after exposure to CH₄/He for 12 h was only three times larger than that for Pt/ZrO₂ after exposure to CH₄/He for only 10 min, indicating that coke is not easily produced on the ZrO₂ support. The peak of CO₂ evolving from Pt/ZrO₂ is symmetric and indicates that it originates from one type of coke. Based on the above arguments the CO₂ peak observed with Pt/ZrO₂ is concluded to result from oxidizing coke on Pt particles. The amount of unsupported metallic Pt metal for the experiment was 10 mg and this is 20 times larger than the amount of Pt loaded in Pt/ZrO₂ for that experiment, but the amount of coke for unsupported metallic Pt was much smaller than that for Pt/ZrO₂. This results from the difference in the number of Pt atoms available on the surface. Indeed, the SEM picture shows that an unsupported metallic Pt sample consists of larger particles (μm sized) after reduction in H₂ (Fig. 11).

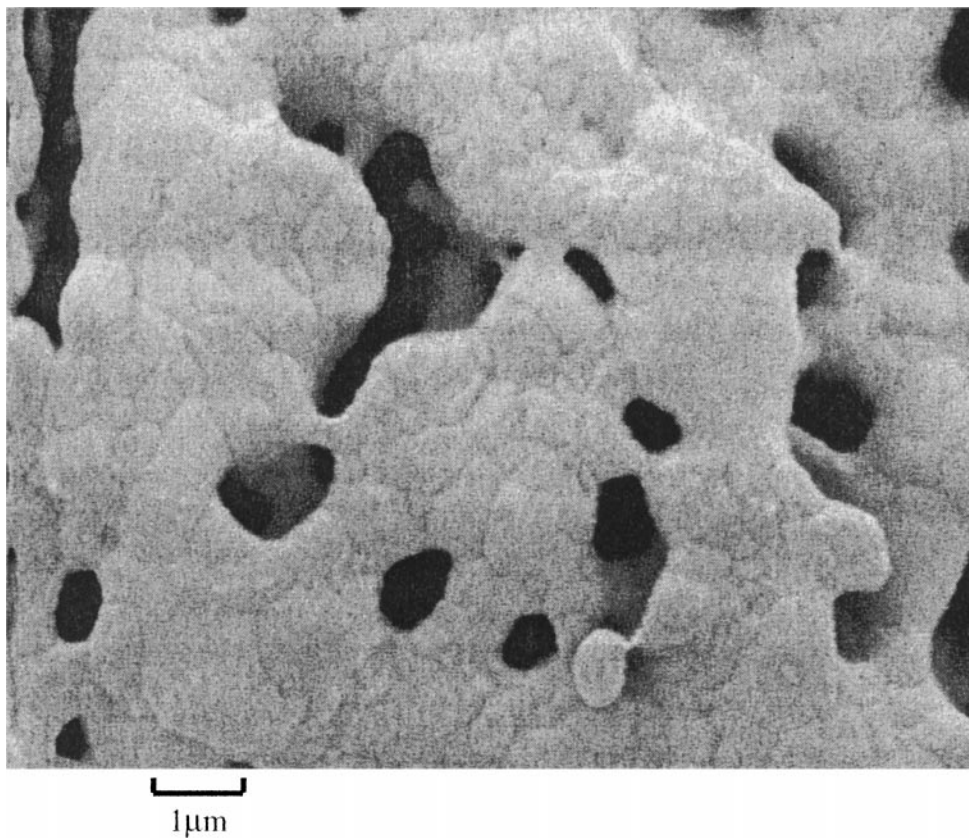


FIG. 11. SEM image for unsupported metallic Pt after reduction at 1120 K.

Acid Site on Support

The amount of coke deposited on the Al_2O_3 support was larger than that on $\text{Pt}/\text{Al}_2\text{O}_3$ (Fig. 4). This observation differs from the earlier results obtained for reactions at lower temperatures (i.e., less coke was found on Al_2O_3 than on $\text{Pt}/\text{Al}_2\text{O}_3$) (17). At lower reaction temperature (875 K), the difference was related to the contributions to hydrogen desorption via metallic Pt facilitating coking (20–24) and in parallel on the support coke was formed by Lewis acid (25) catalyzed decomposition of methane. The contribution from the latter reaction pathway was small at the lower temperature. At the higher temperature (1070 K) the effect of Lewis acid sites catalyzed formation of carbon is concluded to dominate leading to an enhanced coke accumulation on the support. In the case of Pt/ZrO_2 , the absence of appreciable amounts of acids sites on zirconia results in Pt being the dominant sites for coke formation and hence at both high and low temperatures more coke is seen on Pt/ZrO_2 than on ZrO_2 .

The amount of coke on Al_2O_3 exposed to CH_4/He for 12 h (not shown) was almost the same as that exposed to CH_4/CO_2 for 12 h. Thus, coke was produced more easily on Al_2O_3 compared to ZrO_2 . As suggested earlier (17), this is attributed to the higher concentration of Lewis acid sites on Al_2O_3 compared with ZrO_2 .

Relation between Coke and Deactivation

For $\text{Pt}/\text{Al}_2\text{O}_3$, the amount of coke (moles of carbon) during CH_4/CO_2 treatment was evaluated quantitatively and the amounts of coke on Pt and on the support were calculated from the areas of the peaks in Fig. 2. The amount of coke on Pt particles increased strongly at the beginning (Fig. 12) and slowed down considerably after a while. The number of surface Pt atoms in $\text{Pt}/\text{Al}_2\text{O}_3$ was estimated from hydrogen adsorption to be $21 \mu\text{mol g}^{-1}$ catalyst, and the

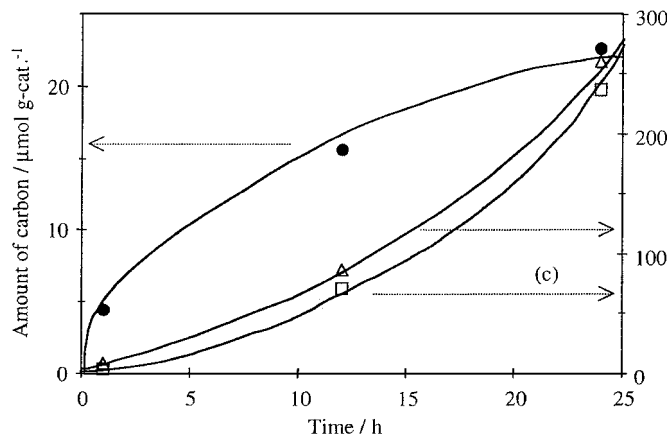


FIG. 12. Amount of coke formed during CH_4/CO_2 reaction at 1070 K over $\text{Pt}/\text{Al}_2\text{O}_3$. ●, Coke on Pt particles; □, coke on support; Δ, total coke (●+○).

amount of the coke seemed to approach this value (Fig. 12). On the other hand, the amount of coke on the support increased initially gradually, while after some time the rate of coke formation accelerated dramatically (Fig. 12). At 1070 K (Fig. 1) catalyst deactivation followed the trend of coke buildup on Pt particles (Fig. 12). This implies that at these higher temperatures the key step of this reaction occurs not only on the $\text{Pt}-\text{Al}_2\text{O}_3$ perimeter as proposed earlier for lower temperatures, but also on Pt metal.

We have shown earlier that a bifunctional mechanism is operative over the supported Pt catalysts at 875 K (14–17). Decomposition of methane occurs on the Pt particle to yield hydrogen (desorbing into the gas phase) and partially dehydrogenated methane (CH_x ; $0 \leq x \leq 3$), which is oxidized by CO_2 chemisorbed on the support in the vicinity of Pt particles. Thus, the key step (oxidation of CH_x) is considered to occur on the Pt-support perimeter and the coke on the perimeter blocks the reaction. At the higher temperature (≥ 1070 K) coke on Pt particles can also be removed by CO_2 (Fig. 7) and provides for an additional route.

Three mechanistic routes may be considered for the reaction of coke with CO_2 on the Pt particles: (a) Methane is adsorbed and decomposed on the metal (Rh) to H_2 and adsorbed carbon as suggested by Mark *et al.* (26, 27). The carbon on the catalyst reacts directly with CO_2 from the gas phase to CO. (b) Methane is decomposed on the metal to yield surface CH_x species and hydrogen (3, 28, 29). Upon adsorption, CO_2 dissociates to CO and adsorbed oxygen. The oxygen reacts with the CH_x species to CO and hydrogen. (c) Partly dehydrogenated methane (CH_x) is oxidized by adsorbed oxygen, transferred from the support in the vicinity of the Pt particles (30).

As the deactivation followed the trend of coke buildup on the Pt particles, our results cannot be explained by direct CO_2 attack from gas phase as suggested in route (a). Activity tests showed that after a fast initial deactivation, $\text{Pt}/\text{Al}_2\text{O}_3$ had relatively stable CO_2 conversion (≥ 1070 K) (Fig. 1), and the concentration of coke approaches that of surface Pt (Fig. 12). So we can conclude that the activity is gradually lost due to coke formation from CH_4 on the Pt surface blocking CO_2 access and this accounts for the initial deactivation. After this, only the perimeter is used for the reaction providing stable activity due to the high activity of the perimeter Pt for oxidation of CH_x with CO_2 as proposed in the bifunctional mechanism.

The coke on Al_2O_3 had low reactivity toward CO_2 compared to coke on Pt particles and could not be removed at the reaction temperature (1070 K) (Fig. 7a), indicating that it is gradually accumulated on the support (Fig. 12). The coking rate increased with time on stream, implying that after nucleation occurred coke formation becomes easier.

The question whether a deactivated $\text{Pt}/\text{Al}_2\text{O}_3$ could be regenerated with CO_2 is therefore interesting. Figure 13 shows the original activity of $\text{Pt}/\text{Al}_2\text{O}_3$ and that after

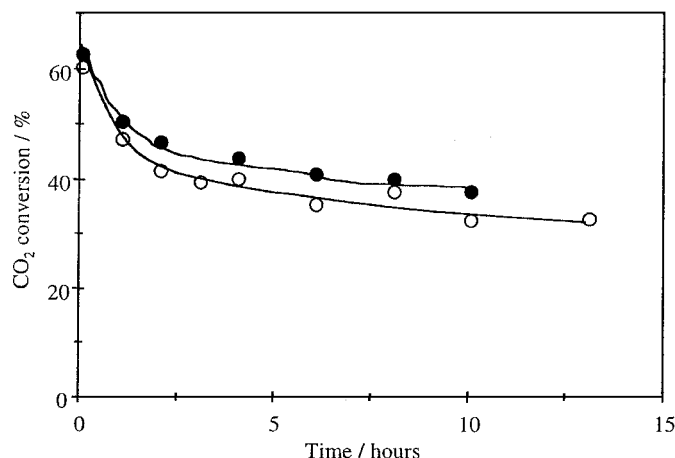


FIG. 13. Carbon dioxide conversion as a function of time on stream for Pt/Al₂O₃ at 1070 K, CO₂/CH₄/Ar + N₂ = 42/42/85/ml min⁻¹, 300 mg catalyst. ●, Freshly reduced; ○, reactivated by CO₂ at 1115 K.

treating by CO₂ (1115 K for 3 h) as a function of time. Initial CO₂ conversion for fresh and regenerated catalyst was 62.6 and 60.2%, respectively, indicating that the activity was almost completely restored by the regeneration and that the coke deactivating the catalyst was removed by CO₂. The results also suggests that the major cause of the deactivation would not be sintering of Pt, but coke deposition on active site, because the activity after regeneration must be decreased if the sintering of Pt is intended to occur (as an earlier work has shown for Pt/ZrO₂ (17)). A slight difference is that the deactivation of the regenerated catalyst was faster than that of fresh catalyst. This suggests that coke on support (not removed by regeneration) contributes to promote nucleating fresh coke on Pt.

In summary, the reaction and coking for Pt/Al₂O₃ at high temperature (≥ 1070 K) is schematically shown in Fig. 14. CH₄ decomposes both on Pt particles and on acid sites of the support to CH_x (coke) species. Only the species on Pt are reactive toward CO₂. CO₂ is also activated both on Pt particles and on the support. Two reaction pathways exist in

which carbon (on the Pt particles) is oxidized by CO₂ to CO, i.e., on the Pt particle (r_1) and on the boundary of Pt and the support (r_2). r_2 is assumed to be fast enough to remove coke in the vicinity of the perimeter (keeping some activity for long time on stream), while the CH₄ decomposition rate on Pt is faster than r_1 (resulting the initial deactivation due to coking) (Fig. 1). After a while, most of Pt is covered by a monolayer of coke, but the perimeter is still available for the reaction. Coke on the support cannot be removed at the temperature and builds up. This process blocks sites (on the perimeter) for CO₂ activation and it finally causes complete catalyst deactivation.

Relevance of Coke Deposition and Its Influence on the Stability between Pt/Al₂O₃ and Pt/ZrO₂

TPRn with CO₂ on Pt/ZrO₂ after exposure to CH₄/He for 5 min (Fig. 7b) indicates two types of coke. However after exposure for 10 min the second peak increased drastically. This indicates that only the coke corresponding to the low-temperature peak appeared initially and the high temperature developed with time on stream. As coke was hardly produced on ZrO₂ (Fig. 5), both of them would be on Pt. On the other hand, coke on Pt (supported on Al₂O₃) reacts with CO₂ at least 70 K higher temperature when compared to reactive coke (first peak) on Pt/ZrO₂. As the reactants are coke (CH_x) and CO₂, the reactivity of those species should cause the different reactivity of coke with CO₂. From above arguments, coke on Pt supported on ZrO₂ would be more reactive toward CO₂ than coke on Pt supported on Al₂O₃ in the presence of a CH₄/CO₂ mixture; hence it is more easily removed by activated CO₂. Note also that the initial CH₄ deposition rate on Pt/ZrO₂ was slower than that on Pt/Al₂O₃ (Fig. 7). So (slow) CH₄ deposition and (fast) removal of coke is balanced on Pt/ZrO₂ and coke does not accumulate on Pt particles. In addition, there is insufficient coke produced on the ZrO₂ support that might cover active sites. As a result, coke does not accumulate on Pt/ZrO₂ giving the catalyst a stable activity.

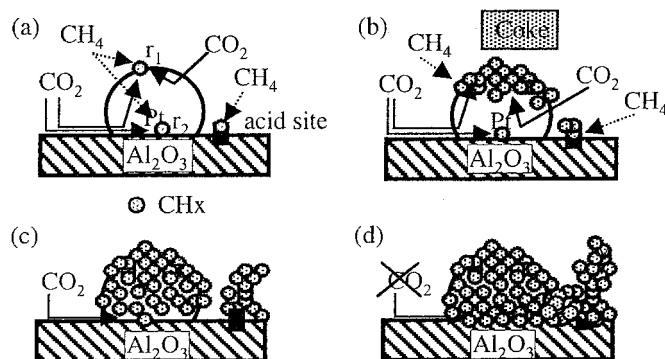


FIG. 14. Model of reaction and coking scheme over Pt/Al₂O₃ at high reaction temperature.

CONCLUSIONS

Pt/ZrO₂ has stable activity for CO₂/CH₄ reforming at all temperatures, while Pt/Al₂O₃ partly deactivates at high temperatures (≥ 1070 K) and completely loses activity at lower temperatures (< 875 K) (16).

The deactivation mechanism of Pt/Al₂O₃ was investigated at 1070 K (industrial condition) in this communication. As regeneration by CO₂ (to remove coke on Pt) recovers catalytic activity, the contribution of Pt sintering to activity loss is trivial and the cause of deactivation is attributed to coking.

During carbon dioxide reforming of methane, CH₄ decomposes to hydrogen-containing carbon species (CH_x: 0 $\leq$

$x \leq 3$) on Pt and on Lewis acid sites of support. At the higher reaction temperature coke on Pt particles can be removed by reaction with activated CO_2 . The rate for removing coke on Pt, which is not in the vicinity of the Pt– Al_2O_3 perimeter, is slow compared to the rate of CH_4 decomposition. Hence, the surface of Pt particles is gradually covered by a monolayer of coke. This process corresponds to the initial deactivation of catalyst. After a while only perimeter Pt in the vicinity of support is available for the reaction and the higher reaction rate of the CH_x oxidation by carbonates at the perimeter (14–16) provides stable activity for a while.

However, at that temperature coke on the support cannot be removed kinetically by activated CO_2 and hence it builds up. This does not affect the catalyst activity immediately, but eventually blocks the CO_2 activation sites on the support (in the vicinity of Pt particle) and induces subsequently complete deactivation.

As coke on Pt (supported on ZrO_2) is more reactive toward CO_2 than coke on Pt (supported on Al_2O_3) under reforming reaction condition (the reactivity of CH_x and/or CO_2 would result in the difference), it is removed more easily (as CO and H_2) as it is formed. Additionally the rate of CH_4 decomposition on Pt/ ZrO_2 is slower than that on Pt/ Al_2O_3 . Therefore, carbon formation on Pt (supported on ZrO_2) and its oxidation by activated CO_2 are balanced. In addition, coke is not deposited on ZrO_2 , because it lacks a significant concentration of strong Lewis acid sites. Because of these factors coke hardly accumulates on Pt/ ZrO_2 and allows the material thus to exhibit stable activity.

REFERENCES

1. Seshan, K., Bitter, J. H., and Lercher, J. A., *Chem. Tech.*, in press.
2. Richardson, J. T., and Paripatyadar, S. A., *Appl. Catal.* **61**, 293 (1990).
3. Solymosi, F., Kutsan, Gy., and Erdöhelyi, A., *Catal. Lett.* **11**, 149 (1991).
4. Ascroft, S. T., Cheetham, A. K., Green, M. L. H., and Vernon, P. D. F., *Nature* **352**, 225 (1991).
5. Udengaard, N. R., Bak Hansen, J.-H., Hanson, D. C., and Stal, J. A., *Oil Gas J.* **90**, 62 (1992).
6. Rostrup-Nielsen, J. R., and Bak Hansen, J.-H., *J. Catal.* **144**, 38 (1993).
7. Rostrup-Nielsen, J. R., *Catal. Today* **18**, 305 (1993).
8. Erdöhelyi, A., Cerenyi, J., and Solymosi, F., *J. Catal.* **141**, 287 (1993).
9. Seshan, K., ten Barge, H. W., Hally, W., van Keulen, A. N. J., and Ross, J. R. H., *Stud. Surf. Sci. Catal.* **81**, 285 (1994).
10. Tsipouriari, V. A., Estathiou, A. M., Zhang, Z. L., and Verykios, X. E., *Catal. Today* **21**, 579 (1994).
11. Swaan, H. M., Kroll, V. C. H., Martin, G. A., and Mirodatos, C., *Catal. Today* **21**, 571 (1994).
12. Seshan, K., Mercera, P. D. L., Xue, E., and Ross, J. R. H., U.S. patent, 537791, 1994; Japan patent, 522634, 1994; International patent, WO 94/224042, 1994.
13. Zhang, Z., Verykios, X. E., MacDonald, S. M., and Affrossman, S., *J. Phys. Chem.* **100**, 744 (1996).
14. Bitter, J. H., Seshan, K., and Lercher, J. A., *J. Catal.* **171**, 279 (1997).
15. Bitter, J. H., Seshan, K., and Lercher, J. A., *J. Catal.* **176**, 93 (1998).
16. Bitter, J. H., Ph.D. thesis, University of Twente, 1997.
17. Bitter, J. H., Seshan, K., and Lercher, J. A., *J. Catal.* **183**, 336 (1999).
18. Staag, S. M., Salazar, E. R., Padro, C., and Resasco, D. E., *J. Catal.* **178**, 137 (1998).
19. Van Keulen, A. N. J., Seshan, K., Hoebink, J. H. B. J., and Ross, J. R. H., *J. Catal.* **166**, 306 (1997).
20. Barbier, J., *Appl. Catal.* **23**, 225 (1986).
21. Iglesia, E., Baumgartner, J. E., and Price, G. L., *J. Catal.* **134**, 549 (1992).
22. Iglesia, E., and Baumgartner, J. E., *Catal. Lett.* **21**, 55 (1993).
23. Narbeshuber, T. F., Brait, A., Seshan, K., and Lercher, J. A., *Appl. Catal.* **146**, 119 (1996).
24. Narbeshuber, T. F., Ph.D. thesis, University of Twente, 1995.
25. Masai, M., Kado, H., Miyake, A., Nishiyama, S., and Tsuruya, S., in "Methane Conversion" (D. M. Bibby, D. Chang, R. F. Howe, and S. Yurchak, Eds.). Elsevier Science, Amsterdam, 1998.
26. Mark, M. F., and Maier, W. F., *Angew. Chim. Int. Ed. Engl.* **33**(15/16), 1657 (1994).
27. Mark, M. F., and Maier, W. F., *J. Catal.* **164**, 122 (1996).
28. Qin, D., and Lapszewicz, J., *Catal. Today* **21**, 551 (1994).
29. Qin, D., Lapszewicz, J., and Jiang, X., *J. Catal.* **159**, 140 (1996).
30. Tomishige, K., Chen, Y.-G., and Fujimoto, K., *J. Catal.* **181**, 91 (1999).