Journal of Catalysis **197,** 34–42 (2001)
doi:10.1006/jcat.2000.3062, available online at http://www.idealibrary.com on IDEAL®

Carbon Deposition during Carbon Dioxide Reforming of Methane—Comparison between Pt/Al_2O_3 and Pt/ZrO_2

Katsutoshi Nagaoka,* Kulathuiyer Seshan,† Ken-ichi Aika,*,[1] and Johannes A. Lercher‡

*Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku Yokohama 226-8502, Japan; †Faculty of Chemical Technology, University of Twente, P.O. Box 217, 7500, AE, Enschede, The Netherlands; and ‡Department of Physical Chemistry, Technical University of Munich, D-85748 Garching, Germany

Received March 13, 2000; revised September 1, 2000; accepted September 18, 2000

The relation between coke formation and the deactivation of supported Pt catalysts during CO_2 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 CO_2 were applied to Pt catalysts (Pt/Al_2O_3 and Pt/ZrO_2) which were exposed to CH_4/CO_2 (reforming reaction conditions) or CH_4/He (facile coke formation) to identify the carbon species. The activity decrease for Pt/Al_2O_3 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 CO_2, but coke on the Al_2O_3 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 CO_2 and CH_4 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 CH_4 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 CO_2 at the metal–support boundary. Gradually, the coke on the support (Al_2O_3) increases to an extent that it blocks the reaction also at that location. In contrast to the situation with Pt/Al_2O_3, coke was not observed on Pt/ZrO_2 even after exposure to reforming gas (CH_4/CO_2) for 12 h. The combination of three factors is concluded to cause the high catalytic stability of Pt/ZrO_2 in CO_2/methane reforming: (i) 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 conditions; (ii) methane decomposition is slower on Pt/ZrO_2 than on Pt/Al_2O_3; and (iii) coke is hardly formed on the ZrO_2 support. © 2001 Academic Press

[1] To whom correspondence should be addressed. Fax: +81-45-924-5441. E-mail: kenaika@chemenv.titech.ac.jp.

INTRODUCTION

CO_2 reforming of methane is attractive to generate synthesis gas with a H_2/CO ratio of unity. This ratio can be adjusted by combining CO_2 reforming with steam reforming from 1 to 3. Note that gas fields sometimes contain CO_2 (≧25 vol%), which may be an incentive to apply in part CO_2 reforming rather than separating methane and CO_2 (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 ($CH_4 \rightarrow C + 2H_2$) and carbon monoxide disproportionation ($2CO \rightarrow C + CO_2$). 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/ZrO_2 has been found to be stable for more than 500 h during reaction at 900 K (12, 14). On the other hand, Pt/Al_2O_3 and Pt/TiO_2 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 ZrO_2 (14, 15), demonstrating that a bifunctional mechanism is operative on Pt/ZrO_2 at relatively low temperatures (875 K). The reaction sequence involves dissociation of methane on Pt to molecular hydrogen and partially dehydrogenated methane (CHx: $0 \leqq x \leqq 3$) as a surface species. This CHx species is oxidized by CO_2 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

0021-9517/01 $35.00
Copyright © 2001 by Academic Press
All rights of reproduction in any form reserved.

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/ZrO_2 and Pt/Al_2O_3 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 CO_2 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 CO_2, and temperature-programmed reaction (TPRn) with CO_2 are used to characterize the reactivity of the coke on supported Pt catalysts which were exposed to CH_4/CO_2 (CO_2 reforming of methane) or CH_4/He (methane as the source of coking).

METHODS

Catalyst Preparation

Pt/ZrO_2 and Pt/Al_2O_3 were prepared by the wet impregnation technique. For this, $H_2PtCl_6 \cdot 6H_2O$ in water (10 mg Pt per ml), ZrO_2 (RC-100, Gimex, Japan), and Al_2O_3 (000-3AQ, AKZO, The Netherlands) were used. The ZrO_2 powder was pressed at 4000 bar for 5 min, while Al_2O_3 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 $PtAl_2O_3$ and Pt/ZrO_2 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/ZrO_2 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 H_2/N_2 (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% CH_4, 25% CO_2, 5% N_2, 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 CO_2

TPO and TPRn with CO_2 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 H_2 for 1 h at 1120 K. After reduction, the temperature was lowered to 1070 K in flowing He and the feed gas mixture (CH_4/CO_2 (1/1) or CH_4/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 O_2/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 CO_2 ($m/e = 44$) 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, $[Pt(NH_3)_4^{2+}](OH)_2$ (15.2 mg) was loaded to the reactor and calcined for 5 h at 923 K (heating rate 3 K min^{-1}) in O_2/He (5/95 with total flow of 30 ml min^{-1}) and subsequently reduced with H_2 at 1120 K and treated in the same way as described above.

For TPRn with CO_2, CO_2/He (10/90 with a total flow of 30 ml min^{-1}) was fed instead of O_2/He in the above experiment. After the temperature reached 1273 K, it was kept for 10 min under CO_2 atmosphere. Only CO ($m/e = 28$) was analyzed. The contribution of CO fragment due to carrier gas CO_2 (11.4%) was subtracted.

Temperature-Programmed Desorption (TDP) of CO_2

For this purpose the same apparatus as for TPO was used. Prior to adsorption, the catalyst was reduced with H_2 at 1120 K. Subsequently, the catalyst was degassed in He and cooled to 325 K. At this temperature CO_2 (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.

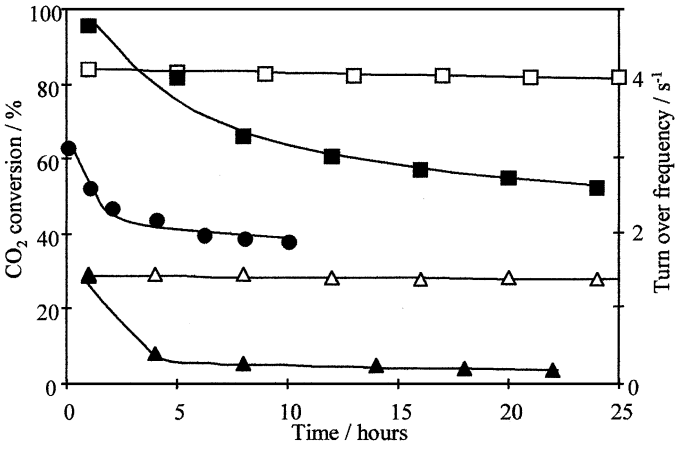

FIG. 1. Stability tests for supported Pt catalysts at different temperatures with $CO_2/CH_4/Ar + N_2 = 42/42/85$/ml min^{-1}. □, Pt/ZrO_2 (0.2 g) at 1125 K; ■, Pt/Al_2O_3 (0.3 g) at 1125 K; ●, Pt/Al_2O_3 (0.3 g) at 1070 K; △, Pt/ZrO_2 (0.3 g) at 875 K; ▲, Pt/Al_2O_3 (0.3 g) at 875 K. (TOF was calculated based on the dispersions shown in the text. TOF values for □ and △ 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 ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) over Pt/Al_2O_3 and Pt/ZrO_2 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/ZrO_2 maintains stable activity for 500 h at all temperatures, while Pt/Al_2O_3 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/Al_2O_3 and Pt/ZrO_2 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/Al_2O_3. Both peaks increased with time of exposure. With Pt/ZrO_2 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 Bouduard reaction ($2CO \rightarrow CO_2 + C$) is thermodynamically feasible under reaction conditions (19). In order to explore coking under the more severe conditions of the present study, Pt/Al_2O_3 and Pt/ZrO_2 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/Al_2O_3 and the peak temperatures coincided approximately with those

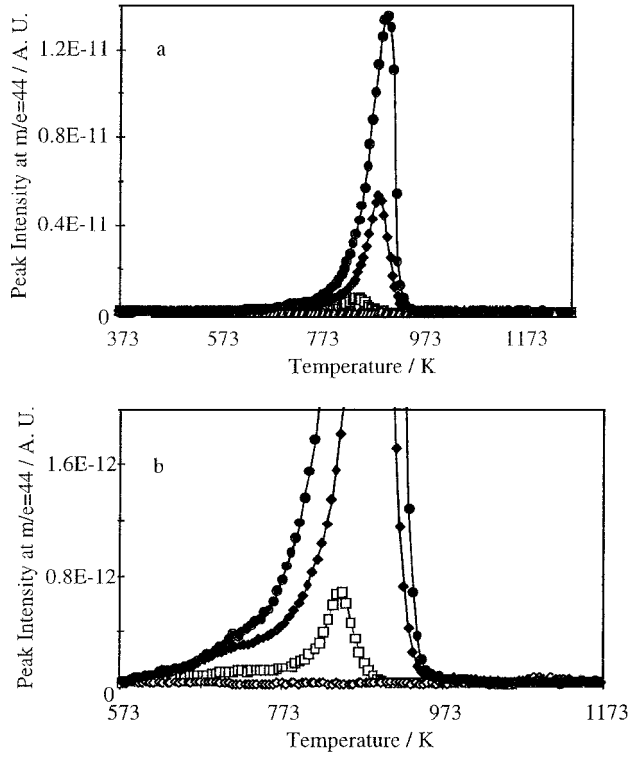

FIG. 2. Temperature-programmed oxidation (TPO) profiles for supported Pt catalysts after exposure to CH_4/CO_2 at 1070 K (Fig. 2b is a expansion of Fig. 2a). ◇, Pt/ZrO_2 for 12 h; □, Pt/Al_2O_3 for 1 h; ◆, Pt/Al_2O_3 for 12 h; ●, Pt/Al_2O_3 for 24 h.

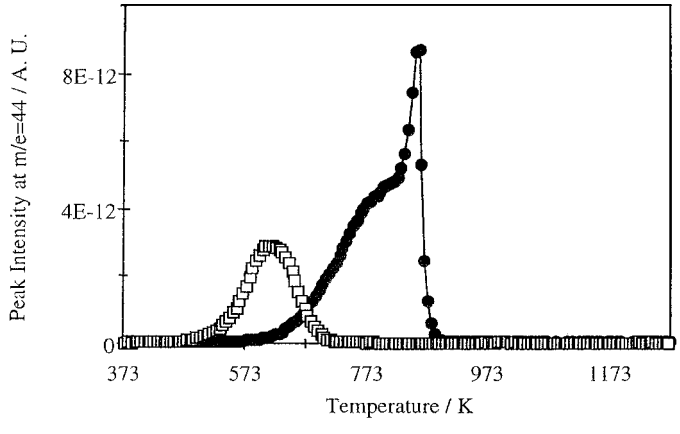

FIG. 3. Temperature-programmed oxidation (TPO) profiles for supported Pt catalysts after exposure to CH_4/He at 1070 K for 10 min. □, Pt/ZrO_2; ●, Pt/Al_2O_3.

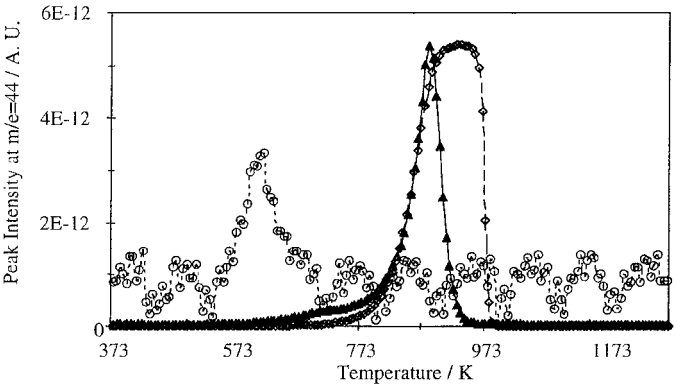

FIG. 4. Temperature-programmed oxidation (TPO) profiles after exposure at 1070 K for (○) unsupported metallic Pt(×50) (CH_4/He for 1 h), (▲) Pt/Al_2O_3 (CH_4/CO_2 for 12 h), and (◇) Al_2O_3(×0.1) (CH_4/CO_2 for 12 h).

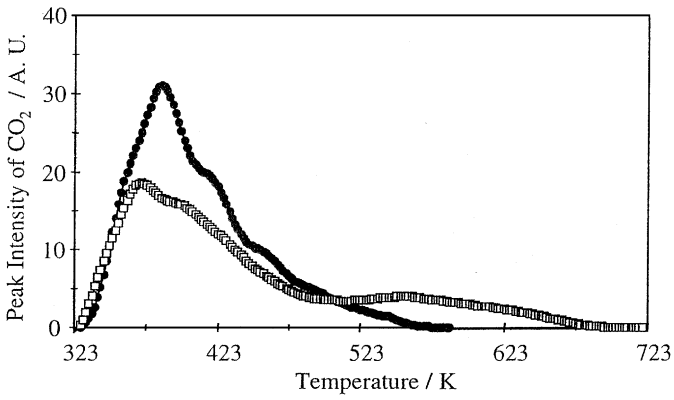

FIG. 6. Temperature-programmed desorption (TPD) profiles of CO_2 for supported Pt catalysts. ●, Pt/Al_2O_3; ○, Pt/ZrO_2.

after exposure to CH_4/CO_2, while a single peak (615 K) was observed for Pt/ZrO_2. The peak temperature for Pt/ZrO_2 was about 140 K lower than that for Pt/Al_2O_3. It should be emphasized that the amount of coke was almost the same when Pt/Al_2O_3 was exposed to CH_4/He for 10 min, or when exposed to CH_4/CO_2 for 24 h. This is in agreement with the conclusion that CH_4 decomposition is the source of coking (19).

To analyze the origin of the TPO peaks, the TPO profile for Pt/Al_2O_3 after exposure to CH_4/CO_2 for 12 h is compared with those for unsupported metallic Pt after exposure to CH_4/He for 1 h and Al_2O_3 after exposure to CH_4/CO_2 for 12 h (see Fig. 4). For unsupported metallic Pt and Al_2O_3 only one peak was seen and the temperatures were about 620 and 930 K, respectively. The peak area for Al_2O_3 was 20 times larger than that for Pt/Al_2O_3 after feeding the same gas (CH_4/CO_2) for 12 h. Similarly, the TPO profile for Pt/ZrO_2 after exposure to CH_4/He for 10 min is compared with that for unsupported metallic Pt after exposure to CH_4/He for 1 h and ZrO_2 after exposure to CH_4/He for 12 h (see Fig. 5). For ZrO_2 a single peak was observed and the temperature maximum of the CO_2 desorption peak was (655 K) was 40 K higher than that for Pt/ZrO_2.

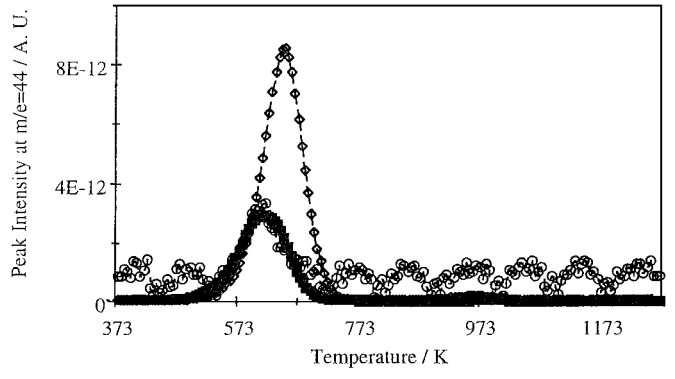

FIG. 5. Temperature-programmed oxidation (TPO) profiles for (○) unsupported metallic Pt(×50) (for 1 h), (■) Pt/ZrO_2 (for 10 min), and (◇) ZrO_2 (for 12 h) after exposure to CH_4/He at 1070 K.

Temperature-Programmed Desorption of CO_2

In order to prove if carbonate on the support contributes to the TPO profiles, TPD of CO_2 was measured for Pt/Al_2O_3 and Pt/ZrO_2 and the results are shown in Fig. 6. Carbonate on Pt/Al_2O_3 and Pt/ZrO_2 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 CO_2

Figure 7 shows TPRn profiles with CO_2 for Pt/Al_2O_3 and Pt/ZrO_2 freshly reduced and treated in CH_4/He for 5 or 10 min. After considering the contribution of the CO_2 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 CO_2 dissociation ($2CO_2 \rightarrow 2CO + O_2$) during TPRn with CO_2. *In situ* IR experiment had earlier shown decomposition of CO_2 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/Al_2O_3 catalyst (Fig. 7a) peaks were observed below and above the reaction temperature at which the kinetic measurements were made (1070 K). For Pt/ZrO_2 (Fig. 7b) two peaks appeared below 1070 K, one of those peaks occurring 70 K lower than that on Pt/Al_2O_3. This indicates that part of the coke on Pt/Al_2O_3 and all of the coke on Pt/ZrO_2 could be removed (by CO_2) at the temperature at which the reforming reaction was carried out. For Pt/Al_2O_3 significantly larger amounts of coke were produced after 5 min exposure than on Pt/ZrO_2, and most of the coke was formed in the initial 5 min, the amount increased rather slowly after that period. The peaks

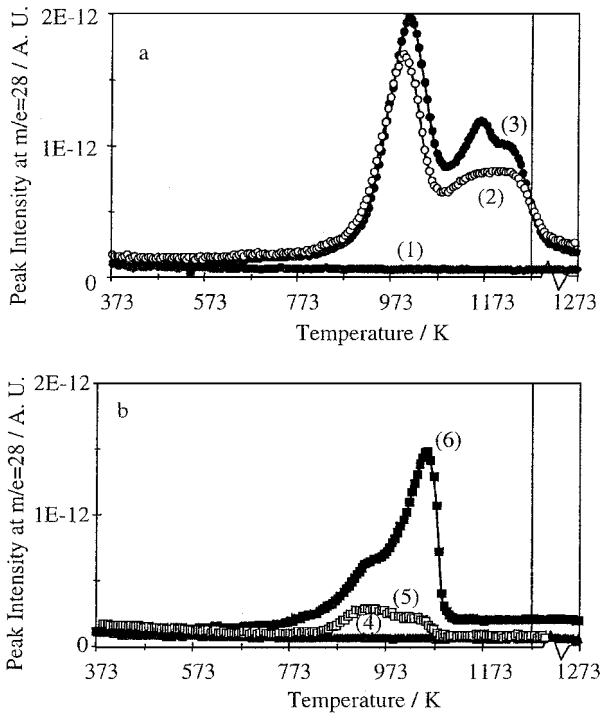

FIG. 7. Temperature-programmed reaction (TPRn) with CO_2 profiles for (a) Pt/Al_2O_3 and (b) Pt/ZrO_2, freshly reduced and exposed to CH_4/He at 1070 K. During TPRn, the temperature was increased up to 1273 K and kept at this temperature for 10 min in CO_2. (1), (4), Reduced in H_2; (2), (5), treated in CH_4/He for 5 min; (3), (6), treated in CH_4/He for 10 min.

for Pt/ZrO_2 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 CO_2, TPO was carried out subsequently (see Fig. 8). The absence of peaks in Fig. 8 indicates that all coke

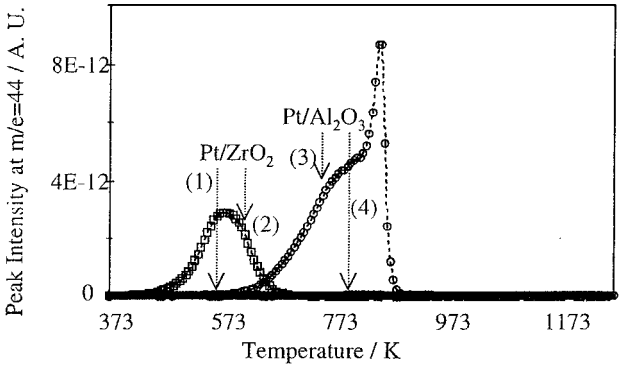

FIG. 8. Temperature-programmed oxidation (TPO) profiles for supported Pt catalysts, coked or after TPRn with CO_2 to 1273 K (all catalysts were treated in CH_4/He for 10 min at 1070 K). (1) Pt/ZrO_2 after TPRn; (2) Pt/ZrO_2 coked; (3) Pt/Al_2O_3 coked; (4) Pt/Al_2O_3 after TPRn.

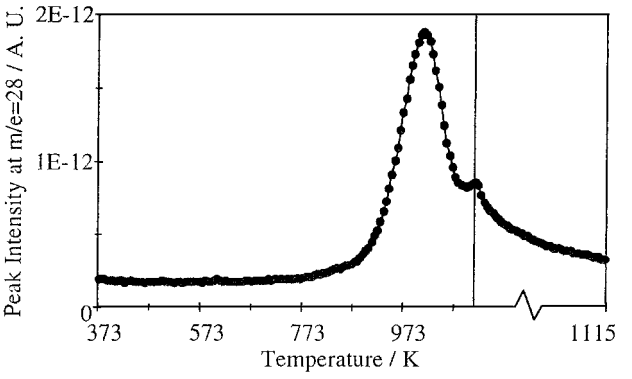

FIG. 9. Temperature-programmed reaction (TPRn) with CO_2 profile for Pt/Al_2O_3 after exposure to CH_4/He at 1070 K for 10 min. During TPRn, the temperature was increased up to 1115 K and kept at this temperature for 25 min in CO_2.

on the catalyst was removed by reaction with CO_2 up to 1273 K.

In order to assign the peaks of TPRn with CO_2 on Pt/Al_2O_3 (treated in CH_4/He for 10 min), the temperature was increased only up to 1115 K during TPRn. The catalyst was kept in CO_2 at this temperature for 25 min and subsequently TPO was measured. The resulting profiles of TPRn with CO_2 and TPO are shown in Figs. 9 and 10, respectively. For comparison, a TPO profile without TPRn with CO_2 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 CO_2 up to 1115 K.

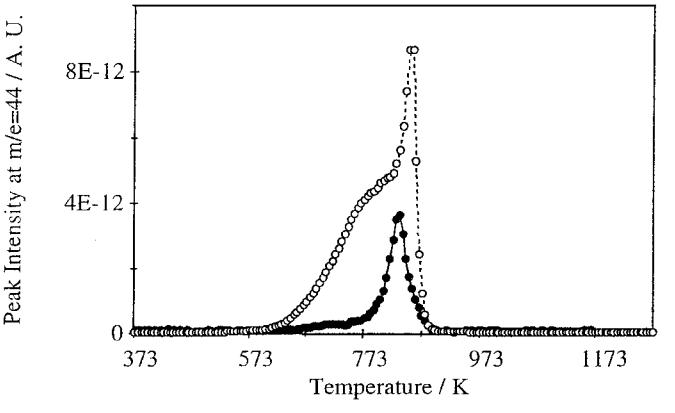

FIG. 10. Temperature-programmed oxidation (TPO) profiles for Pt/Al_2O_3 (both catalysts were treated in CH_4/He at 1070 K for 10 min). ○, Coked; ●, after TPRn to 1115 K.

DISCUSSION

Peak Assignment of TPO and TPRn with CO_2 Profiles

During TPO two peaks were observed on Pt/Al_2O_3 (750 and ≧840 K) and a single peak was observed on unsupported metallic Pt (620 K) or Al_2O_3 (930 K) (see Fig. 4). In this context, Barbier *et al.* (20) identified two types of coke by TPO after cyclopentane reforming over Pt/Al_2O_3. 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/Al_2O_3 used at 875 K for the CO_2 reforming of methane (17). Since coke is more easily removed from metallic Pt than from Al_2O_3 (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/Al_2O_3 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 CO_2 to 1115 K (Figs. 7a, 9). The results also support the conclusion that coke on Pt is more easily combusted than that on Al_2O_3. The resulting single peak (TPO, Fig. 10) corresponds to the high-temperature peak of TPRn with CO_2 (Fig. 7a) and to the high-temperature peak of TPO for coke on Al_2O_3 (Fig. 4). The low-temperature peak of the TPRn with CO_2 (Fig. 7a) therefore corresponds to coke on Pt particles and the high-temperature peak to coke on the Al_2O_3 support.

In contrast to Pt/Al_2O_3, the combustion characteristics of coke on Pt/ZrO_2 (TPO, Figs. 3 and 5), unsupported metallic Pt, and ZrO_2 were almost identical. However, the amount of CO_2 desorbing from ZrO_2 during TPO after exposure to CH_4/He for 12 h was only three times larger than that for Pt/ZrO_2 after exposure to CH_4/He for only 10 min, indicating that coke is not easily produced on the ZrO_2 support. The peak of CO_2 evolving from Pt/ZrO_2 is symmetric and indicates that it originates from one type of coke. Based on the above arguments the CO_2 peak observed with Pt/ZrO_2 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/ZrO_2 for that experiment, but the amount of coke for unsupported metallic Pt was much smaller than that for Pt/ZrO_2. 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 H_2 (Fig. 11).

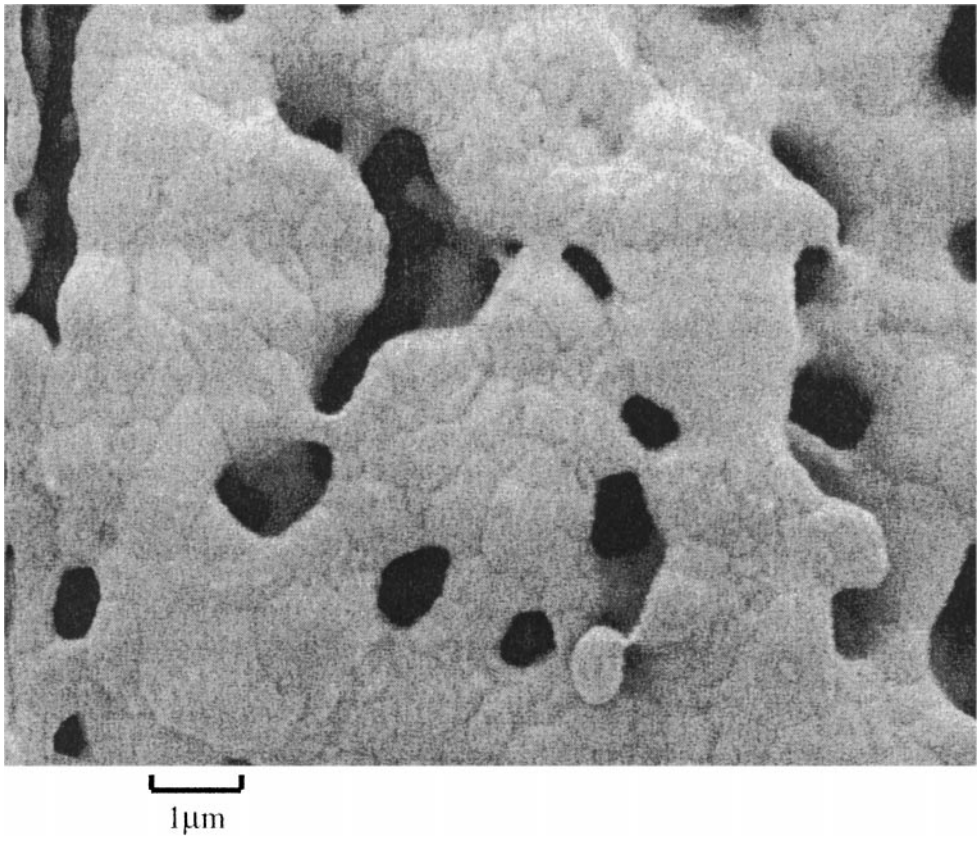

FIG. 11. SEM image for unsupported metallic Pt after reduction at 1120 K.

Acid Site on Support

The amount of coke deposited on the Al_2O_3 support was larger than that on Pt/Al_2O_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 Pt/Al_2O_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 Pt/Al_2O_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 Pt/Al_2O_3 was estimated from hydrogen adsorption to be 21 μmol g^{-1} catalyst, and the 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 Pt-Al_2O_3 perimeter as proposed earlier for lower temperatures, but also on Pt metal.

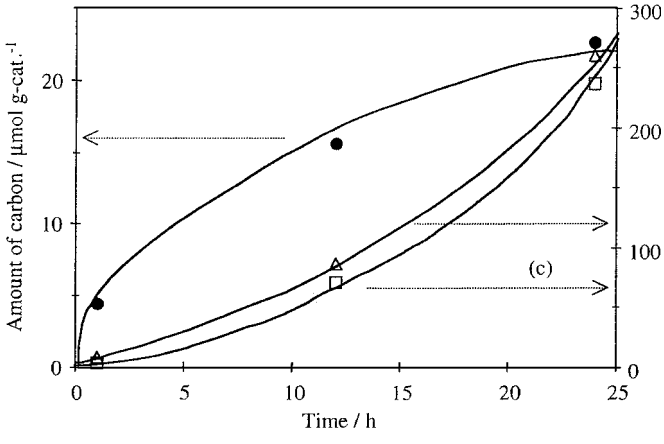

FIG. 12. Amount of coke formed during CH_4/CO_2 reaction at 1070 K over Pt/Al_2O_3. ●, Coke on Pt particles; □, coke on support; △, total coke (● + ○).

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 (CHx: $0 \leqq x \leqq 3$), which is oxidized by CO_2 chemisorbed on the support in the vicinity of Pt particles. Thus, the key step (oxidation of CHx) is considered to occur on the Pt-support perimeter and the coke on the perimeter blocks the reaction. At the higher temperature ($\geqq$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 CHx 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, Pt/Al_2O_3 had relatively stable CO_2 conversion ($\geqq$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 CHx 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 Pt/Al_2O_3 could be regenerated with CO_2 is therefore interesting. Figure 13 shows the original activity of Pt/Al_2O_3 and that after

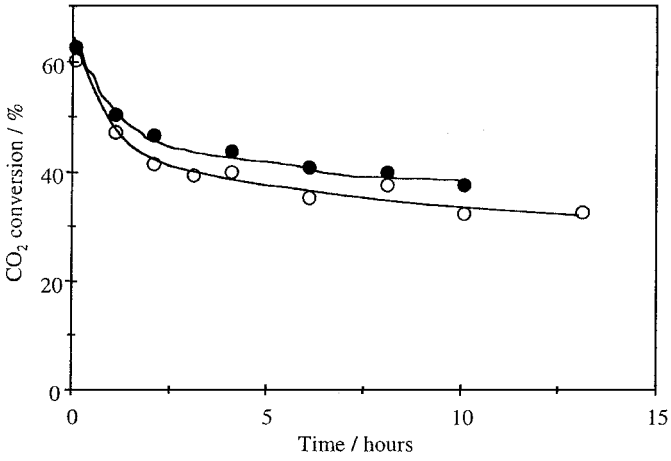

FIG. 13. Carbon dioxide conversion as a function of time on stream for Pt/Al_2O_3 at 1070 K, $CO_2/CH_4/Ar + N_2 = 42/42/85$/ml min^{-1}, 300 mg catalyst. ●, Freshly reduced; ○, reactivated by CO_2 at 1115 K.

treating by CO_2 (1115 K for 3 h) as a function of time. Initial CO_2 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 CO_2. 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/ZrO_2 (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/Al_2O_3 at high temperature (≧1070 K) is schematically shown in Fig. 14. CH_4 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 CO_2. CO_2 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 CO_2 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 CH_4 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 CO_2 activation and it finally causes complete catalyst deactivation.

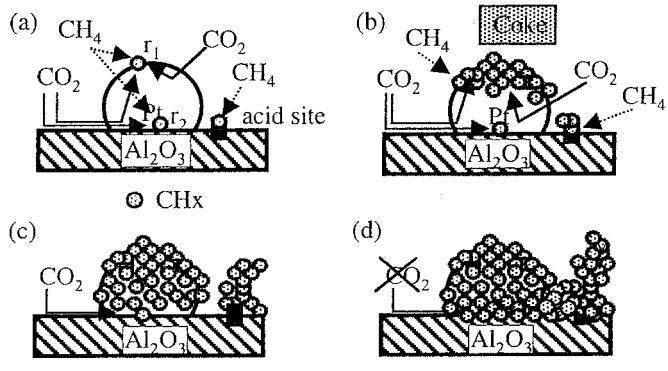

FIG. 14. Model of reaction and coking scheme over Pt/Al_2O_3 at high reaction temperature.

Relevance of Coke Deposition and Its Influence on the Stability between Pt/Al_2O_3 and Pt/ZrO_2

TPRn with CO_2 on Pt/ZrO_2 after exposure to CH_4/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 ZrO_2 (Fig. 5), both of them would be on Pt. On the other hand, coke on Pt (supported on Al_2O_3) reacts with CO_2 at least 70 K higher temperature when compared to reactive coke (first peak) on Pt/ZrO_2. As the reactants are coke (CH*x*) and CO_2, the reactivity of those species should cause the different reactivity of coke with CO_2. From above arguments, coke on Pt supported on ZrO_2 would be more reactive toward CO_2 than coke on Pt supported on Al_2O_3 in the presence of a CH_4/CO_2 mixture; hence it is more easily removed by activated CO_2. Note also that the initial CH_4 deposition rate on Pt/ZrO_2 was slower than that on Pt/Al_2O_3 (Fig. 7). So (slow) CH_4 deposition and (fast) removal of coke is balanced on Pt/ZrO_2 and coke does not accumulate on Pt particles. In addition, there is insufficient coke produced on the ZrO_2 support that might cover active sites. As a result, coke does not accumulate on Pt/ZrO_2 giving the catalyst a stable activity.

CONCLUSIONS

Pt/ZrO_2 has stable activity for CO_2/CH_4 reforming at all temperatures, while Pt/Al_2O_3 partly deactivates at high temperatures (≧1070 K) and completely loses activity at lower temperatures (<875 K) (16).

The deactivation mechanism of Pt/Al_2O_3 was investigated at 1070 K (industrial condition) in this communication. As regeneration by CO_2 (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, CH_4 decomposes to hydrogen-containing carbon species (CH*x*: 0 ≦

$x \leqq 3$) 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).