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CO_2 reforming of methane to syngas over highly active and stable Pt/MgO catalysts

Min Yang, Helmut Papp [*]

Institute of Technical Chemistry, University of Leipzig, Linnéstr. 3, 04103 Leipzig, Germany

Abstract

Pt/MgO catalysts were prepared by wet impregnation. At 800 °C and atmospheric pressure, Pt/MgO catalysts exhibited a high stability at high gas hourly space velocity of 36,000 ml/g h with a CH_4/CO_2 ratio of 1.0. During 72 h time on stream, the conversion of CH_4 and CO_2 remained almost constant, at about 88% and 90%, respectively. There was no loss of Pt. After reaction, the XRD peaks of MgO became broader, indicating amorphization of MgO, which was supported by TEM results. XPS indicated that the reforming reaction had little influence on Pt. CO_2-TPSR results showed that some carbon deposition occurred under stoichiometric feed of CH_4 and CO_2, but it did not result in the deactivation of the catalyst. The deposited carbon came mainly from the decomposition of methane.

Keywords: Reforming; CH_4; CO_2; Pt/MgO; Carbon deposit

1. Introduction

CO_2 reforming of methane to synthesis gas (Reaction (1)) has been a topic of considerable interest for CO_2 utilization and natural gas conversion. This process offers important advantages compared to steam reforming of methane. First, this reaction produces hydrogen and carbon monoxide or/and their mixture with a desired ratio of H_2/CO close to unity [1]. Secondly, this reaction has important environmental implications as two greenhouse gases are converted into a valuable feedstock. Finally, it is well suited for chemical energy transformation systems [2–4].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H_{298} = 247.3\,\mathrm{kJ/mol} \qquad (1)$$

Ni-based catalysts, the traditional catalysts for steam reforming, are widely used for CO_2 reforming of methane as well because of high activity and low cost. However, a rapid deactivation due to carbon deposition and/or sintering of the metal particles has been reported on Ni/oxidic support catalysts [1,5–10]. There is a general agreement about noble metals showing a better activity and lower degree of carbon deposition [11]. Most authors preferred Rh catalyst, owing to its good activity and stability. But, from the perspective of relative price and availability, Pt is a reasonable compromise, and many studies have shown that Pt catalysts have a comparable activity and stability [12–14]. van Keulen et al. [13] showed that Pt is one of the most active and stable metals among zirconia supported group VIII metals and Pt/ZrO_2 has a very high stability for time on stream over 1000 h at 650–700 °C and a feedstock of $CH_4/CO_2 = 2$. There is evidence that the support utilized can have a significant influence on the overall catalytic activity and stability [1,15]. Choudhary et al. [16] found that nickel supported on silica and/or alumina pre-coated with MgO, CaO or rare earth oxides showed much higher activity, selectivity and productivity in the methane-to-syngas conversion process than the catalysts prepared using supports without any precoating. Further study of Choudhary et al. [17] showed that the best performance was shown by MgO among the precoating metal oxides. Mehr et al. [18] studied the influence of MgO in the CO_2 reforming of methane to syngas, and found that addition of MgO reduced the carbon deposition and energy consumption. They attributed the stability and less coking on MgO-promoted catalysts to the Lewis basicity of MgO [19,20]. Considering the catalytic activity of Pt for CO_2 reforming and the special properties based on the basicity of MgO as support, we prepared a series of Pt/MgO catalysts to study their physicochemical properties and catalytic activity. Our earlier work showed that Pt/MgO catalysts have high catalytic activity and

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[*] Corresponding author. Tel.: +49 341 9736301; fax: +49 341 9736349.
E-mail address: papp@chemie.uni-leipzig.de (H. Papp).

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stability for the partial oxidation of methane to syngas due to low carbon deposition [21]. CO_2 reforming of methane over these catalysts was studied under different conditions [22]. The results showed that the temperature and the Pt loading had big influence on the catalytic activity of the catalyst, i.e. low temperature resulting in low conversion and selectivity, and the catalyst with Pt loading 0.80 wt% exhibiting the best performance among all tested catalysts (Pt loading: 0.10–1.50 wt%). In this study, we report about the CO_2 reforming results over a Pt/MgO catalyst with Pt loading 0.80 wt%.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by impregnating the support material MgO (99.95% (metal basis), Alfa Aesar, BET surface area = 9.2 m^2/g) with an aqueous solution of $PtCl_4$ (99.99% (metal basis), Alfa Aesar). To get the desired content of Pt loading, a calculated volume of precursor solution was added to a calculated amount of support MgO. After removal of solvent by heating the mixture slowly under a water evaporator equipped with a magnetic stirrer, the catalyst was dried at 120 °C for 24 h, then, reduced in a mixture of H_2 (50 ml/min) and N_2 (50 ml/min) at 800 °C for 6 h. Finally, the catalysts were crushed and sieved to granules with 200–315 μm after it has been pressed at 2×10^7 Pa for 15 min. The physicochemical properties of the Pt/MgO catalyst are listed in Table 1.

2.2. Characterization

XRD measurements were carried out with a D5000 diffractometer (SIEMENS, Germany) with Cu Kα radiation ($\lambda = 0.15418$ nm) and PSD detector in air at room temperature in the range of 2θ from 8° to 100° with a scanning step of 0.039° every 0.30 s. The sample was finely ground and then placed on a glass slide using a smear mount technique.

ESCA measurements were performed with an UNI-Specs ESCA System (Specs, Germany) equipped with SpecsLab software for data acquisition and a CasaXPS software for data evaluation. A pass energy of 30 eV, at a pressure lower than 2×10^{-9} mbar and Al Kα radiation with 1486.8 eV and 300 W (13 kV, 23.4 mA) was used. A wide range spectrum (0–1386 eV) was recorded, after which the elements of interest were analyzed separately. The binding energy scale was calibrated using the peak of Mg_{2p} (50.5 eV) [23]. The Shirley background subtraction was applied.

Table 1
Physicochemical properties and results of CO chemisorption of a freshly reduced Pt/MgO catalyst

Catalyst	Pt/MgO
Pt loading[a] (wt%)	0.80
BET surface area (m^2/g_{cat})	12.2
CO uptake ($\mu l_{(STP)}/g_{cat}$)	67.1
Dispersion (%)	6.9
Metal surface area (m^2/g_{cat})	0.16
Metal surface area (m^2/g_{Pt})	19.1
Crystallite size[b] (nm)	1.2

[a] Detected by ICP-AES.
[b] Determined from CO uptake.

The catalysts, as prepared and after the catalytic tests, were examined by means of a Philips CM200 transmission electron microscope (TEM) (Holland), operated at 200 kV with magnifications of 13,000 and 30,000. The distribution of Pt particles was analyzed using the SIS software (Soft Imaging Software GmbH, Germany). Samples for TEM were prepared by taking a small quantity of powder into ethanol and ultrasonicated for a few minutes. Then, the resultant slurry was deposited onto a carbon film covering the copper grid (holey 400 mesh).

Temperature-programmed surface reaction (TPSR) measurements were performed in a continuous fixed bed quartz reactor with 100 mg of catalyst. After termination of the catalytic reaction of CO_2 reforming of methane or of reaction of 50% CH_4 (or CO) in N_2 with the catalyst, it was purged with nitrogen (50 ml/min) for 30 min at reaction temperature, and then cooled down slowly overnight to room temperature. The following day the temperature of the sample was ramped at a rate of 10 °C/min from 100 to 900 °C while a gas mixture of 25% CO_2 in N_2 (20 ml/min) was passed through the catalyst bed. During the heating, CO_2 reacted with the surface carbon intermediates to produce CO, which was analyzed by an on-line Advance Optima Modular Process Analysis System (Uras 14).

2.3. Catalytic reaction

Catalytic experiments were carried out by using 100 mg of catalyst Pt/MgO with 0.80 wt% Pt in a quartz tube reactor with an internal diameter of 5 mm, the height of catalyst bed was about 8 mm. The catalytic tests were started by heating the reactor, from room temperature to 800 °C, under a N_2 flow (50 ml/min). Subsequently, the N_2 flow was stopped and H_2 (50 ml/min) was allowed to flow through the reactor to reduce the catalyst for 60 min. Then, it was purged with N_2 at 800 °C. Finally, the reaction mixture (mixed for more than 10 min prior to reaction) was permitted to pass through the reactor. After catalytic reaction the temperature was lowered under N_2 to room temperature at which the used catalyst could be unloaded for various characterizations.

Both the feed gases and products were analyzed simultaneously and continuously by the analytical unit, which consisted of two Advance Optima Modular Process Analysis Systems, Uras 14 for CO, CO_2 and CH_4 components and Magnos 16 for O_2 (Hartmann and Braun, Germany). Water was separated from the product mixture by an electric cooling trap (Hartmann and Braun, Switzerland) before the products were analyzed.

3. Results and discussion

3.1. Catalytic behavior

CO_2 reforming of methane was carried out with a feedstock ratio of CH_4/CO_2 1.0 and 2.0. Fig. 1 shows the catalytic

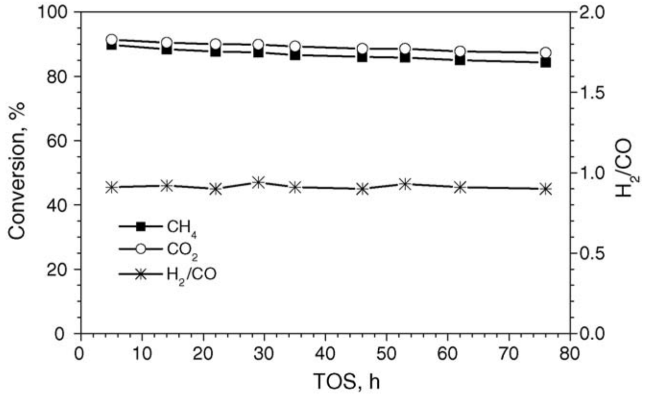

Fig. 1. CH_4/CO_2 reforming over a Pt/MgO catalyst (800 °C, $CH_4/CO_2 = 1.0$, GHSV = 36,000 ml/g h).

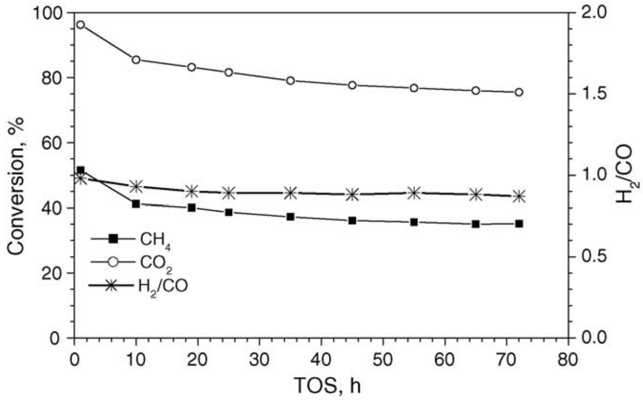

Fig. 2. CH_4/CO_2 reforming over a Pt/MgO catalyst (800 °C, $CH_4/CO_2 = 2.0$, GHSV = 36,000 ml/g h).

behavior of a Pt/MgO catalyst at $CH_4/CO_2 = 1.0$. During 76 h time on stream, the conversion of both methane and CO_2 showed only a slight decrease, i.e. 5% and 4%, respectively. This result shows that Pt/MgO has a very high activity and stability for CO_2 reforming of methane. During the whole time, the conversion of CO_2 is higher than that of CH_4. This indicates that the reverse water gas shift reaction (RWGS) (Reaction (2)) took place additionally during the reforming reaction, because the RWGS reaction is thermodynamically favorable at the reaction temperature 800 °C. In fact, water could be detected at the outlet of the reactor. The ratio of H_2/CO (included in Fig. 1) was at about 0.90, which is less than the stoichiometric value 1.0. This gives more evidence for the existence of the RWGS reaction.

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H_{298} = 41.0\,\mathrm{kJ/mol} \tag{2}$$

A high CH_4/CO_2 feed ratio (>1.0) is considered as severe condition for CO_2 reforming of methane. According to the reforming reaction (Reaction (1)), the stoichiometric ratio of CH_4/CO_2 is 1.0. When the ratio is bigger than 1.0, there will be extra methane left. As reported in the following part of this contribution, the Pt/MgO catalyst is active for the decomposition of methane (Reaction (3)). If there is not enough oxidant (CO_2) in the reaction mixture, the produced carbon will deposit on the surface of the catalyst, and result in its deactivation. Therefore, the higher the CH_4/CO_2 ratio, the more severe the reaction condition for CO_2 reforming. Fig. 2 gives the results over a Pt/MgO catalyst under very severe conditions, i.e. $CH_4/CO_2 = 2.0$.

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298} = 74.9\,\mathrm{kJ/mol} \tag{3}$$

Different from the results at $CH_4/CO_2 = 1.0$, the conversion of both reactants decreased continuously during 72 h reaction. After the initial 10 h, the decrease of both CH_4 and CO_2 conversion is very large, 10% and 11%, respectively. After that, the decrease becomes more gentle. The ratio of H_2/CO changed slightly during the 72 h time on stream from 0.98 to 0.87.

It is worth to note the catalytic behavior of the Pt/MgO catalyst during the first several hours at $CH_4/CO_2 = 2.0$. At the very beginning of the reaction (TOS = 1 h), the conversion of CH_4 and CO_2 is 52% and 96%, respectively. Compared to the results at $CH_4/CO_2 = 1.0$, there is more CH_4 taking part in the reaction. Wang and Xu observed a similar phenomenon [24] when they studied the CO_2 reforming on a Ni/MgO-AN catalyst under high pressure (1.5 MPa). They believed that the conversion of CH_4 was not balanced by that of CO_2 or there was an ‘‘excessive’’ conversion of CH_4 at the beginning of the reaction. In our study, the H_2/CO ratio was 0.98 at the same time, which is very close to the stoichiometric ratio of 1.0. Considering the unavoidable existence of the RWGS reaction, we suggest that the high CH_4 conversion and high H_2/CO ratio resulted from the decomposition of CH_4.

3.2. Characterization

XRD measurements were used to characterize the structural changes of the catalyst before and after the reaction. Fig. 3 shows that both the fresh and used catalysts exhibit the typical pattern of MgO. No diffraction peaks for Pt crystallites were detected. After reforming at 800 °C for 68 h under very severe

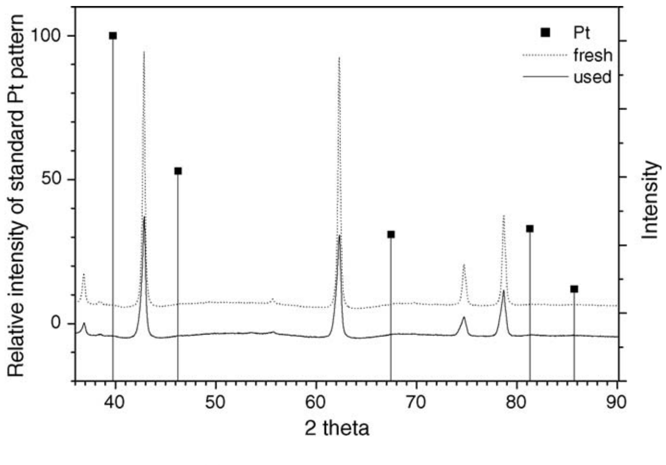

Fig. 3. XRD patterns of freshly reduced Pt/MgO (dotted) and a used Pt/MgO catalyst (solid) (800 °C, $CH_4/CO_2 = 2.0$, TOS 68 h).

Table 2
Surface characterization by XPS after different treatments

Catalyst	Pt $4f_{7/2}$	Pt/Mg	O/Mg	C/Mg
Dried[a]	73.6	0.0037	1.5805	0.1625
Reduced	72.5	0.0100	1.0683	0.1936
$CH_4/CO_2 = 1.0$, 800 °C for 70 h	72.4	0.0078	0.9609	0.1863
$CH_4/CO_2 = 2.0$, 800 °C for 90 h	72.3	0.0089	0.9218	0.3122

[a] The catalyst was dried at 120 °C for 24 h.

conditions ($CH_4/CO_2 = 2.0$), the XRD pattern of MgO changed significantly compared with the fresh catalyst. The intensities of the diffraction peaks of MgO became very low, and the widths very large. After reaction at $CH_4/CO_2 = 1.0$, no change in the XRD pattern was observed. The XRD results of the fresh and used catalysts indicate that the extended reforming reaction under severe reaction condition resulted in sintering of the support MgO. This may be one reason for the loss of activity for CO_2 reforming.

Table 2 gives the ESCA results of the Pt/MgO catalyst treated at different conditions. As described in Section 2, the fresh catalyst was reduced at 800 °C for 6 h, the used catalysts were reduced at 800 °C for 6 h before use as well. In the dried catalyst (120 °C for 24 h), the binding energy of Pt $4f_{7/2}$ was 73.6 eV, indicating that Pt existed in the state of Pt^{4+} ions. The other samples, both freshly reduced and used, showed a binding energy of 72.3–72.5 eV for Pt $4f_{7/2}$. We attribute this binding energy to Pt^0, i.e. metallic Pt. In fact, the temperature-programmed reduction (TPR) of the reduced catalyst showed no hydrogen uptake, supporting the result that Pt existed in the metallic state on the surface of the freshly reduced and used catalysts. The binding energy of Pt $4f_{7/2}$ in the fresh catalyst and in both used catalysts ($CH_4/CO_2 = 1.0$ and 2.0) were almost identical. The fact that an extended CO_2 reforming reaction, even though under very severe reaction conditions, did not change the binding energy of Pt $4f_{7/2}$ indicates that CO_2 reforming could not change the environment of Pt greatly. This means that the Pt/MgO catalyst is very stable.

The surface atomic ratios of Pt/Mg for the fresh and used catalysts support this conclusion. The surface atomic ratios of Pt/Mg did not change significantly after 70 h at $CH_4/CO_2 = 1.0$ and 90 h at $CH_4/CO_2 = 2.0$, indicating that the dispersed Pt atoms did not migrate from the bulk to the surface, i.e. the dispersed Pt is very stable. In order to get more information about the influence of CO_2 reforming on the Pt content of the Pt/MgO catalysts, ICP-AES was used to detect the Pt content of the fresh and used catalysts. The catalyst used for CO_2 reforming for 68 h under $CH_4/CO_2 = 2.0$ at 800 °C had a Pt content of 0.78 wt%, the fresh catalyst of 0.80 wt% (Table 1). There is no Pt loss even after CO_2 reforming under $CH_4/CO_2 = 2.0$ for TOS 68 h. This proves again that Pt is very stable in the Pt/MgO catalyst. We attribute the stability of Pt to the interaction between the dispersed Pt and the support MgO. This interaction hinders the segregation of dispersed Pt.

The surface atomic ratios of C/Mg for fresh and used catalysts give insight into the surface carbon content. After TOS 70 h under a stoichiometric feed of CH_4 and CO_2, the surface carbon content was unchanged, compared to the fresh catalyst. But after TOS 90 h under severe reaction conditions ($CH_4/CO_2 = 2.0$), the C/Mg ratio increased greatly, showing that there is more carbon deposited on the catalyst surface. The deposited carbon is surely responsible for the deactivation of the PtMgO catalyst under severe reaction condition.

Fig. 4 gives the TEM images of the Pt/MgO catalyst before (a) and after the CO_2 reforming reaction for 72 h under stoichiometric feed ($CH_4/CO_2 = 1.0$) (b) and severe conditions ($CH_4/CO_2 = 2.0$) (c). The freshly reduced catalyst showed Pt crystallites dispersed on the surface of MgO crystallites. In this sample, the average size of Pt crystallites was 4.2 nm, which is bigger than that detected by CO chemisorption (Table 1). The TEM image after reaction for 72 h under stoichiometric feed was very similar to that of the freshly reduced catalyst, the average size of Pt crystallites in sample (b) is 4.5 nm, a little bigger than that of the fresh catalyst. The TEM image (c) after reaction for 72 h under $CH_4/CO_2 = 2.0$ shows a big difference compared to the above two images, that is the border of MgO crystallites becoming unclear, indicating the amorphization of the support MgO. This is consistent with the XRD results. The average size of Pt crystallites in the catalyst used under $CH_4/CO_2 = 2.0$ is 4.3, very similar to that of the catalyst used under stoichiometric feed. So, the CO_2 reforming reaction, both under stoichiometric feed and under $CH_4/CO_2 = 2.0$, has no big influence on the size of the dispersed Pt crystallites.

Carbon deposition on the catalysts is a problem always encountered in syngas production. During CO_2 reforming of methane, carbon deposition can originate form CH_4 decomposition (Reaction (3)) and CO disproportionation (Reaction (4)). In this study, temperature-programmed surface reaction was used to investigate the carbonaceous deposits on used catalyst samples.

$$2CO \rightarrow C + CO_2 \quad \Delta H_{298} = -172.0\,\mathrm{kJ/mol} \qquad (4)$$

The fresh Pt/MgO catalyst was exposed to a mixture of CH_4 (50 ml/min) and N_2 (50 ml/min) at 800 °C for 10 min. The decomposition of CH_4 (Reaction (3)) results in carbon deposits on the catalyst surface. TPSR gives some information about the deposited carbon, as shown in Fig. 5a. There are two CO peaks (Fig. 5a), one is at 820 °C, another is higher than 900 °C. This means that there are two kinds of carbon deposited on the surface of Pt/MgO resulting from the decomposition of methane. The size of the peak at low temperature is bigger than that at high temperature. The TPSR profile of the catalyst exposed prior to a mixture of CO (50 ml/min) and N_2 (50 ml/min) at 800 °C for 10 min is shown in Fig. 5b. There is no CO peak detected from the reaction of CO_2 with surface carbon. This indicates that the CO disproportionation does not take place under the applied reaction condition [25]. Based on the TPSR results in profile Fig. 5a and b, we can conclude that the Pt/MgO catalyst has a high activity for methane decomposition, but it is inactive for CO disproportionation.

During TPSR-CO_2 two CO peaks (820 and >900 °C) were observed on the Pt/MgO catalyst after exposure to the mixture

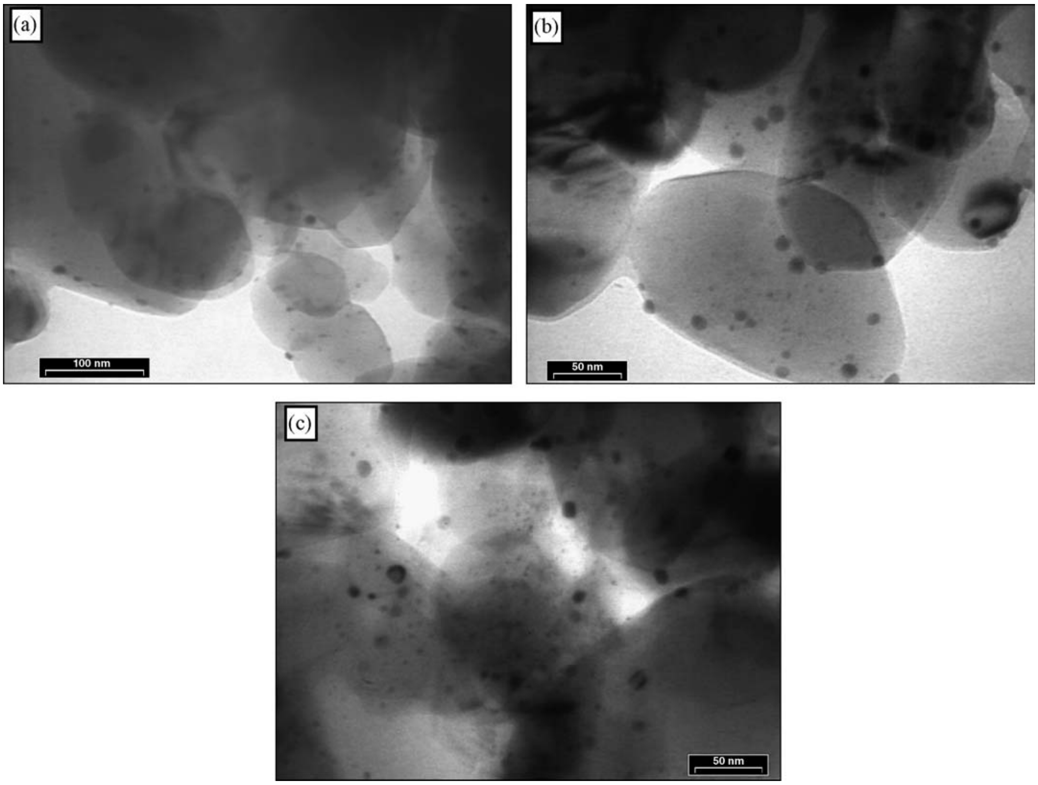

Fig. 4. TEM images of the freshly reduced (a) and used (b and c) Pt/MgO catalyst (b: $CH_4/CO_2 = 1.0$, 800 °C, 72 h; c: $CH_4/CO_2 = 2.0$, 800 °C, 72 h).

of CH_4 and N_2 (Fig. 5a) indicating that there are two kinds of carbon on the catalyst surface. Barbier [26] 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 support. Bitter et al. [27] observed two kinds of coke on Pt/Al_2O_3 catalyst used at 875 K for the CO_2 reforming of methane. Nagaoka et al. [28] also observed two kinds of carbon by using TPO and TPSR-CO_2 on Pt/Al_2O_3 and Pt/ZrO_2 catalysts, which were used for CO_2 reforming reaction. The authors also attributed the more reactive carbon to the coke on Pt and the less reactive carbon to the coke on the support. In this study, we assign the low temperature CO peak (820 °C) to coke on Pt and the high temperature CO peak (>900 °C) to coke on the support MgO. This means that carbon deposits on both Pt and MgO after an exposure of the catalyst to a mixture of CH_4 and N_2 at reaction temperature.

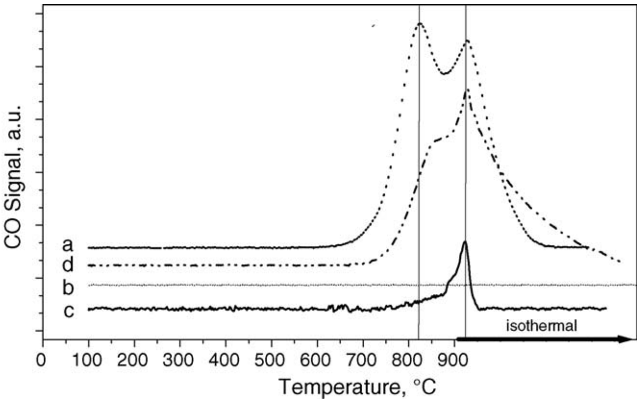

Fig. 5. TPSR-CO_2 profiles of the Pt/MgO catalyst after being (a) exposed to $CH_4 + N_2$ for 10 min; (b) exposed to $CO + N_2$ for 10 min; (c) used for TOS 72 h ($CH_4/CO_2 = 1.0$) (magnified three times); (d) used for TOS 72 h ($CH_4/CO_2 = 2.0$).

The profile Fig. 5c is the TPSR result of the catalyst used for CO_2 reforming (TOS 72 h) at 800 °C with a stoichiometric feed of CH_4 and CO_2. Only one very small CO peak at higher temperature (>900 °C) was observed, which matches very well with the high temperature peak in profile Fig. 5a. Therefore, this peak is assign to coke on support MgO. This means that there was only a small amount of carbon deposited on support MgO after CO_2 reforming for 72 h with a stoichiometric feed of CH_4 and CO_2.

However, the TPSR profile (Fig. 5d) of the catalyst used under severe conditions ($CH_4/CO_2 = 2.0$) gives two CO peaks, a shoulder at low temperature (~850 °C) and a main peak at a temperature higher than 900 °C. The low temperature peak is shifted to higher temperature compared to the profile of Fig. 5a, but the high temperature peak is at the same position as in the profile Fig. 5a. This indicates that more carbon was deposited on the catalyst under severe conditions, which is supported by the ESCA results (Table 2), and it proves that the carbon deposits originate from the decomposition of methane. According to peak assignment mentioned above, the low temperature peak is caused by the carbon on Pt and the high temperature peak by the carbon on MgO. So, the carbon deposited not only on the support MgO but also on Pt after CO_2 reforming used under severe conditions ($CH_4/CO_2 = 2.0$).

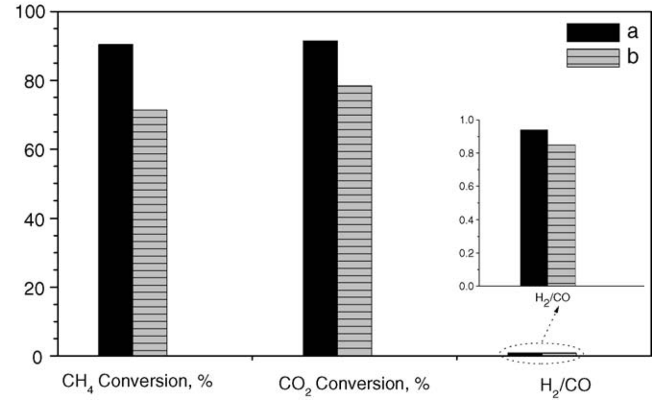

Fig. 6. Catalytic activity of freshly reduced (a) and used (b) catalyst (b: exposed to $CH_4 + N_2$ for 10 min at 800 °C).

Most authors propose also that the carbon deposits causing catalyst deactivation originate from the decomposition of methane [11,29]. van Keulen et al. [29] studied the carbon deposits on supported Pt catalysts by using thermogravimetry. Their results showed that carbon was not formed by CO disproportionation (Reaction (4)), but by decomposition of methane (Reaction (3)), although the CO disproportionation is thermodynamically favored under the reaction condition. Our study showed that much carbon is deposited on the catalyst after catalyst exposure to CH_4, but there is no carbon detected after the catalyst exposure to CO. Considering the fact that there is much more carbon deposited on the catalyst after reforming under severe reaction conditions connected with a severe deactivation (Fig. 2), compared with the catalyst used with a stochiometric feed (Fig. 1), it is proposed that the deactivation of the catalyst under severe reaction conditions results from the carbon deposits formed via CH_4 decomposition, and the very small amount of carbon deposited under the stoichiometric feed of CH_4 and CO_2 is responsible for the high activity and stability of the catalyst. Considering the two kinds of carbon and the difference of the carbon deposited on the catalyst after CO_2 reforming reaction under stoichiometric conditions (Fig. 5c) and severe conditions ($CH_4/CO_2 = 2.0$) (Fig. 5d), the deactivation of the catalyst under severe reaction conditions should be caused by the carbon deposited on Pt. Fig. 6 gives a comparison of the activities of the Pt/MgO catalyst before and after exposure to CH_4. This shows that the catalytic activity of the Pt/MgO catalyst was reduced after exposure to a mixture of CH_4 and N_2 at a reaction temperature of 800 °C for 10 min, supporting the conclusion that the carbon deposits formed via CH_4 decomposition resulted in the deactivation of the catalyst.

4. Conclusions

Pt/MgO catalysts have a high and stable activity for CO_2 reforming of methane at 800 °C with a stoichiometric feed of CH_4 and CO_2. The stability of the catalyst stems from the stable structure and the high resistance to carbon deposition on the catalyst. The carbon deposit formed by the decomposition of methane and the amorphization of the support MgO are the main reasons causing the deactivation of the catalyst under severe reaction conditions.

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