# Dry reforming of $CH_4$ on $Co/Al_2O_3$ catalysts reduced at different temperatures

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A B S T R A C T

The reforming of methane with carbon dioxide has been investigated at 773 K on 10% $Co/Al_2O_3$ reduced at different temperatures up to 1173 K. The catalysts were characterized by BET, TPR, XRD and XPS methods. TPR and XPS results revealed that during the pre-treatment of the catalysts the Co only partially reduced. The reduction degree and the amount of the structured metallic cobalt increased with the reduction temperature. The conversion of the reactants was the highest on the sample reduced at 973 K, but the turnover frequencies of CO and $H_2$ formation increased as the reduction temperature increased.

The amount of surface carbon significantly depended on the pre-treatment temperature of the catalysts. The IR spectra registered at the beginning of the reaction indicate that tilted CO was formed, but the position of the absorption bands depends on the reduction temperature of the catalysts. Similarly, the pre-treatment temperature influenced the type of the surface carbon determined by XPS. We assume that the different structures of the metallic Co formed in pretreatment resulted in the different catalytic behaviors.

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## 1. Introduction

The conversion of $CH_4$ and $CO_2$ – the two main components of biogas and the major greenhouse gases – into synthesis gas is in the focus of academic and industrial research. One of the possibilities to achieve this goal is to react $CH_4$ and $CO_2$ with each other.

All of the Group VIII metals on a variety of supports have been studied as dry reforming catalysts [1–3]. We showed in our previous studies that supported noble metals are active in this reaction [4–7]. Supported Co catalysts have been also extensively investigated in the dry reforming of methane due to their lower cost and availability in larger scale. The results obtained on these catalysts are summarized in different reviews [1,2,8,9].

Ferreira-Aparicio et al. [10] compared the activities of different alumina supported catalysts, and though the Co containing sample was not the best one but it showed good stability in the whole temperature range. Ruckenstein and Wang [11] found that $Co/Al_2O_3$ exhibited a very good activity among Co catalysts supported on different oxides. The stability of $Co/Al_2O_3$ catalyst strongly depends on the Co loading and the calcination temperature [12]. Over the catalyst with high Co concentration (>12 wt%) notable amounts of carbon were accumulated during reforming, and deactivation was observed. It was found that not only the deposition of

surface carbon but also the oxidation of metallic sites could result in the decrease of activity. It was stable when the balance between the formation and oxidation of carbon was achieved. The structural characteristics of the $Al_2O_3$ supported Co (24 wt%) catalyst were strongly affected by the calcination temperature and so was their reducibility [13]. The catalysts lost their activities in time independently of the calcination temperature [11]. Characterization of $Co/\alpha-Al_2O_3$ indicated that the surface species of Co, the reforming activity and the rate of coke formation depend on the calcination temperature and the reduction time [14]. Similar results were found on $\gamma-Al_2O_3$ supported Co catalyst; the amount and the reactivity of surface carbon significantly depended on the calcination temperature [15]. San José-Alonso et al. studied the reaction on $Co/Al_2O_3$ with low Co content [16]. 1% $Co/Al_2O_3$ deactivated during the first minutes of the reaction at 973 K because $CoAl_2O_4$ was formed, while on 2.5% $Co/Al_2O_3$ high stability and low carbon deposition was observed. The effects of the preparation methods on the efficiency of $Co/Al_2O_3$ were also studied [17,18]. The good coking resistivity of the catalysts was attributed to the high surface concentration of OH species, to the small metallic Co particles and to the strong interaction between Co and the support. It was stated that $CoAl_2O_4$ plays an important role in the prevention of coke formation [17]. $Co/Al_2O_3$ prepared by controlled adsorption method showed higher $CO_2$ and $CH_4$ conversion than the sample prepared by dry impregnation; it was attributed to the higher dispersion of Co. On this sample more non-deactivating coke deposit

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was formed, while on the other catalyst deactivating coke built up which drastically hindered the catalytic activity [18].

Rare earth oxide additives improved the anti-coke performance of the 20% $Co/Al_2O_3$ catalyst [19] in the $CO_2 + CH_4$ reaction. Rh additives enhanced the reducibility of Co and the activity of the catalyst [15]. K doping of $Co/Al_2O_3$ also reduces the carbon deposition but the catalytic activity as well; it was explained by its ability to catalyze the carbon gasification and by partial coverage of cobalt active sites for $CH_4$ decomposition [20].

Takanabe et al. [21,22] studied the influence of the reduction temperature on the catalytic behavior of $Co/TiO_2$ in the dry reforming of methane. The great difference in the initial activities of 10% $Co/TiO_2$ reduced at different temperatures corresponds to the different crystal structures of $TiO_2$ after the reduction [21]. 0.5% $Co/TiO_2$ reduced below 1123 K showed rapid and complete deactivation at the beginning of the reaction; the deactivation would be correlated to the coking on the active sites. On the other hand, the $Co/TiO_2$ reduced at and above 1123 K showed relatively stable activity [22].

The present paper gives an account of the effect of the reduction temperature on the structure and catalytic efficiency of $Co/Al_2O_3$ in the $CO_2 + CH_4$ reaction. Earlier we found that when the reducibility of Co on alumina increased, so increased the activity of the catalysts [15]. The changes of the reduction temperature also influenced the ratio of oxidized and reduced Co on the surface of the support. With the present contribution, we would like to show the effect of the above-mentioned ratio on the activity, the stability of the catalyst and on the coke formation.

## 2. Experimental

### 2.1. Preparation of the catalysts

The support ($Al_2O_3$, Degussa P110C) was impregnated with the aqueous solution of $Co(NO_3)_2$ to yield a nominal 10 wt% metal content. The samples were dried at 383 K and calcined at 973 K in air.

Before the measurements, the catalysts were oxidized at 673 K in $O_2$ flow for 30 min and reduced at different temperatures from 773 K to 1173 K in flowing $H_2$ for 60 min in situ. Afterwards the catalyst was flushed with $N_2$ at the reduction temperature for 15 min, and cooled down to the reaction temperature.

### 2.2. Kinetic measurements

Catalytic reactions were carried out in a fixed bed continuous-flow reactor. The ratio of $CH_4/CO_2$ in the reacting gas mixture was 1:1. The amount of catalyst used was usually 0.15 g. The flow rate of the reactants was 60 ml/min at room temperature and pressure. Analyses of the gases were performed with gas chromatograph (Agilent 6890 N) using HP-PLOT Q column. TC and FI detectors detected the gases simultaneously. To increase the sensitivity of CO and $CO_2$ detection a methanizer was applied before the detectors.

Infrared spectra were recorded during the catalytic reaction with an Agilent Cary 670 type FTIR spectrometer equipped with diffuse reflectance attachment (Harrick) with $BaF_2$ windows with a wave number accuracy of $\pm 4\,cm^{-1}$. Typically, 32 scans were registered. The catalysts were pre-treated as mentioned above, and then the $CH_4 + CO_2$ gas mixture was introduced into the cell at the reaction temperature and the IR spectra were recorded. All spectra were rated to the spectra of the catalysts pre-treated before the measurements. When the samples had to be reduced above 873 K (the cell is heatable only to 873 K), the catalysts were treated with $H_2$ ex situ at the given temperature and cooled down in $N_2$ stream to room temperature. Before the measurements the catalyst was reduced again in situ at 773 K. Separate TPR measurements revealed

that this treatment is sufficient to remove the adsorbed oxygen or oxidized species while only one reduction stage was detectable at about 600 K.

### 2.3. Characterization of the catalysts

The amount of surface metal was determined after pretreatment by $H_2$ adsorption using an impulse method.

Temperature programmed reduction and the BET surface measurements of the catalysts were carried out by a BELCAT-A instrument. The BET surface was measured using $N_2$ adsorption at the temperature of liquid nitrogen. Before TPR measurements, the catalysts were treated in oxygen at 673 K for 30 min and flushed with Ar for 15 min. Afterwards the sample was cooled in flowing Ar to room temperature. The pure Ar flow was changed to 10% $H_2$ containing Ar, and the reactor was heated linearly at a rate of 20 K/min up to 1373 K and the $H_2$ consumption was detected.

The amount and the reactivity of surface carbon formed in the catalytic reactions were determined by temperature-programmed hydrogenation. After the catalytic run (2 h) the reactor was flushed with $N_2$ at the reaction temperature, and the sample was cooled down to 373 K. Then the $N_2$ flow was changed to $H_2$ and the sample was heated up to 1173 K and the forming hydrocarbons were determined by gas chromatograph.

For XPS studies, the powder samples were pressed into tablets with ca. 1 cm diameter and a few tenth of mm thickness and placed into the load lock of the spectrometer. Sample treatments were carried out in a high-pressure cell (catalysis chamber) directly attached to the analysis chamber and isolated from that with a gate valve. With the help of the sample manipulators it was possible to transfer the samples from the analysis chamber into the high pressure cell in high vacuum, without the reach of air. The samples were pre-treated in the same way as described above. The high-pressure cell is heatable also only to 873 K; so when the samples had to be reduced above this temperature they were treated as written above. After the pre-treatment, the samples were cooled to room temperature in flowing nitrogen gas and the sample was taken back to the analysis chamber. After spectrum acquisition, the sample was moved back into the catalytic chamber and treated with the reacting gas mixture at the reaction temperature under the same experimental conditions as the catalytic reaction. The experiment was interrupted after the 5th, 30th and 120th minutes of the reaction and the XP spectra were recorded.

XP spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical electron energy analyzer operated in the FAT mode. The excitation source was the K$\alpha$ radiation of an aluminum anode (h$\nu$ = 1486.6 eV). The X-ray gun was operated at 210 W power (14 kV, 15 mA). The pass energy was set to 20 eV, the step size was 50 meV. Typically, five scans were added to get a single spectrum. The binding energy of the Al 2p line in $Al_2O_3$ was used as energy reference: it was taken 74.7 eV. For data acquisition and evaluation both manufacturers' (SpecsLab2) and commercial (CasaXPS) software were used.

The XRD study was carried out on a Rigaku Miniflex II powder X-ray diffractometer equipped with a Cu K$\alpha$ radiation source ($\lambda$ = 0.15418 nm) by applying a scanning rate of 4°/min in the 2$\theta$ range of 3–80°.

## 3. Results and discussion

### 3.1. Characterization of the catalysts

The BET surface area, the amount of $H_2$ – adsorbed at 373 K – and the dispersion of the Co on the $Co/Al_2O_3$ reduced at different temperatures are summarized in Table 1.

**Table 1**
Some characteristic data of the 10% $Co/Al_2O_3$ catalysts reduced at different temperature.

| Reduction temperature | BET surface | Adsorbed $H_2$ at 373 K | Dispersion | Average particle size[a] | $\frac{Co^0}{(Co^0+Co^{2+})}$ [b] | | | |
|---|---|---|---|---|---|---|---|---|
| K | $m^2/g$ | $\mu$mol/g | % | nm | reduced | used in the reaction for 10 min 30 min 120 min | | |
| 773 | 95 | 227 | 24 | 12.6 | 0.37 | 0.37 | 0.31 | 0.30 |
| 973 | 94 | 211 | 22 | 21.5 | 0.39 | 0.35 | 0.35 | 0.31 |
| 1173 | 96 | 129 | 14 | 26.1 | 0.57 | 0.57 | 0.57 | 0.41 |

[a] Determined from XRD data using the Scherrer equation.
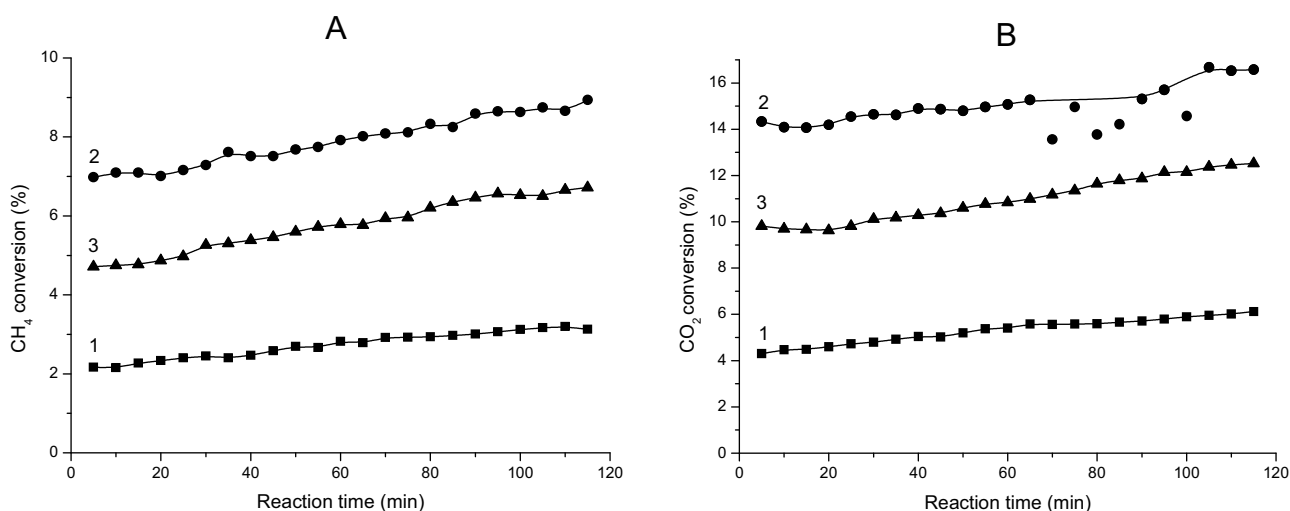[b] Determined from XPS results.



**Fig. 1.** The conversion of $CH_4$ (A) and $CO_2$ (B) in the $CH_4 + CO_2$ reaction at 773 K on $Co/Al_2O_3$ reduced at 773 (1), 973 K (2) and 1173 K (3).

The BET surfaces of the samples were practically the same, 94–96 $m^2/g$, irrespective of the reduction temperature (Table 1).

The Co dispersion calculated from the amount of adsorbed hydrogen decreased as the reduction temperature increased. It was the highest (24%) on the catalyst reduced at 773 K, and the lowest (14%) when the $Co/Al_2O_3$ was treated with hydrogen at 1173 K (Table 1).

The XRD profile of the $Co/Al_2O_3$ calcined at 973 K shows diffraction peaks at 31.5°, 37.1°, 59.5°, and 65.5° [15] corresponding to $CoAl_2O_4$ (JCPDS card No. 82-2248) or $Co_3O_4$ (JCPDS card No. 78-1970) [23–25]. Both have spinel structure with almost identical diffraction patterns [25]. On the reduced samples the diffractions characteristic for the spinel structures disappeared and new peaks were detected at 44.2° and 51.5° corresponding to Co(111) and Co(200) (JCPDS card No. 15-0806) facets. The intensities of these features increased as the reduction temperature increased.

From the XRD data using the Scherrer equation the average crystal size of the reduced catalysts was determined (Table 1). We found that the particle size increased as the reduction temperature increased. It was 12.6 nm on the catalyst reduced at 773 K and 26.1 nm when the sample was treated with hydrogen at 1173 K.

The TPR profile of the catalyst consists of a broad peak between 580 and 980 K with three different maxima at 767, 823, and 885 K, and a high temperature reduction stage ($T_{max}$ = 1103 K) was also observed [15]. The peak at low temperature corresponds to the reduction of large crystalline $Co_3O_4$ particles. The high temperature reduction stage can be attributed to the reduction of CoO and $CoAl_2O_4$. Some authors suggest that the peak at low temperature is in connection with the reduction of large crystalline $Co_3O_4$ particles to $Co^0$ via CoO formation [23], others propose that this low temperature peak can be ascribed to the reduction of $Co_3O_4$ to CoO [26]. There is an agreement that the high temperature peak corresponds

to the reduction of $Co^{3+}$ and $Co^{2+}$ species [23,26], but Ewbank et al. [18] suggested that $CoAl_2O_4$ reduced at this high temperature.

The Co 2p XP spectra of the 10% $Co/Al_2O_3$ sample shows the characteristic doublet (Co $2p_{3/2}$ at 781.4 eV) with shake up satellite peaks both in the as received and the oxidized state, corresponding to $Co^{2+}$. This value agreed well with the earlier findings [27] usually cited in the literature for cobalt-oxides.

After reduction a strong shoulder, more precisely a nearly distinct peak appeared at the low binding energy side of the Co $2p_{3/2}$ component at 778.0 eV, which can be attributed to the metallic cobalt state [28,29]. The intensity of this peak increased with increasing the reduction temperature, but de-convoluting the Co $2p_{3/2}$ envelope after the treatment of the sample at 1173 K, the peak and the satellite characteristic of $Co^{2+}$ are still unequivocally detectable. The ratio of $Co^0/(Co^0+Co^{2+})$ calculated from the XPS peak area shows that the ratio of metallic cobalt is hardly more than 50% even after the high temperature reduction (Table 1).

### 3.2. Reaction of methane with carbon dioxide

The reaction of $CO_2$ and $CH_4$ was studied under isotherm conditions at 773 K. The activities of the samples, the conversion of $CH_4$ and $CO_2$ increased in time in all cases during 2 h of the reaction (Fig. 1).

Only CO, $H_2$ and a small amount of water were detected. It should be mentioned that when the catalysts were used for longer time (at least 100 h) the activity of the catalysts slowly decreased. It was found that the $CO_2$ conversion was higher than that of methane in all cases and the $CO/H_2$ ratio was higher than 1 (Table 2). These observations indicated that the reaction
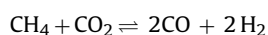
$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

**Table 2**
Some characteristic data for the $CH_4 + CO_2$ reaction at 773 K on 10%Co/Al$_2$O$_3$ reduced t different temperature.

| Reduction temperature | Formation rate (µmol/gs) | | | | Conversion (%) | | | | CO/H$_2$ | | Turnover frequency (1/s) | | | | Surface carbonaceous deposit µmol/g |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CO | | H$_2$ | | CO$_2$ | | CH$_4$ | | | | H$_2$ | | CO | | |
| | 5 min | 115 min | 5 min | 115 min | 5 min | 115 min | 5 min | 115 min | 5 min | 115 min | 5 min | 115 min | 5 min | 115 min | |
| 773 K | 9 | 12.7 | 2 | 3 | 4.3 | 6.1 | 2.2 | 3.1 | 4.4 | 4.2 | 0.005 | 0.01 | 0.025 | 0.036 | 884.8 |
| 973 K | 24.7 | 28.9 | 8.6 | 11.9 | 14.3 | 16.6 | 7 | 8.9 | 2.9 | 2.4 | 0.023 | 0.032 | 0.066 | 0.077 | 7984.7 |
| 1173 K | 17.1 | 22.2 | 5.2 | 8.7 | 9.8 | 12.5 | 4.7 | 6.7 | 3.3 | 2.5 | 0.022 | 0.037 | 0.072 | 0.093 | 6285.3 |

was followed by several secondary processes, including the hydrogenation of CO, $CO_2$ and the water gas shift reaction. It is known that in the equilibrium at 773 K the $CO_2$ conversion is higher than that of methane by about 25% and the CO/H$_2$ ratio is about 1.6 [9], but in our cases the difference in the conversions was near 100% and the CO/H$_2$ ratios were higher. Comparing the conversion of $CH_4$ and $CO_2$ obtained on different catalysts, we can conclude that the activity was the highest on the sample reduced at 973 K and the lowest on the catalyst hydrogenated at 773 K. The order of the hydrogen and CO formation rate was the same as was observed in the $CH_4$ and $CO_2$ (Table 2).

A different order resulted when we calculated the turnover frequencies for CO and H$_2$ formation. The highest value was found in both cases on the sample reduced at 1173 K (Fig. 2 and Table 2) after two hours of the reaction.

How could we explain the differences in the activity of the catalysts reduced at different temperatures? Earlier we assumed [5] in the case of supported Rh catalysts that the first step of the reaction is the methane decomposition to hydrogen and perhaps to CH$_x$ fragments. These species could promote the $CO_2$ dissociation and the adsorbed oxygen facilitated the dissociation of $CH_4$. Recently a theoretical calculation showed that $CO_2$ could be activated on the Co surface and $CO_2^-$ could be formed, but this interaction is structure sensitive [30]. Taking into account that with increasing the reduction temperature increased the area of a specially oriented surface of Co (fcc) particles, we could suppose that the varying structure of Co$^0$ resulted in the different activities of the samples.

The CO/H$_2$ ratio changed in a wide range. It was 4.2–4.4 on the sample reduced at 773 K and 2.4–2.5 on the other samples (Table 2). It means that one of the secondary reactions took place, which consumes H$_2$ and/or produces CO, such as reverse water gas shift reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O,$$
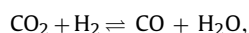
or the methanation of $CO_2$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$
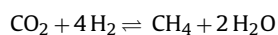
On the catalysts pre-treated at 973 and 1173 K the CO/H$_2$ ratio decreased in time. It is possible that the H$_2$ formation rate increased more rapidly than that of CO, but more probably, the rate of a secondary process changed and resulted in the decrease of the CO/H$_2$ ratio.

After 2 h of the reaction, the amount and the reactivity of surface carbon formed during the dry reforming of methane were determined by hydrogen TPR. The reactivity of the carbon deposit was nearly the same in all cases; the TPR peak maxima were about 820 K independently of the reduction temperature (Fig. 3). On the contrary, the amount of surface carbon determined with temperature-programmed hydrogenation was nearly 8 times less on the sample reduced at 773 K than on the other catalysts (Table 2). If we related the amount of surface carbon formed in the reaction to the converted $CH_4 + CO_2$ we found that less than 3.5% of the transformed gas accumulated on the surface in the worst case.

### 3.3. Hydrogenation of carbon dioxide

To understand the differences in the CO/H$_2$ ratio measured on the samples reduced at different temperatures, the hydrogenation of $CO_2$ was also studied on the samples reduced at 773 and 973 K. At low temperature, at 548 K, the conversion of $CO_2$ was below 3% and the $CH_4$ selectivity was about 90% in both cases. When the reaction was carried out at 773 K, the $CO_2$ conversion increased with increasing the reduction temperature (63 and 85%), but the selectivity of $CH_4$ formation was 99% in both cases. These findings do not support the idea that the differences in the CO/H$_2$ ratio are the results of secondary reactions. When the $CO_2 + H_2$ reaction was carried out on a catalyst which was used earlier in the $CH_4 + CO_2$ reaction, the amount of CO formed in the $CO_2 + H_2$ reaction was three times higher on the sample reduced at 773 K than in the other case. From these results we may assume that the surface of the catalysts changed during the $CO_2 + CH_4$ reaction and it resulted in the different CO selectivity in the reverse water gas shift reaction and so in the different CO/H$_2$ ratios in the dry reforming.

### 3.4. Characterization of the catalysts after the catalytic reaction

The infrared spectra were registered in the DRIFT cell during the catalytic reaction of $CH_4 + CO_2$ at 773 K on 10% Co/Al$_2$O$_3$ reduced at 773 K. They showed that beyond the carbonate bands at the beginning of the reaction a weak absorption was present at 1984 cm$^{-1}$ attributed to adsorbed CO. Features at 1592 and 1353 cm$^{-1}$ could be assigned to the asymmetric and symmetric stretching vibrations of O—C—O groups of formate species. The intensities of the formate bands slightly increased in the first 10 min of the reaction and then remained constant. Between these peaks, some not well-resolved absorbances could be attributed to different carbonates and C—H groups (Fig. 4). The CO band was observed only in the first minutes of the reaction.

Similar spectra were recorded when the catalysts were reduced at higher temperature, only the CO band shifted to higher wave number (2015 cm$^{-1}$). Khassin et al. [29] found also the same differences in the position of CO absorption bands on Co/Al$_2$O$_3$ reduced at 753 and 923 K; those features were attributed to tilted CO bonded to Co$^0$ [29]. It was supposed that the appearance of this type of adsorbed CO could be an indication of the secondary interaction of CO with a neighboring cobalt atom, which should cause the lateral tilt of the CO. The occurrence of this interaction results in the significant lengthening of C—O bond [31]. It means that in our cases the distance between the neighboring cobalt atoms is different when the catalysts were reduced at different temperatures. Another explanation for the appearance of the tilted CO is the electronic changes in the metal atoms on the surface [32,33].

Earlier we found that the formate species located on the alumina support [34]. Cobalt formate decomposes at 470–490 K producing Co$_3$O$_4$ [35,36] so in the present cases we could also accept that the formate groups are located on the support, but in spite of the lower decomposition temperature we cannot rule out that they bonded to cobalt oxides. The CO band was detectable only in the first minutes
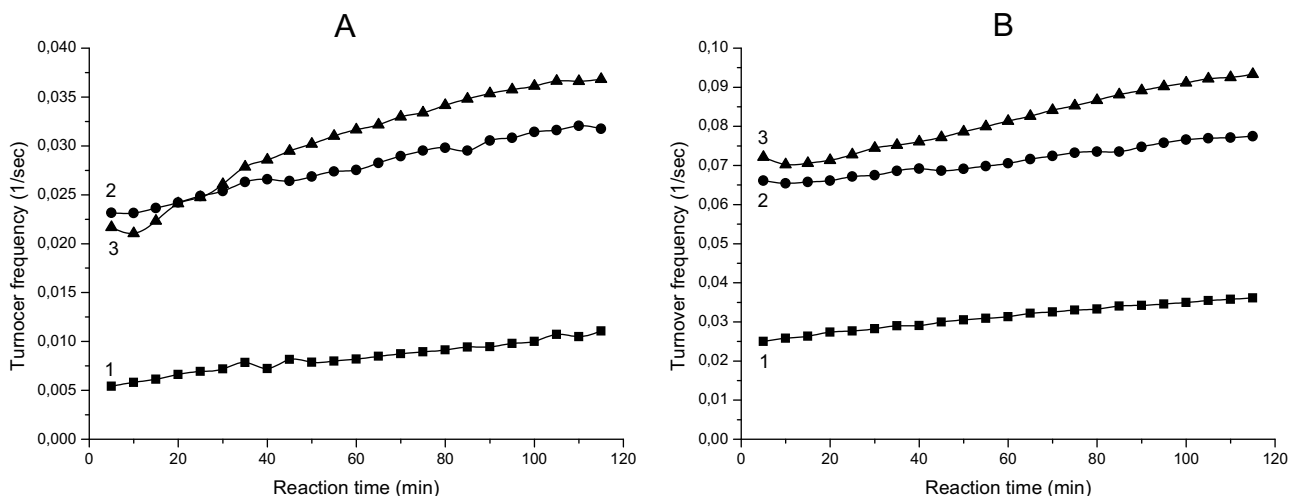
**Fig. 2.** Turnover rate of $H_2$ (A) and CO (B) formation in the $CH_4 + CO_2$ reaction at 773 K on $Co/Al_2O_3$ reduced at 773 (1), 973 K (2) and 1173 K (3).
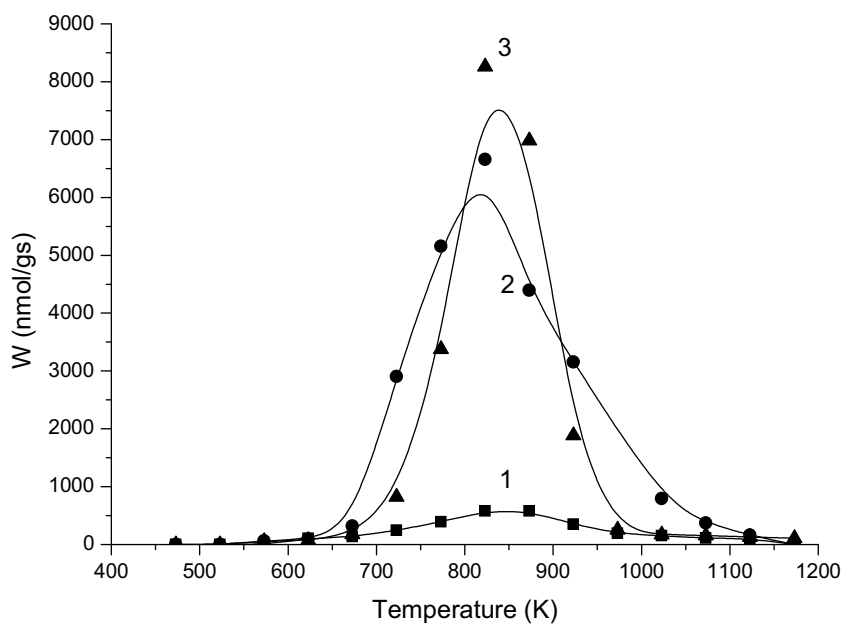


**Fig. 3.** Temperature programmed hydrogenation of surface carbonaceous deposit formed in the $CH_4 + CO_2$ reaction on 10% $Co/Al_2O_3$ catalysts reduced at 773 K (1), 973 K (2) and 1173 K (3).

of the reaction and the intensity of it was very weak. Bands in the C—H region (2800–2900 cm$^{-1}$) were also observed, but these features are not characteristic, while the spectra were registered in the presence of methane in $CH_4 + CO_2$ flow. When the DRIFT cell was flushed with He after the catalytic reaction all bands disappeared immediately from the spectra. It is surprising to detect adsorbed CO and formate groups well above their desorption temperature. It means that the formation rate of these species is higher than their desorption, decomposition or further reaction rates.

The Co 2p XP spectra of 10% $Co/Al_2O_3$ reduced at different temperatures are shown before and after the reaction in Fig. 5. The samples were treated in the catalysis chamber (HPC) of the instrument under the same experimental conditions as in the catalytic tests. The experiment was interrupted after the 10th, 30th, and 120th minutes of the reaction and XP spectra were taken.

The Co 2p spectra of the 10% $Co/Al_2O_3$ sample shows the characteristic doublet (Co $2p_{3/2}$ at 781.4 eV) with satellite peaks in the oxidized state as was mentioned above, corresponding to $Co^{2+}$. These results agreed well with the earlier findings [27].

After reduction and during the reaction a strong shoulder, a nearly distinct peak appeared at the low binding energy side of the Co $2p_{3/2}$ component at 778.0 eV. Its Co $2p_{1/2}$ counterpart could also be detected on the spectra. Therefore, this feature can be attributed to the metallic cobalt state. The binding energy of this feature is in agreement with the literature data [28,29]. The intensity of this peak increased with increasing the reduction temperature, but the surface Co concentration significantly decreased during the reduction (Fig. 5). Deconvoluting the Co $2p_{3/2}$ envelope obtained after the reduction the peak and the satellite characteristic for $Co^{2+}$ is unequivocally detectable even when the catalyst was reduced at 1173 K (Fig. 5). Table 1 shows that the ratio of metallic cobalt on the surface to the whole cobalt content determined by XPS was hardly more than 50%, and these values decreased further during the reaction; it seems that the catalysts slightly oxidized during the reaction. There are some observations that the supported Co catalysts are not oxidized [37] but reduced [38] under the catalytic test, probably due to the reducing nature of the evolved products ($H_2$ and CO). It has to be noted that in both cases the reaction
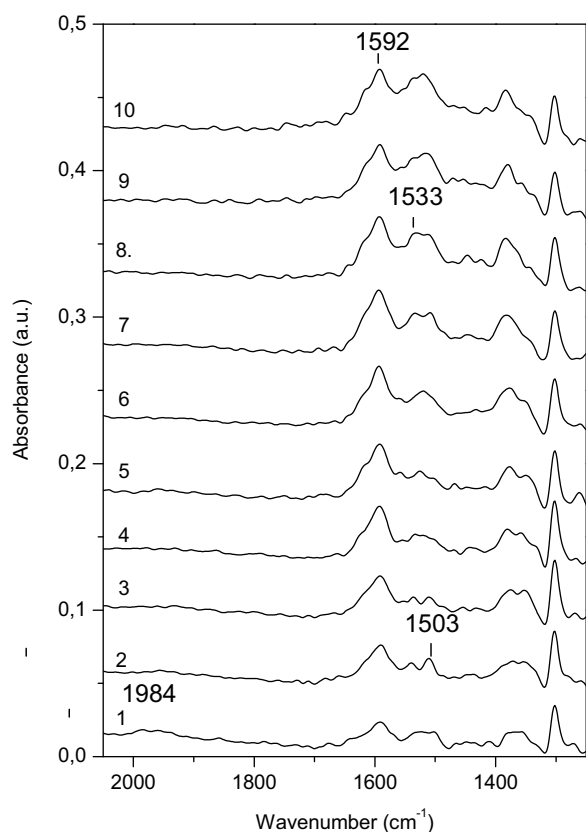
**Fig. 4.** Infrared spectra recorded on 10% $Co/Al_2O_3$ reduced at 773 K in the first (1), 2nd (2), 3rd (3), 5th (4), 10th (5), 15th (6), 30th (7), 60th (8), 90th (9) 120th (10) minutes of the $CO_2 + CH_4$ reaction at 773 K.

temperature was higher (1073 K) than the reduction temperature. In our cases the catalytic tests were carried out only at 773 K, but probably there is a sensitive equilibrium between the reductive and oxidative processes. Our results demonstrated that at 773 K the rate of the oxidative reactions such as the $CO_2$ [39] dissociation or the

formate decomposition [35,36] on Co surface is higher than that of reduction.

It has to be noted that the activity of the catalysts increased in time whilst the ratio of metallic cobalt decreased, although the activity of the unreduced sample was relatively low in the reaction. In spite of this the oxidation of metal has been reported as a deactivation mechanism of cobalt-based catalysts [12,21].

The C 1s peak on the XP spectra was located in the reduced samples at 285.0 eV in all cases, originated from adventitious carbon. The intensity of this peak decreased as the reduction temperature increased (Fig. 6).

There were no changes in the peak position in this region when the sample reduced at 773 K was used in the catalytic reaction but the intensity of it increased significantly especially in the second hour of the reaction (Fig. 6A).

Very different C 1s spectra were detected when the catalysts were reduced at 973 or 1173 K. Already after 10 min of the reaction new peaks were detected at 282.8 eV and later another one was observed at 281.5 eV (Fig. 6B) on the sample reduced at 973 K; this signal became more and more dominant. Similar spectra were detected on the sample reduced at 1173 K.

Ewbank et al. [18] also found a C 1s XPS peak at 281.7 eV after the dry reforming of methane on $Co/Al_2O_3$, which was attributed to the presence of carbidic carbon. In another work, the binding energy of C 1s in $CoC_2$ is reported at 283.2 eV [40,41]. Bulk cobalt carbide decomposed to form graphitic carbon above 700 K [41]. Feng et al. [42] also detected an unusually low binding energy for C 1s, at 281.4 eV, in the conversion of ethanol to acetonitrile on alumina supported Ni or Co catalysts. They supposed that the carbon had combined with Co or Ni in the catalytic runs. Taking into account these observations, the low binding energy C 1s species could be assigned as $CoC_x$ carbide like form, rather than as a structured carbon layer. The differences in the structure of the carbon formed during the reaction on the catalysts reduced at different temperatures could be also explained by the different surface structures of metallic Co produced in the reduction at 773 K and at 973 K or higher temperatures.

Comparing the amount of surface carbon, determined by TPR (Fig. 3 and Table 2), and the C 1s peak intensities on the XPS curves obtained on the samples reduced at different temperatures,
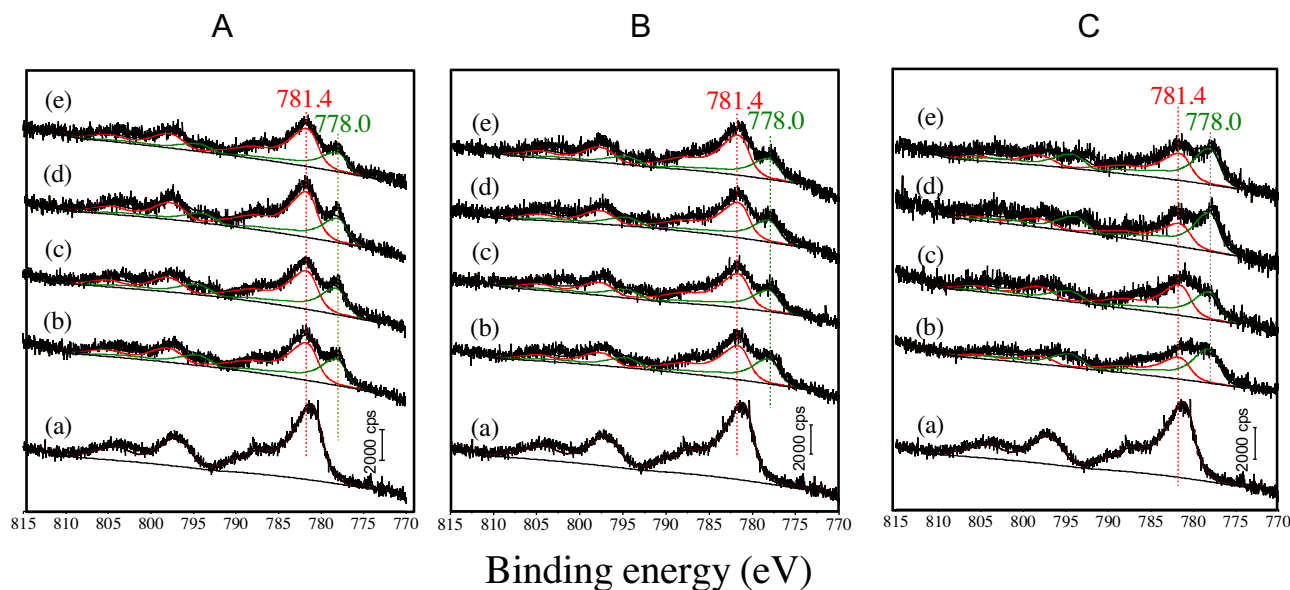


**Fig. 5.** XP spectra of Co 2p recorded after the $CO_2 + CH_4$ reaction at 773 K on $Co/Al_2O_3$ reduced at 773 K (A), 973 K (B), 1173 K (C); oxidized (a), reduced sample (b), after 5th (c), 30th (d) and 120th (e) minutes of the reaction.
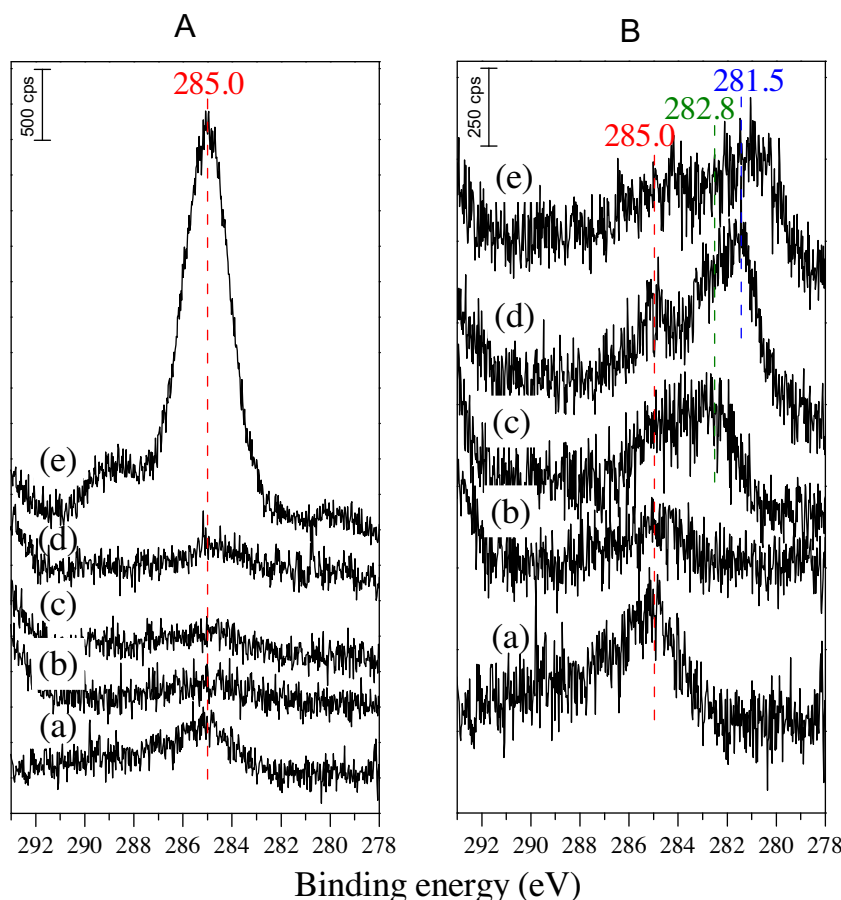
**Fig. 6.** XP spectra of C 1s recorded after the $CO_2 + CH_4$ reaction at 773 K on $Co/Al_2O_3$ reduced at 773 K (A), 973 K (B), oxidized (a), reduced sample (b), after 5th (c), 30th (d) and 120th (e) minutes of the reaction.

it seems that there is a contradiction. On the sample reduced at 773 K, a relatively intensive peak was detected after the reaction on the XPS spectra at 285 eV. It is assigned to surface carbon from C—C or C=C groups, but only a small amount of carbon was detected by TPR. On the samples reduced at higher temperatures, the amount of surface carbon determined by TPR was more than one order of magnitude higher (Fig. 3, Table 2) but the XPS peak intensities, although at lower energies, were much less. These features were assigned to carbide like structures. How could this discrepancy be explained?

We have to suppose that the carbon on the sample reduced at 773 K is directly on the surface and so the XPS signal is not shielded by the cobalt or by the support. On the other samples, the main part of carbon diffuses during the reaction into the bulk and so not detectable by XPS, but segregates to the surface above 770 K during the TPR and reacts with hydrogen.

We may assume that the ratio of the metallic to oxidized Co evolved in the pretreatment resulted in the different catalytic behaviors.

## 4. Conclusion

XRD results revealed that cobalt spinel structures formed in the thermal treatment of $Co/Al_2O_3$. TPR and XPS results revealed that during the pre-treatment of the catalysts the Co only partially reduced. The reduction degree and the amount of the structured metallic cobalt increased with the reduction temperature, but the ratio of metallic cobalt on the surface to the whole cobalt content determined by XPS was hardly more than 50% even after the reduction at 1173 K.

The conversion of the reactant was the highest on the sample reduced at 973 K, but the turnover frequencies of CO and $H_2$ formation increased as the reduction temperature increased.

The amount of surface carbon significantly depended on the pre-treatment temperature of the catalysts. By means of in situ DRIFT spectroscopy in some cases adsorbed CO and formate species were detected during the catalytic run far above their desorption temperature; the formation rate of them is higher than the desorption, decomposition or further reaction rates. From the spectra, we may suppose that a tilted CO was formed, but the position of the absorption bands depends on the reduction temperature of the catalysts.

Similarly, the pre-treatment temperature influenced the type of the surface carbon determined by XPS. On the catalysts reduced at low temperature, the amount of the adventitious carbon increased, but on the other samples, the carbidic type carbon was detected. We may suppose that the different structures of the catalysts formed at different reduction temperatures resulted in the different catalytic behavior.

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