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CO_2 reforming of CH_4 on doped Rh/Al_2O_3 catalysts

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ABSTRACT

The reforming of methane with carbon dioxide has been investigated at 773 K on Rh/Al_2O_3 promoted with TiO_2 and V_2O_5. In addition, the dissociation of carbon dioxide and methane has also been examined. TPR and XPS results revealed that during the pre-treatment of the catalysts not only Rh reduced but also TiO_2 slightly and V_2O_5 significantly to V^{4+} below 600 K. The dissociation of carbon dioxide occurred most easily on vanadia promoted catalyst. Vanadia and titania promoted Rh/Al_2O_3 was found to be more active in the $CO_2 + CH_4$ reaction than the Rh/Al_2O_3. The increase of the conversion observed on V_2O_5 and TiO_2 promoted Rh/Al_2O_3 catalysts could be attributed to the oxygen vacancies which formed on the additives during the pretreatment and the reaction.

1. Introduction

The importance of the catalytic transformation of methane and carbon dioxide is unquestionable both from industrial and environmental point of view and there has been great efforts to convert them into synthesis gas. All of the Group VIII metals on a variety of supports have been studied as dry reforming catalysts [1]. The high efficiency of supported noble metals in this reaction was confirmed by our previous studies [2–5]. The specific activity of the catalyst in the $CH_4 + CO_2$ reaction decreased in the order: Ru, Pd, Rh, Pt, Ir which correspond to their activity order towards the dissociation of CO_2 [2]. There was a debate about the relative reactivities of different metals, though Rh is generally considered to be one of the most effective catalysts for this process.

A significant effect of the support on the catalytic activity was observed, the order being $Rh/A1_2O_3 > Rh/TiO_2 > Rh/SiO_2$ [6]. Contrary to this observation Bitter et al. reported that the activity of Rh catalysts in CO_2/CH_4 reforming is mainly determined by the availability of Rh sites irrespective of the support [7]. The catalytic activity of Rh/SiO_2 was promoted by physically mixing Rh/SiO_2 with metal oxides such as $A1_2O_3$, TiO_2, and MgO [6]. The role of the metal oxides used as support and that of their physical mixtures may be the promotion of the dissociation of CO_2 on the surface of Rh, since the $CH_4 + CO_2$ reaction is first order in the pressure of CO_2, suggesting that CO_2 dissociation is the rate-determining step.

Rostrup-Nielsen and Bak Hansen [8] reported that H_2O reforming rates are much faster than CO_2 reforming rates and that the latter depended on the rate-determining CO_2 activation steps on Rh/Al_2O_3. Studies of the activation of stoichiometric CO_2 and CH_4 mixture on Rh/Al_2O_3 led to the conclusion that both CH_4 and CO_2 limit the overall rates, and first-order rate dependencies on CO_2 and CH_4 were proposed [9]. Bhat and Sachtler [10] reported that the CO_2 reforming of CH_4 is a first-order process in CH_4 and zero-order in CO_2 on Rh/NaY catalyst, indicating that C–H bond activation is the kinetically relevant step in CH_4 reforming reactions and hydrogen desorption to form H_2 and that CO_2 reactions with CH_4-derived chemisorbed species to form CO are fast.

The above mentioned papers clearly show that in spite of the lot of articles published on the $CO_2 + CH_4$ reaction on different supported Rh catalysts, there is not a clear and unambiguous explanation of the true nature of the reaction.

The promotion of Rh/SiO_2 with vanadium oxide in the dry reforming of methane markedly enhanced both the activity and turnover frequency by 15–20 fold [11]. This is attributed to the formation of a partial VO_x overlayer on the Rh surface which breaks up the large ensembles of Rh atoms required for CH_4 dissociation.

Vanadia-promoted Rh catalysts have been reported to have a high activity and selectivity in the syngas conversion for the production of C_2 oxygenates such as ethanol and acetic acid [12,13]. The role of the vanadium oxide promoter is the enhancement of the CO dissociation and/or the insertion of CO into metal–carbon bond.

The present report gives an account of the effect of V_2O_5 and TiO_2 additives on the catalytic efficiency of Rh/Al_2O_3 in the $CO_2 + CH_4$ reaction.

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Table 1
Some characteristic data of the $CO_2 + CH_4$ reaction at 773 K.

	BET surface (m^2/g)	Dispersion (%)	Conversion		Formation rate				CO/H_2 ratio
			CO_2 (%)	CH_4 (%)	H_2 (μmol/g)	CO (μmol/g)	H_2 ($\times 10^{-3}\ s^{-1}$)	CO ($\times 10^{-3}\ s^{-1}$)	
Rh/Al_2O_3	132	65	13.5	7.7	5.9	13.9	93.4	220	2.35
$Rh/5\%V_2O_5–Al_2O_3$	158	60.7	18.4	10.3	7.2	18.0	130	324	2.5
$Rh/10\%V_2O_5–Al_2O_3$	180	57	18.5	10.3	7.9	18.2	142	330	2.07
$Rh/5\%TiO_2–Al_2O_3$	175	74	19.6	13.7	10.6	22.1	148	307	2.32
$Rh/10\%TiO_2–Al_2O_3$	176	78	19.4	11.2	8.0	18.6	105	245	2.32

The space velocity was $2 \times 10^4\ h^{-1}$.

2. Experimental

2.1. Catalysts preparation

The catalysts were prepared by impregnation of the pelletized Al_2O_3 (Akzo CK300) first with NH_4VO_4 or Ti-i-propilate solution. The clean and the impregnated alumina were calcined at 773 K. The V_2O_5 and TiO_2 content of the alumina was 5 or 10 wt%. Afterwards the supports were impregnated with the solution of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey 99.99% metal based) to yield a nominal 1% metal content. Before the measurements the catalysts were oxidized at 673 K in O_2 flow for 30 min and reduced at 773 K in flowing H_2 for 60 min in situ.

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 50–320 ml/min. Analyses of the gases were performed with gas chromatograph (Agilent 7890A) using HP-PLOT Q column. The gases were detected simultaneously by TC and FI detectors.

Infrared spectra during the catalytic reaction were recorded with a Bio-Rad FTIR spectrometer equipped with diffuse reflectance attachment (Spectra-Tech) with BaF_2 windows with a wave number accuracy of $\pm 4\ cm^{-1}$. Typically 32 scans were registered. The whole optical path was purged with CO_2- and H_2O-free air generated by a Balston purge gas generator. The catalysts were pre-treated as mentioned above, then the $CH_4 + CO_2$ gas mixture was introduced into the cell at the reaction temperature or at room temperature and then the catalyst was heated linearly with a heating rate of 10 K/min up to 873 K and the IR spectra were recorded. All spectra were rated to the spectra of the catalysts pre-treated before the measurements.

2.3. Characterization of the catalysts

The dispersion of Rh on these catalysts was determined at room temperature after pretreatment by the adsorption of H_2 using a conventional volumetric apparatus. The BET surface of the catalysts was measured by Micromeritics Gemini 2375 apparatus using N_2 adsorption at the temperature of liquid nitrogen. Some characteristic data of the samples are summarized in Table 1.

The temperature programmed reduction (TPR) of the catalysts was carried out in BEL-CAT catalyst analyzer using a TC detector. The samples were oxidized at 673 K for 30 min and flushed with Ar for 15 min, cooled down to 323 K then Ar flow was changed to 10% H_2 containing Ar and the sample was heated up to 1200 K with 10 K/min heating rate.

The amount and the reactivity of surface carbon formed in the catalytic reactions were determined by hydrogen TPR. After the catalytic run (2 h) the reactor was flushed with Ar the sample was cooled down to 323 K then the Ar flow was changed to H_2 and the sample was heated up to 1000 K and the hydrocarbons were determined by gas chromatograph.

For XPS studies the powder samples were pressed into tablets with cca. 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 main chamber and isolated from that with a gate valve. With the help of the sample manipulator and a second insertion mechanism 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. After the pre-treatment the samples were cooled to room temperature in flowing nitrogen. Afterwards the flow was stopped, the high pressure cell was evacuated and the sample was taken back to the analysis chamber and the XP spectra were recorded. After it the sample was moved back into the catalytic chamber and it was treated with the reacting gas mixture at the reaction temperature with the same experimental conditions as the catalytic reaction.

XP spectra were taken with a SPECS instrument equipped with a PHOIBOS 150 MCD 9 hemispherical electron energy analyser operated in the FAT mode. The excitation source was the K_α radiation of an aluminium anode ($h\nu = 1486.6$ eV). The X-ray gun was operated at 180 W power (12 kV, 15 mA). The pass energy was set to 20 eV, the step size was 25 meV. Typically five scans were added to get a single spectrum. The binding energy of the Al $2p_{3/2}$ was used as energy reference: it was taken 74.4 eV. For data acquisition and evaluation both manufacturers' (SpecsLab2) and commercial (CasaXPS) software were used.

3. Results and discussion

3.1. Characterisation of the catalysts

The dispersion of the samples, determined by hydrogen adsorption, was between 58 and 78%. It seems that there is no correlation between the dispersion of Rh and the support. It was the highest in the case of $Rh/10\%TiO_2–Al_2O_3$ (78%) and the lowest on Rh/10% $V_2O_5–Al_2O_3$ (57%) (Table 1).

The BET surface of the pre-treated samples was higher than 130 m^2/g in all cases; the promoted catalysts have a higher surface area than the unpromoted Rh/Al_2O_3 (Table 1).

The TPR profiles of the catalysts are displayed in Fig. 1. From the figure it is clear that all samples used as catalysts can be reduced in the same temperature range 350–600 K. The reduction of the samples started at about 350 K and in the case of Rh/Al_2O_3 a small but broad peak was detected. In the case of promoted samples the peak intensities increased; on the $Rh/10\%TiO_2–Al_2O_3$ and on $Rh/5\%V_2O_5–Al_2O_3$ the peaks have a shoulder at higher and at lower temperature, respectively.

The TPR peak area i.e. the hydrogen consumption was the smallest in the case of Rh/Al_2O_3 and it increased as the promoter concentration increased. It is ambiguous whether in the case of the vanadia containing samples the peak areas were higher than

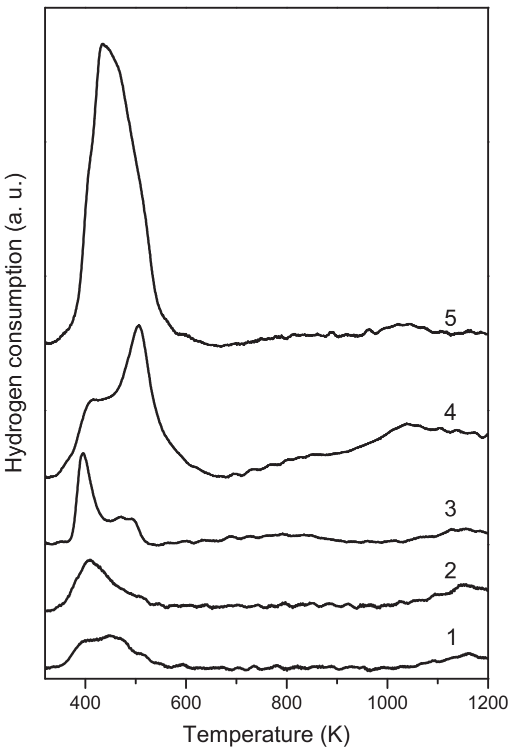

Fig. 1. Temperature programmed reduction of Rh/Al_2O_3 (1), $Rh/5\%TiO_2–Al_2O_3$ (2), $Rh/10\%TiO_2–Al_2O_3$ (3), $Rh/5\%V_2O_5–Al_2O_3$ (4), $Rh/10\%V_2O_5–Al_2O_3$ (5) catalysts.

on the $TiO_2–Al_2O_3$ supported samples. While in the case of 1% $Rh/5\%TiO_2–Al_2O_3$ the amount of reacted hydrogen was about 30% higher than on Rh/Al_2O_3, on $Rh/10\%V_2O_5–Al_2O_3$ one order of magnitude more hydrogen consumed. The hydrogen consumption was calculated from the TPR peak area.

The experimental hydrogen uptake was higher in the case of promoted samples than the theoretical one assuming the reduction of Rh^{3+} to Rh°. These results clearly show that in the case of promoted samples not only Rh but the oxide was also reduced. The average oxidation state of Ti in the TiO_2 was +3.9 and that of V was about +4 instead of +5 in both cases. These results agree well with our XPS measurements (see later).

The enhanced reducibility of the promoted catalysts, especially of vanadia containing samples is surprising at first. When the temperature programmed reduction of V_2O_5 was earlier investigated the reduction of vanadium pentoxide started at about at 830 K and peaked at 955 K. These values were lower, 690 and 940 K, respectively, when the V_2O_5 was supported on Al_2O_3 [14]. In the case of 1% $Rh/10\%V_2O_5–Al_2O_3$ the onset temperature of the reduction was about 340 K and the peak maximum was at 424 K. Kip et al. found the same results [15] on rhodium alumina promoted by vanadium oxide, they also observed that the reduction of V_2O_5 occurred in the same temperature range in the presence of Rh as mentioned before. These results suppose that Rh catalyses the reduction of the oxide, probably hydrogen spill over can explain the co-reduction of Rh and V_2O_5.

3.2. Interaction of methane and carbon dioxide with the catalysts

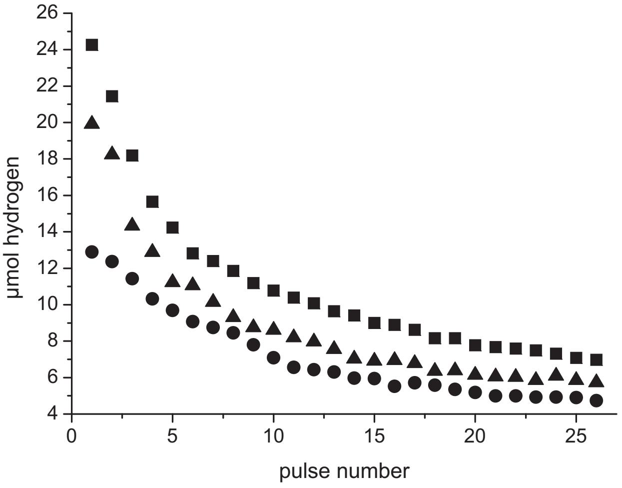

Fig. 2. The amount of hydrogen formed in the decomposition of methane on Rh/Al_2O_3 (■), $Rh/5\%TiO_2–Al_2O_3$ (▲), $Rh/5\%V_2O_5–Al_2O_3$ (●) at 773 K. One pulse contains 14 μmol CH_4, and 0.2 g catalyst was used.

The interaction of methane with the different catalysts was studied by pulse method at 773 K at the reaction temperature of carbon dioxide and methane. The amount of hydrogen formed in the decomposition of methane decreased in all cases as a function of pulse number. There were no significant differences in the efficiency of the different catalysts with the exception of the first pulse (Fig. 2). The highest amount of hydrogen was produced on Rh/Al_2O_3. The methane conversion in the first pulse was about 85% on this catalyst, but only 46% on $Rh/5\%V_2O_5–Al_2O_3$. The amount of surface carbon, calculated from the hydrogen evolution, formed in this process on Rh/Al_2O_3 already in the first pulse and on $Rh/5\%V_2O_5–Al_2O_3$ in the first two pulses was nearly the same as the number of surface metal atoms. This suggests an accumulation of carbonaceous residue on the catalysts during methane decomposition and results in a significant decay in the reaction, which, however did not cease. This may mean that the carbon species formed a cluster on the rhodium or migrate onto the support. Similar results were obtained earlier, supported Rh was found to be active in the decomposition of CH_4 to give hydrogen, traces of ethane and carbonaceous residues [3]. Significant effect of the support was detected; Rh/Al_2O_3 exhibited the best performance but in our cases there were no significant differences in the efficiencies of the catalysts with the exception of the first pulse.

The dissociation of carbon dioxide was monitored by DRIFT spectroscopy. This is one of the most sensitive methods for following the interaction of CO_2 and the supported Rh catalyst, as CO, the primary product of this process is strongly bonded to the metal.

The adsorption of CO_2 on a clean Rh surface is a well-studied process; it is weak and non-dissociative. Under ultrahigh vacuum (UHV) conditions CO_2, adsorbed at 100 K, completely desorbs below 300 K without dissociation. The results obtained in this field are summarized in two excellent reviews [16,17]. On supported Rh the situation is basically different. In this case the dissociation of CO_2 occurs, but it also depends on the nature of the support. The most effective support was TiO_2, but even on these samples the CO_2 dissociation was detected only above 373 K [18,19]. It was found that the dissociation of CO_2 on Rh/TiO_2 depends on the reduction temperature the higher the reduction temperature the greater the CO evolution [20,21]. These observations were explained by the speculation that oxygen vacancies produced by the reduction of the catalysts promote the dissociation of CO_2.

Heating up the pretreated catalyst in CO_2 flow only a very weak CO band was detected on $Rh/V_2O_3–Al_2O_3$, but in other cases absorption band in the CO region was not observed.

Fig. 3 shows the DRIFT spectra of different Rh samples in a CO_2 flow but under isotherm conditions. On $Rh/V_2O_5–Al_2O_3$ the CO band indicating the dissociation of CO_2 was observed already after 20 min of CO_2 treatment at 373 K. Absorptions were detected at 2132, 2090, 2063 and 2027 cm^{-1}. Further increase of the

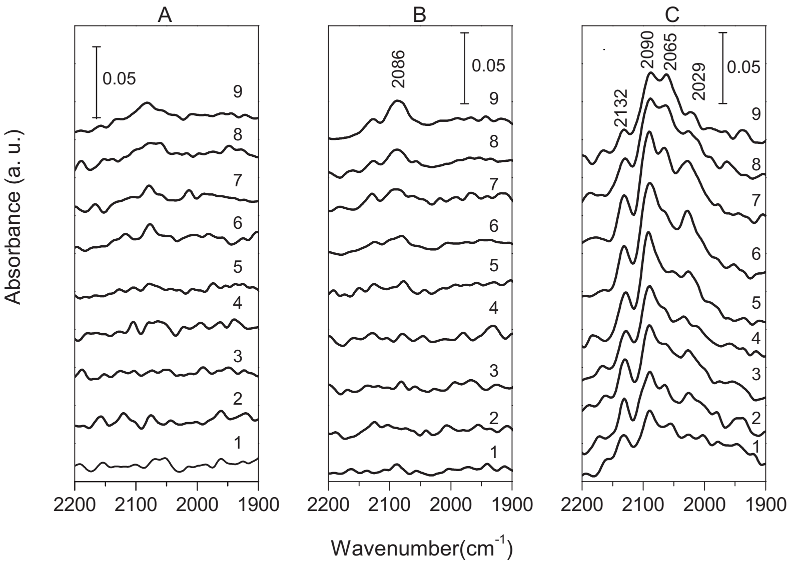

Fig. 3. DRIFT spectra recorded on Rh/Al_2O_3 (A), $Rh/10\%TiO_2–Al_2O_3$ (B), $Rh/10\%V_2O_5–Al_2O_3$ (C) in CO_2 flow at 373 for 20 min (1), at 398 K for 10 (2), 30 min (3) at 423 K for 1 (4), 5 (5), 10 min (6), at 448 K for 1 (7), 5 (8), 30 min (9).

temperature of the catalysts causes an increase of the CO band intensities up to 348 K. On $Rh/TiO_2–Al_2O_3$ only weak bands were registered and on Rh/Al_2O_3 only traces of adsorbed CO were observed under the same experimental conditions as mentioned above. CO adsorbed on Rh-based catalysts has been investigated extensively and different CO species have been identified. The band at 2063 cm^{-1} can be assigned as the linearly bonded CO (Rh–CO), the absorption at 2090 and 2027 cm^{-1} could be identified as the ν_{as} and ν_{sym} vibration of the gem-dicarbonyl $Rh^+(CO)_2$ [22]. The band above 2100 cm^{-1} could be assigned to CO adsorbed on oxidized rhodium [23,24]. According to our XPS data (see later) after reduction of the catalysts the Rh is in 0 valence state in all cases. So the formation of the oxidized form could be imagined as the Rh oxidized during this process.

The interaction of $CO_2 + CH_4$ mixture with the catalysts was also studied by IR spectroscopy. After introducing the reacting gas mixture at room temperature onto Rh/Al_2O_3 catalyst bands at 1650, 1443, 1348 and 1302 cm^{-1} appeared on the spectra, which were attributed to hydrogen carbonate and to other carbonates [25]. With increasing temperature the intensities of these bands decreased and above 623 K disappeared from the spectra. At 548 K a new single peak was detected at about 2050 cm^{-1} characteristic of adsorbed CO. The intensity of this peak increased as a function of temperature and shifted to lower wave number. At 623 K the maximum of this band was found at 2022 cm^{-1} but at higher temperature the position and the intensity of this peak did not change significantly up to 873 K.

The spectral feature of adsorbed CO produced in this reaction differed basically from that observed during the adsorption of gaseous CO on Rh/Al_2O_3: the doublet due to $Rh(CO)_2$ was missing, and the band due to linearly bonded CO appeared above 573 K at lower frequencies. Nearly the same spectra were earlier detected in the $CO_2 + CH_4$ interaction [3] and it was supposed that Rh carbonyl hydride was formed and resulted in the CO band appearing at low frequencies [25,26]. Fig. 4 clearly shows that in the CO region only one peak was developed indicating carbonyl hydride formation.

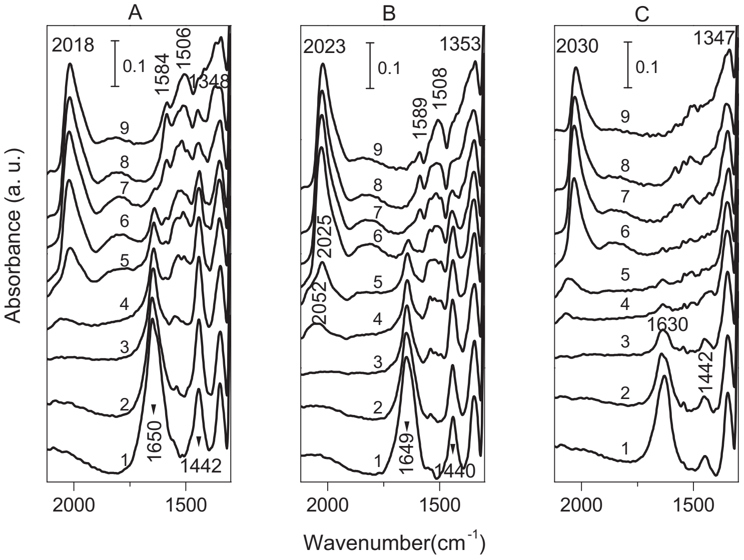

Fig. 4. Infrared spectra recorded on Rh/Al_2O_3 (A), on $Rh/TiO_2–Al_2O_3$ (B) and on $Rh/V_2O_5–Al_2O_3$ (C) heated in the $CH_4 + CO_2$ gas mixture at 300 (1), 373 (2), 473 (3), 573 (4), 598 (5), 623 (6), 673 (7), 773 (8), 873 K (9).

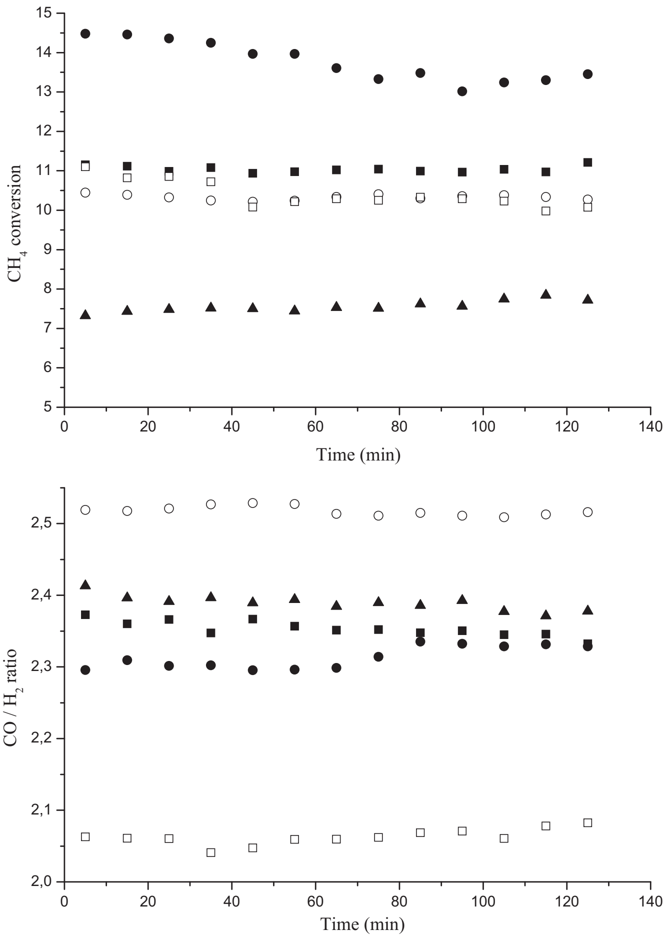

Fig. 5. Conversion of CH_4 (A) and CO/H_2 ratio (B) in the $CH_4 + CO_2$ reaction on Rh/Al_2O_3 (▲), $Rh/5\%TiO_2–Al_2O_3$ (●), $Rh/10\%TiO_2–Al_2O_3$ (■), $Rh/5\%V_2O_5–Al_2O_3$ (○) $Rh/10\%V_2O_5–Al_2O_3$ (□) catalysts at 773 K.

Above 673 K a small band was detected at about 1589 cm^{-1} characteristic of the ν_{as} frequency of the O–C–O vibration of formate ion adsorbed on alumina. The ν_{sym} and the C–H vibrations of this group could not be separated from the different carbonate bands below 1400 cm^{-1}.

Similar spectra were recorded on $Rh/V_2O_5–Al_2O_3$ as on Rh/Al_2O_3 but in this case the bicarbonate bands disappeared (598 K) and the CO band appeared (573 K) at lower temperature. In this case the formate bands were not detectable (Fig. 4).

On $Rh/TiO_2–Al_2O_3$ nearly the same spectra were recorded as on Rh/Al_2O_3 only the adsorbed CO was formed at lower temperature (Fig. 4).

3.3. 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 were stable, only negligible deactivation of the catalysts occurred during 2 h of the reaction (Fig. 5). Only CO, H_2 and a small amount of water were detected. The addition of V_2O_5 or TiO_2 to the Al_2O_3 support increased both the CO_2 and the CH_4 conversion at 773 K by about 34–36 and 44–45%, respectively (Table 1). The CO/H_2 ratios were between 2.05 and 2.55 at 773 K (Fig. 5). 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. These observations indicated that the reaction

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

was followed by several secondary processes, including the hydrogenation of CO, CO_2 and the water gas shift reaction. The differences in the CO/H_2 ratio observed on 5 and 10% V_2O_5 containing samples could be also explained by secondary reaction; earlier it was found that the vanadia promoted the CO hydrogenation on Rh catalysts [12,13].

Comparing the hydrogen and the CO formation rate related to the number of surface metal atoms we can conclude that the activity of $Rh/V_2O_5–Al_2O_3$ is higher than that obtained on $Rh/TiO_2–Al_2O_3$ (Table 1) The turnover rate of the CO formation decreased in the following order: $Rh/V_2O_5–Al_2O_3 > Rh/TiO_2–Al_2O_3 > Rh/Al_2O_3$.

After the 2 h reaction we found relatively small amount of carbon on all samples. The carbon was determined by hydrogen TPR. It was found that the reactivity of this surface residue was the same in all cases; the carbon reacted with hydrogen only above 850 K. On $Rh/V_2O_5–Al_2O_3$ more CH_4 was detected than in the other cases. CO formation was also observed from the promoted samples above 850 K probably the surface carbon reacted with the V_2O_5 or TiO_2.

The infrared spectra registered in the DRIFT cell during the catalytic reaction of $CH_4 + CO_2$ at 773 K showed that on Rh/Al_2O_3 from the beginning of the reaction absorption bands were present at 2025 and1842 cm^{-1} attributed to adsorbed CO, and at 1587 and 1353 cm^{-1} which could be assigned to the asymmetric and symmetric stretching vibrations of O–C–O groups of formate species. Between these peaks there are some not well resolved absorbances that could be attributed to different carbonates and C–H groups (Fig. 6). The amount of formate species increased during the reaction on the unpromoted Rh/Al_2O_3. Earlier it was stated that the formate species were located on the alumina [25] while these species are stable on Rh only up to 200 K. On the other samples the intensity of it achieved a steady state value. The intensities and the position of CO band did not change significantly during the reaction. The appearance of a single peak at so low wave number, at 2025 cm^{-1}, could be attributed to the carbonyl hydride formation. 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 rate.

Similar spectra were recorded on $Rh/10\%TiO_2–Al_2O_3$ and on $Rh/10\%V_2O_5–Al_2O_3$ only the intensity of the formate bands were weaker, and the CO band appeared at somewhat higher wave numbers (Fig. 6).

XP spectra of supported Rh samples before and during the reaction are shown in Figs. 7 and 8. The binding energy of the Rh $3d_{5/2}$ electrons in the calcined sample was 309.2–309.8 eV which is nearly the same as observed for Rh^{3+} ions. After reduction at 673 K the peak shifted in all cases to lower binding energies; the Rh $3d_{5/2}$ orbital was centered at 307.4 eV for Rh/Al_2O_3, 307.1 eV for $Rh/TiO_2–Al_2O_3$ and 307.3 eV for $Rh/V_2O_5–Al_2O_3$ and neither the intensities nor the positions change during the reaction (Fig. 7). These peak positions lay some tenth eV higher than that for metallic bulk rhodium. Similar feature was observed after reduction of different supported Rh [27] or when Rh supported on TiO_2 was reduced at different temperatures [20]. According to the considerations of Mason [28] the higher binding energy reflects the fact that the particle sizes are small. In the dispersed system there are less neighboring atoms than in the bulk and therefore there are less screening electrons.

So we can state that the Rh is reduced to 0 valence state during the pretreatment in all cases and the oxidation state of it did not change during the reaction (Fig. 7).

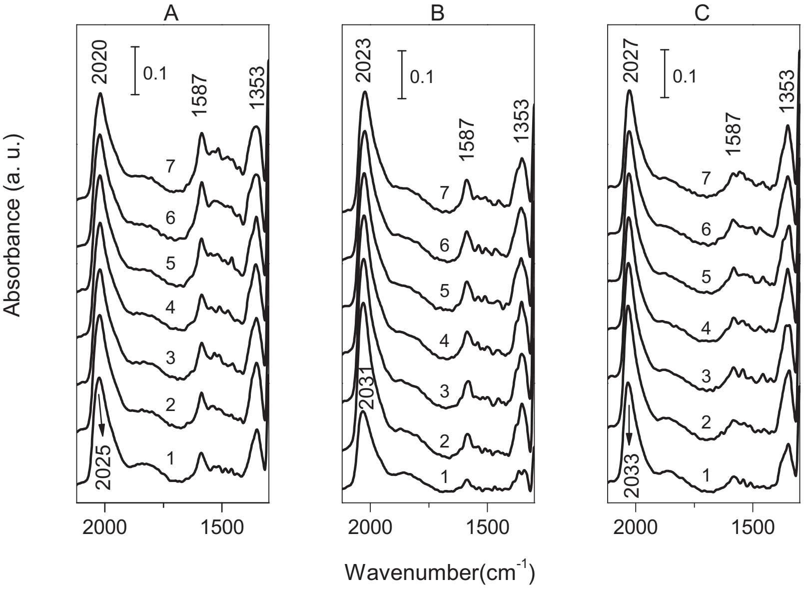

Fig. 6. Infrared spectra recorded during the $CO_2 + CH_4$ reaction at 773 K on Rh/Al_2O_3 (A), on $Rh/TiO_2–Al_2O_3$ (B) and on $Rh/V_2O_5–Al_2O_3$ (C) in the 30th second (1), first (2), 5th (3), 15th (4), 30th (5), 60th (6), 120th (7) minute of the reaction.

The binding energy of Ti 2p electrons in the $Rh/TiO_2–Al_2O_3$ shifted only few tenth eV downwards after the reduction of the catalyst, but did not change further during the reaction (Fig. 8).

On the contrary, significant shift was observed in the binding energy of V 2p electrons in the case of V_2O_5 promoted sample. After subtracting the X-ray satellites of the O 1s peak and comparing the results obtained on the as received sample with the reduced catalyst (Fig. 8) we found that the binding energy of V $2p_{3/2}$ in the reduced sample shifted to 516.4 eV that could be assigned to V^{4+}. These results are in good harmony with our TPR measurements.

Earlier Sigl et al. [11] found that on vanadia promoted Rh/SiO_2 only a weak shoulder developed at lower binding energy on the V $2p_{3/2}$ peak in the reduced sample as well as after the $CH_4 + CO_2$ reaction on used catalyst compared to the as calcined sample. This

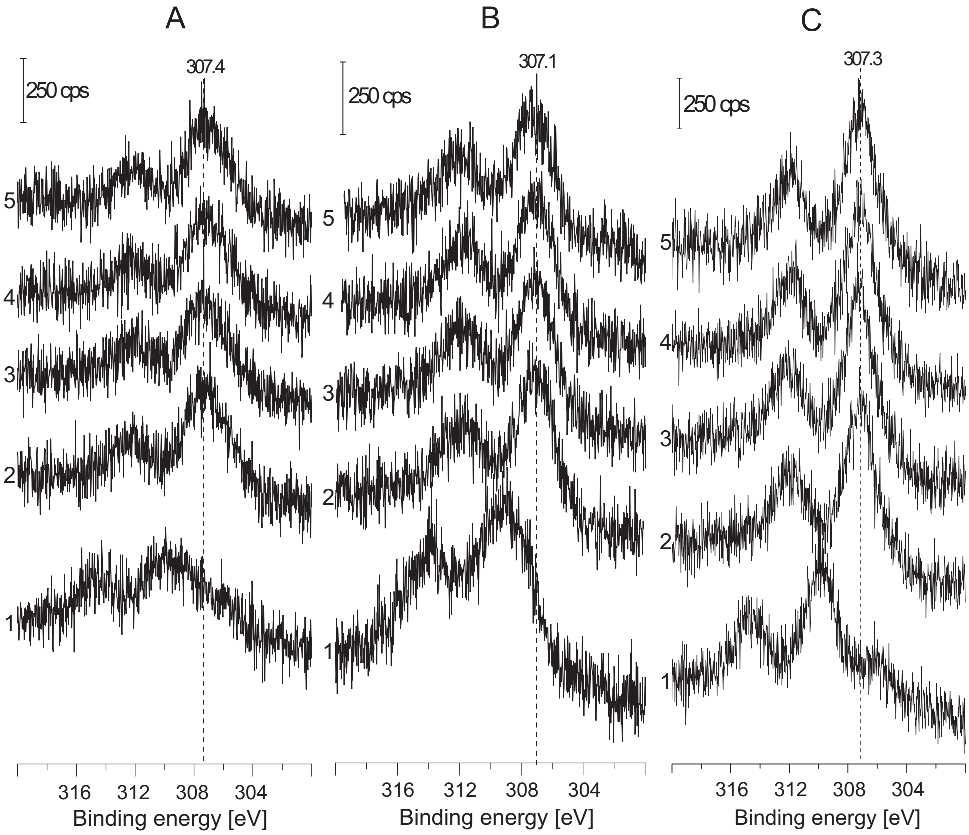

Fig. 7. The XP spectra of Rh 3d registered on Rh/Al_2O_3 (A), on $Rh/10\%TiO_2–Al_2O_3$ (B) and on $Rh/10\%V_2O_5–Al_2O_3$ (C) as received sample (1), the reduced sample (2), after 5th (3), 30th (4) 120th minute (5) of the $CH_4 + CO_2$ reaction at 773 K.

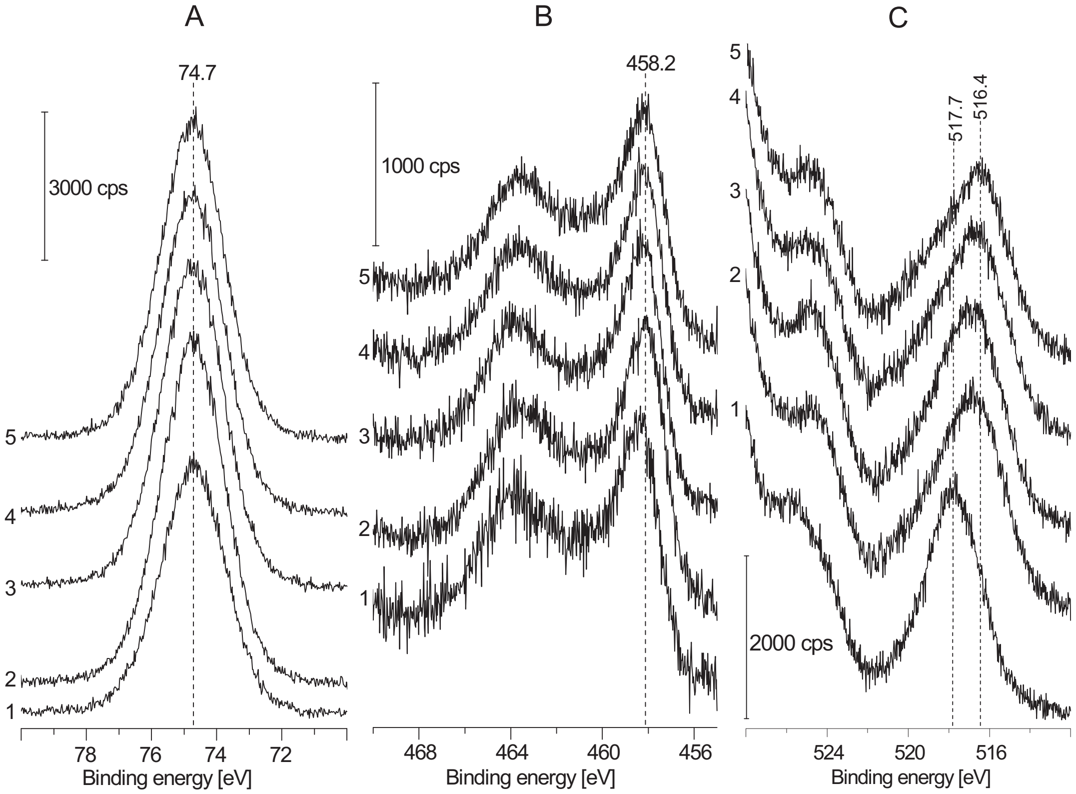

Fig. 8. The XP spectra of Al 2p on 1% Rh/Al_2O_3 (A), Ti 2p on $Rh/10\%TiO_2–Al_2O_3$ (B), V 2p on $Rh/10\%V_2O_5–Al_2O_3$ (C) as received sample (1), the reduced sample (2), after 5th (3), 30th (4) 120th minute (5) of the $CH_4 + CO_2$ reaction at 773 K.

suggested that the major V species does not undergo any change in the reduction state. This is in contrast with our results because we detected a significant shift after reduction. On the other hand this observation does not agree with the earlier finding that the vanadia is reduced from V^{5+} in $RhVO_4$ to V^{3+} in V_2O_3 during high temperature treatments [29], however, it was an ex situ treatment. We suppose that the formation of V^{3+} could be excluded in our cases because the binding energy of V $2p_{3/2}$ in this species is below 516 eV [30] and in our vanadia promoted Rh/Al_2O_3 sample the binding energy was 516.4 eV (Fig. 8).

In the position of C 1s signal no significant change could be detected during the reaction but the intensity of it increased comparing the reduced and the used sample in all cases.

The question is that how the effect of the promoters on the activity of the Rh/Al_2O_3 catalyst could be explained. The turnover rates of CO formation were about 50% higher on $Rh/V_2O_5–Al_2O_3$ than on Rh/Al_2O_3.

Earlier we assumed [3] that hydrogen formed in the decomposition of CH_4 and perhaps CH_x fragments promoted the CO_2 dissociation and the adsorbed oxygen facilitated the dissociation of methane. Fig. 2 shows that the methane decomposition rate is similar on all the samples used. Although in the first pulse there was a significant difference in the hydrogen formation observed in the presence of our samples, on Rh/Al_2O_3 the highest rate for methane decomposition was found and the lowest efficiency in the $CH_4 + CO_2$ reaction. These observations exclude that this process results in the higher reaction rate on the promoted samples. The amount of surface carbon was nearly the same on all samples so the carbon deactivation could not result in the difference in dry reforming rate.

Fig. 3 shows that the carbon dioxide dissociation i.e. the CO formation occurred on $Rh/V_2O_5–Al_2O_3$, a small amount of CO was detected on $Rh/TiO_2–Al_2O_3$ and only traces of CO was detected on Rh/Al_2O_3. This order was obtained in the reaction rate of $CO_2 + CH_4$ reaction. From these results we may conclude that not only the methane decomposition but the CO_2 dissociation could influence the rate of the $CO_2 + CH_4$ reaction.

Former investigations of CO_2 reforming of CH_4 have indicated that when TiO_2 is used as a support, TiO_x species formed during reduction at the metal–TiO_x interface which promotes catalyst activity [31]. It was also stated that the addition of cerium to Pt/ZrO_2 led to an increase in the number of oxygen vacancies which is necessary for CO_2 dissociation during the $CO_2 + CH_4$ reaction [32].

Our TPR (Fig. 1) and XPS (Fig. 8) results demonstrated that the titania only slightly reduced while the vanadia reduced from V^{5+} to V^{4+} during the pre-treatment of the catalysts. It means that oxygen vacancies formed mainly on the interface. The carbonate or the CO_2 reoxidized the reduced oxide while CO and formate are formed. The formate decomposes rapidly to CO. The hydrogen and the CH(x) species produced in the methane decomposition reduced the oxide promoter again.

For the interpretation of the higher efficiency of the vanadia and especially titania promoted samples the electronic interaction between the metal and the promoters [33] has to be taken into consideration.

4. Conclusion

TPR and XPS results revealed that during the pre-treatment of the catalysts not only Rh reduced but TiO_2 slightly and V_2O_5 significantly to V^{4+} below 600 K.

There were no significant differences in the CH_4 decomposition at 773 K on different catalysts but the dissociation of carbon dioxide occurred on $Rh/V_2O_5–Al_2O_3$ much faster and at lower temperature than on the other samples.

Vanadia and titania promoted Rh/Al_2O_3 was found to be more active in the $CO_2 + CH_4$ reaction than the Rh/Al_2O_3.

By means of in situ DRIFT spectroscopy adsorbed CO and in some cases formate species were detected during the catalytic run on the catalysts far above their desorption temperature; the formation rate of them is higher than the desorption, decomposition or further reaction rate.

The increase of the conversion observed on V_2O_5 and TiO_2 promoted Rh/Al_2O_3 catalysts could be attributed to the oxygen vacancies which formed on the additives during the pre-treatment and the reaction.

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