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Promoting Mechanism of Potassium in the Reforming of Ethanol on Pt/Al_2O_3 Catalyst

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Abstract The reaction of ethanol and water has been investigated over K doped 1% Pt/Al_2O_3 catalysts. The presence of K resulted at room temperature in upward shift of the IR band of CO formed in the ethanol adsorption. At higher temperature the presence of surface acetate species was also detected which, according to the TPD results decomposed above 600 K to form CH_4 and CO_2. The K destabilized these forms. In the catalytic reaction the H_2 selectivities were similar and much higher over all promoted Pt/Al_2O_3 than on the pure catalyst. In this study it was proved that the K had a destabilizing effect onto the surface acetate groups and thus improved the steam reforming activity of 1% Pt/Al_2O_3.

Keywords Ethanol reforming · K promoted Pt/Al_2O_3 · Reaction of ethanol with water

1 Introduction

The use of hydrogen in a fuel cell represents one of the cleanest sources of electric energy. Several studies can be found that are focused on the development of the most successful catalytic processes to produce hydrogen. It can be generated from hydrocarbons, by the electrolysis of water, from biomass or different organic compounds that have adequate hydrogen content. Among these sources biomass or other raw materials produced from sustainable material have attracted a particular attention recently since they are considered a zero CO_2 emission energy source.

In our previous works we studied the steam reforming reactions of ethanol over Al_2O_3 supported noble metal (Pt, Ir, Ru, Pd) catalysts [1]. It was found that while the selectivity of hydrogen decreased in time, the formation of ethylene increased parallel to it in all cases. Namely, the sequence of the selectivity values of hydrogen in the quasi steady state conditions was Ru > Rh > Ir = Pd > Pt and the selectivity of C_2H_4 increased in the opposite way. On the TPD spectra of adsorbed ethanol on different alumina supported noble metals there was a high temperature desorption stage, and the T_{max} of this peak depended on the material of the metal (Rh < Pd < Ru < Ir < Pt). The IR spectra of the ethanol adsorbed on pure Al_2O_3 and Al_2O_3 supported noble metals have revealed that not only molecularly adsorbed ethanol, mono-and bidentate ethoxy groups and adsorbed CO were present on the surfaces, but acetaldehyde and a great amount of acetate groups were also detected. The latter were stable even in the temperature range of 700–770 K. We have also pointed out that the presence of water increased the stability of the molecularly bonded ethanol but decreased that of monodentate ethoxy species. It was presumed that the surface acetate species were located mainly on the support.

According to the steam reforming reaction on Pt-containing catalysts was the highest change in the hydrogen selectivity, therefore these samples were examined in detail [2, 3]. As the Pt content was increased from 0% to 1% and 5% the changes in the selectivity of hydrogen decreased while the selectivity of ethylene increased in smaller extent [2]. The same result was obtained by increasing the reaction temperature (from 723 to 823 and 923 K). All these observations mean that during the reaction the metal was poisoned and the effect of the support came to the front.

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We have come to the conclusion that the surface acetate species were the cause of the poisoning as they were the only species present on the surface at the reaction temperature. In order to hinder the poisonous effect the stability of the acetate species has to be lowered or their formation has to be prevented.

It was found in the study of acetic acid adsorption on Rh (111) surface that K additives lowered the stability of acetate species bonded on the metal surface [4]. So we prepared Pt/Al_2O_3 samples promoted with potassium.

The effect of alkali metal promoters are widely studied almost in all catalytic reactions.

Frustreri et al. [5, 6] studied the steam reforming process over Ni/MgO catalysts promoted with 1% and 3% potassium. They found that the catalytic activity decreased in smaller rate in time in the case of K-containing catalysts than over pure Ni/MgO. The presence of potassium did not effect significantly the product distribution, only the selectivity of methane increased slightly. They stated that the potassium caused changes in the electron structure of the catalyst. This means that the alkali metal donated electrons to the nickel which made the C–Ni bonds stronger and weakened the C–O bond in the meantime.

Llorca et al. [7] found that sodium had a positive effect on the steam reforming of ethanol on Co–ZnO-based catalyst; the production of hydrogen increased with the sodium content. The effect of K on surface acetate species was proven in the work of Parida and Mishara [8], who examined the catalytic ketonization of acetic acid over alkali metal doped ZrO_2 catalysts. Comparing the yield of acetone at 573 K they found that in the presence of an alkali metal the amount of this product increased, except Li, where less acetone formed than over pure ZrO_2. This negative effect of Li was explained by the fact that this metal significantly decreased the surface of the catalyst.

It was also found that the addition of potassium to Mo_2C/Norit enhanced the catalytic efficiency of Mo_2C in the ethanol decomposition and increased the formation of hydrogen [9].

The promoting effect of K was observed in the ethanol oxidation, too [10]. Alkali metal doped catalysts did not produce acetic acid and these samples were significantly more active than the un-promoted Pt/Al_2O_3 [10].

In the present paper we report on the catalytic performance of K promoted Pt/Al_2O_3 catalysts in the ethanol desorption and in the ethanol + water reaction.

2 Experimental

The Pt/Al_2O_3 was prepared by impregnating the support with the aqueous solution of $H_2PtCl_6 \times 6\ H_2O$ to yield 1 wt% metal content. The impregnated powder was dried at 383 K. Al_2O_3 (Degussa P 110 C1 100 m^2/g) was used as support.

When the K doped catalysts were prepared the support was impregnated with the mixture of the aqueous solution of $H_2PtCl_6 \times 6\ H_2O$ to yield 1 wt% metal content and the proper amount of the solution of KNO_3 to yield 0.04, 0.2 and 0.4 w/w% K. Prior to the catalytic tests, the TPD experiments and the DRIFTS analyses the catalysts were heated in situ to 473 K in inert gas flow (Ar) and kept in O_2 stream (40 mL/min) at this temperature for 30 min. Then the temperature was raised to 673 K in Ar flow again where the catalysts were reduced in H_2 flow (40 mL/min) for 60 min. After the pre-treatment the reactor was cooled to room temperature for adsorption or it was heated to the reaction temperature (723 K) in inert gas flow.

The dispersions of these catalysts were determined at room temperature after pre-treatment by adsorption of H_2. The dispersion data are summarized in Table 1.

Infrared spectra were recorded with a Bio-Rad FT-IR FTS 135 spectrometer with a wave number accuracy of $\pm 4\ cm^{-1}$. Typically 64 scans were registered. The whole optical path was purged with CO_2- and H_2O-free air generated by a Balston purge gas generator. All spectra were rated to the spectra of the catalysts pre-treated before the measurements. The pre-treatment of the samples were performed in a high vacuum cell as follows: The catalysts were heated in vacuum up to 473 K, after the evacuation the sample was treated in 133.3 kPa of O_2 for 30 min. Then the catalyst was kept at 673 K in 133.3 kPa of H_2 for 1 h. For IR studies the catalysts' powders were pressed to a self

Table 1 Some characteristic data of ethanol steam reforming at 723 K on different K containing 1% Pt/Al_2O_3 catalysts in the 120th min of the reaction

	D (%)	Conversion (%)	Selectivity (%)								
			CH_4	C_2H_6	C_2H_4	C_2H_4O	H_2	CO	CO_2	$(C_2H_5)_2O$	C_6H_6
1% Pt/Al_2O_3	49	94.0	0.6	0.3	79.2	7.0	5.7	1.8	1.4	7.7	0
0.04% + 1% Pt/Al_2O_3	67	94.5	19.3	8.1	37.4	4.3	30.8	6.2	23.4	0.3	1.0
0.2% K + 1% Pt/Al_2O_3	50	87.2	28.5	7.6	20.2	6.8	32.2	7.1	27.6	1.2	0.9
0.4% K + 1% Pt/Al_2O_3	86	81.7	29.3	5.0	12.8	13.1	34.3	11.8	25.6	2.1	0.2

supporting disc (30 × 10 mm, 5 mg/cm^2). After the pre-treatments 266 Pa of ethanol was introduced at room temperature into the chamber and the catalyst was kept in this ethanol vapour for 15 min. After this, the sample was evacuated at room temperature and the spectrum was recorded; then the adsorbed layer was heated to different temperatures in order to examine the thermal stability of surface species. The chamber was continuously evacuated; all spectra were registered at room temperature.

The catalytic experiments were carried out in a fixed bed continuous flow reactor (8 mm o.d. quartz tube), which was heated externally. The dead volume of the reactor was filled with quartz beads. For catalytic studies small fragments (1–3 mm) of slightly compressed pellets were used. Typically 50 mg of catalysts was taken. Ethanol–water mixture of 1:3 molar ratio was introduced into an evaporator by an infusion pump (Infusens 5188.21; flow rate: 0.3 mL liquid/h); the evaporator was flushed with Ar-flow (60 mL/min). After the pre-treatment of the catalyst the Ar-flow containing the ethanol-water mixture entered the reactor through an externally heated tube avoiding condensation.

Analysis of the products and reactants was performed with an Agilent 6890 N gas chromatograph using HP-PLOT Q column. The gases were detected simultaneously by TC and FI detectors.

Hydrogen and different product selectivities were defined as

$$S_{H_2} = \frac{x_{H_2}}{\sum x_i n_i} \qquad S_i = \frac{x_i n_i}{\sum x_i n_i}$$

where x_i and x_{H_2} denote the mole fraction of product (i) and H_2, respectively, and n_i is half of the number of hydrogen atoms (in S_{H_2}), or the number of carbon atoms (S_i) in each molecule of the product.

The adsorption and temperature programmed desorption (TPD) studies were carried out in a microbalance (Netzsch STA 409 PC) connected to a mass spectrometer (Pfeiffer QMS 200). During the measurements the changes in the mass spectrometer signal intensity of the main fragments of ethanol, water and the possible products were followed. With the help of a home made algorithm one can calculate the intensity characterizing only the given product (generally the most intense fragment signal of a molecule) by taking into account the contributions of any other fragments to this signal. The contributions were calculated on the basis of intensity ratios between the fragments characteristic of the individual molecules. The intensity ratios measured in our system during MS analyses of the starting materials and the possible products did not differ considerably from the intensity ratios published in the literature.

The adsorption of ethanol was performed by bubbling the carrier gas through the ethanol at 273 K for 30 min. The amount of adsorbed ethanol was followed by weight-change measurements performed with the help of the microbalance. After ethanol adsorption the sample was flushed again with He-flow at 300 K for 15 min and then the catalyst was heated with a heating rate of 20 K/min up to 900 K in dry He stream (30 mL/min).

The DRIFTS analyses were performed in a diffuse reflectance infrared cell (Spectra Tech) with CaF_2 windows, adapted to a BioRad FTS-135 type FT-IR spectrometer. In all cases the catalyst was first pretreated in a flow system as described above and then it was flushed with the same reaction mixture used in the catalytic reaction. The spectra were recorded in different intervals during the reaction. The spectrum of the sample after the reduction step was used as background.

3 Results and Discussion

The IR spectra of ethanol adsorbed on K-promoted 1% Pt/Al_2O_3 catalysts did not differ significantly from the spectra of the adsorbed layer on 1% Pt/Al_2O_3 that were published earlier [2]. Introducing ethanol onto the catalysts at room temperature resulted in the appearance of bands at 2973, 2930, 2902, 2877, 1450, 1392, 1164 cm^{-1} which can be attributed to different C–H vibrations. The band due to adsorbed CO appeared at 2017 cm^{-1}. The peaks at 1106, 1073 and 1052 cm^{-1} can be assigned to monodentate and bidentate ethoxy species, respectively. The band characteristic for δ(OH) vibration in molecularly adsorbed ethanol was detected at 1276 cm^{-1}. The positions and the intensities of these bands did not change with the evacuation at room temperature. The negative features at 3727 and 3680 cm^{-1} can be connected to the consumption of the surface OH-groups during the interaction of ethanol with the surface. The bands, with the exception of adsorbed CO, monotonously lost their intensities as the temperature increased up to 673 K. At and above 373 K new bands appeared at 1577–1570 and 1467–1477 cm^{-1} that were the only stable bands above 723 K. These absorptions can be assigned to surface acetate species bonded to the support [2, 3]. It was found in the case of alumina supported noble metals that the formation of acetate exhibited a maximum around 573 K and these species were stable even above 723 K and these values proved to be independent of the nature of the noble metal [1].

The presence of K slightly affected the positions and the intensities of the bands on the IR spectra formed during the adsorption of ethanol (Figs. 1, 2). The change in the intensity of the band at 1574–1578 cm^{-1} due to surface acetate had a similar feature in all cases. It is remarkable that above 673 K it disappeared from the surface at 0.4% K content (Fig. 2), while the same result occurred only at

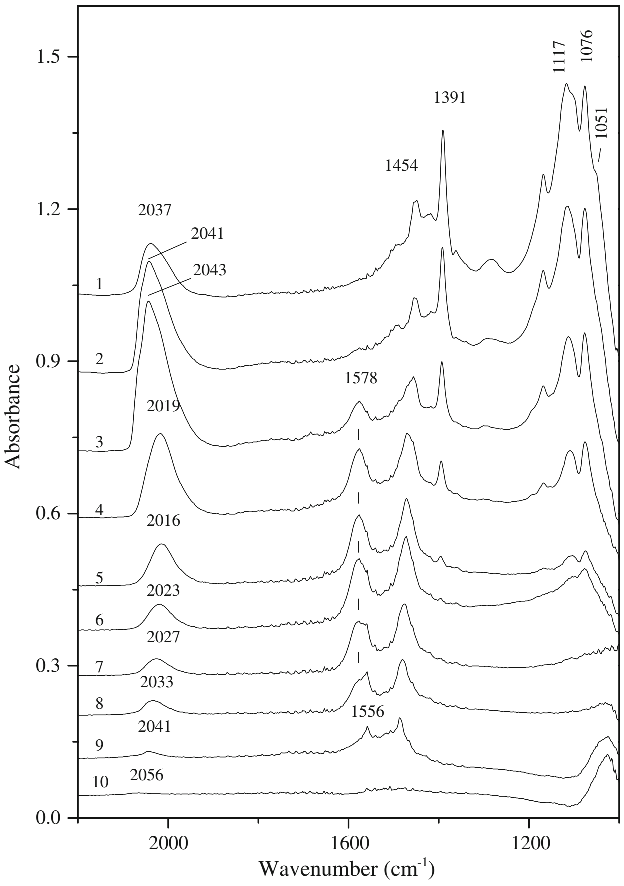

Fig. 1 Infrared spectra registered after the adsorption of ethanol at 300 K on 0.04% K + 1% Pt/Al_2O_3 and then evacuated at room temperature (1), at 373 K (2), 423 K (3), 473 K(4), 523 K (5), 573 K (6), 623 K (7), 673 K (8), 723 K (9), 773 K (10)

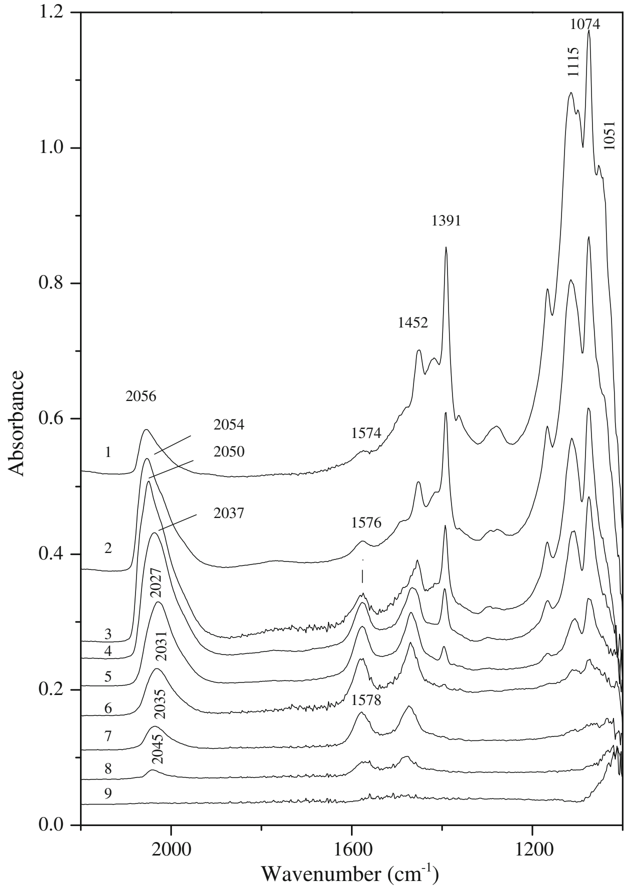

Fig. 2 Infrared spectra registered after the adsorption of ethanol at 300 K on 0.4% K + 1% Pt/Al_2O_3 and then evacuated at room temperature (1) at 373 K (2), 423 K (3), 473 K(4), 523 K (5), 573 K (6), 623 K (7), 673 K (8), 723 K (9)

higher temperatures (723 K) at smaller amounts of K (Fig. 1) or on the potassium-free sample (above 723 K) [1, 2]. These results clearly demonstrate the decreasing stability of the surface acetate on K-doped catalyst in contrast to the case of 1% Pt/Al_2O_3.

The position and the intensity of the band due to adsorbed CO on 1% Pt/Al_2O_3 showed a hysteresis as a function of temperature [2]. The band observed at 2017 cm^{-1} at room temperature shifted upward to 2044 cm^{-1} as the temperature increased form 300 K to 473 K. Above this temperature the intensity of this band decreased and its position shifted to lower wave numbers. It could be observed at 2009 cm^{-1} even after the treatment at 673 K [2]. When the catalyst contained 0.04% potassium (Fig. 1) the main difference as compared to 1% Pt/Al_2O_3 was that the CO band appeared at significantly higher wave number at 2037 cm^{-1} even at room temperature. As the K content of the catalysts increased its position shifted further upwards namely on 0.2% K + 1% Pt/Al_2O_3 catalyst the CO band was observed at 2048 cm^{-1} and on the 0.4% K + 1% Pt/Al_2O_3 at 2056 cm^{-1} (Fig. 2) at room temperature. By raising the evacuation temperature the intensities of the CO band increased up to 423–473 K while its position shifted to lower wave numbers. Above 523 K, although the peak intensity decreased, its position shifted upwards again.

Earlier there was an enormous interest in the CO adsorption on Pt single crystal or on supported Pt catalysts since CO takes part in many important reactions in which Pt is among the most active catalysts. Most of the papers dealing with CO/Pt systems depicted only one band in the range of 2100–2000 cm^{-1} that was attributed to linear (on top) CO adsorbed on Pt atoms surrounded by only Pt atoms. It was found that the real position of this band depends on the surface coverage [10], and the reduction degree of Pt [11]. There is another model explaining the band position of adsorbed CO, the CO island formation model [12–14], in which the CO stretching frequency was constant over a wide range of coverage. In some cases more absorption were registered in the 2100–2000 cm^{-1} range, which were attributed to CO adsorbed on the corner Pt atoms or on the edges [15]. The upward shift with the increase of the intensity of the CO band obtained after ethanol adsorption on Pt/Al_2O_3 was explained by the increase of surface CO concentration causing lateral electron repulsion between adsorbed CO species and/or the change of the extent of the back donation [2].

Derrouiche et al. [16] found that the addition of K to the Pt/Al_2O_3 catalyst significantly modified the adsorption of CO on Pt particles, as the linearly bonded CO absorbed at lower wave numbers-at about 2050 cm^{-1}-than on the potassium free Pt/Al_2O_3 (2074 cm^{-1}). Our results agree well with this finding, on Pt/Al_2O_3 after CO adsorption band was observed at 2065 cm^{-1} and on 0.4% K + Pt/Al_2O_3 this peak was detected at lower wave number 2055 cm^{-1}. The effect of K on the CO adsorbed on Pt surface was explained by a dominant attractive short-range interaction between CO and K but also the existence of a weaker long-range interaction was supposed [17]. A new adsorbed CO species was also detected on Pt promoted with K at 1763 cm^{-1} corresponding to an adsorbed CO denoted X_{Pt-K} CO [16]. It has been also suggested that the peak around 1760 cm^{-1} can be assigned to the threefold coordinated CO on the Pt atoms interacting with potassium species [18]. Figure 2 clearly shows that between 373 and 473 K a weak band appeared at about 1760 cm^{-1} which could be assigned to this species. It has to be mentioned that the *v* (C=O) vibration of acetaldehyde was registered also at about 1753 cm^{-1} [19].

It is surprising that after the adsorption of ethanol on K doped Pt/Al_2O_3 the CO band was detected at higher wave number (at 2037 cm^{-1}on 0.04% K + 1% Pt/Al_2O_3) than on Pt/Al_2O_3 (at 2017 cm $^{-1}$) [2] and its position shifted to higher wave number with increasing the K content (2056 cm^{-1} on 0.4% K doped catalyst) (Fig. 2). If we accept that the CO band appeared on Pt/Al_2O_3 at 2017 cm^{-1}, because Pt carbonyl hydride was formed [1], than the effect of potassium can be explained by the inhibition of carbonyl hydride formation.

It was shown earlier in TPD experiments that ethanol adsorbed on Al_2O_3 desorbed in one stage in the temperature range of 350–550 K and mainly ethylene was formed [3]. In the case of supported Pt a second desorption stage was observed above 600 K with CO_2 and CH_4 as the main products, which was explained with the formation and decomposition of surface acetate species. In the low temperature range only traces of ethylene were found while mainly acetaldehyde, CO_2, and smaller amounts of ethanol, hydrogen and CO were detected [3].

There were no significant differences between the TPD curves obtained either in the case of Pt/Al_2O_3 or on K promoted samples in the low temperature range (Fig. 3a). Only the signal intensity of m/e = 39 was near one order of magnitude higher in the case of 0.4% K + 1% Pt/Al_2O_3 than on the K free sample. This fragment could be assigned as C_3–C_4 hydrocarbons, as their other characteristic fragments were also detectable in traces, but it is mainly due to the desorption of K. Earlier it was found that the potassium already desorbed below 600 K from Pt single crystal when the coverage was higher than 0.7 ML [20]. After CO adsorption on 0.25 ML K/Pt (111) surface, CO and K desorbed in the 530–650 K temperature range [21]. On the basis of these results we may suppose that in our experiments at above 520 K potassium desorbed from the 0.4% K + 1% Pt/Al_2O_3 surface. This observation could explain the shift of the CO band at high temperature observed after ethanol adsorption on K promoted Pt/Al_2O_3 catalyst.

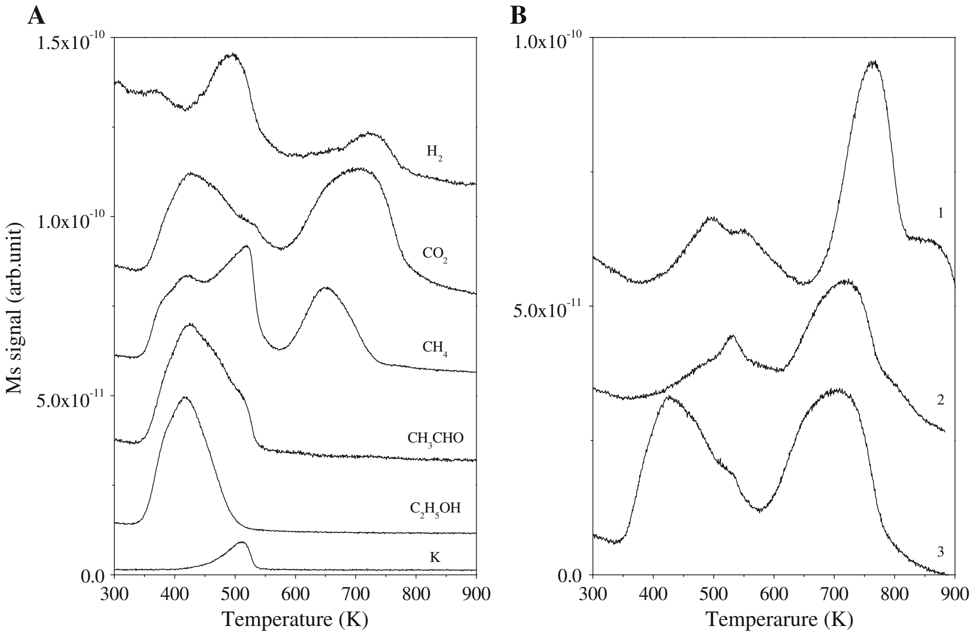

Fig. 3 Temperature programmed desorption of adsorbed ethanol on 0.4% K + 1% Pt/Al_2O_3 (**a**); CO_2 evolution in the TPD of adsorbed ethanol on 1% Pt/Al_2O_3 (1), 0.04% K + 1% Pt/Al_2O_3 (2), 0.4% K + 1% Pt/Al_2O_3 (3) (**b**)

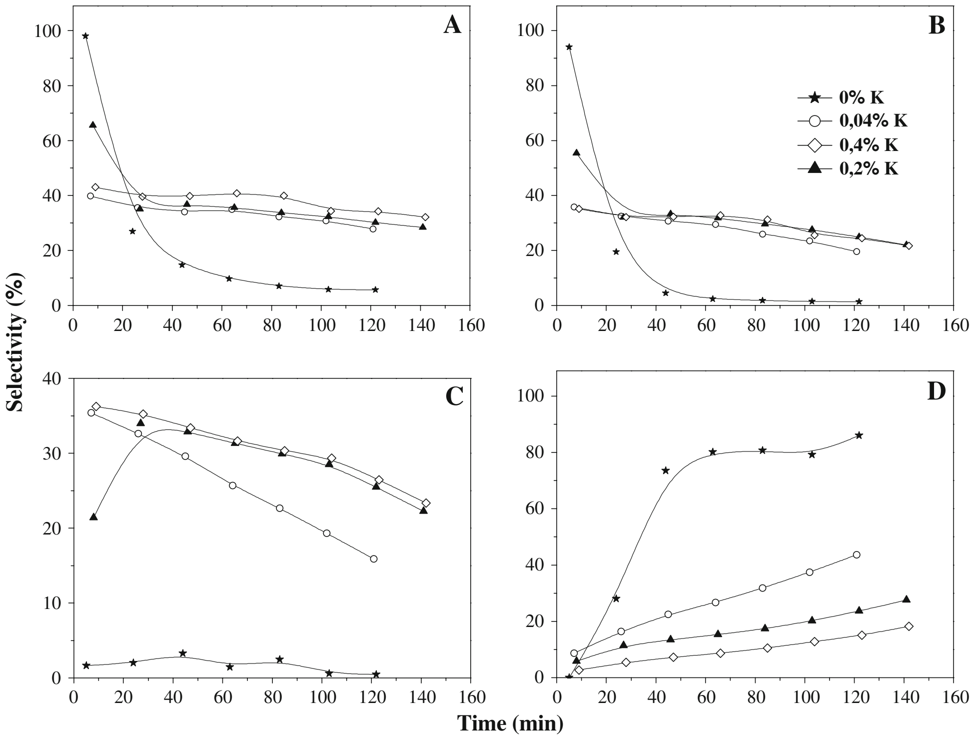

Fig. 4 The selectivity of H_2 (**a**), CO_2 (**b**), CH_4 (**c**), and C_2H_4 (**d**) formation in the ethanol + water reaction at 723 K on K free (*), 0.04% K (○), 0.2% K (▲), 0.4% K (□) containing Pt/Al_2O_3 catalysts

The temperature increase resulted in the decrease of the K coverage and so the CO absorption band shifted to higher wave numbers because the effect of K on the adsorbed CO also decreased. Nevertheless the CO band intensity also decreased.

The presence of potassium significantly influenced the features of the second desorption stage. Figure 3b represents the changes in the amount of CO_2 formed in the ethanol TPD. As the K content of 1% Pt/Al_2O_3 increased the temperature of the desorption peak maxima of CO_2 shifted to lower temperatures (at 1% Pt/Al_2O_3 $T_{\max} =$ 760 K, at 0.4% K + 1% Pt/Al_2O_3 $T_{\max} = 700$ K). These results are in good agreement with IR measurements at high K content namely that surface acetate species decomposed at lower temperature.

In the steam reforming of ethanol (ethanol/water = 1:3 molar mixture) at 723 K over 1% Pt/Al_2O_3 the conversion was high (about 94%) and constant, H_2, ethylene and CO_2 formed as main products while the presence of acetaldehyde and CO was also detected. The initial, almost 100% selectivity of H_2 and CO_2 suffered a sudden decrease as the reaction proceeded and after 60 min of the reaction it had values under 10%. In the meantime the selectivity of ethylene changed oppositely than that of H_2, meaning that it increased from 0% to almost 90% [2]. In the presence of K the ethanol conversion slightly decreased; when the catalyst contained 0.4% K the conversion was about 86% (Table 1). The potassium caused significant changes in the product distribution of the steam reforming reactions compared to the results described above (Fig. 4). Over K containing catalysts higher selectivity of H_2, CO_2, and CH_4 was obtained in the steady state than over pure 1% Pt/Al_2O_3, and the potassium also suppressed the formation of ethylene. Namely, while under near steady state conditions the selectivity of H_2, CO_2 and CH_4 were below 10% over 1% Pt/Al_2O_3, these values were much higher over the promoted catalysts. The selectivities of these products changed in proportion to the amount of potassium especially in the case of CH_4 and C_2H_4. In the S(H_2) nearly the same results were obtained over all K concentrations (Table 1).

The infrared spectra registered in a DRIFT cell during the catalytic reaction at 723 K on Pt/Al_2O_3 and on different K promoted samples were nearly the same in all cases. From the 1st min of the reaction absorption bands were observed at 1574 cm^{-1} and 1466–1468 cm^{-1} which can be attributed to the acetate species. The intensities of these bands increased almost linearly in time until the 30th min of the reaction and then achieved a nearly steady state value (Fig. 5).

Below 1200 cm^{-1} where the ethoxy species would be detectable only very weak bands, if any were found and their intensities were comparable with the noise.

In the CO region on the un-promoted and on the K doped samples a band was detected at 2041 and 2052 cm^{-1}, respectively (Fig. 5). The intensities of these bands decreased in time and their positions shifted to lower wave numbers. After 2 h of the reaction the bands were

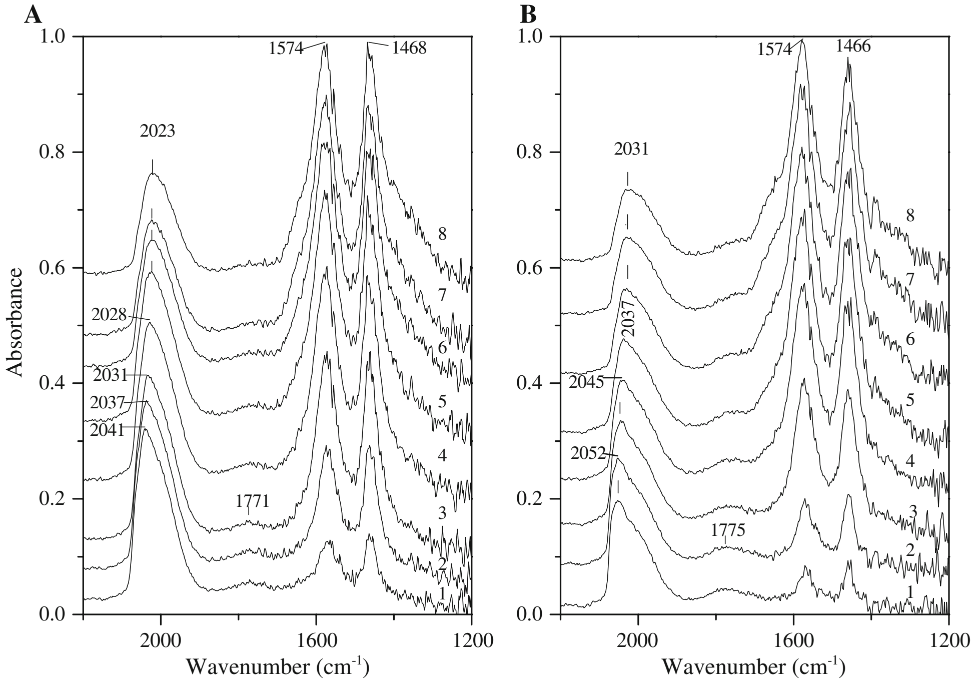

Fig. 5 Infrared spectra registered on 1% Pt/Al_2O_3 (**a**), 0.4% K + 1% 1% Pt/Al_2O_3 (**b**) during the ethanol + water reaction at 723 K in the 0.5th (1), in the 1st (2), 5th (3), 15th (4), 30th (5), 60th (6), 90th (7), 120th (8) min of the reaction

detected at 2023 and 2031 cm^{-1}. At about 1770 cm^{-1} a small absorbance was also observed which can be assigned to the three fold coordinated CO [18]. It is surprising that at this high temperature intensive CO bands can be detected.

When the DRIFT cell was flushed with He after the reaction, the intensities of the CO and acetate bands decreased. It means that during the reaction the formation rate of CO and acetate species was higher than the further reaction or decomposition of these species. It is interesting that the CO adsorbed either at room temperature or during the treatment at 723 K disappeared in the 1st min from the IR spectra when the cell was flushed with He stream. From these observations we may conclude that the CO detected during and after the reaction formed continuously from the acetate species or from the carbonaceous deposit.

Discussing the results of Figs. 1 and 2 it was assumed that the differences in the CO bands on the spectra obtained in the case of Pt/Al_2O_3 and K promoted samples at low temperature range were the results of the potassium bonded to the metal; by means of the TPD and FT-IR experiments we may suppose that the K desorbed from the Pt surface in the 500–600 K temperature range (Fig. 3a). This observation supports the fact that the presence of K did not influence the CO band on the spectra registered during the reaction at 723 K as it is shown on Fig. 5.

On the IR spectra stable bands at 1574 and 1466–1468 cm^{-1} were recorded during the reaction. Similar bands (1574 and 1465 cm^{-1}) were found after the adsorption of acetic acid on Al_2O_3 [22], which are tentatively assigned to surface acetate species. The question is still open whether these species are located on the support or on the metal. EELS [23] and HREELS [24] studies revealed that after the adsorption of acetic acid on Pt acetate species formed; but the TPD spectra of it in the case of polycrystalline Pt show that CO, CO_2 and H_2 desorbed in a single peak with a maximum of 435–450 K [25].

Cordi and Falconer [26] found by TPD that acetic acid adsorbed on Al_2O_3 decomposes only above 550 K and the reaction was not complete at 873 K; CO, CO_2, CH_4 and H_2 were found as products. Taking into account these results we may conclude that the acetate species are located rather on the support than on the metal at the reaction temperature.

The significant decay in the H_2 and CO_2 selectivity in the early stage of the steam reforming reaction over 1% Pt/Al_2O_3 (Fig. 4) [2] hints at the effect of a byproduct which inhibited the reaction on the metal. When the surface species formed in the reaction were desorbed, or the reaction was studied at higher temperatures (823 and 923 K) this decay reduced significantly, moreover, at 923 K it practically could not be detected. These findings are supported by the observation that the surface acetate species decompose above 750 K (the $T_{\max}$ of the TPD curves is at 753 K [3]).

We stated that the acetate species are bonded mainly on the support, so the question is still open, how a species located on the support can influence the catalytic activity of the metal.

We cannot rule out the presence of carbon located on the metal which may hinder the occurrence of the reaction on the Pt. We may suppose, however, that the acetate species can also poison the H_2 formation as these species may be located close to the metal particles. The surface diffusion of the species formed on the metal or on the support could be reduced by the close vicinity of the acetate species.

This feature could explain the selectivity change on Pt/Al_2O_3. On K promoted samples by raising the K content the hydrogen selectivity increased and the ethylene formation decreased. It is worth noting that the ethanol conversion decreased and the CH_4 and the CO selectivities increased. It seems that these observations contradict to the explanation for the selectivity change observed on Pt/Al_2O_3 while in the DRIFT experiments the intensity of acetate bands during the reaction were nearly the same on Pt/Al_2O_3 and on $K + Pt/Al_2O_3$ (Fig. 5). It seems that the alumina support functions as a pool for the intermediates and for the products or byproducts such as acetate species while the intensities of the acetate bands increased in time during the reaction (Fig. 5).

It was found that K additives suppressed the ethylene formation. The dehydration of ethanol is catalyzed by the acidic center of alumina but the potassium neutralizes these centers and therefore hinders ethylene production. The same arguments were used explaining the decay of ethylene formation in the ethanol oxidation on K doped Pt/Al_2O_3 catalysts [10].

This idea can explain that the ethanol conversion decrease as a function of potassium content (Table 1).

We supposed that the acetate hindered the reforming reaction on Pt [2] and it was found that the stability of these species decreased in the presence of potassium. In spite of these observations the surface concentration of the acetate species increased with the same rate on K doped and K free catalysts but the rate of ethanol reforming changed slightly on $K + Pt/Al_2O_3$ sample compared to the Pt/Al_2O_3.

The answer for this discrepancy can be looked for in the further surface reactions of the acetate species. The reforming of acetate was studied by several authors from the viewpoint of the reaction mechanism, catalyst deactivation and resistance to coking. Wang et al. [27] found that on commercial Ni-based catalysts acetic acid forms coke, which is subsequently gasified by steam. The proposed mechanism for this coke formation involves an adsorbed acetate species that decarboxylates to form the coke precursor, (CH_{1-3}), and also ketene, a dehydration product, that decomposes to form carbonaceous deposit [27]. A bi-functional mechanism has been proposed for the steam reforming of acetic acid over Pt/ZrO_2 [28], Pt/Al_2O_3 and Pt/CeO_2–ZrO_2 catalysts [29] which means that the support is an active component of the catalysts. The bi-functional mechanism has been suggested for the ethanol steam reforming, too [30]. The support was shown to be active for the dehydrogenation, dehydration and cracking reaction.

The question is still open how the K additives bonded to the support can influence the reaction occurring on the Pt. Earlier significant differences were observed in the reaction rate and in the product distribution in the water gas shift reaction obtained on alkali promoted or on unpromoted Al_2O_3 sample. Amenomiya and Pleizier [31] found that the rate of the $CO + H_2O$ reaction increased on alumina with the concentration of the promoter until the surface was saturated with alkali metal ions. For example the reaction rate on 9 wt% K/Al_2O_3 was about 20 times higher than on alumina in the 670–870 K temperature range. They also found that the addition of alkali salts to the Al_2O_3 increased the catalyst activity in the $CO_2 + H_2$ reaction as well [31].

In the TPD experiments the shift of the temperature of the desorption peak maxima caused by the presence of the promoter means that the K decreased the stability of the surface acetate species and for this reason they decomposed at lower temperatures as the K-content of the catalysts increased (Fig. 3). In spite of this the intensities of the acetate bands during the catalytic reaction at 723 K were nearly the same both on K promoted and on the unpromoted Pt/Al_2O_3 (Fig. 5). It means that the formation rate of the acetate species has to be higher on $K + Pt/Al_2O_3$ than on the pure catalyst. In the catalytic tests over the clean 1% Pt/Al_2O_3 a great decrease was observed in the formation of H_2 and CO_2 while the amount of ethylene increased in time. In the presence of K the steam reforming activity of the catalysts was improved in proportion with the potassium content. Besides the H_2 and CO_2 methane was also detected in higher quantities than over the pure supported Pt. We may suppose that the surface acetate species had an inhibiting effect on the steam reforming activity of the Pt catalysts tested that caused the great drop in the amounts of the main products in time and improved the formation of ethylene on the support. The presence of K resulted in a stable steam reforming activity of the promoted 1% Pt/Al_2O_3 in proportion with the amount of the promoter. This means that potassium destabilized the surface acetate species to produce CO_2 and CH_4.

In the presence of hydrogen CO can form from CO_2 on Pt/Al_2O_3 [32] and the K promoted alumina is an active catalyst for the water gas shift reaction [31]. These earlier observations support the finding that the K additives enhanced the hydrogen and methane selectivity on Pt/Al_2O_3 catalyst.

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