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Hydrogen formation in ethanol reforming on supported noble metal catalysts

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Abstract

The formation and stability of surface species generated in the interaction of ethanol and ethanol–water mixture with Al_2O_3 and CeO_2-supported noble metal catalysts were studied by FT-IR, TPD and TPR methods. It was found that water enhanced the stability of ethoxide surface species formed in the dissociation of ethanol. Dehydrogenation of molecularly adsorbed ethanol was proposed as a key reaction step. The TPD spectra of ethanol adsorbed on supported noble metals exhibited a high temperature desorption stage which was explained by the formation and decomposition of surface acetate species. Ethylene (product of the dehydration of ethanol) was mainly formed on Al_2O_3-supported noble metals, while on CeO_2-supported noble metals significant amount of acetaldehyde (originated from the dehydrogenation of ethanol) was also formed. In the steam reforming of ethanol the selectivity of H_2 formation decreased but that of C_2H_4 increased in time, while the conversions were stable on alumina-supported noble metals. These observations were explained by the inhibiting effect of surface acetate species.

Keywords: Ethanol steam reforming; Surface acetate species; TPD of ethanol; Reaction of ethanol with water; Oxide-supported noble metal catalysts

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1. Introduction

The increasing demand for alternative energy sources drew a great attention to the steam reforming of ethanol producing H_2 [1–12]. The use of ethanol is favoured because it can be readily produced from renewable biomass. Alumina-supported catalysts are very active at low temperatures in the dehydration of ethanol to ethylene. At higher temperatures ethanol is converted into H_2, CO, CO_2 and CH_4 [8]. The activity order of metals is Rh > Pd > Ni = Pt. When ceria/zircona was the support ethylene formation was not observed and the order of activity at higher temperature was Pt ≥ Rh > Pd. Auprêtre et al. [7] studied the effect of both the metal and the support in the steam reforming of bio-ethanol. They found that the hydrogen yield on alumina-supported metal catalysts decreased in the following order at 973 K: 9.7% Ni > 1% Rh > 0.5% Pd > 1% Pt > 9.1% Cu = 9.8% Zn > 0.67% Ru = 8.7% Fe. They concluded that the high activity of the metals in the ethanol steam reforming and their poor efficiency in the water gas shift reaction would give active and selective catalysts for ethanol reforming. Liguras et al. [9] also found that among the low-loaded catalysts, Rh was significantly more active and selective towards hydrogen formation than Ru, Pt and Pd. The catalytic performance of Rh and, particularly, Ru was greatly improved by the increase of metal loading. It was shown that the catalytic activity and selectivity of highly loaded Ru catalysts were comparable to those of Rh. Rh/MgO showed the best performance in the steam reforming of ethanol at 923 K in terms of activity and stability. It was not so selective, however, towards hydrogen formation [10]. Kinetic measurements revealed large difference in metal specific activities: Rh sites were 2.3, 3.7, and 5.8 times more active than Pd, Co and Ni sites, respectively. Although the number of publications on this reaction has been growing [1–11], only few attempts can be found in the literature on the detailed study of surface species formed during the adsorption and reaction of ethanol, the steam reforming of ethanol and on their relations with the gas phase products. In the present work the reforming of ethanol was studied on different noble metals supported on Al_2O_3 and on reducible CeO_2. The surface species formed during the

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interaction of ethanol and ethanol–water mixtures with the supported metals and with the pure supports were also examined.

2. Experimental

The catalysts were prepared by impregnating the supports with the aqueous solution of noble metal salts ($RhCl_3 \times 3H_2O$, H_2IrCl_6, $RuCl_3 \times 3H_2O$, $PdCl_2$, $H_2PtCl_6 \times 6H_2O$) to yield 1 wt.% metal content. The impregnated powders were dried at 383 K. Al_2O_3 (Degussa P 110 C1 100 m^2/g), and CeO_2 (Ventron, 5 m^2/g) were used as support.

For IR studies the catalyst powders were pressed onto a Ta-mesh (30 mm × 10 mm, 5 mg/cm^2). It was resistively heated and the temperature of the sample was measured by a NiCr–Ni thermocouple spot-welded directly to the mesh. The pre-treatments of the samples were performed in a stainless steel ultra vacuum IR cell (base pressure 10^{-7} Torr) and corresponded to those applied in our previous work [2]. Briefly, the samples were oxidized in 1 Torr (133.3 Pa) O_2 for 30 min at 673 K, evacuated for 15 min and reduced in 1 Torr H_2 for 60 min at 573 K. Infrared spectra were recorded either with a Genesis (Mattson) or a Bio-Rad FTS 135 FT-IR spectrometer with a wave number accuracy of ± 4 cm^{-1}. Typically 136 scans were collected. The spectrum of the pre-treated sample (background spectrum) and the actual vapour spectrum were subtracted from the spectrum registered in the presence of vapour.

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. Before the experiments the catalysts were pre-treated in the following way: (a) heating in Ar-flow (40 ml/min) up to 473 K; (b) keeping the sample in O_2-flow (40 ml/min) at 473 K for 20 min; (c) heating in Ar-flow (40 ml/min) up to 673 K; (d) treatment with H_2 (40 ml/min) at 673 K for 60 min; (e) heating (or cooling) in Ar-flow (40 ml/min) to the reaction temperature. Ethanol or ethanol–water mixtures of 1:3 molar ratio were introduced into an evaporator with the help of an infusion pump (Infusens 5188.21; flow rate: 0.3 ml liquid/h); the evaporator was flushed with Ar-flow (60 ml/min). Ethanol or ethanol–water containing Ar-flow 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 i.

The amount of surface carbonaceous deposit formed in the catalytic reaction was determined by temperature programmed reaction (TPR). After performing the reactions of ethanol and ethanol–water mixtures at 723 K for 110 min the reactor was flushed with Ar at the reaction temperature, the sample was cooled to 373 K, then the Ar flow was changed to H_2, the sample was heated up to 1170 K with a 10 K/min heating rate and the hydrocarbons formed were determined.

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). Before the TPD experiments the sample was oxidized and reduced. 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 measuring the weight changes by 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 or wet (water concentration was 3%) He stream (30 ml/min).

3. Results and discussion

3.1. IR spectra of adsorbed ethanol on supported noble metals

The formations of surface species in C_2H_5OH adsorption at 300 K, their further reactions in vacuum and in the presence of water at different temperatures were investigated by IR spectroscopy. We present here detailed spectra only for Ir/Al_2O_3, as on the other samples very similar features were observed.

After the adsorption of 1.33 hPa ethanol (300 K, 15 min) and subsequent evacuation (300 K, 15 min) the bands of molecularly adsorbed ethanol (spectrum 1 on Fig. 1A) and ethoxide were detected on 1% Ir/Al_2O_3 (Table 1). Other bands not involved in Table 1 originate from the products of surface reaction(s) and they will be assigned later. The negative spectral features at 3718 and 3677 cm^{-1} and the broad absorptions centered at 3405 cm^{-1} (not shown) are from the adsorption of molecular ethanol through the formation of hydrogen bridge bonding with the OH groups of the support. In the spectral range of 2200–1800 cm^{-1} bands of adsorbed CO were detected even at 300 K on Ir/Al_2O_3 (Fig. 1A).

The adsorbed layer was heated up quickly to different temperatures under evacuation the samples were kept at the given temperature for 1 min and then cooled down to room temperature. The spectra were always registered at 300 K (Fig. 1A).

The bands observed at 300 K in the C–H stretching region (3100–2600 cm^{-1}) monotonously lost their intensities with the increase of the temperature up to 573 K. Above this temperature the intensities of these bands dramatically decreased. On the spectra of Al_2O_3 and other alumina-supported noble metal samples similar characteristics could be observed in the 1800–900 cm^{-1} range. On supported metals, however, at and above 373 K new bands appeared at 1575 and

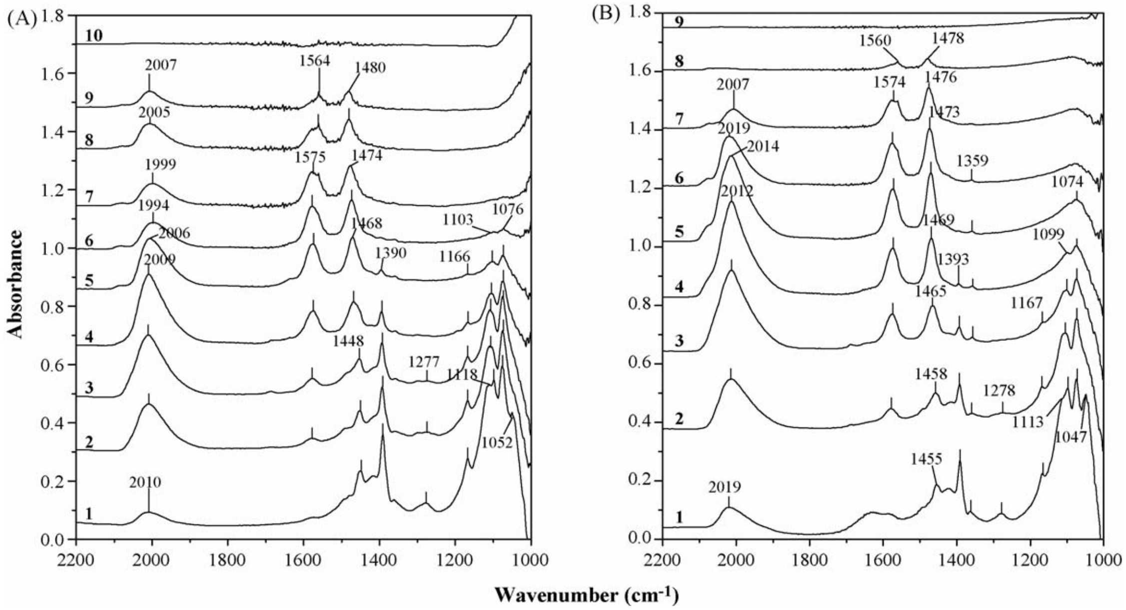

Fig. 1. IR spectra registered at 300 K on 1% Ir/Al_2O_3 after heating the adsorbed C_2H_5OH layer to different temperatures under constant evacuation (A) and in 1.33 hPa water (B)—1: 300 K; 2: 373 K; 3: 423 K; 4: 473 K; 5: 523 K; 6: 573 K; 7: 623 K; 8: 673 K; 9: 723 K; 10: 773 K.

1474–1468 cm^{-1} (attributed to surface acetate species [20]), which were the only stable bands at 673 K (Fig. 1A). Band due to δ(OH) in molecularly adsorbed ethanol (1277 cm^{-1}) could be observed up to 473 K on the surfaces. Spectral features due to H-bridge bonding of molecular ethanol (not shown) were detected up to 573 K on Al_2O_3 [11] and up to 623 K on 1% Ir/Al_2O_3.

In the following experiments the stability of adsorbed ethanol layer on 1% Ir/Al_2O_3 was investigated in the presence of water. For this purpose 1.33 hPa water was added to the adsorbed layer (produced via the adsorption of 2.67 hPa ethanol for 15 min and evacuation for 15 min at 300 K) at room temperature and the sample was heated up quickly to different temperatures. After keeping the sample at the given temperature for 5 min, the gas phase was evacuated for 5 min at the same temperature and then the sample was cooled down to 300 K. The spectra were always taken at 300 K after the above treatments (Fig. 1B).

From the comparison of the corresponding spectra on Fig. 1A and B it turned out that the presence of water led to the appearance of the 1574 and 1458 cm^{-1} bands even at 300 K. In the presence of water, on the other hand, the band at 1074 cm^{-1} could be observed even after the treatment at 673 K.

Ethanol was found to adsorb on various metal oxide surfaces by the dissociation of the OH bond, with the proton going to a surface lattice oxygen and the ethoxide species bonded to the surface cation. For example adsorbed ethoxide species were detected upon the adsorption of ethanol on various oxide surfaces including TiO_2 [2], CeO_2 [12,15] and Al_2O_3 [13].

Over oxides both dehydrogenation to acetaldehyde and dehydration to ethylene occurred depending on the nature of the oxides. The dimerization of aldehydes is also possible through aldolization reaction. From two acetaldehyde molecules crotonaldehyde formation also occurred through dehydration.

Table 1
Bands (in cm^{-1}) of surface species produced by the adsorption of ethanol on noble metal/Al_2O_3 catalysts

Assignments	Al_2O_3 [13]	Al_2O_3 [14]	Pt/Al_2O_3 [14]	Ir/Al_2O_3[a]	Pd/Al_2O_3[a]	Ru/Al_2O_3[a]	Rh/Al_2O_3[a]
$\nu_a(CH_3)$	2970	2967	2974	2973	2973	2972	2977
$\nu_a(CH_2)$ [13] or $\nu_s(CH_3)$ [14]	2930	2923	2930	2931	2933	2932	2933
$\nu_s(CH_2)$	2900		2892	2903	2903	2903	2906
$\nu_s(CH_3)$	2870	2875		2875	2877	2876	2881
$\delta_a(CH_3)$	1450	1446	1446	1448	1449	1449	1449
$\delta_s(CH_3)$	1390	1391	1391	1390	1391	1390	1390
$W(CH_2)$				1361	1361	1360	1360
δ(OH) in ethanol		1272	1272	1277	1277	1276	1276
ν(C–O), ν(C–C)	1170	1167	1167	1166	1167	1167	1167
ν_a(CCO) monodentate	1115			1118	1112	1112	1116
ν(C–C)		1096	1096	1095	1097	1098	1098
ν_s(CCO) bidentate	1070			1076	1075	1075	1076
ν_a(CCO) bidentate		1052	1052	1052	1052	1050	1052

[a] This work.

This reaction was observed on the surface of CeO_2 [16] and TiO_2 [17] upon the adsorption of acetaldehyde.

IR bands recorded during ethanol adsorption on some oxides and on oxide-supported noble metal catalysts and their possible assignments have been collected in Table 1.

In order to distinguish bands of adsorbed ethanol molecules and ethoxide(s) formed in the dissociation of ethanol, we follow the method proposed by Hussein et al. [18]: they attributed the band at 1380 cm^{-1} ($\delta(CH_3)$ in ethanol) and 1270 cm^{-1} ($\delta(OH)$ in ethanol) to ethanol molecularly adsorbed on TiO_2 surface. They suggested that the 1270 cm^{-1} band is from strongly held C_2H_5OH probably coordinatively bonded to Lewis acid sites [2,11].

The negative features and the broad absorptions above 3400 cm^{-1} on the spectra of Ir/Al_2O_3 catalyst show that a part of the ethanol molecules was adsorbed by hydrogen bridge bonding to the surface OH groups of the catalyst.

It has also been proposed [18] that bands below 1200 cm^{-1} could be assigned to ethoxides ($C_2H_5O_{(a)}^-$). The band around 1120 cm^{-1} was attributed [19] to ethoxide coordinated to a single surface cation of the support (monodentate ethoxide) and the band around 1070 cm^{-1} to an ethoxide bridge-bonded (bidentate) to adjacent surface cations of the supporting oxide [20,21].

Based upon the above assignments, our data clearly show that ethanol could adsorb in two molecular forms on the surfaces of the catalysts studied in the present work: in an adsorbed form coordinated to Lewis acid sites of the supports and in a hydrogen bridge bonded form through the OH groups of supporting oxides. The dissociation of ethanol to form $C_2H_5O_{(a)}^-$ species occurs already at 300 K.

The positions and the relatively small intensities of the bands of CO adsorbed on noble metal (Ir) showed the limited occurrence of the surface reaction at 300 K resulting in the formation in $CO_{(a)}$. Intensity increased as a function of increasing temperature. This feature indicates the greater extent of CO producing surface reaction of ethanol; the maximum values of these parameters were achieved at 373–473 K (Fig. 2B). Above these temperatures band intensities decreased and maxima shifted downwards probably due to the disappearance of the surface species, the reactions of which led to the formation of CO adsorbed on the metallic part of the catalysts. Similar features were observed for CO bands on all supported noble metal catalysts. These CO spectra significantly differed from those registered after the adsorption of CO gas [22]. The CO bands from the decomposition of adsorbed ethanol appeared at lower wave number, than those from CO adsorption. In all cases only one peak was observed, while, for example, on supported Rh the twin structure was also formed [22]. These differences were explained by the formation of metal carbonyl hydride [23,24].

At 373 K (in ethanol decomposition) and already at 300 K in the presence of water other surface reactions occurred, the result of which is the appearance of the stable bands at 1575 and 1474–1458 cm^{-1}. These bands are tentatively assigned to surface acetate species. After ethanol adsorption on Pt/TiO_2. Rachmady and Vannice [20] found bands at 1550 and 1442 cm^{-1} assigned to $\nu_a(COO)$ and $\nu_s(COO)$ vibrations in the surface acetate species.

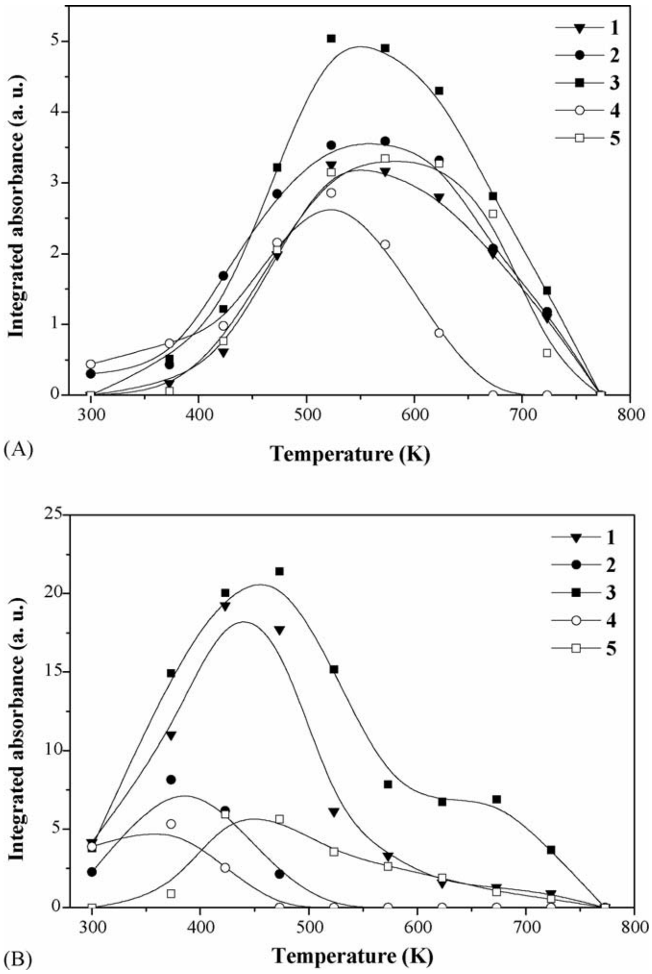

Fig. 2. Integrated absorbances change of the surface acetate (A) and adsorbed CO band (B) in the vacuum treatments (see text) as a function of temperature on—1: 1% Pt/Al_2O_3; 2: 1% Pd/Al_2O_3; 3: 1% Ir $/Al_2O_3$; 4: 1% Rh/Al_2O_3; 5: 1% Ru/Al_2O_3.

The formation of acetate (characterized here by the integrated absorbance of the 1574 cm^{-1} band) exhibited a maximum around 573 K and this value proved to be independent on the nature of the noble metal (Fig. 2A). The data presented on Fig. 2A and B clearly show that the surface centers for ethanol decomposition to CO are the metallic sites, while acetate formation occurs more probably on the supporting oxides [11]. It was earlier found that the acetate formed on the metal surfaces is stable at lower temperatures. For example in the case of Pt up to 450 K [25]. This observation is in harmony with our explanation. Similar spectral features can be observed on other oxide-supported noble metal catalysts, too.

The stability of most surface species formed in ethanol adsorption has only slightly changed in the presence of water at different temperatures. The bands of ethoxide species, however, became more stable when the adsorbed ethanol layer was treated with water.

After heating the C_2H_5OH layer on oxide-supported noble metal catalysts in vacuum ethanol, acetaldehyde, ethylene, methane and hydrogen appeared in the gas phase. Ethanol desorption showed a maximum at 423 K from all surfaces, which is in good agreement with IR data indicating that hydrogen bridge bonded ethanol was detected up to 423 K on these surfaces. The formation of H_2 started already at 323 K on all surfaces. The source of H_2 is the dehydrogenation of molecularly adsorbed ethanol at least up to 473 K. Above 473 K, no molecularly adsorbed ethanol was detected, so the decomposition of ethoxide led to the formation of H_2 and methane. Acetaldehyde (as the product of ethanol dehydrogenation, mainly observed on CeO_2-supported noble metals, see later) may undergo further decomposition below 500 K according to the reaction:

$$C_2H_4O_{(a)} \rightarrow CH_{4(g)} + CO_{(g)} \tag{1}$$

A slight increase in the amount of gas phase CO was detected accordingly on Pt/CeO_2 above 423 K.

During ethanol adsorption acyl groups can also form. The conversion of these species to form acetate can be explained by the equation:

$$CH_3CO_{(a)} + O_{(l)} \rightarrow CH_3COO_{(a)} \tag{2}$$

where $O_{(l)}$ designates a lattice oxygen atom.

It is also possible that the adsorbed aldehyde reacts with surface OH groups:

$$CH_3CHO_{(a)} + HO_{(a)} \rightarrow CH_3COO_{(a)} + H_2 \tag{3}$$

These reactions (1)–(3), however, do not occur on the clean supports.

3.2. Temperature programmed desorption and temperature programmed reaction of adsorbed ethanol

The temperature programmed desorption of ethanol was also studied in a flow system after the adsorption of ethanol at room temperature. The amount of adsorbed ethanol was nearly the same on all the metals on the same support. On noble metal/alumina sample and on the support alone, too, 14.4–16 mg/g, on ceria-supported samples 1.5–2.5 mg/g ethanol was adsorbed.

After C_2H_5OH adsorption on Al_2O_3 mainly C_2H_4 desorbed in TPD experiments, but small amounts of CH_3CHO, CO_2 and CH_4 were also detected. C_2H_4 appeared in a narrow peak ($T_{max} = 565$ K). CO_2 and acetaldehyde desorbed in a lower and broader temperature range, at 420–570 K, where the ethanol desorption was also detected.

When ethanol was adsorbed on noble metal/Al_2O_3 catalysts, the main products were CO_2 and CH_3CHO in the TPD experiments. Much less ethylene formed on noble metal/Al_2O_3 catalysts than on Al_2O_3 alone. In the low temperature range (up to 600 K) small amounts of diethyl ether, benzene, crotonaldehyde and ethyl acetate were also detected on Ru/Al_2O_3 and Ir/Al_2O_3 samples.

Interestingly, the addition of water to the carrier gas did not influence the feature of TPD experiments on noble metal/Al_2O_3 catalysts. For illustration the results obtained on 1% Ir/Al_2O_3 are presented on Fig. 3A and B. T_{max} values of CO_2, CH_4 and H_2 desorptions at higher temperature (above 600 K), however, depended significantly on the nature of the noble metals. TPD curves of CO_2 obtained on different noble metal/Al_2O_3 catalysts are collected on Fig. 4. The peak maxima for CO_2 desorption both in the absence (Fig. 4A) and in the presence

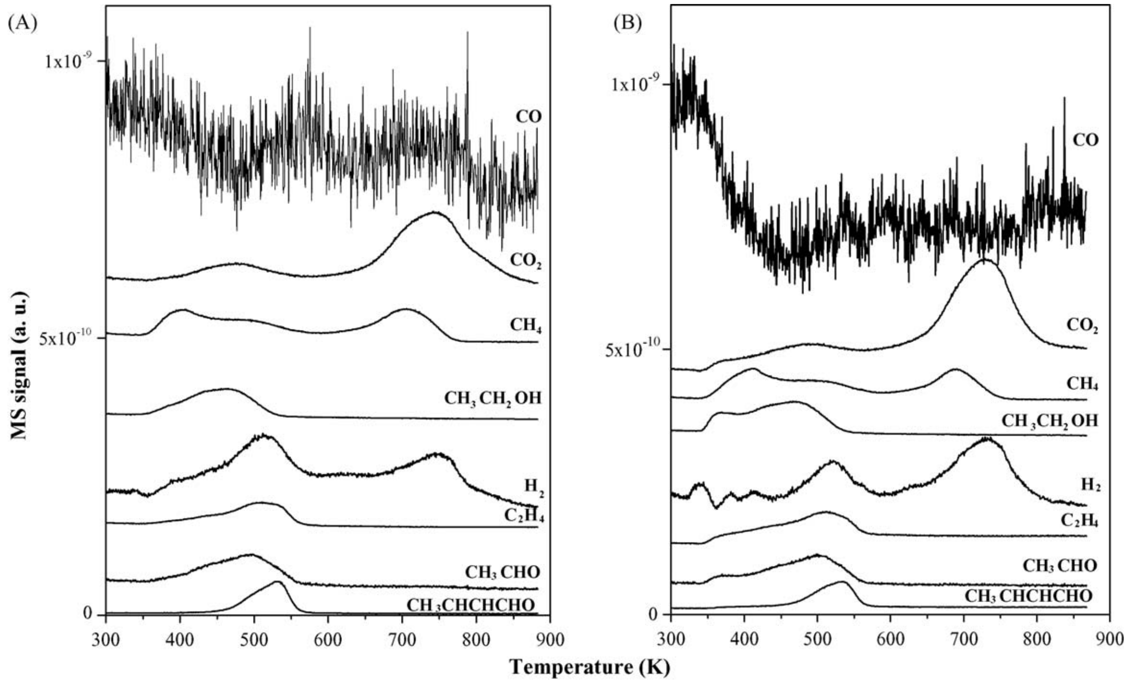

Fig. 3. Temperature programmed desorption of adsorbed ethanol (A) temperature programmed reaction of ethanol with water (B) on Ir/Al_2O_3.

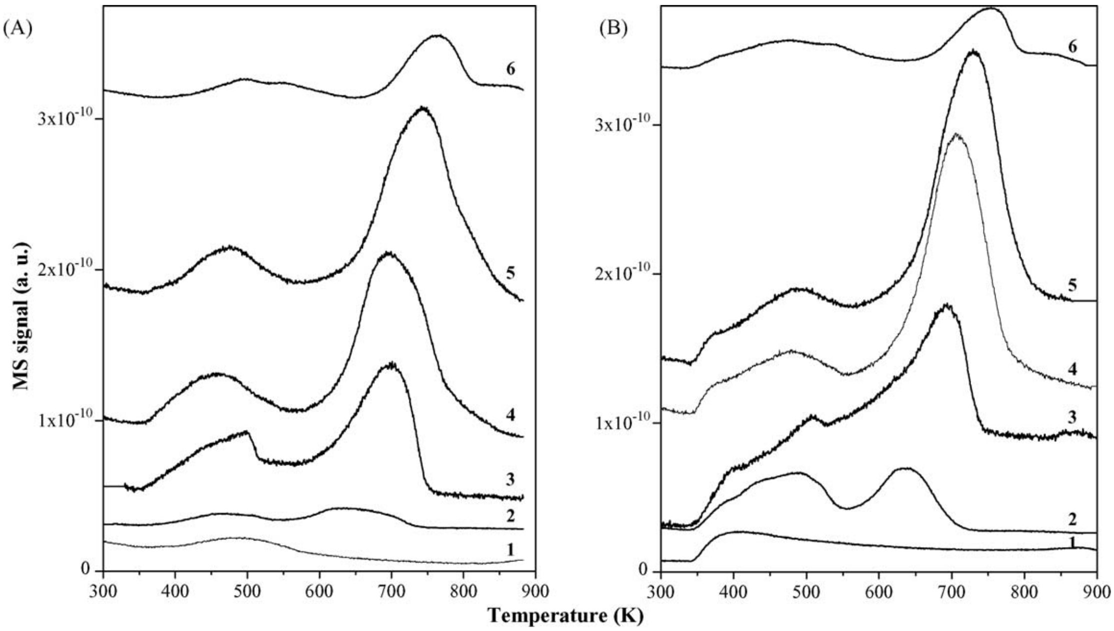

Fig. 4. CO_2 formation in the temperature programmed desorption of adsorbed ethanol (A) and in the temperature programmed reaction of adsorbed ethanol with water (B) on—1: Al_2O_3; 2: 1% Rh/Al_2O_3; 3: 1% Pd/Al_2O_3; 4: 1% Ru/Al_2O_3; 5: 1% Ir/Al_2O_3; 6: 1% Pt/Al_2O_3.

(Fig. 4B) of water shifted to higher temperature in the order of $Rh/Al_2O_3 < Pd/Al_2O_3 < Ru/Al_2O_3 < Ir/Al_2O_3 < Pt/Al_2O_3$.

Our IR data clearly show that the formation of acetate surface species is independent of the nature of the noble metals (Fig. 2). The nature of noble metal, however, has a significant effect on the CO_2 formation (Fig. 4). CO_2 is presumably the product of the high temperature decomposition of the surface acetate species. From these findings it can be concluded that acetate species formed on the supporting oxide migrate to the vicinity of the metal at high temperature and decompose there (reverse spillover). Cordi and Falconer [21] 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 decomposition products. They supposed that the carbon–carbon bond was cleft to form CO and CO_2 from α carbon and some of the resulting CH_3 groups were hydrogenated to CH_4. The amount of CH_4 was much smaller than that of $CO + CO_2$, the rest of the β carbon, however, remained on the surface.

When CeO_2 or CeO_2-supported noble metals were the adsorbents, the features of the TPD spectra were similar. In these cases the products formation was detected also in two stages during the TPD.

3.3. Decomposition of ethanol

The decomposition of ethanol was studied on alumina- and ceria-supported noble metal catalysts and (for comparison) on the supports at 723 K. The main features of the ethanol decomposition were nearly the same on the catalysts and on the supports. The ethanol conversion was more than 90% both on Al_2O_3 and alumina-supported metal catalysts and the activity of the samples were constant in time. In the decomposition mainly ethylene was formed ($S_{\text{ethylene}} > 95\%$), but on supported metal catalysts small amounts of other products were also observed. For example, in the presence of Ru/Al_2O_3 acetaldehyde ($S = 2.5\%$), CO, CO_2, H_2 and crotonaldehyde (1.5%) were detected.

The activity of the samples significantly decreased in time at 723 K on CeO_2-supported samples: it was only between 35 and 5% in the steady state. The highest activity was observed on Ir/CeO_2; the activity of the other samples decreased in the following order: $Pt/CeO_2 > Pd/CeO_2 > Rh/CeO_2 \geq Ru/CeO_2 \geq CeO_2$. The product distribution was completely different; on CeO_2 mainly ethylene was detected, on the ceria-supported metals, however, acetaldehyde was observed at the beginning of the reaction. The selectivity of acetaldehyde on Pt, Rh and Ru containing samples remained constantly high during the reaction, but on Ir/CeO_2 and on Pd/CeO_2 it decreased in time while the selectivity of ethylene and diethyl ether formation increased significantly.

3.4. The reaction of ethanol + water

The reaction of ethanol with water was studied in flow reactor at 723 K. The ethanol conversion on Al_2O_3 support was high (about 95%) and stable. The main product was ethylene, but at the beginning of the reaction acetaldehyde ($S = 14\%$) and H_2 ($S = 3\%$) were also formed. When the reaction was carried out on alumina-supported noble metal catalysts the conversion was above 90% in all cases and it was also nearly constant. The product selectivity, however, remarkably changed in time. On Fig. 5A the time dependence of selectivities on 1% Ir/Al_2O_3 is shown. In the first minutes of the reaction CO, CO_2 and H_2 selectivities decreased but that of ethylene increased. We identified a number of other products (diethyl ether, benzene, ethyl acetate, crotonaldehyde, acetone, ethane); all of them could form in different secondary reactions. The selectivities of

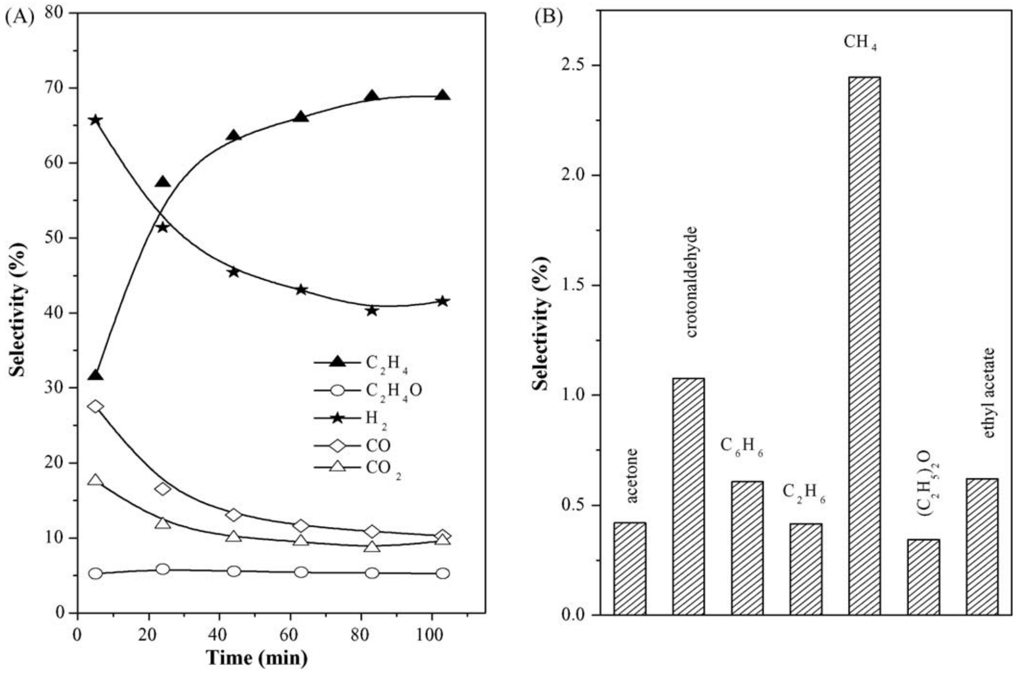

Fig. 5. Product selectivities in the reaction of ethanol + water (A) and selectivities of the products formed in smaller quantities determined in the 110th min of the reaction (B) on 1% Ir/Al_2O_3 at 723 K.

these minor products determined in the 110th min of the reaction were depicted on Fig. 5B.

On 1% Ir/CeO_2 the conversion considerably decreased in time. The main products (C_2H_4, H_2, CO and CO_2) formed in the reaction of ethanol + water with smaller selectivities (Fig. 6A) than on 1% Ir/Al_2O_3. The selectivities of acetaldehyde and other products formed in secondary reactions, however, were much higher on Ir/CeO_2 (Fig. 6B).

For better comparison the H_2 and C_2H_4 selectivities were collected for Al_2O_3-supported noble metals (Fig. 7) and conversion, H_2 and CH_3CHO selectivity data for CeO_2-supported noble metals (Fig. 8). It was found that in all cases the hydrogen selectivity decreased but ethylene and acetaldehyde selectivity increased in time. The highest changes were observed on Pt/Al_2O_3 where the hydrogen selectivity was near 100% in the first minutes of the reaction, but after 60 min it was

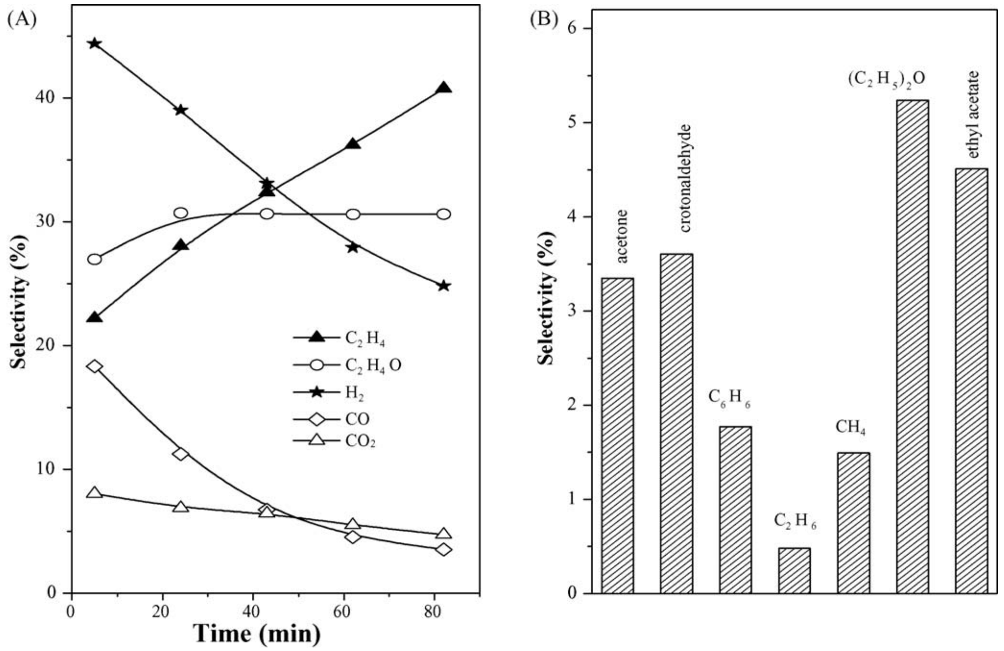

Fig. 6. Product selectivities in the reaction of ethanol + water (A) and selectivities of the products formed in smaller quantities determined in the 110th min of the reaction (B) on 1% Ir/CeO_2 at 723 K.

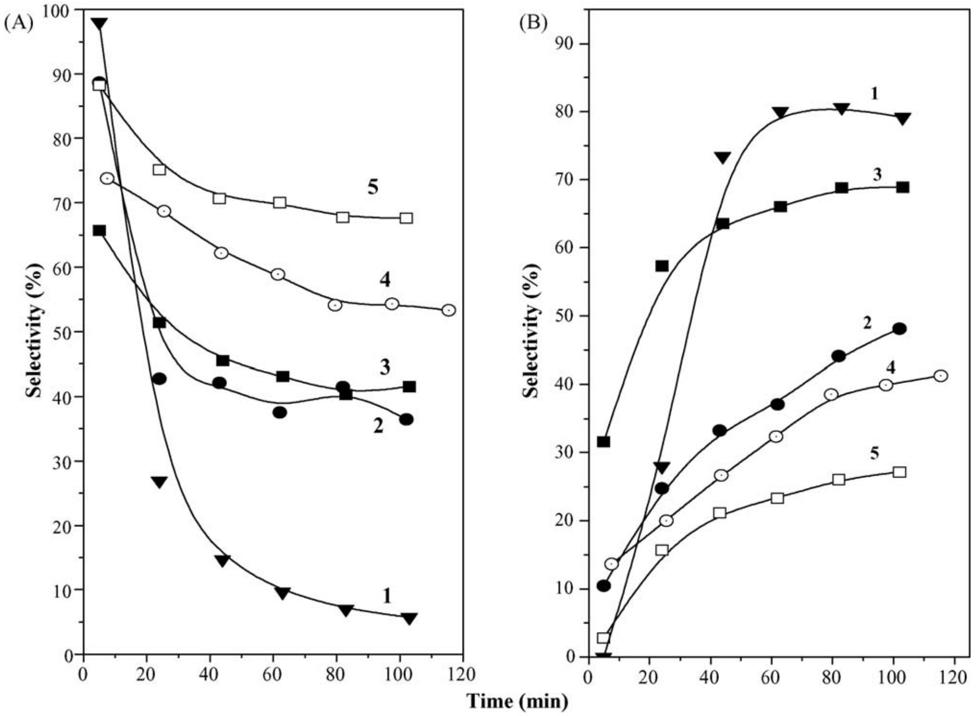

Fig. 7. Selectivity of H_2 (A) and of ethylene (B) in the reaction of ethanol + water at 723 K on—1: 1% Pt/Al_2O_3; 2: 1% Pd/Al_2O_3; 3: 1% Ir/Al_2O_3; 4: 1% Rh/Al_2O_3; 5: 1% Ru/Al_2O_3.

only about 10%. In contrast with this observation, on alumina-supported Ru or Rh the selectivity changes were only about 20%. Ethylene selectivity varied oppositely, on Pt/Al_2O_3 in the first minutes ethylene formed only in traces but after one hour the C_2H_4 selectivity was more than 80%. Similar features were observed on CeO_2-supported metals, in these cases not only the ethylene but also the acetaldehyde selectivity increased in time.

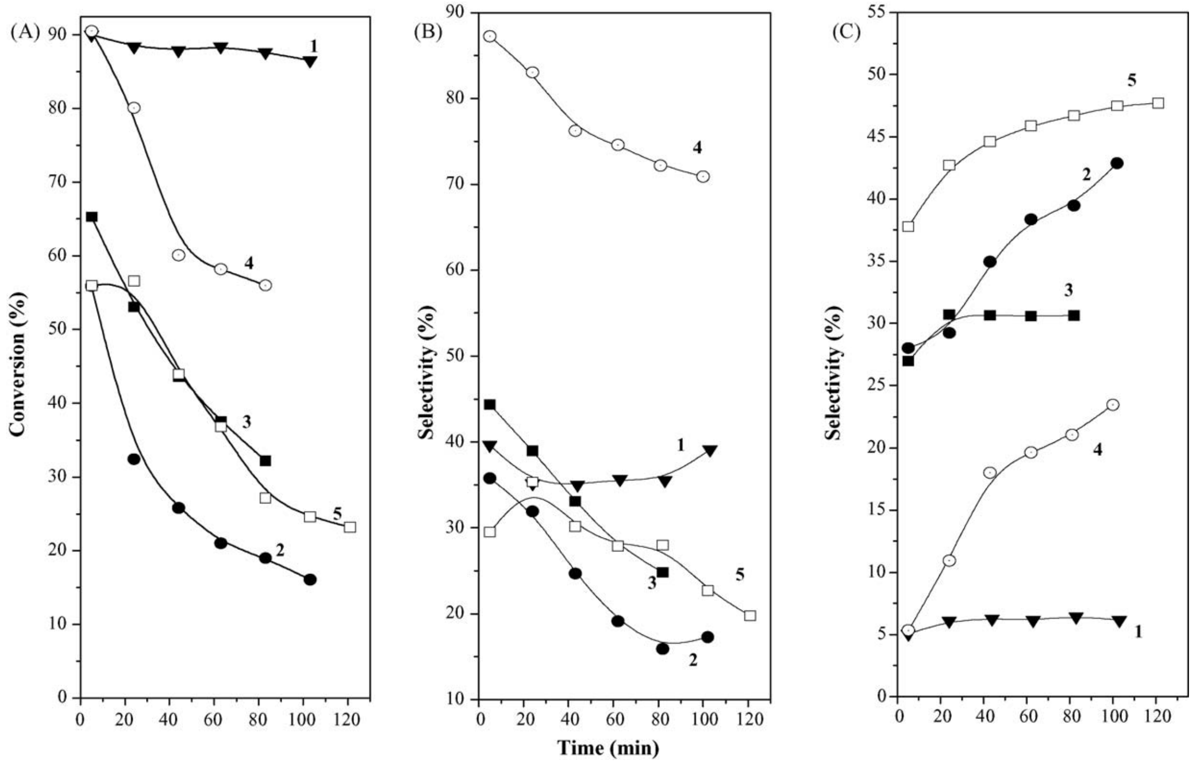

Fig. 8. Conversion (A), selectivity of H_2 (B) and acetaldehyde (C) in the reaction of ethanol + water at 723 K on—1: 1% Pt/CeO_2; 2: 1% Pd/CeO_2; 3: 1% Ir/CeO_2; 4: 1% Rh/CeO_2; 5: 1% Ru/CeO_2.

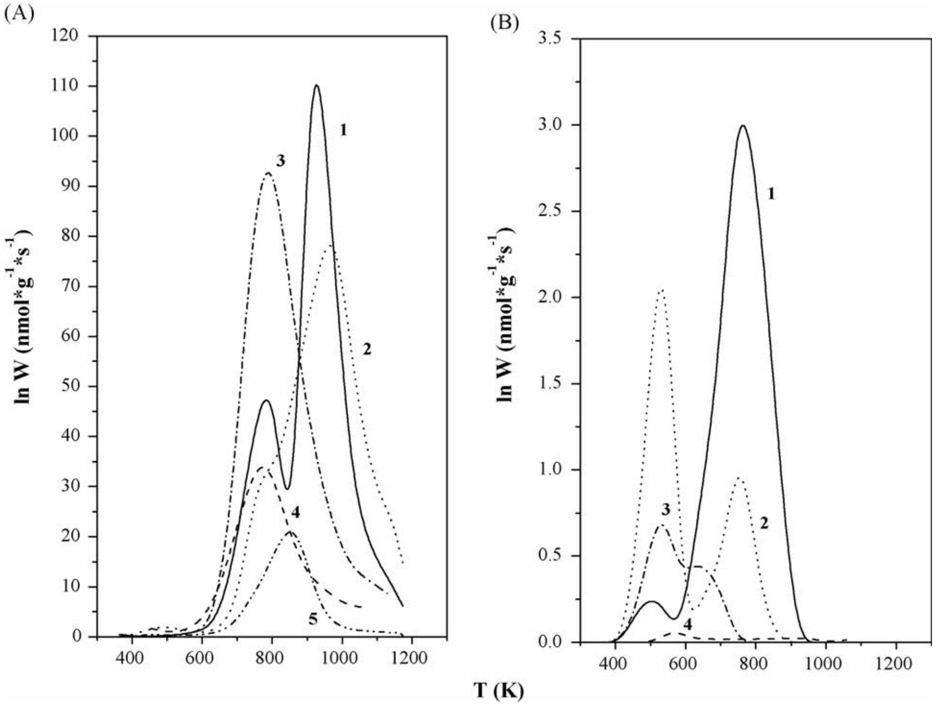

Fig. 9. Temperature programmed reaction of surface carbonaceous deposit formed in the reaction of ethanol + water at 723 K for 110 min on Al_2O_3-supported noble metals: (A) CH_4 and (B) C_2H_6 formation; 1: 1% Pt/Al_2O_3; 2: 1% Pd/Al_2O_3; 3: 1% Ir/Al_2O_3; 4: 1% Rh/Al_2O_3; 5: 1% Ru/Al_2O_3.

Taking into account that H_2 selectivity decreased in the course of reaction we can state that the metal surface (the active surface site for the dehydrogenation of ethanol) is poisoned, consequently the efficiency of the support comes to the forefront. The IR measurements clearly show that at the reaction temperature only acetate species are on the surface. The TPD experiments revealed that the high temperature desorption stage of adsorbed ethanol depends on the metal. On Rh/Al_2O_3 the acetate species decompose at the lowest temperature and this sample has one of the highest hydrogen selectivity. On Pt/Al_2O_3 the situation is the opposite. We have stated that acetate is located primarily on the support but these groups can poison the reaction. On the basis of these observations we may assume that the acetate groups hindered the migration of ethoxide to the metal, which may cause the decrease of hydrogen formation on the metal sites.

After the catalytic reaction of the ethanol + water mixture at 723 K, the amount and the reactivity of surface carbonaceous deposit was determined with temperature programmed reaction. On Al_2O_3-supported noble metals (Fig. 9) during the TPR not only CH_4 but C_2H_6 was formed, too. The surface carbonaceous deposit reacts with hydrogen between 600 and 800 K. On Pt/Al_2O_3 and Pd/Al_2O_3, however, the existence of a less active carbonaceous deposit producing CH_4 at T_{max} = 920–970 K was also experienced. On Ru/Al_2O_3 and Rh/Al_2O_3 significantly less amount of methane was detected. We cannot rule out that acetate species are still present at these temperatures, after all C_2H_6 was also formed. Interestingly, the temperature of the first appearance was much lower for C_2H_6 than for CH_4. On Pt/Al_2O_3 and Pd/Al_2O_3 another peak around 770 K appeared on the curve of C_2H_6 formation, which agrees well with the first T_{max} (770–830 K) of CH_4 TPR peaks. No C_2H_6 formation was observed on 1% Rh/Al_2O_3.

Similar features were observed for CeO_2-supported noble metals with two maxima (590 and 910 K) on the TPD curve of methane. Only traces of C_2H_6 were detected in these cases.

4. Conclusions

1. Ethanol adsorbs molecularly (to form hydrogen-bonded weakly adsorbed species and to produce strongly adsorbed molecular ethanol on the Lewis-sites of the supports) and disassociatively (forming ethoxide and proton) on Al_2O_3- and CeO_2-supported noble metal catalysts.
2. High-temperature treatment of the adsorbed species caused the formation of surface acetate species on the supports. The presence of water lowered the temperature of the appearance of acetate species, and increased the stability of monodentate ethoxide species.
3. Dehydrogenation of ethanol up to 423 K proceeded on the metal part of the catalysts producing H_2 and carbonyl–hydride surface species. At higher temperature the decomposition of ethoxide (at the metal/support interface) led to the formation of H_2.
4. In the high-temperature reaction of ethanol and ethanol–water mixture the initial H_2 selectivity decreased in the course of the reaction. Presumably the highly stable acetate species hindered the migration of ethoxide species, thus the H_2 formation in the decomposition of ethoxide at the metal/support perimeter.
5. The reducibility of the supports caused differencies in the catalytic data: at the beginning of the reaction the main

products were H_2 and ethylene on Al_2O_3-supported noble metal catalysts, on noble metals supported on reducible CeO_2, however, H_2 and acetaldehyde formed in the highest amounts in the initial period of the reaction.

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