Cobalt supported on zirconia and sulfated zirconia
II. Reactivity of adsorbed NO_x compounds toward methane

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Abstract

In order to evaluate the effect of sulfate ions in zirconia-supported cobalt catalysts on the reactivity of adsorbed NO_x species toward methane, experiments involving the interaction of the hydrocarbon with NO_x-free and NO_x-precovered catalysts are performed. The nitrate species formed at room-temperature adsorption of NO/O_2 over the CoO_x/ZrO_2 catalysts are inert toward the methane in the 573–723 K temperature range. Over NO_x-precovered CoO_x/SO_4^{2-}–ZrO_2 catalysts, oxidation of the hydrocarbon starts at 573–623 K with the participation of reactive nitro-nitrato species coordinated to cobalt sites. It is proposed that in the catalytic reduction of NO over the sulfated cobalt catalysts, the activation of methane occurs on cobalt sites and the products of the latter process—formate species and formic acid—are key intermediates capable of selectively reducing the nitro-nitrato species.
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1. Introduction

Catalytic systems based on cobalt supported on sulfated zirconia exhibit high activity and selectivity in the reduction of nitrogen oxide with propane [1] and methane [2] in excess oxygen. The role of the sulfate ions is in the stabilization of the +2 oxidation state of the active component and prevention of the formation of Co_3O_4 clusters, which are active for hydrocarbon combustion [1,2]. According to other authors [3] the presence of sulfate ions in cobalt–zirconia catalysts hinders the formation of H–N–C–O deposit when methane interacts with the NO_x-precovered catalyst.

In general, the mechanism of selective catalytic reduction of nitrogen oxides in excess oxygen on various oxide catalysts involves the interaction of strongly adsorbed NO_x^- species (x is 2 or 3) with the hydrocarbon [3–9]. The results of our previous investigation [7] have shown that the presence of sulfate ions in zirconia-supported copper(II) catalysts strongly modifies the reactivity of adsorbed NO_x species toward saturated long-chain hydrocarbon (decane). The aim of this paper is to investigate the effect of

sulfate ions in zirconia-supported cobalt catalysts on the reactivity of adsorbed NO_x species toward methane. The catalysts studied contain 2.8 and 5 wt% of cobalt supported on sulfated zirconia with the surface concentration of the SO_4^{2-} ions close to the monolayer. Parallel experiments with sulfate-free catalysts containing the same amount of cobalt have also been carried out. The structural characteristics of the catalysts studied and the results on the identification of the NO_x species obtained upon adsorption of NO and its coadsorption with oxygen are reported in the first part of this paper [10].

2. Experimental

2.1. Samples

The samples were obtained by impregnation of zirconia and sulfated zirconia with an aqueous solution of cobalt(II) acetate. The method of preparation of these materials was reported previously [10]. The samples with an analytical cobalt content of 2.6 and 4.8 wt% were denoted according to their nominal content by 2.8CoZ and 5CoZ, respectively, whereas for the materials with an analytical composition

of 2.7 and 5.1 wt% of Co supported on sulfated zirconia (3.9 wt% analytical content of sulfate ions) the notations 2.8 and 5CoSZ were used (2.8 and 5 correspond to the nominal weight percentage of Co).

According to the chemical analysis, the sulfate content of the catalysts used in the experiments remains at the level of the fresh samples.

2.2. Infrared spectroscopy

The FT-IR spectra were recorded with a Bomem-MB102 (Hartmann & Braun) FT-IR spectrometer at a spectral resolution of 4 cm^{-1} (128 scans). Self-supporting pellets were prepared from the samples and treated in situ in the IR cell connected to a vacuum/adsorption apparatus [10]. The activation procedure of the catalysts was described previously [10]. The spectra of the samples that had been subjected to elevated temperatures were recorded after the IR cell had been cooled to room temperature. All the spectra presented were obtained by subtraction of the corresponding background reference.

In order to evaluate the ability of the catalyst containing preadsorbed NO_x species for methane activation, the following experiments were performed:

(i) "Blank NO_x" experiment involving formation of NO_x adsorbed species by NO/O_2 coadsorption, followed by evacuation at room temperature and heating of the closed IR cell containing the NO_x-precovered catalyst at 623 and 723 K, respectively;

(ii) "Blank CH_4" experiment consisting of the interaction of the activated catalyst with methane at elevated temperatures;

(iii) The interaction of methane with the catalyst containing preadsorbed NO_x species at various temperatures.

The ability of the NO_x-precovered catalysts to activate the hydrocarbon can be evaluated by measuring the temperature dependence of the consumption of the adsorbed nitro–nitrato species in a methane atmosphere. If the catalyst contains NO_x species that can be reduced with methane, their surface concentration, after interaction with the hydrocarbon at elevated temperatures, should be lower than that obtained in the blank NO_x experiment. In the absence of an interaction, the spectra detected should be similar to those obtained in the blank NO_x experiments. Since the NO_x species formed on the sulfated catalyst containing 5 wt% of cobalt display the highest reactivity, detailed data are reported for this sample and compared with those for the sulfate-free 5CoZ sample.

3. Results

3.1. CoOx/ZrO2 catalysts: blank NOx experiment

Coadsorption of NO and O_2 (1.33 kPa, NO:O_2 = 1:1) on the 5CoZ catalyst for 30 min followed by evacuation at room temperature for 10 min (Fig. 1, spectrum a) gives rise to strong absorption in the 1650–1000 cm^{-1} region due to various types of nitrate species [10]. The band at 1930 cm^{-1} corresponds to the ν(NO)-stretching vibration of a cobalt(II) nitrosyl-nitrato complex, ON–Co^{2+}–NO_3^- [10]. Heating the closed IR cell (Fig. 1) for 30 min at 623 (spectrum b) and 723 K (spectrum c) causes a decrease in the intensities of the nitrate bands. At the same time, new bands at 1448 and 1424 cm^{-1} are detected, which are assigned to the ν(N=O)-stretching vibration of two types of monodentate nitrito species [7]. These bands grow with an increase in the temperature at the expense of the nitrate bands. The spectrum taken after heating at 773 K shows, in addition to the nitrito species, the presence of bidentate nitrates (at 1589 cm^{-1} with a shoulder at 1610, 1234, and 1004 cm^{-1}) and bridged nitro species (at 1542 and 1187 cm^{-1} [10]). The intensity of the nitrosyl band at 1930 cm^{-1} increases and shifts to 1872 cm^{-1}. The latter absorption corresponds to the ν(NO) mode of the Co^{2+}–NO species [10] and shows that transformation of cobalt(II) nitrosyl-nitrato complex into cobalt(II) mononitrosyl has occurred. The decrease in the intensities of the bands due to H-bonded OH groups indicates that some of the altered isolated hydroxyls are restored (reduced intensity of the negative band at 3680 cm^{-1}). According to the spectra in Fig. 1, the nitro and nitrito species are formed mainly by the decomposition of the bridged and monodentate nitrates. In this process, NO is evolved producing cobalt(II) mononitrosyls at room temperature, after the IR cell is cooled for recording the spectra.
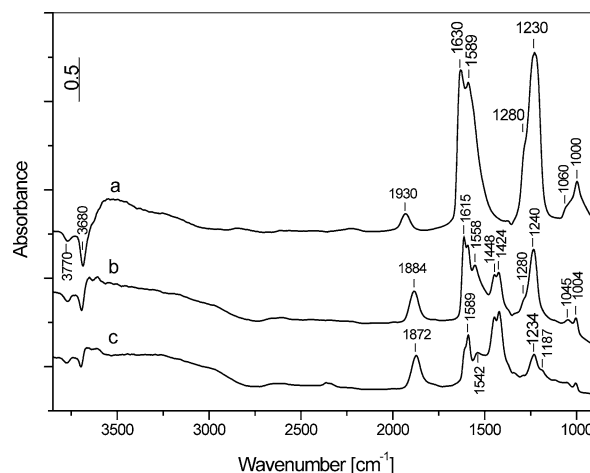

Fig. 1. FT-IR spectra of the 5CoZ catalyst taken after adsorption of NO/O_2 mixture (1.33 kPa, NO:O_2 = 1:1) for 30 min at room temperature followed by evacuation for 15 min (a) and after heating of the closed IR cell for 30 min at 623 K (b) and 723 K (c). The spectrum of the activated sample is used as a background reference.

The nitrate species formed on the 2.8CoZ sample display analogous behavior.

3.2. CoO$_x$/ZrO$_2$ catalyst: blank CH$_4$ experiment

Heating of the activated 5CoZ sample at 573 K (Fig. 2, spectrum a) and 723 K (Fig. 2, spectrum b) in presence of 6.7 kPa of CH$_4$ leads to the appearance of bands in the carbonate region, which are attributed [11] to monodentate (1436 and 1418 cm^{-1}) and bidentate carbonates (1545 cm^{-1}). The negative band at 1356 cm^{-1} corresponds to adsorbed CO$_2$ arising during the activation of the sample [10]. The increased intensities of the bands at 3750 and 3690 cm^{-1} (due to the Zr^{4+}–OH groups) and the broad absorption between 3600 and 2800 cm^{-1} suggest that water is formed, which adsorbs dissociatively. The sharp band at 3019 cm^{-1} is due to the ν_3 mode of the gaseous methane. The weak absorption at 1848 cm^{-1} is characteristic of the ν(CO) mode of bridged carbonyl species adsorbed on metallic cobalt sites [12]. These experimental facts show that the oxidation of methane has occurred. Since the experiment is performed in absence of gaseous oxygen, the oxidation of the hydrocarbon is caused by surface oxide ions coordinated to the cobalt ions, which leads to reduction of the latter.

In the case of the 2.8CoZ sample, no bands that can be attributed to reaction products are detected, indicating that this material is inert toward the oxidation of methane in the absence of molecular oxygen.

3.3. Interaction of methane with the NO$_x$-precovered CoO$_x$/ZrO$_2$ catalysts

Fig. 3A shows the FT-IR spectrum of the 5CoZ catalyst obtained after introduction of 1.33 kPa of NO/O$_2$ mixture (NO:O$_2$ = 1:1) for 30 min followed by evacuation at room temperature for 10 min and subsequent addition of 6.7 kPa of methane (spectrum a). The closed IR cell, containing the catalyst treated in this way, was heated at various temperatures (spectra b, c, and d). Heating of the sample at 573 and 623 K leads mainly to the conversion of the nitrates into monodentate nitrito species (bands at 1449 and 1415 cm^{-1} in the subtraction spectrum c-b in Fig. 3B). The increase in the intensity of the nitrosyl band at 1930 cm^{-1} and its shift to 1875 cm^{-1} (Fig. 3A, spectrum c, see also subtraction spectrum c-b) show that the cobalt(II) nitrosyl-nitrato complex converts into Co^{2+}–NO species due to the loss of a coordinated nitrate ion. The decrease in the intensities of the bands in the ν(OH)-stretching region suggests that there is no oxidation of the methane after heating at 623 K (assuming formation of water). The cause of this decrease is the same as in the blank NO$_x$ experiment: it is due to the restoration of altered isolated hydroxyls. Increasing the temperature to 723 K results in a considerable increase in the intensities of the nitrito bands. At the same time, enhancement in the absorption in the region of the H-bonded OH groups relative to that observed at 623 K is detected. By a comparison with spectrum c in Fig. 1, it can be concluded that the broad absorption with a maximum at 1606 cm^{-1} corresponds to superimposed bands due to the bending mode of adsorbed water and ν(N=O)-stretching vibrations of residual bidentate nitrates. This is supported by the subtraction
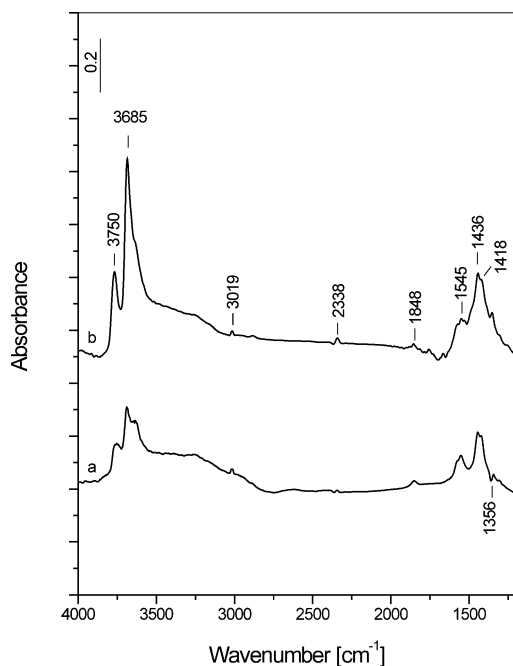

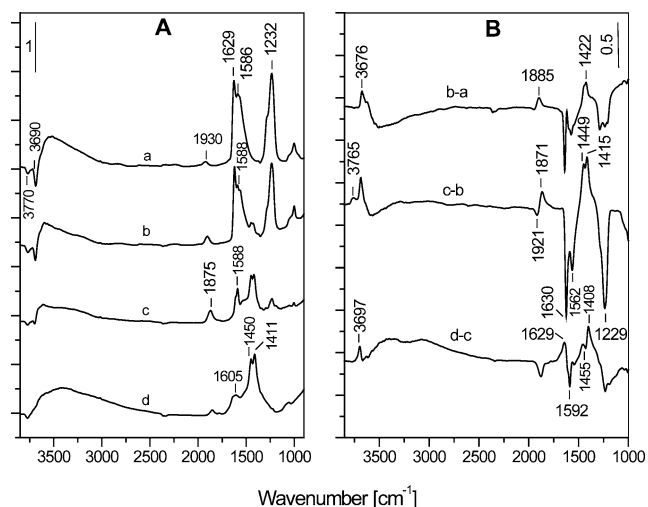Fig. 2. FT-IR spectrum of the 5CoZ catalyst taken after addition of methane (6.7 kPa) at room temperature followed by heating of the closed IR cell for 30 min at 573 K (a) and 723 K (b). The spectrum of the activated sample is used as a background reference.

Fig. 3. (A) FT-IR spectra of the 5CoZ catalyst taken after adsorption of NO/O$_2$ mixture (1.33 kPa, NO:O$_2$ = 1:1) at room temperature followed by evacuation for 10 min and addition of 6.7 kPa of methane (a) and after heating of the closed IR cell for 30 min at 573 K (b), 623 K (c), and 723 K (d). The spectrum of the activated sample is used as a background reference. (B) FT-IR subtraction spectra of the catalyst 5CoSZ obtained from the spectra shown in panel A.
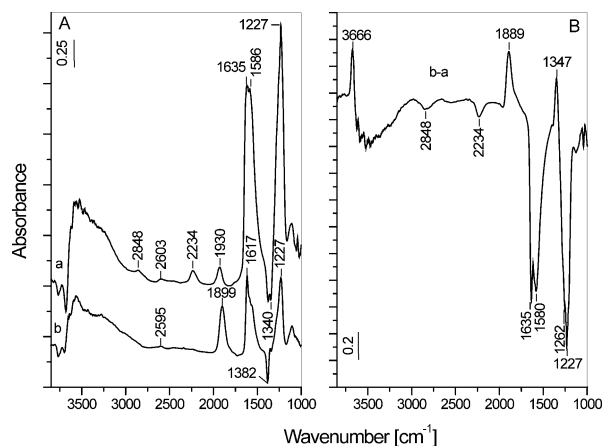
Fig. 4. FT-IR spectra of the 5CoSZ catalyst taken after adsorption of NO/O$_2$ mixture (1.33 kPa, NO:O$_2$ = 1:1) for 30 min at room temperature followed by evacuation for 15 min (a) and after heating of the closed IR cell for 30 min at 623 K (b). The spectrum of the activated sample is used as a background reference.

spectrum d-c in Fig. 3B. Obviously, some oxidation of the methane has occurred. The characteristic absorption bands of the other products of the oxidation, such as carbonates, are difficult to distinguish because of overlap with the nitrito bands (compare with Figs. 1 and 2).

The results of the blank CH$_4$ experiment show that the oxidation of methane over the NO$_x$-free 5CoZ sample takes place already at 573 K. Contrary to this, the oxidation of methane on the NO$_x$-precovered catalyst becomes noticeable at a much higher temperature (723 K). This difference shows that the nitrate species formed at room temperature on the surface of the 5CoZ catalyst are unreactive and they block the active sites for methane oxidation. With an increasing temperature, the nitrates undergo transformation into nitrito species, thus liberating active sites for methane oxidation. By heating at 723 K, the number of the latter is enough in order for the oxidation of CH$_4$ to be detected.

No interaction between the methane and the nitrate species on the 2.8CoZ sample is observed in the 573–723 K temperature range. The increase in the temperature causes continuous a decrease in the intensities of the bands in the ν(OH)-stretching region (positive and negative) and transformation of the surface nitrates into NO$_2^-$ species.

3.4. CoO$_x$/SO$_4^{2-}$–ZrO$_2$ catalysts: blank NO$_x$ experiment

The behavior of the surface NO$_x$ species on both 2.8- and 5CoSZ samples upon heating of the closed IR cell at various temperatures is similar. This is illustrated with the spectra of the 5CoZS catalyst. The preadsorbed NO$_x$ species were obtained by keeping the sample in contact with 1.33 kPa of NO/O$_2$ gas mixture (NO:O$_2$ = 1:1) for 30 min followed by evacuation for 10 min at room temperature (Fig. 4A, spectrum a). Heating the closed IR cell for 30 min at 623 K (Fig. 4A, spectrum b) results in a decrease in the intensities of the unresolved bands in the 1630–1550 cm^{-1} region and

1227 cm^{-1} due to nitro-nitrato species [10]. The subtraction spectrum b-a in Fig. 4B shows that this decrease is due to the disappearance of the bridged nitrates characterized by fundamental bands at 1635 and 1227 cm^{-1} and combination bands at 2848 and 2235 cm^{-1} [10]. The NO$_x$ species with absorption bands at 1580 and 1262 cm^{-1} (assigned to monodentate nitrates) desorb as well. The remaining bands in the fundamental region with maxima at 1617 and 1227 cm^{-1} and the weak combination band at 2595 cm^{-1} (Fig. 4A, spectrum b) correspond to bidentate nitrates [10], which possess high thermal stability and do not decompose under the conditions of the experiment. The low-frequency shoulders at about 1580 and 1560 cm^{-1} are probably due to the ν_{as}(NO$_2$) modes of bridged nitro species, which appear at elevated temperatures as a result of the transformation of the bidentate nitrates [10]. At the same time the band at 1930 cm^{-1} due to the ν(NO)-stretching mode of the mixed cobalt(II) nitrosyl-nitrato complex shifts to 1899 cm^{-1} increasing in intensity. As in the case of the 5CoZ catalyst, the increase in the intensity of the latter band indicates that the unstable nitrate species decompose producing NO, which forms Co^{2+}–NO nitrosyls during cooling of the IR cell to room temperature. The heating causes partial restoration of the isolated OH groups altered during the NO/O$_2$ adsorption and the regeneration of perturbed sulfate groups characterized by the ν(S=O) mode at 1340 cm^{-1}. The negative band at 1382 cm^{-1} indicates that altered SO$_4^{2-}$ groups are still present.

3.5. CoO$_x$/SO$_4^{2-}$–ZrO$_2$ catalysts: blank CH$_4$ experiment

After activation of the 5CoZS catalyst, 6.7 kPa of methane was added to the IR cell. Heating the closed IR cell at temperatures ranging from 573 to 723 K for 30 min (Fig. 5, spectra a, b, and c) leads to the appearance of a growing absorption in the carbonate-carboxylate region. The band at 1570–1565 cm^{-1} and the absorption between 2950 and 2600 cm^{-1} are typical of formate ions [7,8,11,14], whereas the bands at 3667 and 1650 cm^{-1} are assigned to ν(OH) and ν(C=O)-stretching modes, respectively, of adsorbed formic acid [7, 8,11,14]. These facts lead to the conclusion that under the conditions described, partial oxidation of the methane has occurred. Increasing the temperature to 723 K causes a noticeable increase of the intensity of the band at 1616 cm^{-1} and an enhancement in the absorption in the 3500–3000 cm^{-1} region. At the same time, the band at 3667 cm^{-1} (due to the ν(OH)-stretching mode of adsorbed formic acid) appears in the spectrum with reduced intensity and a new band at 1896 cm^{-1} is detected. The latter absorption, according to the literature data [12,15], is assigned to ν(CO)-stretching vibration of linear or bridged carbonyls of cobalt in a zero oxidation state. Based on these facts, it is concluded that at 723 K the decomposition of formic acid to CO and H$_2$O prevails. The considerably high decomposition temperature is consistent with the observed high thermal stability of formates produced by alkane adsorption [16].
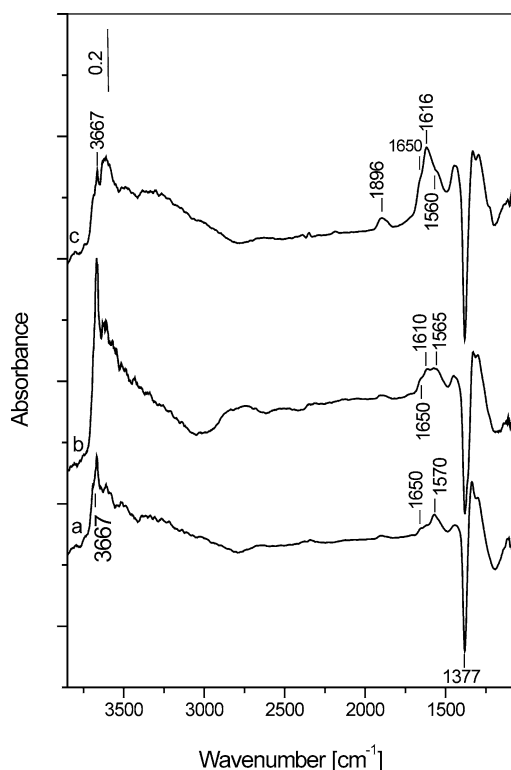
Fig. 5. FT-IR spectra of the 5CoSZ catalyst taken after addition of methane (6.7 kPa) at room temperature followed by heating of the closed IR cell for 30 min at 573 K (a), 623 K (c), and 723 K (b). The spectrum of the activated sample is used as a background reference.

The oxidation of methane in the presence of the 2.8CoSZ sample starts at somewhat higher temperature (623 K). Again, products of partial oxidation are detected. However, their amount is lower than that on the 5CoSZ catalyst.

It should be noted that no interaction between the methane and sulfated zirconia is observed after heating up to 723 K. Under these conditions, the sulfate bands remain with practically unchanged intensities. Therefore, it is concluded that the oxidation of the methane on the sulfated cobalt catalysts is caused by surface oxide ions coordinated to the Co^{n+} sites. The negative band at 1377 cm^{-1} observed in all spectra in Fig. 5 is due to perturbed sulfate groups by the adsorbed species.

3.6. Interaction of methane with the NO_x-precovered CoO_x/SO_4^{2-}–ZrO_2 catalysts

Previously, it has been shown [10] that part of the bidentate nitrates formed on the 5CoSZ catalyst transform to NO_2^- (nitro) species upon evacuation at 373 K. It is of importance to investigate the reactivity of adsorbed NO_x species toward methane that are stable at higher temperatures. Therefore, stable nitro-nitrato species preadsorbed on the 5CoSZ catalyst were formed by keeping the sample in contact with 1.33 kPa of NO/O_2 gas mixture ($NO:O_2 = 1:1$) for 30 min at room temperature followed by evacuation for 10 min. Then the closed IR cell was heated for 30 min at 623 K and after cooling to room temperature, 6.7 kPa of methane was added (Fig. 6A, spectrum a). The rise in the temperature from room temperature to 623 K for 30 min (Fig. 6A, spectrum b) leads to a decrease in the intensities of
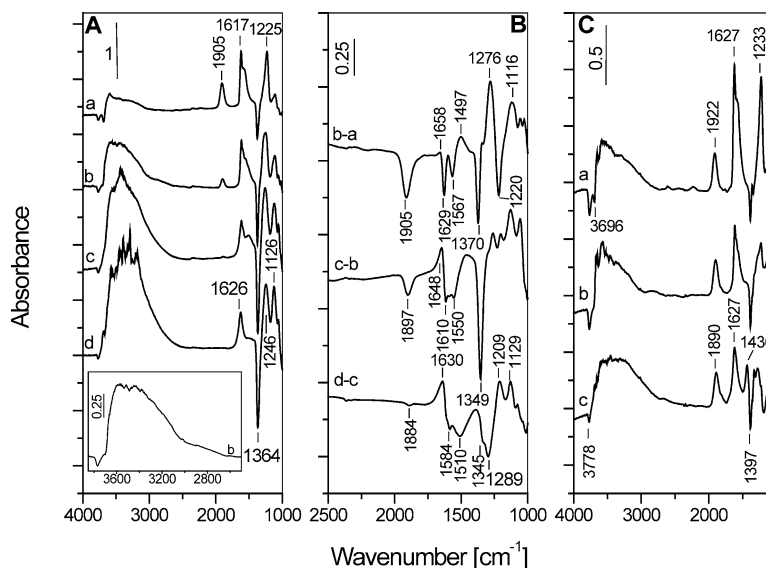

Fig. 6. (A) FT-IR spectra of the catalyst 5CoSZ taken after adsorption of NO/O_2 mixture (1.33 kPa, $NO:O_2 = 1:1$) at room temperature followed by evacuation for 15 min and heating of the closed IR cell for 30 min at 623 K and subsequent addition of 6.7 kPa of methane after cooling to room temperature (a), and after heating of the closed IR cell (containing methane) for 30 min at 623 K (b), 673 K (c), and 723 K (d). The spectra in Figs. 5 and 6A are obtained using the same sample pellet. (B) FT-IR subtraction spectra of the catalyst 5CoSZ obtained from the spectra shown in panel A. (C) FT-IR spectra of the catalyst 2.8CoSZ taken after adsorption of NO/O_2 mixture (1.33 kPa, $NO:O_2 = 1:1$) at room temperature followed by evacuation for 15 min and heating of the closed IR cell for 30 min at 623 K and subsequent addition of 6.7 kPa of methane after cooling to room temperature (a), and after heating of the closed IR cell (containing methane) for 30 min at 623 K (b) and 723 K (c). The spectra of the activated samples are used as a background reference.

the bands corresponding to adsorbed NO (1905 cm^{-1}) and nitro-nitrato species. The subtraction spectrum b-a in Fig. 6B shows that new bands at 1658 and 1497 cm^{-1} are formed. The former band (partially masked by the negative band at 1629 cm^{-1}) is assigned to carboxylic acid coordinately bonded through the carbonyl oxygen to a Lewis acid site [7, 8,11,14]. The presence of a very weak positive absorption in the 2900–2600 cm^{-1} region (see the inset in Fig. 6A) characteristic of formate moiety [7,8,11,13,14] suggests formation of a formic acid. The band at 1497 cm^{-1} can be attributed to a $\nu_{as}(CO_2)$ mode of monodentate carbonate species [11]. A further increase in the temperature to 673 K (Fig. 6A, spectrum c) leads to a significant decrease in the concentration of the nitro-nitrato species, which is accompanied by an additional increase in the absorption in the $\nu(OH)$ stretching region. The positive absorption at 1648 cm^{-1} (visible in the subtraction spectrum c-b in Fig. 6B) is assigned to superimposed bands due to $\nu(C=O)$-stretching vibrations of formic acid and $\delta(HOH)$ modes of adsorbed water molecules. Heating at 723 K causes complete consumption of the adsorbed nitro-nitrato species and disappearance of the formic acid and Co^{2+}–NO nitrosyls. The spectrum taken under these conditions (Fig. 6A, spectrum d) contains strong positive absorption between 3600 and 3000 cm^{-1} and a band at 1626 cm^{-1} corresponding to adsorbed water molecules and a negative band at 1364 cm^{-1} due to water-perturbed sulfate groups [17] (positive bands at 1246 and 1126 cm^{-1}). The subtraction spectrum d-c in Fig. 6B contains positive unresolved absorption with the maximum at 1630 cm^{-1} due to the bending mode of adsorbed water and negative bands in the nitro-nitrato region. These results indicate that interaction between the methane and the NO_x species adsorbed on the surface of the catalyst has occurred. The reactivity of the latter depends on the temperature. The species characterized by the bands at 1629 and 1220 cm^{-1} (bridged nitrates) and at 1567 cm^{-1} (most probably monodentate nitrates) possess the highest reactivity toward the methane and disappear from the spectrum after heating at 623 K (Fig. 6B, spectrum b-a). The bridged and monodentate nitrates are characterized by the lowest thermal stability (see Blank NO_x experiment, Fig. 4) and probably are present at lower concentrations on the 5CoSZ catalyst after the preheating at 623 K for the formation of NO_x species stable at higher temperatures. At 673 K the species characterized by bands at 1610–1550 cm^{-1} (bidentate nitrates and bridged nitro species) are involved in the interaction with the hydrocarbon (Fig. 6B, spectrum c-b). The corresponding concomitant bands are superimposed on the negative band at 1349 cm^{-1} due to the altered sulfate groups. The species, giving rise to the bands at 1584, 1510, and 1289 cm^{-1} (bridged nitro compounds [10]) display the lowest reactivity—they disappear after heating at 723 K (spectrum d-c). The unresolved band at approximately 1345 cm^{-1} is assigned to perturbed sulfate groups (positive bands at 1209 and 1129 cm^{-1}).

It should be pointed out that the interaction between the methane and the NO_x species produced by NO/O_2 adsorption at room temperature (without preheating at 623 K) on the 5CoSZ catalyst leads to an identical result. The consumption of the nitro-nitrato species starts at 573 K.

Noticeable interaction of methane with the NO_x-precovered 2.8CoSZ catalyst (Fig. 6C) starts at 623 K (spectrum b): there is a considerable decrease in the intensity of the nitro-nitrato band at 1627 cm^{-1}. The slight increase in the absorption due to H-bonded OH groups and the restoration of the isolated OH groups at 3696 cm^{-1} indicates that water molecules are produced, which adsorb dissociatively. The appearance of a very weak absorption in the 2900–2600 cm^{-1} region provides evidence for the formation of formate species. The increase in the temperature up to 723 K (spectrum c) leads to an additional increase in the absorption due to H-bonded OH groups with simultaneous decrease in the intensity of the band at 1627 cm^{-1}. The band at 1430 cm^{-1} is assigned to carbonate species based on its absence in the spectra obtained in the Blank NO_x experiment. The different enhancement of the absorption due to the H-bonded hydroxyls observed after the final heating at 723 K indicates that the activity of the NO_x-precovered sulfated catalysts toward the methane is different, being higher for the 5CoSZ sample (compare spectrum c in Fig. 6C with spectrum d in Fig. 6A).

4. Discussion

The results of the blank experiments with methane show that in the absence of gaseous oxygen oxidation of the hydrocarbon takes place on both 5CoZ and 5CoSZ catalysts. This process is detected occurring at temperature as low as 573 K. However, the oxidation products adsorbed on the catalysts are different. In the case of the sulfate-free sample carbonates, adsorbed H_2O and CO are observed, suggesting that mainly the process of complete oxidation of the methane has occurred. The interaction of methane with the sulfated cobalt catalysts leads to the formation of products of partial oxidation, such as formate species and formic acid. The loading of cobalt in 5CoZ catalyst is 7.7 atoms/nm^2, which exceeds the theoretical monolayer capacity by approximately two times [10]. This leads to the formation of multinuclear cobalt(II) oxo ions and Co_3O_4 clusters, which favor the complete oxidation of methane. Pietrogiacomi et al. [15] reported that the reodox couples Co(III)/Co(II) on the surface of the Co_3O_4 particles are very active in the complete oxidation of the hydrocarbon. The 5CoSZ catalyst also contains small amounts of Co_3O_4 particles [10], although the surface concentration of cobalt (3.3 atoms/nm^2) is close to that corresponding to the theoretical monolayer (3.8 atoms/nm^2). The application of sulfated zirconia as a support decreases the average crystallite size [10] and increases the dispersion of the redox centers. As a result, the reducibility of cobalt(III) [10] and cobalt(II) [1] is suppressed and partial oxidation of methane is favored.
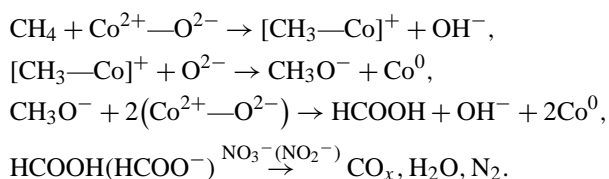
The 5CoZ and 5CoSZ catalysts do not contain exposed coordinatively unsaturated Zr^{4+} ions detectable by room-temperature adsorption of NO [10]. Therefore, we believe that the NO_x species obtained upon NO/O_2 coadsorption on these catalysts are coordinated mainly to cobalt sites. Modification of zirconia with sulfate ions affects the reactivity of the adsorbed NO_x species toward methane. In the absence of sulfate ions, the nitrate species formed at room temperature upon NO/O_2 adsorption on the 2.8- and 5CoZ catalysts do not react with methane. Up to 723 K, mainly the transformation of bridged and monodentate nitrates to nitrito species and adsorbed NO is observed to take place in a methane atmosphere. Some oxidation of the hydrocarbon is detected at 723 K in the case of the 5CoZ catalyst and the nitrito species do not participate in this process. It can be assumed that under these conditions the oxidation of the CH_4 is caused by sites that are restored during the thermal decomposition of bridged nitrates to monodentate nitrito species:

$$Co^{2+}-[ON(O)O]^{-}-Co^{2+} \rightarrow Co^{3+}-O^{2-} + Co^{3+}-ONO^{-}.$$
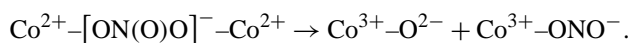
The higher the temperature, the greater the number of active sites liberated for the complete oxidation of methane. Despite the different catalysts and methods of investigation, the results of Li et al. [2] show the same trend: the Co/ZrO_2 catalyst (4 wt%) is practically inactive in the SCR of NO with methane from 623 to 923 K. We believe that the decomposition of monodentate nitrates takes place without a change in the oxidation state of cobalt(II) according to the reaction:

$$2NO_3^{-} \rightarrow 2NO + 1.5O_2 + O^{2-}.$$
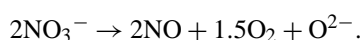
Contrary to the 5CoZ sample, the oxidation of the hydrocarbon on the NO_x-precovered 5CoSZ catalyst starts at a much lower temperature (573 K) with the involvement of the surface nitro-nitrato species. At the same temperature, over the NO_x-free catalyst the formation of formate species and formic acid is observed to take place. It can be proposed that the interaction between the CH_4 and the adsorbed NO_x species begins with the partial oxidation of the hydrocarbon and the formate species, respectively formic acid, play a role of intermediates that are capable of selectively reducing the nitro-nitrato species. Studies with oxide systems [18,19] have shown that methane is adsorbed dissociatively over strong Lewis acid-base pairs with generation of strongly bound metal–alkyl or methoxy species. The formate species (formic acid) can be produced by fast oxidation of the methoxide. Reaction Scheme 1 summarizes the steps assumed:

$$CH_4 + Co^{2+}-O^{2-} \rightarrow [CH_3-Co]^{+} + OH^{-},$$

$$[CH_3-Co]^{+} + O^{2-} \rightarrow CH_3O^{-} + Co^{0},$$

$$CH_3O^{-} + 2(Co^{2+}-O^{2-}) \rightarrow HCOOH + OH^{-} + 2Co^{0},$$

$$HCOOH(HCOO^{-}) \xrightarrow{NO_3^{-}(NO_2^{-})} CO_x, H_2O, N_2.$$

Scheme 1.

The fact that in the case of 5CoSZ catalyst there is a continuous decrease in the concentration of the surface nitro-nitrato species increasing the temperature and that no other adsorbed NO_x species are detected after the interaction at 723 K can be used as evidence that the nitro-nitrato species are reduced to dinitrogen. The reduction of surface nitrates by formate ions has been suggested earlier as a possible step in the SCR of NO with decane over CuO_x/SO_4^{2-}–ZrO_2 [7] and MnO_x/TiO_2 [8] catalysts. It should be pointed out that under identical experimental conditions the amount of adsorbed water molecules produced after interaction of CH_4 at 723 K with the NO_x-precovered 5CoSZ catalyst is much larger than that observed on the NO_x-free 5CoSZ sample (compare spectrum c in Fig. 5 with spectrum d in Fig. 6A). This fact confirms the conclusion that the formate species and formic acid formed are further oxidized by the nitro-nitrato species leading to the products of CH_4–SCR. Although a difference in the catalyst composition and experimental conditions, this conclusion is in agreement with the lower conversion of CH_4 in the CH_4–O_2 than in the NO–CH_4–O_2 reaction reported for Co/SO_4^{2-}–ZrO_2 catalyst with 4 wt% of Co [2].

The lack of strong Lewis acid-base pairs in the sulfate-free 2.8CoZ catalyst makes this material inert in the interaction with methane in absence of molecular oxygen. In contrast, under the same conditions the 2.8CoSZ catalyst shows activity toward the partial oxidation of methane, although lower than that observed on the 5CoSZ catalyst. Increasing the cobalt loading at the sulfate content close to the monolayer provides a higher concentration of strong Lewis acid-base pairs, which ensures higher conversion of the methane to partially oxidized hydrocarbons for interaction with the surface nitro-nitrato species.

Modification of the support with sulfate ions results in the formation of less thermally stable NO_x species [10] that transform at elevated temperatures to adsorbed NO and nitro compounds without affecting the oxidation state of the cobalt sites. Consequently, enough active sites for the methane activation and sufficient amount of reactive bidentate nitrates and bridged nitro species coordinated to cobalt ions are available for the reaction to occur at considerably lower temperatures. The onset temperature (573–623 K), at which interaction between the products of methane activation (formic acid and formate ions) and the nitro-nitrato species begins, is comparable to that reported for Co-exchanged zeolites (593 K) [20].

5. Conclusions

Interaction of methane with CoO_x/ZrO_2 (4.8 wt% cobalt loading) at 573 K in the absence of gaseous oxygen results in products of complete oxidation (surface carbonates, adsorbed water) due to the presence of some amount of Co_3O_4. The sample with a lower cobalt content (2.6 wt%) is inert toward the methane on heating up to 723 K. The nitrate

species formed at room-temperature adsorption of NO/O_2 over these catalysts do not react with methane in the 573–723 K temperature range. In the case of the NO_x-precovered CoO_x/ZrO_2 catalyst with 4.8 wt% of cobalt, some oxidation of CH_4 is observed at 723 K due to the liberation of active sites as a result of thermal decomposition of surface-bridged nitrates to monodentate nitrito species.

The sulfate ions (3.9 wt%) of the $CoO_x/SO_4^{2-}–ZrO_2$ catalysts containing 2.7 and 5.1 wt% of cobalt, respectively, modify the reactivity of the surface oxygen. As a result, after contact of the catalysts with methane at 573–623 K in the absence of gaseous oxygen, products of partial oxidation (adsorbed formate species and formic acid) are observed. Over the NO_x-precovered catalyst with 5.1 wt% of cobalt, oxidation of the hydrocarbon starts at 573 K with the participation of reactive nitro-nitrato species coordinated to cobalt sites. It is proposed that in the catalytic reduction of NO on $CoO_x/SO_4^{2-}–ZrO_2$ catalysts the products of methane activation—formic acid and formate species—are key intermediates capable of reducing selectively the surface nitro-nitrato species.

Acknowledgment

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