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In situ FTIR study of the formation and consumption routes of nitroorganic complexes—Intermediates in selective catalytic reduction of nitrogen oxides by propene over zirconia-based catalysts

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ABSTRACT

The results of this study show that the adsorption and catalytic properties of bulk ZrO_2 and nanoscale ZrO_2 pillars in pillared clay are significantly different. The NO + O_2 interaction with the surface of bulk zirconia results in the formation of three types of surface nitrate complexes (bridging, bidentate and monodentate), while over ZrO_2 pillars monodentate nitrates are not revealed.

The interaction of the propene–oxygen mixture with the surface of bulk zirconia leads to the formation of the acetate complexes only. Meanwhile, the main activation form of propene over ZrO_2 pillars is the isopropoxide complex; the acetate complexes are observed only in small amounts at elevated temperatures. Complexes of three types are formed on the surface of Pt,Cu/ZrPILC after interaction with the propene–oxygen mixture flow: isopropoxide complexes, coordination-bound acetone, and acetates. Modification of ZrO_2 pillars by Pt and Cu results in a significant change in the concentration and the temperature range of existence of C–H–O surface compounds.

The difference in the forms of reagents activation results in different structures of nitroorganic complexes. Over bulk zirconia the acetate and nitrate complexes form surface complexes with the structure similar to that of adsorbed nitromethane, monodentate nitrate being the most reactive species. Under reaction conditions at relatively low temperatures, over both modified and unmodified ZrO_2 pillars, interaction of isopropoxide and nitrate complexes produces surface complexes structurally similar to adsorbed dinitropropane.

IR spectral kinetic studies revealed that the rates of surface nitrate and nitroorganic complexes transformation are in general close to each other and to the rate of catalytic reaction, significantly increasing due to Pt + Cu supporting on pillars. This demonstrates that these complexes are real intermediates of NO_x HC–SCR over studied catalysts.

1. Introduction

Selective catalytic reduction of nitrogen oxides by hydrocarbons in excess of oxygen is a promising method for NO_x removal from the automotive and industrial sources [1]. The mechanism of this process has been studied in a number of papers (see e.g. [2–26]).

The participation of nitrate complexes in this reaction is considered to be reliably established to date. Numerous papers devoted to the investigation of the role of nitrite–nitrate species in NO_x HC–SCR suggest that nitrate complexes and/or their decomposition product NO_2 react with hydrocarbons and/or their activated forms (radicals, allylic complexes, oxygenates, etc.) generating nitrogen-containing organic compounds, primarily organic nitrates $O_2N–C_mH_n$ and organic nitrites $ONO–C_mH_n$ [13,23–35].

Some results of studies of the processes of hydrocarbons activation on the surface of oxide catalysts are summarized by Finocchio et al. [36]. Activation of propylene on Brönsted acid sites proceeds via primary formation of isopropoxide complex which is then transformed into acetone and, finally, to acetate species. In the case of propylene activation on Lewis acid sites, first acrolein or acrylic acid are formed with subsequent

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appearance of acrylate and, finally, acetate species. Hence, in dependence upon the nature of the surface sites of catalysts, any of the above-mentioned forms of propylene activation could be involved in the formation of nitrogen-containing organic compounds. Thus, according to Anderson and Rochester [21,22], namely acrolein and acrylic acid as products of propylene partial oxidation are involved in NO_x reduction. On the other hand, results obtained by Shimizu et al. [12] and Burch et al. [19] are in favor of acetate species participation in NO_x reduction.

At elevated temperatures nitrogen-containing organic compounds react with $NO + O_2/NO_2$ yielding molecular nitrogen. In addition (see for summary the paper of Gorce et al. [20]), nitrogen-containing organic substances may decompose to form OCN^-, ammonia [26,29,32], organic nitriles [29], cyanogens [38] and prussic acid [38,39]. Surface isocyanates are the most stable and, consequently, the most frequently registered by IR spectroscopy products of nitroorganics decomposition. Isocyanates as well as surface cyanides easily react with the $NO + O_2$ mixture and/or NO_2 yielding molecular nitrogen and N_2O as reaction products [13,34,37,39–41].

Another route could include isocyanate hydrolysis yielding ammonia which reacts with NO_x producing NH_4NO_2 [23–26]. Decomposition of ammonium nitrite easily produces molecular nitrogen. Some mechanistic schemes leading to N_2 formation based upon results of kinetic and spectroscopic studies of NO_x HC–SCR by present authors' teams for different catalysts and hydrocarbons are also given in [16,43].

Hence, interaction between surface nitrates and activated hydrocarbons results, first of all, in the appearance of nitrogen-containing organic substances that either react directly with $NO_x + O_2$ to yield NO_x HC–SCR products or decompose to NCO^-, CN^- and ammonia—intermediates in the molecular nitrogen formation.

In the excess of oxygen, undesirable oxidation of nitrogen-containing organic substances may take place leading to an over-equilibrium concentration of NO_2 in the gas phase [32]: $C_mH_nNO_2 + O_2 \rightarrow NO_2 + CO_2 + H_2O$

The above literature data indicate that some of the most general properties of the surface nitroorganic compounds have been established to date. At the same time, there is a lack of information on the stages of the process leading to formation of these complexes, the structure of their organic constituents, transformation mechanism of nitrate complexes into molecular nitrogen and the role of oxygen and nitrogen oxides in this process. The information on the role of the nature of a catalyst in the surface reactions listed above is especially important from the viewpoint of controlling the HC–SCR activity and selectivity.

Considering all this, detailed studies devoted to elucidation of the formation and consumption routes of nitroorganic complexes—intermediates in selective catalytic reduction of nitrogen oxides by propene over zirconia-based catalysts (bulk mesoporous zirconia (ZrO_2), zirconia-pillared clays (ZrPILC), zirconia-pillared clays promoted with noble metals and/or transition metal oxides (Pt,Cu/ZrPILC)) using *in situ* FTIR spectroscopy were undertaken. Zirconia-based systems are promising low-temperature catalysts for NO_x HC–SCR (by propene, propane, and decane) in excess of oxygen, which possess good hydrothermal properties and sulfur poisoning stability as well [42–45]. A special attention is paid here on elucidating the specificity of the mechanistic features for nanosized zirconia pillars as related to their structural arrangement being apparently responsible for their unique catalytic properties [42–45].

2. Experimental

ZrO_2 sample was synthesized by the precipitation of amorphous hydroxide from $ZrO(NO_3)_2$ with ammonia solution, followed by hydrothermal treatment at 90–110° and calcination at 500 °C as was earlier described by Chuah [46]. Detailed characterization of the real structure of sample by TEM, XRD, Raman and IR spectroscopy of lattice modes is given in [47,48]. It is mainly comprised of hydrated monoclinic zirconia phase with some admixture of the tetragonal or cubic-type phase.

The synthesis of pillared clays, procedures of the pillars modification by supporting Cu + Pt and samples characterization by structural and spectroscopic methods have been described in details earlier [43–45]. The sample studied in this work contained 1 wt.% Cu and 0.2 wt.% Pt.

Interaction of reagents and their mixtures with the surface of sample was studied by transmission FTIR spectroscopy in the flow regime in transient as well as steady-state conditions. The FTIR spectra were recorded using a PerkinElmer "Spectrum RX I FT-IR System" spectrometer. The weight of the samples pellets used in these experiments was 10–20 mg/cm^2. Prior to recording the FTIR spectra, the samples were subjected to standard heat treatment in N_2 flow at 400 °C. The IR cells-reactors used in this study allowing to record the IR spectra at elevated temperatures have been described earlier [49]. The intensity of absorption bands (a.b.) in transmission spectra was measured in the optical density units (A).

From the experimental IR spectra obtained by exposing the sample to a flow of reaction mixture, the spectra obtained in nitrogen flow under the same conditions were subtracted and resulting difference spectra were used for analysis throughout this paper.

Specificity of NO_x species adsorption on the samples surface was also studied by the thermal desorption (TPD) method. TPD under flow conditions in the IR cell-reactor was combined with registration of the IR spectra of surface complexes. Prior to the thermal desorption experiment, the sample was pretreated in the IR cell-reactor in the flow of N_2 at 400–500 °C. Unless otherwise stated, the samples were cooled down in a closed reactor (without N_2 flow) to a room temperature, after which nitrogen oxides were adsorbed from the flow of 0.2% NO/N_2 for 20 min. The NO excess was removed for 25 min under flowing N_2. The IR spectra of surface complexes were recorded during the thermal desorption. Each spectrum provided information on the change of the surface after heating for 20 °C.

In all experiments, GHSV was 9000 h^{-1}. All gases were purified using traps containing anhydrone and ascarite. The basic feed composition was $(0.2\%\ NO + 0.2\%\ C_3H_6 + 2.5\%\ O_2)/N_2$. During investigation of the effect of the mixture composition on the properties of surface compounds, the NO concentration was varied from 0 to 0.5%, the C_3H_6 concentration was varied from 0 to 1.0%, and the O_2 concentration was varied from 0 to 4.0%. The compositions of gases before and after the reactor were measured continuously using a Beckman-951A chemiluminescence NO/NO_x analyzer (carrier gas, nitrogen; heating rate, 5 °C/min) and a Beckman-950 infrared HC/CO analyzer.

3. Results and discussion

3.1. Steady-state measurements

3.1.1. Interaction of binary reaction mixtures with the catalysts' surface

3.1.1.1. $(0.2\%\ NO + 2.5\%\ O_2)/N_2$ feed. Fig. 1 presents the FTIR spectra recorded after achieving the steady state under contact of ZrO_2

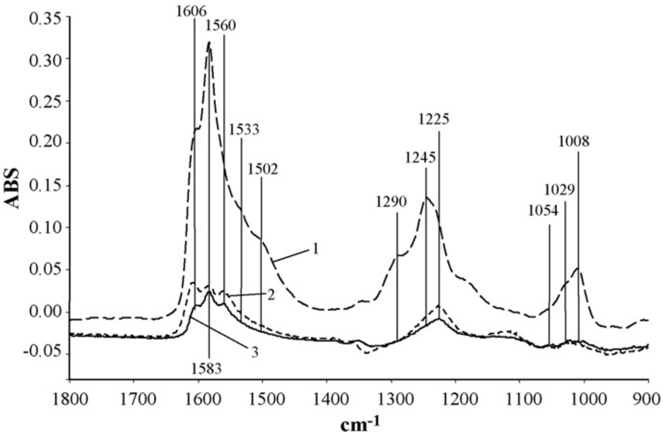

Fig. 1. FTIR spectra recorded after interaction of (0.2% NO + 2.5% O_2)/N_2 mixture with ZrO_2 surface at 250 °C (1), 300 °C (2) and 350 °C (3).

Table 1
Assignment of absorption bands in the spectra recorded after interaction of (0.2% NO + 2.5% O_2)/N_2 mixture with ZrO_2 surface

Band position (cm^{-1})	Complex
1606, 1225, 1029	Bridging nitrate
1583, 1245, 1054	Bidentate nitrate
1560, 1228, 1008	Monodentate nitrate
1502, 1290	Monodentate nitrite
1533, 1174	Bidentate nitrite

surface with the (0.2% NO + 2.5% O_2)/N_2 flow at different temperatures. The bands of both nitrate and nitrite complexes are present. No bands corresponding to nitrosyl complexes are observed. Detailed assignment of observed bands based upon known published data [50–55] is given in Table 1.

Fig. 2a and b presents spectra recorded after interaction of the (0.2% NO + 2.5% O_2)/N_2 mixture flow with the pillared clay surface at 100–300 °C. Absorption bands of bridging (1617 cm^{-1}) and bidentate (1589 cm^{-1}) nitrate complexes are present in the spectra (Fig. 2a).

As found by integration of NO_x TPD peaks, approximately five times less NO_x molecules are adsorbed over ZrO_2-pillared clay than on bulk ZrO_2 [56]. Since ZrO_2 content in the clay is 20 wt.%, this suggests that nitrate complexes are located on ZrO_2 pillars. This conclusion is supported by the fact that NO_x is not adsorbed in the form of nitrates over aluminosilicates.

In contrast to bulk ZrO_2, monodentate nitrates are not formed in significant amounts over the pillared clay (Fig. 2a). This can be explained by a much lower number of centers able to stabilize such species on the surface of nanosized zirconia pillars, namely, Lewis acid sites—coordinatively unsaturated Zr^{4+} cations [45,57]. This is due to specificity of these pillars structure mainly comprised of separate $Zr_4(OH)_n$ tetramers with strongly bound bridging hydroxyls [58].

The data presented in Fig. 2b also show that the interaction of the (0.2% NO + 2.5% O_2)/N_2 mixture with the surface results in the decrease of the intensity of bands of ZrO_2 hydroxyl groups (3740 and 3645 cm^{-1}) [45] and simultaneous growth of the intensity of absorption bands in the range of 3100–3300 cm^{-1}. Similar features were earlier observed by Kantcheva et al. in studies of NO + O_2 adsorption on zirconia-based systems [59,60] and explained by participation of bridging hydroxyls in stabilization of bridging nitrates with appearance of hydrogen bonded hydroxyl groups.

The obtained data indicate that the interaction of the (0.2% NO + 2.5% O_2)/N_2 mixture with the surface of bulk ZrO_2 and ZrO_2 pillars in the pillared clay has a qualitative difference: whereas NO_x surface coverages are close, monodentate nitrates are not formed over ZrO_2 pillars.

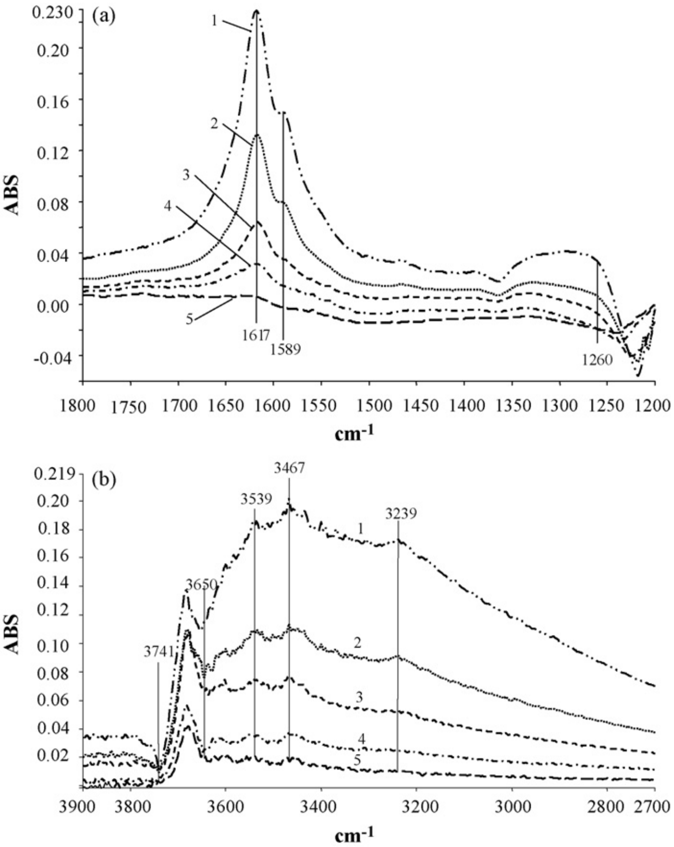

Fig. 2. IR spectra recorded after interaction of 0.2% NO + 2.5% O_2 in N_2 mixture with the pillared clay surface at 100 °C (1), 150 °C (2), 200 °C (3), 250 °C (4), 300 °C (5); (a) in the 1200–1800 cm^{-1} range and (b) in the 2700–3900 cm^{-1} range.

Like in the case of unmodified pillared clay [61], absorption bands of bridging (1617 cm^{-1}) and bidentate (1588 cm^{-1}) nitrate complexes are observed in the FTIR spectra of Pt + Cu-doped Zr-pillared clay. Under identical conditions, concentration of nitrate complexes is higher over Pt,Cu/ZrPILC than over ZrPILC (Fig. 3). Hence, modification of zirconia pillars by Pt + Cu apparently favors formation and stabilization of these surface species.

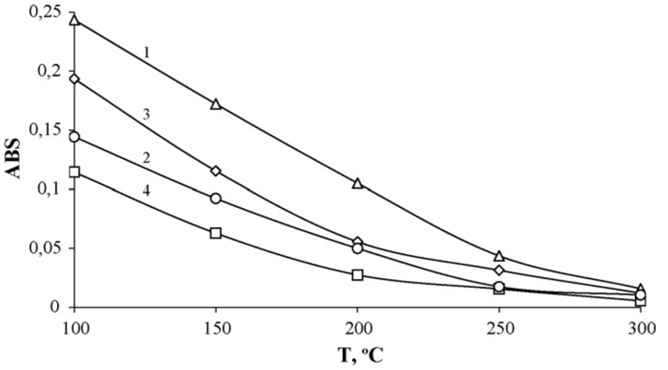

Fig. 3. Absorption bands intensity of the nitrate complexes on the surface of Pt,Cu/ZrPILC (1) bridging (1617 cm^{-1}), (2) bidentate (1588 cm^{-1}) and ZrPILC ((3) bridging and (4) bidenate) in the presence of NO_x in the gas phase as a function of temperature.

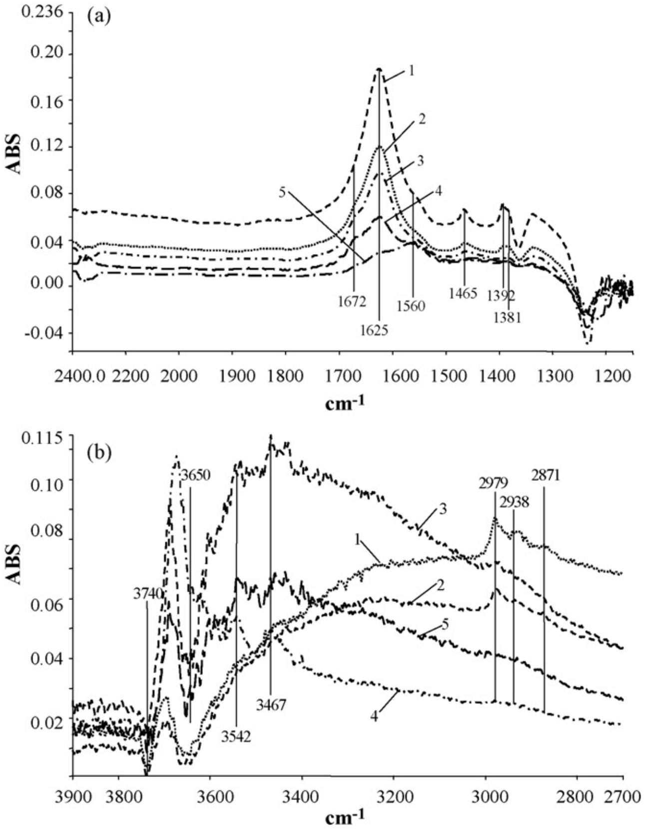

Fig. 4. IR spectra recorded after interaction of 0.2% C_3H_6 + 2.5% O_2 in N_2 mixture with the pillared clay surface at 100 °C (1), 150 °C (2), 200 °C (3), 250 °C (4), 300 °C (5); (a) in the 1150–2400 cm^{-1} range and (b) in the 2700–3900 cm^{-1} range.

3.1.1.2. (0.2% C_3H_6 + 2.5% O_2)/N_2. After interaction of (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture with ZrO_2 surface at different temperatures, low intensity bands corresponding to monodentate carbonate (1560, 1250 and 1134 cm^{-1}) and acetate (1545 and 1440 cm^{-1}) complexes [50] are observed. The intensity of these bands goes through a maximum when the temperature is increased [44,56].

The spectra recorded after interaction of the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture with the pillared clay surface at 100, 150, 200 and 250 °C are presented in Fig. 4a and b. The analysis of changes in the bands intensities as dependent upon the time of adsorption at different temperatures and comparison with available literature data [36,50,57,62–69] revealed that three types of complexes are present on the surface: isopropoxide complex, coordination-bound acetone and acetate. The formation of the isopropoxide complex is also confirmed by the decrease in the intensity of bands at 3740 and 3650 cm^{-1} (Fig. 4b) corresponding to vibrations of 2- and 3-coordinated hydroxyl groups located on ZrO_2 pillars [45].

An open structure of zirconia nanopillars derived from that of Zr_4 tetramer provides a plenty of bridging hydroxyls revealed by broad IR bands in the range of 3650–3740 cm^{-1} [45,57]. Neutralization of the excessive negative charge of aluminosilicate sheets by positively charged Zr_4 species completely suppresses the initial acidity of clays, as manifested by disappearance of bands at 3540–3615 cm^{-1} corresponding to hydroxyls bound with aluminosilicate layers [45,57]. The total acidity of Zr-pillared clays estimated by NH_3 TPD is much higher than that of the initial clay being proportional to the pillars density [70,71]. NH_3 TPD curves for ZrPILC are usually characterized by the maximum in the range of 250–300 °C with desorption continuing up to 500 °C [72]. This indicates the presence of both moderate and strong acid sites comparable by strength with those in H-ZSM-5 [73]. Since the amount of Lewis acid sites probed by IR spectroscopy of adsorbed CO test molecules is very low (less than several % of Zr cations in the samples) [57], this means that regular bridging hydroxyls in zirconia nanopillars are indeed acidic. This explains their efficiency in the low-temperature activation of propylene molecules and stabilization of respective oxygenates—products of propylene transformation. Indeed, the isopropoxide complex is observed during the heating of the sample to 250 °C. The absorption bands of adsorbed acetone appear in the spectrum after the sample is heated above 150 °C. The acetate complex bands appear after heating above 250 °C.

In the spectra of the initial sample there is a band at 1624 cm^{-1} belonging to vibrations of adsorbed water molecules. It should be noted that the pillared clay holds adsorbed water molecules unusually strongly: the corresponding band remains in the spectrum even after the sample is heated in an inert gas flow to 250 °C. These water molecules are certainly retained by highly charged Zr^{4+} cations in the structure of nanosized pillars comprised of $Zr_4(H_2O)_n(H_2O)_m$ units [74]. Assignment of bands observed for Zr-pillared clay under contact with C_3H_6 + O_2 feed based upon known published data [36,50,57,62–69,75] is reported in Table 2.

Earlier, for bulk ZrO_2, only acetate complexes were observed after sample contact with C_3H_6 + 2.5% O_2 mixture at temperatures exceeding 250 °C [56]. Hence, appearance of isopropoxide complexes and coordination-bound acetone on ZrO_2-pillared clay surface after contact with the same mixture at lower temperatures indicate increased Brönsted acidity of ZrO_2 pillars in comparison with the bulk material.

The analysis of variation of the absorption bands intensity with time of sample contact with the (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture at various temperatures and comparison with the literature data [36,50,62–67,72,75] revealed that for Pt, Cu-pillared clay, as for unmodified pillared clay, the same three types of surface complexes (isopropoxide, coordination-bound acetone and acetates) are formed. In addition, for Pt,Cu/ZrPILC sample, bands corresponding to vibrations of CO molecules adsorbed over Pt in linear and bridging forms (2047 and 1830 cm^{-1}) are observed.

The temperature dependences of intensity of corresponding absorption bands recorded under contact of (0.2% C_3H_6 + 2.5% O_2)/N_2 mixture flow with Pt,Cu/ZrPILC and ZrPILC samples are shown in Fig. 5a and b, respectively. One can see that for Pt + Cu-modified pillared clay, isopropoxide complex is observed at lower temperatures (curve 3), while the concentration of the acetate complexes (curve 2) is significantly higher. This result agrees well with the data presented in [76] where it has been shown that Pt deposition on mesoporous Al_2O_3 results in a significant increase of propene adsorption. In other words, in the presence of Pt, formation of the acetate complex proceeds more easily.

Hence, deposition of Pt and Cu on zirconia pillars changes the concentration and the temperature range of existence of surface compounds as compared to unmodified Zr-pillared clay.

Table 2
Assignment of absorption bands in the spectra observed after interaction of 0.2% C_3H_6 + 2.5% O_2 in N_2 mixture with the pillared clay surface

Band position (cm^{-1})	Complex
1672,1419,1370,1240	Coordination-bound acetone
1392, 1381, 1465, 1335, 2979, 2938, 2870	Isopropoxide
1555, 1445	Acetate
1625	H_2O_{ads}

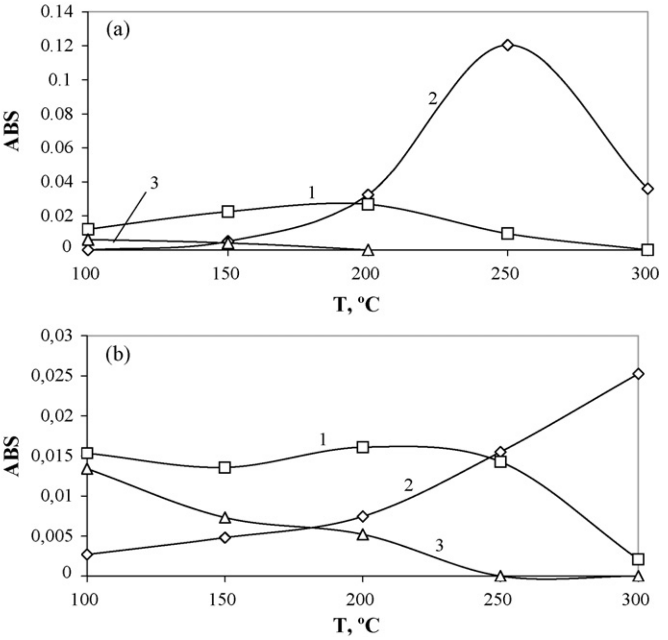

Fig. 5. Temperature dependences of the absorption bands intensity of (a) coordination bonded acetone (1670 cm^{-1}) (1), acetate (1555 cm^{-1}) (2) and isopropoxide (1463 cm^{-1}) (3) complexes on Pt,Cu/ZrPILC surface and (b) coordination bonded acetone (1), acetate (2) and isopropoxide (3) complexes on ZrPILC surface.

3.1.2. Interaction of (0.2% NO + 0.2% C_3H_6 + 2.5% O_2)/N_2 reaction mixture with the catalysts' surface

In the case of ZrO_2 absorption bands corresponding to nitrate and nitrite complexes and bands at 1565, 1383 and 1363 cm^{-1} are observed (Fig. 6). According to the published data [13,33–35,77,78], the latter bands can be assigned to symmetric and asymmetric vibrations of the nitro group and C–H bending vibration in a nitroorganic surface complex. Such assignment is confirmed by the fact that these bands are not observed in the absence of either NO or C_3H_6 in the gas phase (Fig. 1), as well as by special experiments on adsorption of various nitroorganic substances under similar conditions. For comparison, the spectrum of nitromethane adsorbed under similar conditions is shown in Fig. 6 (spectrum 4, 5). Comparison of these spectra with the spectra recorded under reaction conditions shows that the spectrum of the surface nitroorganic complex is the most similar to that of adsorbed nitromethane. Additional TPD, IR, and ESR data on the formation of nitroorganic complexes in this system are reported in [79].

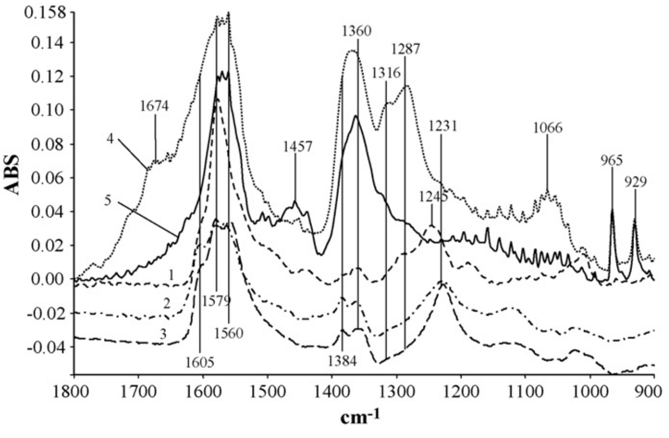

Fig. 6. FTIR spectra recorded after interaction of reaction mixture with ZrO_2 surface at 250 °C (1), 300 °C (2), 350 °C (3) and after interaction of nitromethane with ZrO_2 surface at 250 (4) and 350 °C (5).

The positions of the bands of these complexes are relatively close to each other. Therefore, to determine the dependence of the intensity of each surface complex bands on temperature, complex experimental spectra were decomposed into the components using a standard computer software with the assumption of the Lorentz or Gauss shape of the absorption bands

In the case of pillared clay (Fig. 7a and b), the spectra consist of overlapping bands of coordination-bound acetone and nitrates. Other absorption bands are also present in the spectra: bands at 1386 and 1575 cm^{-1}, which may be assigned to symmetric and asymmetric vibrations of the nitro group [13,34,35,78,80,81]; bands at 1435 and 1340 cm^{-1} assigned to bending C–H vibrations in the nitroorganic surface complex; bands at 2887, 2945 and 2985 cm^{-1} belonging to stretching vibrations of the latter. These absorption bands are not observed in the absence of either NO or C_3H_6 in the gas phase.

To determine the structure of the nitroorganic complex, adsorption of various nitroorganic substances was studied under similar conditions (T = 150 °C, concentrations of nitromethane, nitroethane, 1-nitropropane and 2-nitropropane in the nitrogen flow about 3%). The results of these experiments are presented in Fig. 8. One can see that the spectra contain bands of the nitro group vibrations and bands of the C–H vibrations. Comparison of the spectra recorded under reaction conditions with the spectra recorded after the interaction of the sample with the nitroorganic compounds shows that the spectrum of the surface nitroorganic

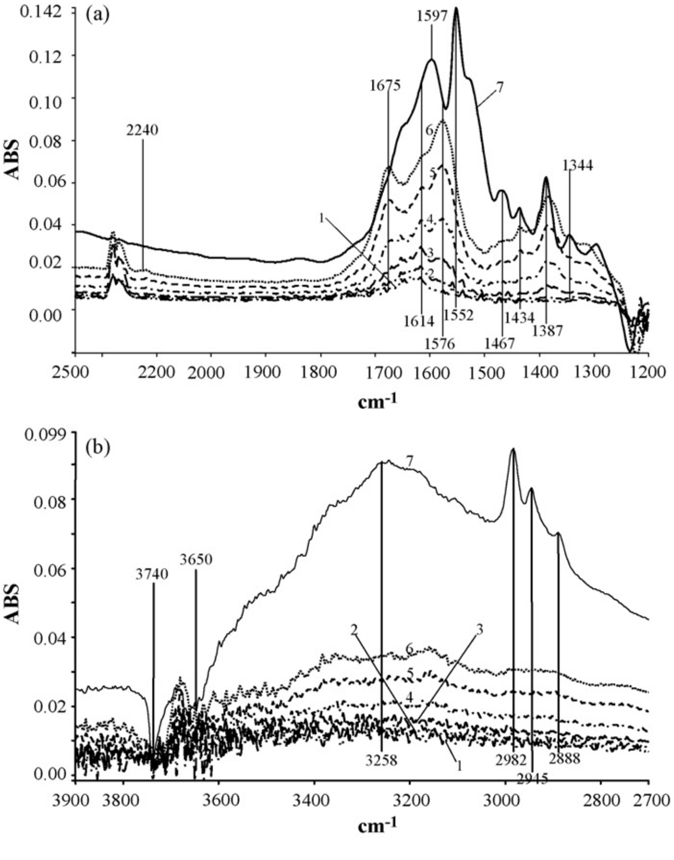

Fig. 7. IR spectra recorded after interaction of 0.2% NO + 0.2% C_3H_6 in N_2 mixture with the pillared clay surface at 150 °C for 1 min (1), 2 min (2), 5 min (3), 10 min (4), 20 min (5), 30 min (6), spectrum of adsorbed nitroporopane (7); (a) in the 1200–2500 cm^{-1} range and (b) in the 2700–3900 cm^{-1} range.

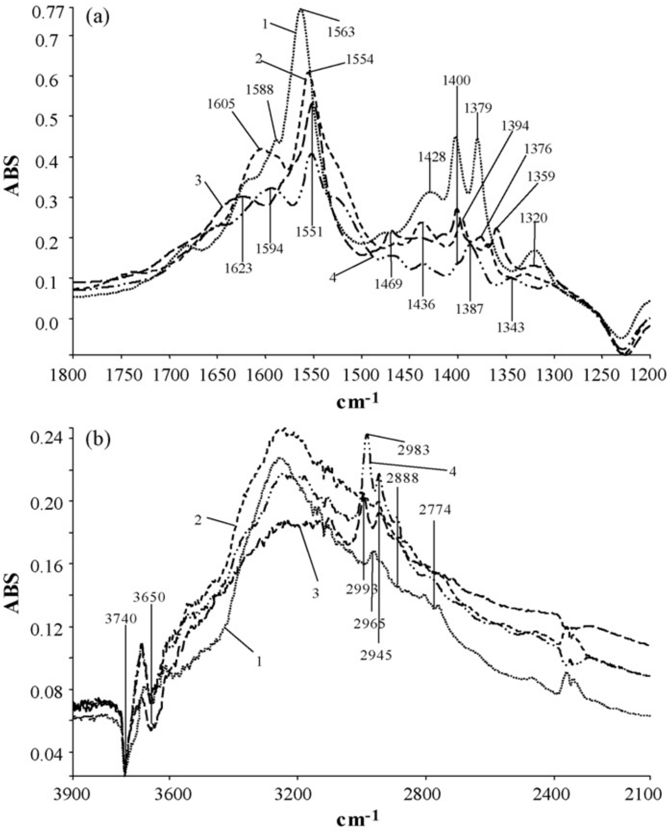

Fig. 8. IR spectra recorded during interaction of nitromethane (1), nitroethane (2), 2-nitropropane (3), 1-nitropropane (4) with the pillared clay surface at 150 °C; (a) in the 1200–1800 cm^{-1} range and (b) in the 2100–3900 cm^{-1} range.

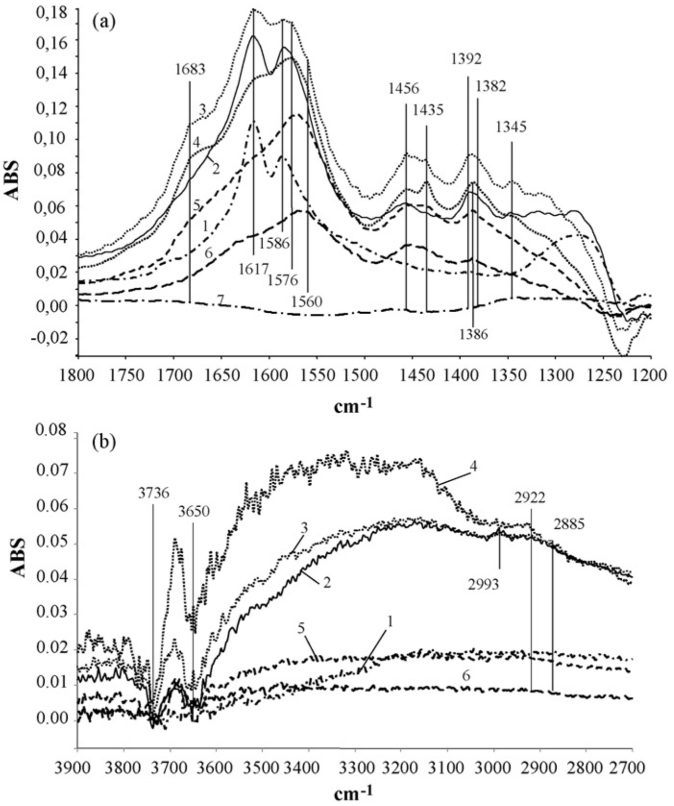

Fig. 9. FTIR spectra recorded during interaction of the 0.2% NO + 0.2% C_3H_6 + 2.5% O_2/N_2 mixture with Pt,Cu/ZrPILC surface at 50 °C (1), 100 °C (2), 150 °C (3), 200 °C (4), 250 °C (5), 300 °C (6) and 400 °C (7); (a) in the 1200–1800 cm^{-1} range and (b) in the 2700–3900 cm^{-1} range.

complex is the most similar to that of adsorbed 1-nitropropane (Figs. 7 and 8). The difference consists in a higher vibration frequency of the asymmetric nitro group vibrations and somewhat broader symmetric vibration band. According to [78,82], higher frequencies of the asymmetric nitro group vibrations are observed in the case when a nitro compound has two nitro groups, whereas the increased half-width of the symmetric vibration is due to splitting of these bands. This reasoning allows us to suggest that the structure of the adsorbed nitroorganic complex observed under reaction conditions is similar to that of adsorbed dinitropropane [78,82]. The case of two NO_2 groups joining an olefin molecule in NO_x HC–SCR over zeolite catalysts is described in [83,84].

In the high-frequency part of Fig. 7a, band at 2240 cm^{-1} corresponding to isocyanate complexes are observed. There are two possible reasons for their formation. The first one is that CO molecules formed during propene oxidation may react with NO to yield surface isocyanate. The second one is related to possible deeper transformations of the nitroorganic complex.

The spectral features of nitroorganic compounds stabilized on bulk ZrO_2 [56] and ZrO_2 pillars in the clay were found to be substantially different. This is caused by a fundamental difference in the propene activation forms over these catalysts at relatively low temperatures (vide supra). One may expect that the nitroorganic complexes will have similar structures over these two catalysts at higher temperatures when propene is mainly transformed into the same oxygenate complex (acetate) over both catalysts.

The interesting results for variation of the surface complexes bands with temperature were obtained for Pt,Cu/PILC sample.

In the 50–200 °C range the spectrum (Fig. 9, spectra 1–4) consists of overlapping bands of the isopropoxide complex, coordination-bound acetone and nitrates. In addition, two group of bands at 1386, 1435, 1576, and at 2993, 2922, 2885 cm^{-1} are observed. According to the literature data [13,34,35,77,78,80,81,85] and adsorption of various nitroorganic substances (vide supra) these bands can be assigned to vibrations of nitrogroup as well as bending (1435) and stretching (2993, 2922 and 2885 cm^{-1}) C–H vibrations in adsorbed dinitropropane surface complex [61].

In the 250–400 °C range the general decrease in the intensities of all bands takes place (Fig. 9, spectra 5–7). Nitroorganic compound bands change as well: the frequency of the asymmetric vibration decreases, while the half-width of the band corresponding to the symmetric vibration of the nitro group increases, so the latter has two poorly resolved maxima at 1392 and 1383 cm^{-1}. For comparison, Fig. 10 presents the spectra of nitromethane adsorbed at 150 (curve 1) and 300 °C (curve 4). One can see that increase in the adsorption temperature decreases the intensity and splitting of bands at 1402 and 1380 cm^{-1}, so that at 300 °C a poorly resolved doublet with the maxima at 1394 and 1385 cm^{-1} is observed. These results suggest that at higher reaction temperature when there are no isopropoxide complexes left on the surface (Fig. 9), the acetate and the nitrate complexes form the nitroorganic complexes close in structure to adsorbed nitromethane, just like over the bulk zirconia [56].

The obtained data suggest that over Pt,Cu/ZrPILC, as opposed to ZrPILC, two surface forms of activated propene exist in noticeable amounts: the low-temperature form (isopropoxide) and the high-temperature form (acetate). It seems that their presence is responsible for domination of different types of nitroorganic species in different temperature ranges: the dinitropropane complex exists at low temperatures, while nitromethane, at high temperatures.

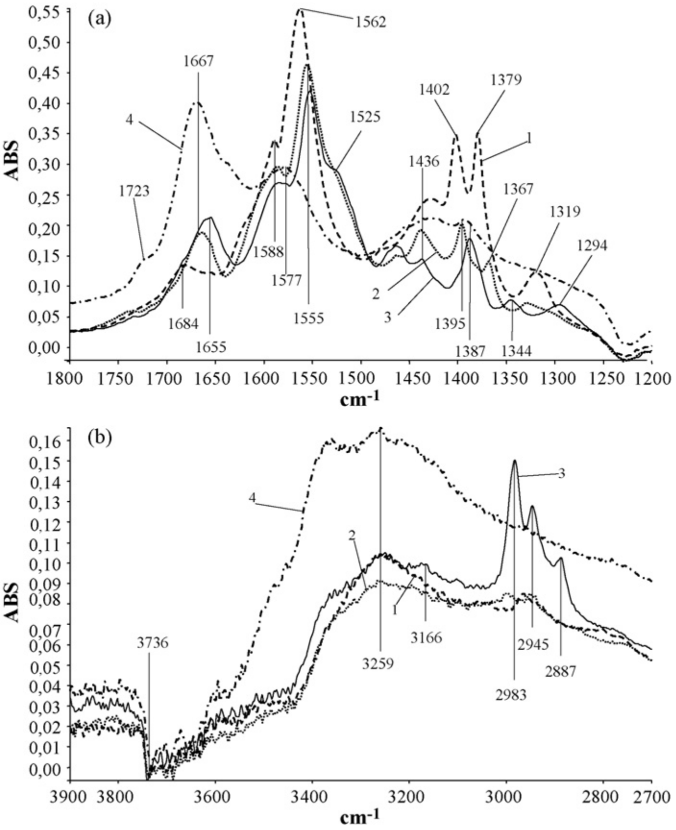

Fig. 10. FTIR spectra recorded during adsorption of nitroorganic substances on Pt,Cu/ZrPILC surface: (1) nitromethane, 150 °C; (2) nitroethane, 150 °C; (3) nitropropane, 150 °C; (4) nitromethane, 300 °C; (a) in the 1200–1800 cm^{-1} range and (b) in the 2700–3900 cm^{-1} range.

3.2. Unsteady-state measurements

Unsteady-state experiments were carried out in a broad (100–300 °C) temperature range where the catalytic activity was measured along with recording the spectra of surface complexes.

3.2.1. ZrO_2

The data presented in Figs. 1 and 6 show that the interaction of the $(C_3H_6 + O_2)/N_2$ or $(NO + O_2)/N_2$ mixtures with the ZrO_2 surface results in the formation of strongly bound complexes, namely, acetate and nitrate species. It can be seen that these complexes are not removed from the surface when the catalyst is purged with N_2 flow.

Fig. 11 presents results on studies of the reactivity of surface acetate complexes. When NO is added, the preformed acetate complexes are consumed (Fig. 11c), whereas the concentrations of the nitroorganic compounds and nitrate complexes go through the maximum (Fig. 11a and b). Simple estimates show that the intensity of nitroorganic compound band is approximately proportional to the product of the concentrations of the nitrate and acetate complexes. This implies that the nitroorganic compound is formed in the reaction between the nitrate and acetate surface complexes. An additional decrease in the intensity of the band corresponding to the nitroorganic compound may be caused by its subsequent consumption in the reaction with NO or NO_2 resulting from decomposition of the surface nitrates to yield the reaction products.

Similar data on the investigation of the reactivity of surface nitrate complexes for ZrO_2 sample are presented in Fig. 12. These complexes are consumed under sample contact with a mixture of propene and oxygen (Fig. 12b). Meanwhile, the concentration of the nitroorganic compounds goes through the maximum (Fig. 12a). Note that the monodentate nitrate is the most reactive complex (Fig. 12b, curve 3). The intensity of the acetate complex bands grows with time (Fig. 12c). In this case, the estimates show once again that the intensity of the nitroorganic compound bands is approximately proportional to the product of the concentrations of the nitrate and acetate complexes.

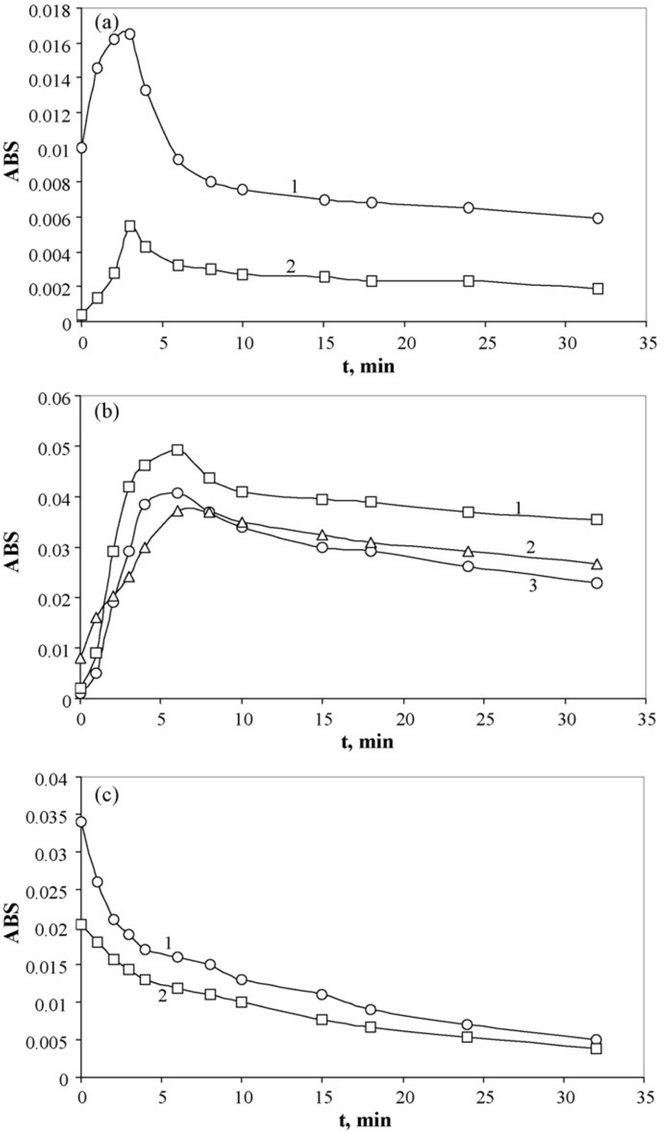

Fig. 11. Time dependence of the intensity of bands corresponding to (a) nitroorganic complex (1: 1565 cm^{-1}, 2: 1383 cm^{-1}), (b) nitrate complexes (1: 1582 cm^{-1}, 2: 1560 cm^{-1}, 3: 1605 cm^{-1}), and (c) acetate complexes (1: 1440 cm^{-1}, 2: 1550 cm^{-1}) in the 0.2% NO + N_2 flow at 350 °C for ZrO_2 sample.

The data on the consumption of the nitroorganic compounds for ZrO_2 sample are shown in Fig. 13. The nitroorganic compounds were formed after interaction of a mixture of propene, NO, and oxygen with the catalyst surface. Beside the nitroorganic complex, the nitrate and the acetate complexes are formed as well. Fig. 13 depicts the time dependences of the surface compounds concentrations during purging the cell with nitrogen. Concentrations of the nitroorganic (Fig. 13a) and nitrate (Fig. 13b) complexes decrease while that of the acetate complexes (Fig. 13c) remains constant. Because the nitrate and acetate complexes which exist individually on the surface are not desorbed in the nitrogen flow,

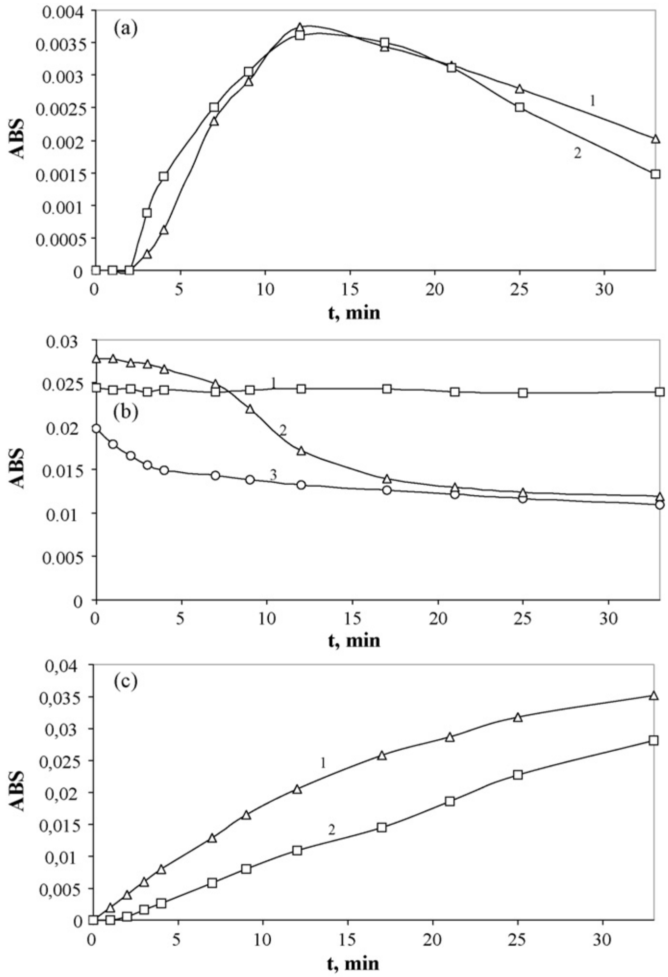

Fig. 12. Time dependence of the intensity of bands corresponding to (a) nitroorganic complex (1: 1383 cm^{-1}, 2: 1363 cm^{-1}), (b) nitrate complexes (1: 1582 cm^{-1}, 2: 1560 cm^{-1}, 3: 1605 cm^{-1}), and (c) acetate complexes (1: 1550 cm^{-1}, 2: 1440 cm^{-1}) in the 0.2% C_3H_6 + 2.5% O_2 + N_2 flow at 350 °C for ZrO_2 sample.

this fact unambiguously shows that the nitroorganic compounds are consumed in the reaction with the nitrate complexes, monodentate nitrate being the most reactive (Fig. 13a, curve 1).

Similar experiments were also performed at 300 and 250 °C. Their results allowed to estimate the reaction rate constant and activation energy of the nitroorganic compound interaction with monodentate nitrate over the ZrO_2 surface given in Table 3.

The data reported in Table 3 indicate that at 250 °C the nitroorganic complexes are formed but are practically not consumed. This conclusion agrees with the fact that ZrO_2 does not show noticeable catalytic activity at 250 °C [44,79].

Close values of the consumption rate constant of the nitroorganic complex and monodentate nitrate species suggests that their interaction is the main surface reaction leading to formation of SCR products. This conclusion is confirmed by the estimation of the activation energies of the nitroorganic and monodentate nitrate complexes consumption. These values turned out to be about 60 kJ/mol, which is relatively close to the activation energy of the overall NO_x SCR process [79].

3.2.2. ZrPILC, Pt,Cu/ZrPILC

Quantitative characteristics of nitrate complexes transformation under the conditions of NO_x HC–SCR over Pt,Cu/ZrPILC and ZrPILC obtained following earlier described approaches [49,79] are given in Table 4. Data in Table 4 allow to make two conclusions:

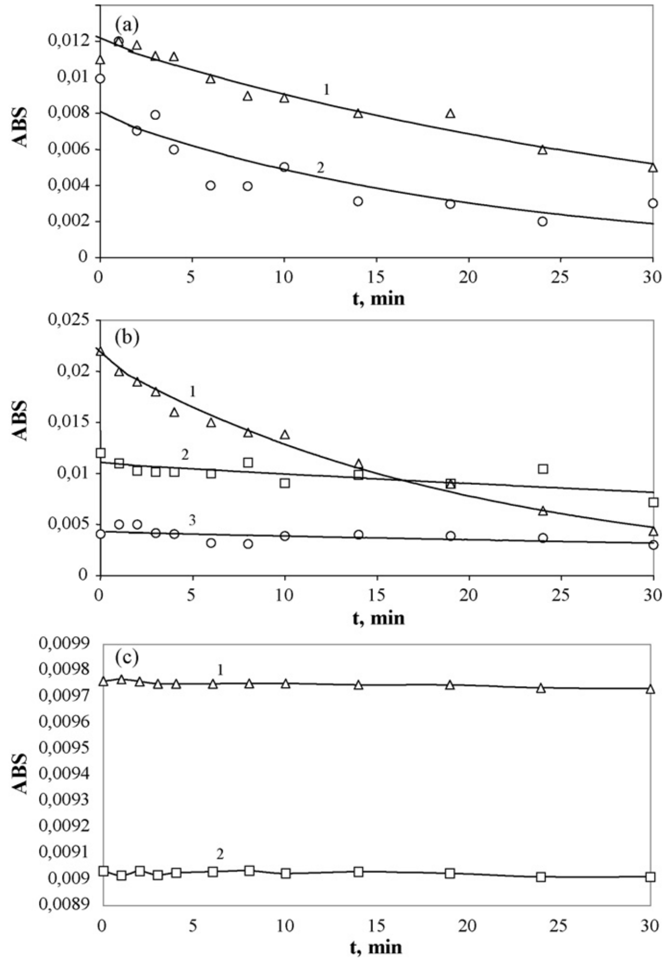

Fig. 13. Time dependence of the intensity of bands corresponding to (a) nitroorganic complex (1: 1363 cm^{-1}, 2: 1383 cm^{-1}), (b) nitrate complexes (1: 1560 cm^{-1}, 2: 1582 cm^{-1}, 3: 1605 cm^{-1}), and (c) acetate complexes (1: 1550 cm^{-1}, 2: 1440 cm^{-1}) in the nitrogen flow at 350 °C for ZrO_2 sample.

- the rate of transformation of surface nitrate complexes is close to the rate of NO_x HC–SCR. This fact suggests participation of nitrate complexes in the reaction as key intermediates;
- the reactivity of nitrate complexes significantly increases from bulk ZrO_2 to pillared clay (ZrPILC) to modified pillared clay (Pt,Cu/ZrPILC).

At lower (100 °C) temperatures, only isopropoxide complexes are formed on the surface of Pt,Cu/ZrPILC sample under contact with C_3H_6 + O_2 feed, which provides a good chance to study their reactivity and transformation routes. They are not removed when the catalyst is purged with the N_2 flow. Under contact with (0.2%

Table 3
Kinetic parameters of the nitroorganic compound reaction with monodentate nitrate over ZrO_2 surface

	T (°C)		
	250	300	350
Consumption rate constant of the nitroorganic compound, k (min^{-1})			
1383 cm^{-1} band	~0	0.021	0.042
Consumption rate constant of the nitrate complexes, k min^{-1}			
1560 cm^{-1} band	~0	0.019	0.040
1582 cm^{-1} band	~0	~0	0.012
1605 cm^{-1} band	~0	~0	0.010

Table 4
Characteristics of transformation of surface nitrate complexes

Sample	T (°C)	Effective rate constant of transformation of surface nitrate complexes k, $\min^{-1}$	Rate of transformation of nitrate complexes W ($\times 10^{18}$ molec $\times$ $\min^{-1}$)	Reaction rate (molec $\times$ $\min^{-1}$)	Ref.
ZrO_2	350	0.038	5	5.6	[56]
ZrPILC	250	0.035	2	1.8	[61]
Pt,Cu/ZrPILC	150	0.070	2.7	3	This work

NO + 2.5% O_2)/N_2 mixture, the isopropoxide complexes are rather rapidly consumed (Fig. 14, curves 4 and 5). Meanwhile, the concentrations of the nitroorganic complexes (curve 2) and acetone (curves 1 and 3) also increase. This implies that the isopropoxide complexes are the source for the formation of both the nitroorganic complexes and acetone.

Fig. 14c presents changes in the intensity of the acetate complexes bands after Pt,Cu/ZrPILC sample purging by N_2 (spectrum 1) or (0.2% NO + 2.5% O_2)/N_2 (spectrum 2) flow at 300 °C. After interaction with the (0.2% NO + 2.5% O_2)/N_2 flow, a weak broad absorption band at 1390–1380 cm^{-1} was observed assigned to nitromethane surface complexes (vide supra). This implies that at relatively high temperatures acetate complexes are the source for the formation of nitroorganic complexes structurally similar to adsorbed nitromethane.

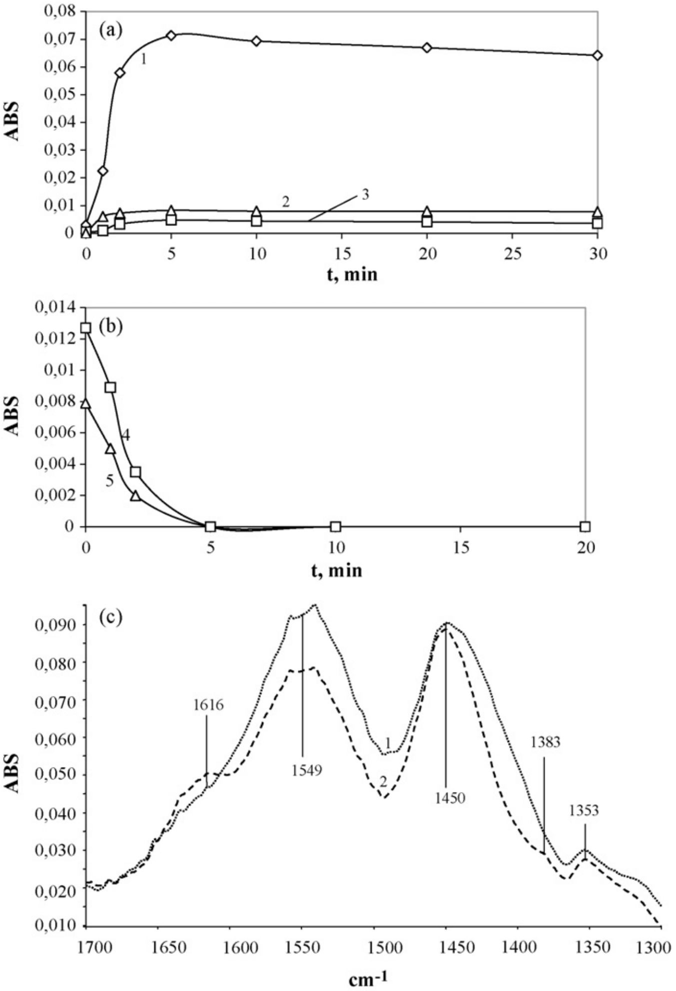

Fig. 14. Absorption bands intensity of (a) acetone (1: 1670 cm^{-1}, 3: 1420 cm^{-1}), nitroorganic (2: 1386 cm^{-1}); (b) isopropoxide (4: 1392, 5: 1463 cm^{-1}) complexes on Pt,Cu/ZrPILC surface as a function of time after introduction of 0.2% NO + 2.5% O_2/N_2 mixture on preformed isopropoxide complexes at 100 °C and (c) FTIR spectra recorded after contact of nitrogen (1) or 0.2% NO + 2.5% O_2/N_2 mixture (2) with preformed acetate complexes on Pt,Cu/ZrPILC surface at 300 °C.

Table 5
Characteristics of transformation of surface nitroorganic complexes

Sample	T (°C)	Effective rate constant of transformation of surface nitroorganic complexes k ($\min^{-1}$)
ZrO_2	350	0.032
ZrPILC	250	0.040
Pt,Cu/ZrPILC	150	0.070

Quantitative characteristics of transformation of nitroorganic complexes under the NO_x HC–SCR conditions over Pt,Cu/ZrPILC, as well as comparison with analogous parameters for bulk ZrO_2 and ZrPILC are given in Table 5.

It can be seen that the effective rate of consumption of surface nitroorganic complexes significantly increases from bulk ZrO_2 to pillared clay (ZrPILC) to modified pillared clay (Pt,Cu/ZrPILC). Moreover, for each catalyst the effective rate of consumption of surface nitroorganic complexes is close to that for nitrate complexes (Tables 4 and 5). Similarity of these values implies that for studied catalysts, nitroorganic complexes are real intermediates of NO_x HC–SCR.

Note that the rates of the nitroorganic complexes transformation in the 2.5% O_2/N_2 or 0.2% NO/N_2 flow match those observed in the inert gas (N_2) flow. This suggests that the consumption of the nitroorganic compound is related to the presence of NO_2 complexes under reaction conditions. As the equilibrium concentration of NO_2 is low at elevated temperatures, the existence of such complexes on the surface may be due to the decomposition of surface nitrates. Experiments carried out in a wide temperature range (100–300 °C) confirm this supposition. The reaction of the nitroorganic complexes with the NO_2 complexes starts at temperatures about 200 °C. According to the thermal desorption data, this is exactly the temperature range where the surface nitrate complexes start to decompose with the formation of activated NO_2 complexes [56,61].

4. Conclusion

Detailed spectroscopic and kinetic study of the mechanistic features of NO_x C_3H_6 SCR on zirconia-containing catalysts (bulk zirconia, zirconia-pillared clays and zirconia-pillared clays promoted with noble metals and transition metal oxides) revealed pronounced effect of the atomic-scale surface features on the nature and reactivity of key reaction intermediates.

Over rather basic bulk zirconia, the main form of C_3H_6 activation at increased temperatures with participation of gas-phase oxygen is acetate complex. Its interaction with the most reactive monodentate nitrate complexes produces intermediate with the structure similar to that of adsorbed nitromethane. In agreement with earlier results of' Shimidzu et al. for Cu/alimuna catalyst [12], this reaction could proceed by substitution of the carboxyl group in the acetate complex by a NOO group.

Over both modified and unmodified ZrO_2 pillars with structural bridging hydroxyls-rather strong Brönsted acid sites, propene activation proceeds quite easily even at low temperatures producing isopropoxide complex. Its interaction with nitrate complexes generates the surface complexes structurally similar to adsorbed dinitropropane. The dinitropropane complexes over ZrO_2 pillars are consumed in the reaction with the surface nitrates. In the absence of $NO + O_2$ in the gas phase and almost complete absence of nitrate complexes on the surface, the dominating reaction is decomposition of dinitropropane complexes resulting in the formation of surface acetate complexes and ammonia—an efficient reducing agent. While for unmodified ZrO_2 pillars concentration of acetate complexes is low, over doped pillars the acetate complexes react at elevated temperatures with nitrate species to form surface nitromethane complexes. The reaction of the latter with the surface nitrates also yields reaction products—molecular nitrogen and CO_2.

IR spectral kinetic studies have shown that the effective rate of consumption of surface nitrate and nitroorganic complexes significantly increases due to Pt + Cu supporting on pillars. Moreover, for each catalyst, the effective rate of consumption of surface nitroorganic complexes is close to the value for nitrate complexes and to the steady-state rate of overall catalytic reaction. Similarity of these values demonstrates that nitroorganic complexes are real intermediates of NO_x HC–SCR over studied catalysts.

The observed differences in the forms of reagents activation and their thermal stability also explain the difference in the activity of bulk ZrO_2, unmodified and modified nanoscale ZrO_2 pillars in pillared clay in selective catalytic reduction of nitrogen oxides by propene in excess of oxygen [56,61,86].

Acknowledgement

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