FT-IR study of the nature and reactivity of surface NO_x compounds formed after NO adsorption and $NO + O_2$ coadsorption on zirconia- and sulfated zirconia-supported cobalt

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Abstract

Infrared spectroscopy has been applied to the study of NO adsorption, $NO + O_2$ coadsorption and interaction of surface nitrates with methane on four samples: ZrO_2, $SO_4{}^{2-}$–ZrO_2, Co/ZrO_2 and $Co/SO_4{}^{2-}$–ZrO_2. Adsorption of NO on zirconia is negligible, while nitrosyls of the $Zr^{4+}(SO_4{}^{2-})$–NO type are formed on $SO_4{}^{2-}$–ZrO_2. Adsorption of NO on Co/ZrO_2 results mainly in formation of cobalt mononitrosyls (band at $1872\,cm^{-1}$) and dinitrosyls (1855 and $1777\,cm^{-1}$), which are stable during evacuation at room temperature. The same types of compounds are also formed after NO adsorption on $Co/SO_4{}^{2-}$–ZrO_2. However, in this case the mononitrosyls are characterized by a band at $1922\,cm^{-1}$ whereas the dinitrosyls have bands at 1903 and $1814\,cm^{-1}$. Both types of nitrosyls decompose slowly during evacuation. Addition of oxygen to the NO-sample systems causes decomposition of the nitrosyls and appearance of various kinds of surface nitrates, part of them formed on the support. The nitrates produced with the participation of cobalt ions react with methane at relatively low temperatures (about 473 K), which indicates that they are intermediate compounds during selective catalytic reduction (SCR) of NO_x with methane. The effect of preliminary sulfatation of zirconia on the properties of deposited cobalt cations has been discussed.
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1. Introduction

At present selective catalytic reduction (SCR) of NO_x with ammonia is used for elimination of nitrogen oxides emitted by stationary sources. Catalysts such as V_2O_5/TiO_2 and similar compositions are utilized [1]. However, the problem associated with nitrogen oxides from mobile sources has not yet been solved. At present three-way catalysts based on noble metals are applied to gasoline engines. However, they are not active in the presence of excess oxygen [1]. That is why effective catalysts for reduction of nitrogen oxides from exhaust gases from diesel engines should be found. With both mobile and stationary nitrogen oxide sources, the application of hydrocarbons as reducing agents in SCR (HC-SCR) [2,3] seems promising. This would not only solve the problem of the NO_x emission from diesel engines but would, in cases of

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stationary NO sources, permit replacement of ammonia, as a reducing agent, by methane which is cheaper and less toxic [1].

The HC-SCR of NO_x was for the first time performed about 10 years ago with Cu-ZSM-5 [4,5], which is still considered to be one of the most active catalysts in this process. Reduction of nitrogen oxides on Cu-ZSM-5 can be performed with alkenes and C^{3+} alkanes [4,5]. Series of Cu, Fe, Pt, Co, Ga and Ge exchanged zeolites as well as the H forms have shown a significant activity during SCR with hydrocarbons [3]. The main disadvantage of zeolites is their low hydrothermal stability.

Regardless of some initial contradictory reports, it has been established that transition metal cations well dispersed on metal oxides also show high activity during HC-SCR [6]. An advantage of the metal oxides as supports is their high thermal stability. In this respect zirconia is promising since it is characterized by high thermal stability, mechanical hardness and chemical inertness.

An important stage of SCR studies is the discovery of Li and Armor [7], according to which NO_x reduction over Co-ZSM-5 can be performed with methane. At first it has been reported [8] that oxide-supported cobalt catalysts are inactive in HC-SCR. However, other investigations [9,10] have been established that in cases when Al_2O_3- and SiO_2-supported cobalt ions have a high dispersion, the resulting catalytic systems are active in the reaction. The activity of Co/ZrO_2 is also disputable. According to some authors [11], Co/ZrO_2 shows good catalytic properties during SCR with propane. Other authors [12] have reported that among the series of Co-ferrierite, Co-β and Co/ZrO_2, the Co/ZrO_2 catalysts possess the lowest activity. These contradictions are probably due to differences in cobalt dispersion on the samples used by the different authors. And indeed, Ciambelli et al. [12] have synthesized their sample by impregnation with a $CoSO_4$ solution whereas Pietrogiacomi et al. [11] have used cobalt acetate as a precursor of the active phase, which leads, in principle, to a higher cobalt dispersion [9,10]. These authors [11] have also established that an increase in cobalt concentration results in formation of Co_3O_4, which is active towards complete oxidation of methane. In this connection, it should be mentioned that preliminary sulfatation of zirconia favors the high dispersion of

deposited cations which leads to a high activity in SCR [13].

Beutel et al. [14] are of the opinion that surface nitrites, characterized by a band at about $1526 \, cm^{-1}$ in the IR spectra, are key compounds in SCR with methane. These species are formed on Co-ZSM-5 but not on Cu-ZSM-5 which activity in SCR with methane is negligible [7]. More recently the band at $1526 \, cm^{-1}$ has been attributed to monodentate cobalt nitrates [15–17]. These nitrates are also detected on Co/SiO_2 (highly dispersed cobalt) where they are reduced easily by methane and the intermediate compounds isolated are organic nitro compounds and isocyanates [16]. It is evident that the ability of supported cobalt ions to form monodentate nitrates, which is favored by the high dispersion of these ions, is decisive for their activity in SCR with methane [15,16].

The subject of the present study is to elucidate the nature and reactivity of the surface compounds appearing during NO adsorption and $NO + O_2$ coadsorption on Co/ZrO_2 and $Co/SO_4^{2-}–ZrO_2$ samples characterized by a high cobalt dispersion. In order to distinguish the surface compounds formed with the participation of the active phase and those appearing on the support, parallel experiments with ZrO_2 and $SO_4^{2-}–ZrO_2$ have been carried out. IR spectroscopy has been used for direct determination of the kind of the surface compounds.

2. Experimental

2.1. Samples and reagents

Commercially available zirconia (Degussa) with a specific surface area of $53 \, m^2 \, g^{-1}$ was used. Sulfated zirconia (SZ) was prepared by suspending ZrO_2 in a solution of $0.5 \, M \, H_2SO_4$. After 90 min stirring the mixture was filtered and washed with $0.05 \, M \, H_2SO_4$. The precipitate was dried at 383 K and calcined for 1 h at 773 K. The specific surface area of the SZ obtained was $55 \, m^2/g$. The electron microphotographs revealed that the main particle size zirconia is about 70 nm. The particles of SZ are similar, but form small aggregates.

The Co/ZrO_2 (Co–Z) sample was prepared by impregnation of zirconia with a 0.9 M solution of Co $(CH_3COO)_2$. The sample of cobalt deposited on sulfated zirconia (Co–SZ) was obtained by impregnating

the SZ with 1.35 M $CoCl_2$ solution. The nominal cobalt concentrations in Co–Z and Co–SZ were 6 and 8 wt.%, respectively.

The nitrogen oxide (>99.5%) and oxygen (>99.95%) were supplied by Merck and the methane (>99.9%) by Messer Griesheim

2.2. Methods

The IR investigations were carried out using a Nicolet Avatar 320 spectrometer with a spectral resolution of $2 \, cm^{-1}$ and accumulating 128 scans. Self-supporting pellets ($\sim$10 mg cm^{-2}) were prepared by pressing the samples at 10^4 kPa and were directly treated in the IR cell. The latter was connected to a vacuum apparatus with a residual pressure of about 10^{-3} Pa. Prior to the adsorption measurements, the samples were activated by heating for 1 h at 673 K under oxygen and evacuation for 1 h at the same temperature.

The electron microphotographs were taken by a JEM-200CX electron microscope.

The XPS experiments were performed in an ES-CALAB MkII VG scientific system using Mg Kα radiation with an energy of 1253.6 eV in a vacuum chamber (residual pressure 2×10^{-7} Pa).

3. Results and discussion

3.1. Preliminary investigations on the synthesis of highly dispersed cobalt catalysts

Preliminary investigations on the synthesis of supported cobalt catalysts were performed with a view to obtain a high-dispersion active phase. One of the methods ensuring atomic dispersion of the supported phase is the so-called grafting or adsorption of cobalt cations from a solution. We have synthesized a Co/SiO$_2$ sample by adsorption of cobalt ions from solution of a $[Co(NH_3)_6]^{3+}$ cobalt–ammonia complex. The sample obtained was characterized by a high dispersion of the deposited cobalt ions. However, the adsorption capacity of zirconia towards cobalt ions was very low. As a result the samples obtained had a quite low cobalt content (below 0.2 wt.%). For that reason we studied the samples prepared by impregnation with different solutions of cobalt salts (nitrates, chlorides, acetates), synthesizing series of samples

with increasing cobalt concentrations. The estimation of cobalt dispersion was based on the ratio between the areas of the CO 2p$_{1/2}$ and Zr 3d peaks in the XPS spectra. This technique gives reliable results when comparing samples with the same support [18]. With rising cobalt concentration its dispersion exhibited an initial slight decrease followed by a sharp drop. High-dispersion cobalt was obtained on zirconia by impregnation with cobalt acetate at cobalt concentrations of less than 8 wt.%. On the sulfated support highly dispersed cobalt was obtained by impregnation with a cobalt chloride solution at cobalt concentrations below 10 wt.%. On the basis of the results obtained, the samples chosen for further studies were Co–Z with a nominal cobalt concentration of 6 wt.% and Co–SZ with a nominal cobalt concentration of 8 wt.%.

A more precise determination of the cobalt dispersion on these two samples was made by TPD of pre-adsorbed NO [18]. The results showed that, using the Co–SZ sample as a standard (assuming a 100% dispersion), the cobalt dispersion on the Co–Z sample is about 90%. No evidence of a separate cobalt-containing phase was found in the electron microphotographs.

3.2. Adsorption of NO

3.2.1. ZrO$_2$

Adsorption of NO on the ZrO$_2$ and SZ samples was studied in details [19]. Therefore, only the most important results directly associated with the supported catalysts will be described here. The adsorption of NO (4 kPa equilibrium pressure) on zirconia produced a series of bands with a very low intensity. Their maxima were at 3445, 2243 (not shown), 1621, 1560, 1443, 1423, 1322, 1233, 1189, 1142, 1057 and 982 cm^{-1} (Fig. 1, spectrum a). The band at 2243 cm^{-1} was attributed to the ν(N–N) stretching modes of adsorbed N$_2$O. The corresponding ν(N–O) mode appeared at 1233 cm^{-1}. The bands at 3445, 1621, 1142 and 982 cm^{-1} were attributed to adsorbed nitric acid [20] while those at 1560, 1189 and 1057 cm^{-1}, to bidentate nitrates [19]. Bands at 1443, 1423 and 1322 cm^{-1} were assigned to nitro compounds [19,21,22]. A careful analysis of the spectra revealed the presence of a band with an extremely low intensity at 1906 cm^{-1} which was assumed to belong to nitrosyls of the Zr^{4+}(NO$_3^-$)–NO type, i.e. they
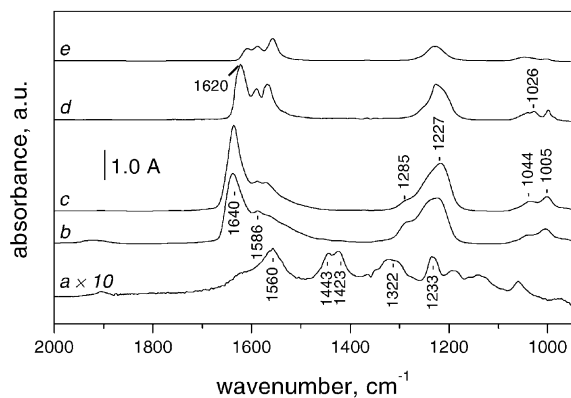
Fig. 1. FT-IR spectra of NO and O_2 coadsorption on ZrO_2. Adsorption of NO (equilibrium pressure of 4 kPa) (a), introduction of O_2 (1.3 kPa) (b), followed by evacuation at 293 K (c), 573 K (d) and 673 K (e).

have been formed with the participation of zirconium cations whose acidity has been enhanced as a result of the inductive effect of nearby nitrates. This interpretation is supported by the fact that the 1906 cm^{-1} band rises in intensity when small amounts of oxygen is added to the NO–ZrO_2 system and when the nitrate bands develop.

3.2.2. SO_4^{2-}–ZrO_2

The spectrum of the activated SZ sample contains an intense band at about 1385 cm^{-1} (spectrum not shown), which is due to the ν(S=O) stretching modes of surface sulfates [23]. The adsorption of NO (2.4 kPa equilibrium pressure) on SZ (Fig. 2, spectrum a) leads, similarly to the case of zirconia, to the appearance of relatively intense N_2O bands at 2243 and 1226 cm^{-1}. A series of bands with very low intensities are seen after a careful examination of the spectra, their maxima being at 1945, 1910, 1618, 1554, 1333, 1300, 1174, 1144 and 1113 cm^{-1}. Simultaneously, a negative peak at about 1380 cm^{-1} is visible due to the shift of the sulfate band to 1350–1330 cm^{-1}. The decrease in equilibrium pressure followed by evacuation result in disappearance of the bands in the region around 1900 cm^{-1} (see the inset in Fig. 2). These bands have a relatively high intensity as compared to the case of NO adsorption on zirconia and have been assigned to nitrosyls formed on the zirconium cations which acidity has been affected by neighboring sulfate ions. The remaining bands have a lower intensity than is the case
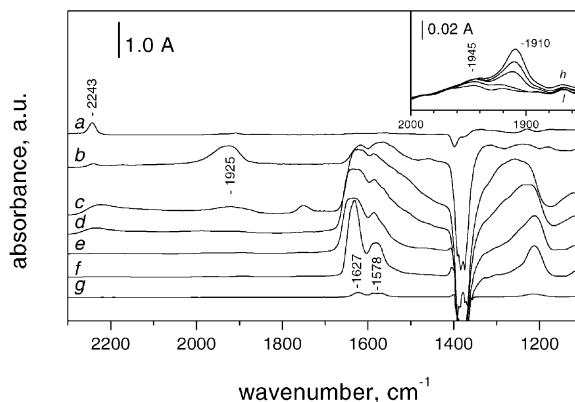

Fig. 2. Surface NO_x species on SO_4^{2-}–ZrO_2. Adsorption of NO (equilibrium pressure of 2.4 kPa) (a), introduction of O_2 (0.27 kPa) (b) and after addition of more O_2 (2.7 kPa) (c), followed by 15 min evacuations at 298 K (d), 473 K (e), 573 K (f) and 673 K (g). Inset: FT-IR spectra of NO adsorbed on SO_4^{2-}–ZrO_2: equilibrium pressures of 2400 Pa (h), 1200 Pa (i) and 130 Pa NO (j) and after evacuation (k and l).

of zirconia and are due to adsorbed nitric acid and bidentate nitrates (see above). The results show that SZ is characterized by enhanced acidity as compared to zirconia whereas its ability to form surface nitrates is weaker. In addition, no nitro complexes have been observed on this sample.

3.2.3. Co/ZrO$_2$

Adsorption of NO (0.4 kPa equilibrium pressure) on Co/ZrO_2 (Fig. 3, spectrum a) produces two intense
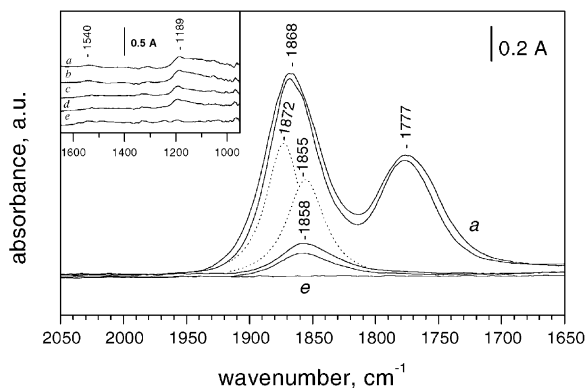

Fig. 3. Adsorption of NO (equilibrium pressure of 0.4 kPa) (a) on Co/ZrO_2, followed by evacuation at 298 K (b), 373 K (c), 423 K (d) and 473 K (e).

bands with maxima at 1868 and 1777 cm^{-1}. As these bands have not been detected on the pure support, they are obviously due to nitrosyl complexes of the cobalt. In agreement with data from the literature [14–16,18,19,24–30] the bands at 1868 and 1777 cm^{-1} can be assigned to ν_s and ν_{as} stretching modes, respectively, of $Co^{2+}(NO)_2$ type dinitrosyls. However, it is known that the ν_s stretching mode is of a lower intensity than is the case of the corresponding antisymmetric vibration [31]. This indicates the presence of another band at about 1870 cm^{-1} which is superimposed on the ν_s of $Co^{2+}(NO)_2$.

In the low-frequency region there is a low-intensity band with a maximum at 1189 cm^{-1} (see the inset in Fig. 3) whose appearance is probably caused by nitro compounds or NO^- [11,31]. A decrease in the equilibrium pressure and evacuation practically does not lead to intensity changes of the registered bands (Fig. 3, spectrum b). Evacuation at 373 K causes disappearance of the band at 1777 cm^{-1}, while a low-intensity band at 1858 cm^{-1} is found instead of the band at 1868 cm^{-1} (Fig. 3, spectrum c). The intensity of this band slightly decreases after evacuation at 423 K (Fig. 3, spectrum d) and vanishes after evacuation at 473 K (Fig. 3, spectrum e). In the latter case the band at 1189 cm^{-1} also disappears.

Computer deconvolution of the nitrosyl bands (see Fig. 3) clearly shows that the component at 1868 cm^{-1} consists of two bands with maxima at 1855 and 1872 cm^{-1}. The component intensity ratio makes one to assume that cobalt dinitrosyls are characterized by ν_s at 1855 cm^{-1} and ν_{as} at 1777 cm^{-1}, while the band at 1872 cm^{-1} obviously corresponds to another type of cobalt nitrosyls. The band at 1858 cm^{-1} is probably due to linear Co^{2+}–NO nitrosyls [16] produced as a result of the decomposition of the dinitrosyls.

The results obtained show that NO adsorption on Co/ZrO_2 leads to the formation of relatively stable mono and dinitrosyls. It should be mentioned, for the sake of comparison, that dinitrosyls on Co^{2+}/SiO_2 decompose already at room temperature while cobalt nitrates on zeolite matrices are in some cases stable up to 573 K [16].

3.2.4. Co/SO$_4$$^{2-}$–ZrO$_2$

Adsorption of NO (equilibrium pressure 1.3 kPa) on Co–SZ results in three bands in the nitrosyl region, their maxima being situated at 1922, 1903 and
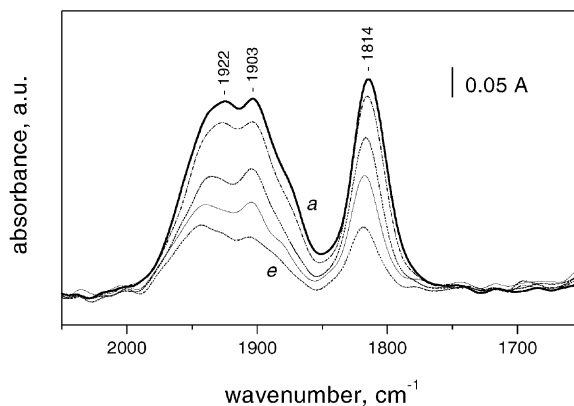

Fig. 4. FT-IR spectra of NO adsorbed on $Co/SO_4$$^{2-}$–$ZrO_2$: equilibrium pressures of 1330 Pa (a) and 130 Pa NO (b) and evolution of the spectra in dynamic vacuum (c–e).

1814 cm^{-1} (Fig. 4, spectrum a). A decrease in the equilibrium pressure (Fig. 4, spectrum b) and evacuation (Fig. 4, spectra c and d) cause a drop in intensity of the three bands, the one at 1922 cm^{-1} exhibiting a higher stability. In agreement with these results and with literature data [31], we assign the bands at 1903 and 1814 cm^{-1} to ν_s and ν_{as} stretching modes, respectively, of $Co^{2+}(NO)_2$ species. These bands are registered at higher frequencies as compared to the geminal dinitrosyls formed on Co/ZrO_2. This is obviously due to the effect of sulfate ions and possibly to residual chlorine ions. The stability of nitrosyls is lower than is the case of sample Co–Z. Hence, regardless of the fact that sulfation enhances the acidity of the support, the acidity of the deposited cobalt ions is lower. Analysis of the literature data [15,16] and special studies [32] have shown that no relationship exists between the stability and the spectral behavior of the $Co^{2+}(NO)_2$ complexes.

The band at 1923 cm^{-1} can be attributed to linear Co^{n+}–NO mononitrosyls [18]. In this case the probable oxidation state of the cobalt ions is +3 since, as a rule, Co^{2+}–NO compounds absorb at lower frequencies.

3.3. Coadsorption of NO and O$_2$

3.3.1. ZrO$_2$

Introduction of O_2 (1.3 kPa) into the NO–ZrO_2 system leads to the appearance of a series of intense

bands with maxima at 1640, 1586, 1560, 1285, 1237, 1227, 1044 and 1005 cm^{-1} (Fig. 1, spectrum b). The bands at 1640, 1227 and 1005 cm^{-1} have been assigned to surface bridged nitrates while those at 1586, 1285 and 1044 cm^{-1} are assumed to be due to bidentate nitrates [11,31]. In addition, a low-intensity band has been detected at 1921 cm^{-1} which is attributed to $Zr^{4+}(NO_3^-)$–NO nitrosyls [19]. The bands at 1443 and 1423 cm^{-1} (characterizing nitro compounds) decrease in intensity, which evidences the oxidation of NO_2^-–NO_3^- in NO + O$_2$ atmosphere.

Subsequent evacuation do not cause changes in the IR spectra (Fig. 1, spectrum c). A decrease in concentration of the surface compounds is observed after evacuation at 573 and 673 K (Fig. 1, spectra d and e). In these conditions the bands of the bridged nitrates decrease visibly in intensity while the bands of bidentate nitrates show a slight intensity increase which suggests conversion of one kind of nitrates into another. Analysis of the intensity ratio of the bands at 1600 and 1200 cm^{-1} shows that with rising the temperature of evacuation this ratio decreases. This indicates the presence of an additional adsorption species at about 1230 cm^{-1} which is attributed to surface nitrites appearing during autoreduction of the nitrates. All bands of adsorbed compounds disappear after evacuation at 723 K (spectrum not shown).

3.3.2. SO_4^{2-}–ZrO_2

Introduction of O$_2$ to the NO–SZ system also results in formation of surface bridged (1638, 1229, 1121 cm^{-1}) and bidentate (1578, ca. 1280 cm^{-1}) nitrates (Fig. 2, spectrum c). Simultaneously, the band of sulfates at 1395 cm^{-1} is shifted to 1320 cm^{-1} and the amount of adsorbed N$_2$O (2243 cm^{-1}) decreases. In addition, a band at 2236 cm^{-1} assigned to NO$^+$ [33,34], another one at 1925 cm^{-1} ascribed to nitrosyls and a third at 1751 cm^{-1} attributed to N$_2$O$_4$ [31], emerge.

Evacuation at room temperature (Fig. 2, spectrum d) leads to the disappearance of nitrosyls and N$_2$O$_4$ and to a strong decrease in NO$^+$ concentration. An more pronounced decrease in nitrate concentration is established after evacuation at 573 K (Fig. 2, spectrum f) and all nitrates are practically decomposed after evacuation at 673 K (Fig. 2, spectrum g). The results obtained show that the surface nitrates on SZ are somewhat less stable than are the nitrates on ZrO$_2$.
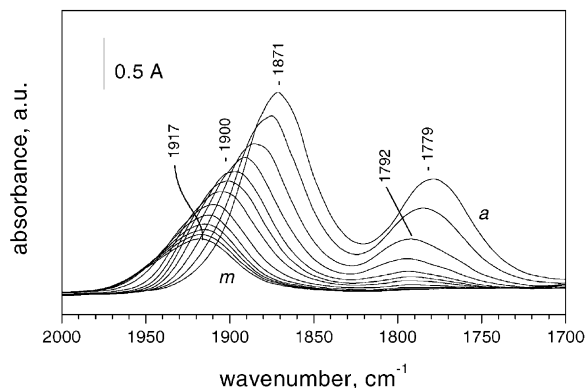

Fig. 5. FT-IR spectra (2000–1700 cm^{-1} region) of NO and O$_2$ coadsorption on Co/ZrO$_2$. Adsorption of 0.7 kPa NO (a) and admission of 1.3 kPa O$_2$ (b), followed by time evolution of the spectra (c–m).

Similar results have been reported very recently by Kantcheva and Ciftikli [20].

3.3.3. Co/ZrO$_2$

Addition of O$_2$ to the NO–Co–Z system results in erosion of the bands at 1871 and 1779 cm^{-1} which characterize cobalt mononitrosyls and dinitrosyls (Fig. 5, spectra b–m). Simultaneously, a band whose maximum is gradually established at 1917 cm^{-1}, is formed. In the region of lower frequencies, bands at 1620, 1560, 1285 and 1230 cm^{-1} develop gradually while the band at 1189 cm^{-1} decreases in intensity (Fig. 6, spectra b and c). After a prolonged contact
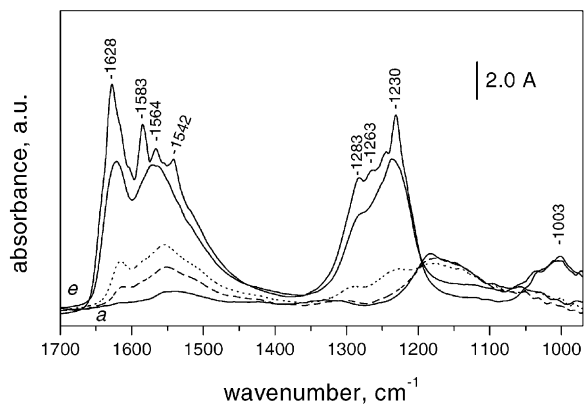

Fig. 6. FT-IR spectra (1700–950 cm^{-1}) of NO and O$_2$ coadsorption on Co/ZrO$_2$. Adsorption of 0.7 kPa NO (a) and admission of 1.3 kPa O$_2$ (b), followed by time evolution of the spectra (c–e).

between the sample and the gas mixture (Fig. 6, spectra d and e), intense bands with maxima at 1628, 1583, 1564, 1542, 1283, 1263, 1230 and $1003 \, cm^{-1}$ appear. The band at $1189 \, cm^{-1}$ (attributed to nitro compounds or NO^-) completely disappears. In addition, there is an isosbestic point between the bands at 1189 and $1230 \, cm^{-1}$ which is an indication for direct conversion (oxidation) of nitrites to nitrates.

Comparison with spectra obtained after coadsorption of NO and O_2 on the pure support reveals two peculiarities:

- The bands in the 1600–1500 and $1300–1250 \, cm^{-1}$ regions are much more intense with sample Co–Z. On this basis, the bands can be associated with cobalt nitrates. The band at $1583 \, cm^{-1}$ could be due to bidentate nitrates while those at 1564 and $1542 \, cm^{-1}$ correspond to monodentate nitrates. Unfortunately, no explicit interpretation of the band at $1628 \, cm^{-1}$ is possible. It may be due to both nitrates formed on the support and cobalt nitrates as well as bridged nitrates of the $Zr^{4+}–(NO_3{}^-)–Co^{2+}$ type.
- The band at ca. $1560 \, cm^{-1}$ assigned to monodentate nitrates of cobalt is the first to appear during coadsorption of NO and O_2.

The development of the nitrate bands simultaneously with the band at $1917 \, cm^{-1}$ allows one to assume that the latter corresponds to $Co^{3+}(NO_3{}^-)–NO$ type nitrosyls. A similar oxidation of surface cations has been observed during coadsorption of NO and O_2 on Cu/SiO$_2$ [35]. It has been established that addition of small amounts of oxygen to the NO–Cu/SiO$_2$ system leads to a fast oxidation of Cu^+ to Cu^{2+}. The band at $1917 \, cm^{-1}$ could hardly correspond to adsorbed N_2O_3 because in this case an intense contaminant band at about $1300 \, cm^{-1}$ should have been detected. However, this possibility cannot be totally ruled out.

Evacuation at room temperature (Fig. 7, spectrum b) only leads to an intensity decrease of the band at $1917 \, cm^{-1}$. This favors the supposition that the band characterizes nitrosyl compounds since adsorbed N_2O_3 is, as a rule, removed very easily by evacuation [15,16]. After evacuation at 373 K the intensity of the nitrate bands strongly decreases and low-intensity bands (1622 and $1552 \, cm^{-1}$), probably due to nitrites and nitrates formed on the support, remain (Fig. 7, spectrum c). These compounds are, as expected, char-
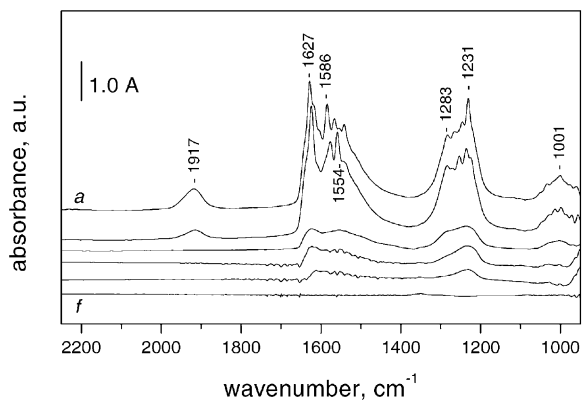
Fig. 7. Coadsorption of NO and O_2 (0.7:1.3 kPa) on Co/ZrO$_2$ (a), followed by evacuation at 298 K (b), 373 K (c), 473 K (d), 573 K (e) and 673 K (f).

acterized by a high thermal stability (Fig. 7, spectra d–f). The above results allow to assume that the larger part of the nitrates detected on Co–Z have been formed with the participation of cobalt ions.

3.3.4. Co/SO$_4{}^{2-}$–ZrO$_2$

Addition of O_2 to the NO–Co–SZ system causes, similarly to the case of Co–Z, a smooth decrease in intensity of the dinitrosyl bands at 1907 and $1812 \, cm^{-1}$ (Fig. 8, spectra b–d). The band at $1925 \, cm^{-1}$ characterizing Co^{3+}–NO species at first slightly increases
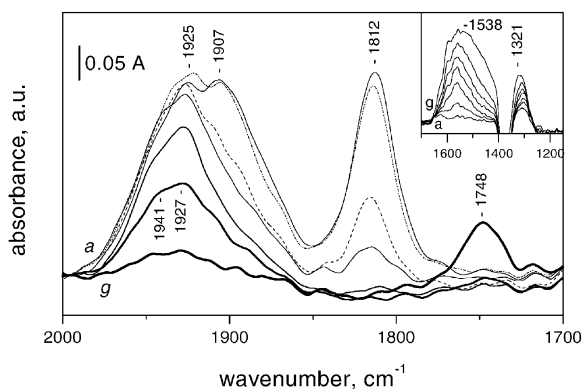
Fig. 8. Adsorption of NO (2.1 kPa equilibrium pressure) on Co/SO$_4{}^{2-}$–ZrO$_2$ (a), followed by addition of small amount of O_2 (530 Pa) (b), evolution with the time (c–e), addition of more O_2 (to totally 2.1 kPa O_2) (f) and addition of another big amount of O_2 (to totally 4 kPa O_2) (g).

in intensity (Fig. 8, spectrum b), which indicates oxidation of Co^{2+} to Co^{3+}, then the intensity begins to decrease (Fig. 8, spectra c–g). This band almost disappears under conditions where adsorbed N_2O_4 ($1748 \, cm^{-1}$) exists.

Simultaneously with these changes, a broad band with a maximum at $1538 \, cm^{-1}$ is observed in the low-frequency region, while the sulfate band at $1380 \, cm^{-1}$ is partly shifted to $1321 \, cm^{-1}$ (see Fig. 8, inset). The spectral characteristics of the nitrates obtained strongly differ from the characteristics of the nitrates formed on the pure support (see Fig. 2 for comparison). The shift of the sulfate band after adsorption, however, is an indication that part of the nitrates has been formed on the support.

Similarly to the case of Co–Z, evacuation at room temperature has almost no effect on the nitrate bands (Fig. 9, spectrum b) but the concentration of the latter noticeably decreases after evacuation at 373 K (Fig. 9, spectrum c). The component at $1606 \, cm^{-1}$ observed after evacuation at 573 K (Fig. 9, spectrum d) probably corresponds to nitrates formed on the support.

3.4. Reactivity of surface nitrates

Potential candidates for intermediates in SCR are compounds which have sufficient stability at the temperature of the catalytic process but are also highly reactive. Many investigations have shown that sur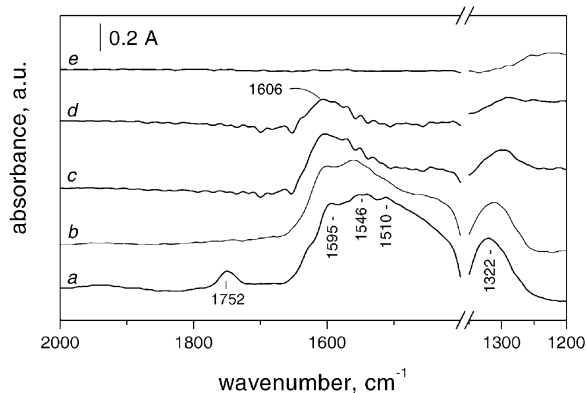face nitrates are key compounds in the process. The results of the present study are in agreement with this point of view since the only stable compounds formed on the catalysts during NO adsorption under aerobic conditions are various surface nitrates. For that reason, we studied their reactivity towards methane. In order to determine the role of nitrates formed with the participation of cobalt, we also investigated the interaction with methane of the nitrates formed on the supports. It should be noted that no comparison between the thermal stability of the surface compounds in vacuum and the stability in the conditions of catalytic process is possible. Separate experiments have shown that the stability of the nitrates under static conditions is much higher probably due to re-adsorption of the products of their decomposition.

3.4.1. Reactivity of surface nitrates on ZrO$_2$

Surface nitrates were formed on ZrO_2 during coadsorption of NO and O_2, followed by evacuation. The introduction of methane (equilibrium pressure 7 kPa) to the cell did not change the IR spectrum (Fig. 10, spectrum a). The heating of the sample under methane at temperatures up to 573 K (Fig. 10, spectra b and c) practically do not cause change of the spectrum. Only a slight drop in intensity of the bands at 1640 and $1215 \, cm^{-1}$ and appearance of low-intensity bands at 1443 and $1423 \, cm^{-1}$ (characterizing NO_2^-) and $1912 \, cm^{-1}$ (due to nitrosyls) were observed. These results evidence the high inertness of the nitrates towards methane up to 573 K. After heating at 673 K
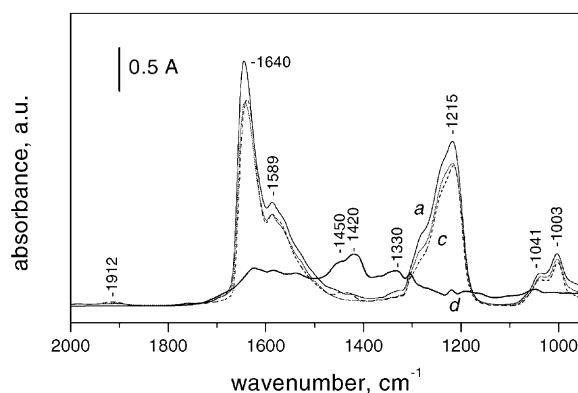

Fig. 9. Surface NO_x species on Co/SO_4^{2-}–ZrO_2. FT-IR spectra of NO and O_2 (2.1:4 kPa) (a) coadsorbed on Co/SO_4^{2-}–ZrO_2, followed by 15 min evacuations at 298 K (b), 373 K (c), 573 K (d) and 673 K (e).

Fig. 10. Reactivity of the surface NO_x species on ZrO_2 towards methane. Coadsorption of NO and O_2 (4:1.3 kPa), followed by evacuation and introduction of methane (7 kPa) (a) and heating in this atmosphere for 15 min at 373 K (b), 573 K (c) and 673 K (d).

(Fig. 10, spectrum d) the nitrate bands practically disappear and bands of nitro compounds (1450, 1420 and 1330 cm^{-1}) develop. Probably the band at 1630 cm^{-1} corresponds to adsorbed water resulting from the reaction. The other bands at 1600–1200 cm^{-1} are difficult to be identified. According to data from the literature [19], the bands can be denoted as a H–C–N–O deposit.

The results obtained show that the NO$_x$ compounds formed on ZrO$_2$ are inert towards CH$_4$ and cannot act as intermediates in SCR.

3.4.2. Reactivity of the surface nitrates on SO$_4{}^{2-}$–ZrO$_2$

In this case, again the addition of methane (6.4 kPa) to the SZ sample with pre-adsorbed nitrates causes no substantial change in the IR spectrum (Fig. 11, spectrum a). After heating under methane atmosphere at 473 K, negligible reduction is established, which is evidenced by the appearance of a nitrosyl band at 1931 cm^{-1} (Fig. 11, spectrum b). A slight drop in intensity of the nitrate bands is observed after reduction at 573 and 673 K (Fig. 11, spectra c and d) which, however, is probably caused by thermal decomposition of the nitrates since no bands which can be attributed to reaction products, are visible. A more pronounced decrease of nitrate band intensities is established after reduction at 723 K (Fig. 11, spectrum e). Simultaneously, the nitrosyl band at 1931 cm^{-1} shows a slight intensity rise. The results indicate that, similarly to
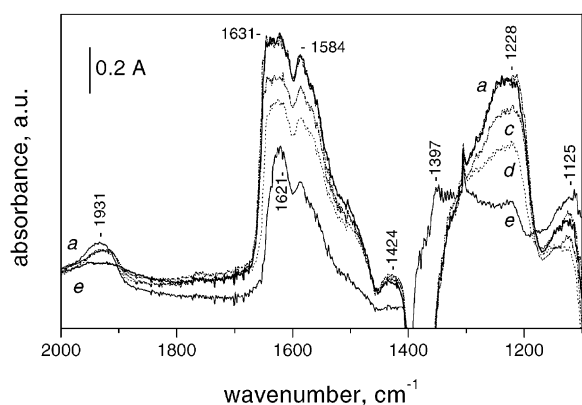

Fig. 12. Reactivity of the surface NO$_x$ species on Co/ZrO$_2$ towards methane. Coadsorption of NO and O$_2$ (0.7:1.3 kPa) followed by evacuation (a), introduction of methane (1.3 kPa) and heating in this atmosphere for 15 min at 473 K (b), 573 K (c) and 673 K (d), followed by evacuation at 573 K (e) and 673 K (f).

the case of ZrO$_2$, the nitrates on SZ are inert towards methane. No H–C–N–O deposit was registered with this sample, probably because its high acidity favors the C–H bond activation.

3.4.3. Reactivity of surface nitrates on Co/ZrO$_2$

Addition of CH4 (equilibrium pressure 1.3 kPa) to Co–Z with pre-adsorbed nitrates causes no spectrum changes (Fig. 12, spectrum a). After heating under methane at 473 K, the nitrate bands at 1577, 1544, 1254 and 1225 cm^{-1} vanish while that at 1917 cm^{-1} is shifted to 1898 cm^{-1} (Fig. 12, spectrum b). Simultaneously, a band with a maximum at 1505 cm^{-1} becomes visible. Heating in methane at 573 K leads to disappearance of the band at 1558 cm^{-1} and a significant intensity decrease of the bands at 1624 and 1237 cm^{-1} (Fig. 12, spectrum c) whereas the band at 1505 cm^{-1} becomes more distinct. The 1898 cm^{-1} band is additionally shifted to 1874 cm^{-1}. Heat-treatment in methane atmosphere at 673 K produces a broad absorption region below 1700 cm^{-1}, maxima being observed at 1628, 1505 and 1350 cm^{-1}, which, according to the literature data [36–45], is typical of H–C–N–O deposition (Fig. 12, spectrum d). The band at 1628 cm^{-1} is most probably due to adsorbed water, the bands at 1779 and 1736 cm^{-1} can be assigned to C=O modes of partly oxidized organic compounds, and the band at 1858 cm^{-1} may correspond to cobalt nitrosyls.

Fig. 11. Interaction of the nitrates on sulfated zirconia with methane. FT-IR spectra of NO and O$_2$ (2.4:2.4 kPa) coadsorbed on SO$_4{}^{2-}$–ZrO$_2$, followed by 15 min evacuation, and after interaction with CH$_4$ (6.4 kPa equilibrium pressure) at 298 K (a), 473 K (b), 573 K (c), 673 K (d) and 723 K (e).
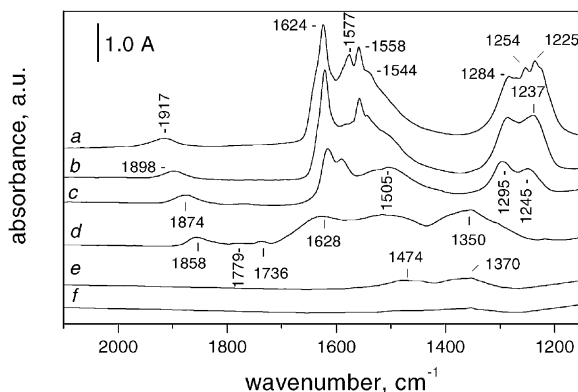
Evacuation at room temperature does not change the spectrum (not shown). Visible changes occur after evacuation at high temperatures only. The intermediate surface compounds, denoted as H–C–N–O deposit, are decomposed to a large extent after evacuation at 573 K (Fig. 12, spectrum e). After this treatment bands at 1350 and 1474 cm^{-1} only are observed in the spectrum, to vanish upon evacuation at 673 K (Fig. 12, spectrum f).

In contrast to the case of pure zirconia, the nitrates on Co/ZrO$_2$ show a higher reactivity towards methane. However, these nitrates are heterogeneous and possess various reactivity. Their reaction with methane begins at 473 K. As a result of this reaction, an organic H–C–N–O coverage is formed.

3.4.4. Reactivity of surface nitrates on Co/SO$_4{}^{2-}$–ZrO$_2$

Introduction of CH$_4$ (equilibrium pressure 6.7 kPa) to Co–SZ with pre-adsorbed nitrogen oxides causes no substantial changes of spectra (Fig. 13, spectrum a). Heating of the sample under methane at 373 K results in slight changes of the spectra: the band at 1594 cm^{-1} shows an intensity drop, while a band at 1607 cm^{-1} is formed (Fig. 13, spectrum b). The intensity decrease of the nitrate bands is more pronounced at 473 and 573 K (Fig. 13, spectra c and d). In these cases nitrosyls (band at 1934 cm^{-1}) are detected as reaction products. Interaction at 673 K results in complete disappearance of the nitrates. A band at 1617 cm^{-1} due

to adsorbed water is detected. It is this water that is responsible for the partial shift of the sulfate band from 1380 to 1305 cm^{-1} (Fig. 13, spectrum e). Unfortunately, data for intermediate compounds, which definitely elucidate the stages of interaction, are missing. This is probably due to the strong surface acidity of the sample, which hinders the formation of an H–C–N–O deposit. Indeed, such a deposit has been registered on zirconia although at higher temperatures but has not been found on the sulfated support. However, the results obtained indicate that the nitrates formed on Co–SZ have a higher reactivity than that found with nitrates present on the pure support. Hence, in this case again the cobalt nitrates are key compounds of SCR with methane.

Finally we may say, similarly to the case of some cobalt-containing catalysts, the nitrates formed on Co–Z and Co–SZ are reactive towards methane. The reaction temperature is higher as compared to other SCR catalysts such as Co-ZSM-5 and Co/SiO$_2$. Preliminary sulfatation of the support causes no change in kind of the surface compounds appearing during adsorption of NO$_x$ and does not affect substantially their reactivity. However, on sulfated samples formation of a H–C–N–O deposit is hindered.

4. Conclusions

Adsorption of NO on SO$_4{}^{2-}$–ZrO$_2$ leads to the formation of nitrosyls of Zr^{4+}(SO$_4{}^{2-}$)–NO type. On pure zirconia Zr^{4+}(NO$_3{}^{-}$)–NO species are obtained only after addition of oxygen and appearance of nitrates. This is due to the fact that the nitrates, which, similarly to the sulfates, increase the Lewis acidity of the Zr^{4+} sites.

Adsorption of NO on Co/ZrO$_2$ and Co/(SO$_4{}^{2-}$)–ZrO$_2$ results in formation of cobalt Co^{3+}–NO and Co^{2+}(NO)$_2$ dinitrosyls species. They are oxidized easily and play no essential role in the SCR with methane.

Coadsorption of NO and O$_2$ on ZrO$_2$ and SO$_4{}^{2-}$–ZrO$_2$ leads mainly to the formation of thermally stable nitrates which are, however, inert with respect to interaction with methane.

The main products of NO + O$_2$ coadsorption on Co/ZrO$_2$ and Co/SO$_4{}^{2-}$–ZrO$_2$ are thermally stable nitrates which react with methane at 473–573 K. These temperatures are, however, by about 100 K higher than

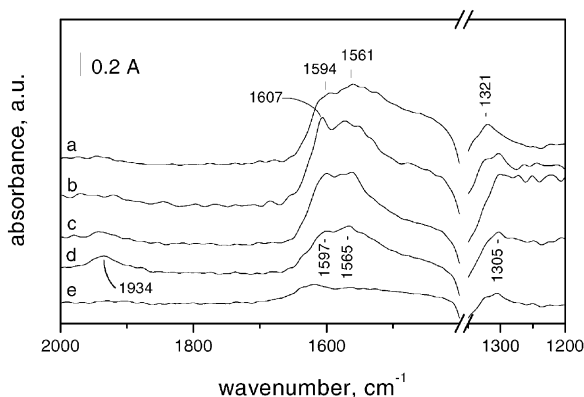Fig. 13. Changes in the FT-IR spectra of Co/SO$_4{}^{2-}$–ZrO$_2$ with pre-adsorbed nitrates (2 kPa NO + 6.4 kPa O$_2$) after interaction with methane (6.7 kPa) at 300 K (a), 373 K (b), 473 K (c), 573 K (d) and 673 K (e).

the interaction temperature of methane with the nitrates on Co-ZSM-5, which is the classical catalyst of SCR with methane.

Preliminary sulfatation of zirconia does not affect the nature of the surface species formed during $NO + O_2$ coadsorption on supported cobalt catalysts but hinders the formation of H–N–C–O deposit.

Acknowledgements

References

[1] F.P. Boer, L.L. Hegedus, T.R. Gouker, K.P. Zak, Chemtech (1990) 312.
[2] M.D. Amiridis, T. Zhang, R.J. Farrauto, Appl. Catal. B 6 (1996) 203.
[3] D.K. Captain, K.L. Roberts, M.D. Amiridis, Catal. Today 42 (1998) 93.
[4] W. Held, A. König, T. Richter, L. Puppe, SAE Paper, 900496, 1990.
[5] M. Iwamoto, H. Hamada, Catal. Today 10 (1991) 57.
[6] M.D. Fokema, J.Y. Ying, Catal. Rev. Sci. Eng. 43 (2001) 1.
[7] Y. Li, J.N. Armor, Appl. Catal. B 1 (1992) L31.
[8] Y. Li, J.N. Armor, in: H.E. Curry-Hyde, R.F. Howe (Eds.), Natural Gas Convertion II, Elsevier, Amsterdam, 1994, p. 103.
[9] H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari, H. Tsuchida, Catal. Today 29 (1996) 53.
[10] M. Inaba, Y. Kintaichi, M. Haneda, H. Hamada, Catal. Lett. 39 (1996) 269.
[11] D. Pietrogiacomi, S. Tuti, M.C. Campa, V. Indovina, Appl. Catal. B 28 (2000) 43.
[12] P. Ciambelli, P. Corbo, M.C. Gaudino, F. Migliardini, D. Sannino, Top. Catal. 16/17 (2001) 413.
[13] J. Pasel, V. Speer, C. Albrecht, F. Richter, H. Papp, Appl. Catal. B 25 (2000) 105.
[14] T. Beutel, B.J. Adelman, W.M.H. Sachtler, Appl. Catal. B 9 (1996) L1.
[15] B. Djonev, B. Tsyntsarski, D. Klissurski, K. Hadjiivanov, J. Chem. Soc., Faraday Trans. 93 (1997) 4055.
[16] K. Hadjiivanov, B. Tsyntsarski, T. Nikolova, Phys. Chem. Chem. Phys. 1 (1999) 4521.
[17] E. Ivanova, K. Hadjiivanov, D. Klissurski, M. Bevilaqua, T. Armaroli, G. Busca, Micropor. Mesopor. Mater. 46 (2001) 299.
[18] K. Hadjiivanov, D. Panayotov, V. Avreyska, B. Tsyntsarski, D. Klissurski, Ts. Marinova, Surf. Interf. Anal. 34 (2002).
[19] K. Hadjiivanov, V. Avreyska, D. Klissurski, Ts. Marinova, Langmuir 18 (2002) 1619.
[20] M. Kantcheva, E.Z. Ciftlikli, J. Phys. Chem. B 106 (2002) 3941.
[21] D. Pozdnyakov, V. Fillimonov, Kinet. Katal. 14 (1973) 760.
[22] K. Hadjiivanov, Catal. Lett. 68 (2000) 157.
[23] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Mir, Moscow, 1966.
[24] J.H. Lunsford, P. Hutta, M.J. Lin, K.A. Windhorst, Inorg. Chem. 17 (1978) 606.
[25] Y. Li, T.L. Slager, J.N. Armor, J. Catal. 150 (1994) 388.
[26] C.Y. Zhu, C.W. Lee, P.J. Chong, Zeolites 17 (1996) 483.
[27] M.C. Campa, S. De Rossi, G. Ferraris, V. Indovina, Appl. Catal. B 8 (1996) 315.
[28] M.C. Campa, D. Pietrogiacomi, S. Tuti, G. Ferrarisa, V. Indovina, Appl. Catal. B 18 (1998) 151.
[29] M. Yamada, N. Koizumi, M. Yamazaki, Catal. Today 50 (1999) 3.
[30] F. Geobaldo, B. Onida, P. Rivolo, F. Di Renzo, F. Fajula, E. Garrone, Catal. Today 70 (2001) 107.
[31] K. Hadjiivanov, Catal. Rev. Sci. Eng. 42 (2000) 71.
[32] B. Tsyntsarski, D. Klissurski, K. Hadjiivanov, in: L. Petrov, Ch. Bonev, G. Kadinov (Eds.) Proceedings of the 9th International Symposium on Heterogeneous Catalysis, Varna, Bulgaria, 23–27 September 2000, p. 133.
[33] K. Hadjiivanov, J. Saussey, J.L. Freysz, J.-C. Lavalley, Catal. Lett. 52 (1998) 103.
[34] K. Hadjiivanov, V. Bushev, M. Kantcheva, D. Klissurski, Langmuir 10 (1994) 464.
[35] K. Hadjiivanov, H. Knözinger, Phys. Chem. Chem. Phys. 3 (2001) 1132.
[36] T. Tabata, H. Ohtsuka, M. Kokitsu, O. Okada, Bull. Chem. Soc. Jpn. 68 (1995) 1905.
[37] B. Adelman, T. Beutel, G. Lei, W.M.H. Sachtler, J. Catal. 158 (1996) 327.
[38] N. Hayes, R. Joyner, E. Shpiro, Appl. Catal. B 8 (1996) 343.
[39] M. Haneda, Y. Kintaichi, M. Inaba, H. Hamada, Appl. Surf. Sci. 121/122 (1997) 391.
[40] H.Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, J. Catal. 180 (1998) 171.
[41] K. Hadjiivanov, H. Knözinger, B. Tsyntsarski, L. Dimitrov, Catal. Lett. 62 (1999) 35.
[42] T. Tanaka, T. Okuhara, M. Misono, Appl. Catal. B 4 (1994) L1.
[43] T. Sun, M.D. Fokema, J.Y. Ying, Catal. Today 33 (1997) 251.
[44] T. Beutel, B. Adelman, W.M.H. Sachtler, Catal. Lett. 37 (1996) 125.
[45] J. Connerton, R.W. Joyner, M. Stockenhuber, Chem. Commun. (1997) 185.