SITING AND REACTIVITY OF THE Co IONS IN FERRIERITE IN SELECTIVE CATALYTIC REDUCTION OF NO WITH CH$_4$

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Catalytic activity of Co ions in CoNaK- and CoH-ferrierites in selective catalytic reduction of NO with methane depending on Co loading was investigated. The previously determined distribution of the exchanged Co ions in Co-ferrierites at three different cationic sites, differring in coordination of the Co ions to framework oxygens, has been utilized to analyze catalytic activity of the Co ions. The type of coordination of the Co ions dramatically affects their reactivity in the selective catalytic reduction of NO with methane. The Co ions coordinated to four framework oxygens of the wall of the main channel exhibit the highest activity, while the Co ions placed in a "boat shape", the most packed site of ferrierite show the lowest activity.
Key words: Selective catalytic reduction of NO with methane; Co-zeolite; Co-ferrierite; Nitric oxide; Zeolites; Heterogeneous catalysis; Cobalt.

Selective catalytic reduction (SCR) of NO$_x$ with low alkanes has appeared to be a promising way for NO$_x$ abatement from flue exhaust gases with an excess of oxygen. If a suitable structure of the catalyst is found, highly active even in the presence of water vapour, moreover, enabling advantageous application of methane as a reducing agent, then a highly advanced technology for NO$_x$ elimination from exhaust gases from combustion of natural gas might be introduced. First patents[1–3] disclosed activity in the SCR of NO with methane for the Co ions exchanged in zeolites of ZSM-5 (MFI) and ferrierite (FER) structures, *i.e.* zeolites containing in their framework low content of aluminium (so called "high-silica" zeolites with the framework Si/Al > 8). Ga and In in ZSM-5 were found to provide a comparable activity in a higher temperature range[4–6]. However, such activity, high and stable with time-on-stream, was not observed for these cations if exchanged in zeolites of faujasite structure consisting of framework

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with high concentration of aluminium and regular six rings in contrast to MFI and FER structures, frameworks of which contain pentasil rings. Co ions supported as various oxides on ZSM-5 zeolite do not provide comparable activity in SCR of NO with methane[7,8] either.

This indicates a dramatic effect of the zeolite matrix on the Co ion bonding resulting in their unique redox properties and catalytic activity. Two factors have been considered, which might affect the activity of the Co ions in SCR of NO with methane: (i) specific coordination of the Co ions in "high-silica", "pentasil-ring" zeolites and (ii) negative charges on the framework oxygens, to which the Co ions are coordinated, given by the framework composition.

As the type of coordination of transition metal ions can be assumed as a highly important factor affecting the reactivity of the cations, our attention has been at first focused on the effect of coordination of the Co ions in high-silica zeolites of MFI and FER structures on their activity in SCR of NO with methane. However, siting and coordination of the Co ions (and of transition metal ions in general) to framework oxygens were not known for high-silica zeolites, in contrast to well-established cationic sites for exchanged metal ions in aluminium-rich zeolites of Type A and faujasite structures obtained from XRD (ref.[9]). The reason for the absence of XRD data for high-silica zeolites is a low concentration of the metal ions, because of low concentration of aluminium, moreover, divided among several cationic sites, and low symmetry of these frameworks. Therefore, our attempt to obtain an insight into the function of the metal ions exchanged in these zeolites had to include both determination of the siting-coordination of the Co ions in MFI and FER structures, population of individual Co ion types, and investigation of the catalytic activity of Co zeolites in SCR of NO with methane.

Recently, we have identified coordination and siting of the exchanged Co ions and population of the individual sites in mordenite[10], ferrierite[11] and ZSM-5 (ref.[12]) structures on the basis of VIS spectra of Co ions in zeolites of various compositions. This has enabled evaluation of the catalytic activity of the Co ions variously coordinated in high-silica zeolites in this study.

SCR of NO with methane is a complex reaction, for which detail mechanism was not established up to now, but the presence of an excess of oxygen is a necessary condition[2]. This fact already excluded the original assumption that the SCR can occur *via* NO decomposition, and oxygen formed *in statu nascendi* being removed by hydrocarbons. On the contrary, the necessary presence of an oxygen excess and investigation of SCR of NO_2 supports conclusion that the oxidation of NO to NO_2 is the first step of the process, followed by the reduction of NO_2 (and NO_x) with methane, which is oxidized to CO_2 and/or CO. However, depending on the activity/selectivity of the catalyst and reaction conditions, simultaneous oxidation of methane with oxygen takes place. Thus, while oxygen is necessary to produce NO_x, it competes with NO_x for methane oxidation. As for the function of the Co ions in SCR of NO, it has been assumed that single

Co ions are responsible for SCR of NO_x with methane, while oxidic Co_xO_y species, which can also be formed by some cobalt precipitation in the zeolite during cobalt ion exchange, provide activity only for NO oxidation to NO_2 (refs[7,8]).

This contribution deals with the activity of the Co ions exchanged in ferrierite structure in SCR of NO with methane. Three types of the Co ion coordinations to framework oxygens at cationic sites in ferrierite structure have been recently established[11]. Population of the individual cationic sites differs depending on the Co loading and co-cation presence. This knowledge has been employed to evaluate the activity of the individual Co ions by investigating the conversion of NO to various products, mainly to N_2 over Co-ferrierites with different Co loading and co-cation presence. Besides, participation of protonic sites and undefined Co_xO_y species within ferrierite in the SCR catalytic reaction is shortly discussed.

EXPERIMENTAL

Catalyst Preparation

Na,K-Ferrierite with chemical composition (wt.%): SiO_2 75.5, Al 4.01, Na 1.89, K 2.59 and H_2O 16.01 was obtained from TOSOH Corp., Japan. NH_4-Ferrierite was prepared from NaK-ferrierite by ion exchange with 1.0 M NH_4NO_3 using 10 ml of the solution per 1 g of the zeolite. The procedure was repeated four times at room temperature to reach a complete NH_4^+ ion exchange. Then the zeolite was washed three times with distilled water and dried on air.

$CoNH_4$- and CoNaK-ferrierites with Co concentration ranges 0.40–3.62 wt.% and 0.12–2.60 wt.%, respectively, were prepared by ion exchange of NH_4-ferrierite with 0.05–0.10 M $Co(OCOCH_3)_2$ and NaK-ferrierite with 0.001–0.05 M $Co(NO_3)_2$. The ion exchange was carried out at room temperature or at 343 K to obtain highly loaded samples. pH value of cobalt salt solutions with the zeolite was kept at a constant value of 5.5 during ion exchange using 0.01 M HNO_3. After ion exchange, the samples were washed three times with distilled water and dried on air. Detailed conditions for the Co ion exchange are given in Table I. Co-Ferrierites were analyzed, after their dissolution in hydrofluoric acid or by alkali melting, by gravimetric analysis (Si), chelatometric analysis (Co, Al) and atomic absorption spectrometry (Na and K), Table II.

Catalyst Characterization

UV-VIS spectra of dehydrated Co-ferrierites in a reflectance mode were obtained by using a Perkin–Elmer Lambda 19 spectrometer equipped with diffuse reflectance attachement with integrated sphere coated by $BaSO_4$. The parent zeolite treated at the same conditions as the investigated samples served as a reference. IR spectra of dehydrated Co-ferrierites in the region of 4 000–400 cm^{-1} were recorded at room temperature on a Magna-IR system 550 FTIR spectrometer (Nicolet), using a MCT-B detector cooled with liquid nitrogen, equipped with a heatable cell with NaCl windows connected to a vacuum system.
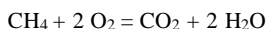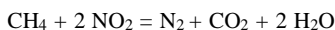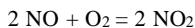
Catalytic Experiments

SCR of NO with methane was carried out in a quartz down-flow microreactor typically with 400 mg of the catalyst. Activation of the catalyst took place in a helium stream at 450 °C (temperature in-

crease 5 °C min^{-1}) for 1.5 h. Then the temperature of the reactor was decreased to 300 °C, the lowest reaction temperature investigated, kept constant, and helium was replaced by a reactant stream (total flow of 100 cm^3 min^{-1}). Concentration of reactants was 800–900 ppm NO, 1 200 ppm CH$_4$, 25 000 ppm O$_2$ and the rest helium. Steady-state conditions corresponding to a constant product composition were obtained typically after 30 min. Between the catalytic measurements at different temperatures, the temperature of the catalyst was increased (10 °C min^{-1}) under stream of reactants. When an opposite sequence of temperatures of the catalytic test was used, the same conversion values and product composition were obtained. Concentrations of NO and NO$_2$ in the inlet and outlet of the reactor were monitored by an NO/NO$_x$ analyzer (VAMET-CZ). CH$_4$, N$_2$, CO and N$_2$O were analyzed by gas chromatography method using a Hewlett–Packard 5890 II equipped with fused silica column (molecular sieve 5A, length 30 m, i.d. 0.53 mm, inner coating 25 µm).

For the selective catalytic reduction of NO with methane

$$2\ NO + CH_4 + O_2 = N_2 + 2\ H_2O + CO_2$$
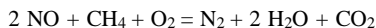
with the assumed individual steps

$$2\ NO + O_2 = 2\ NO_2$$

$$CH_4 + 2\ NO_2 = N_2 + CO_2 + 2\ H_2O$$

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$

total conversion of NO (x_{NO}, %), and conversion of CH$_4$ to CO$_2$ (x_{CH_4}) were calculated as follows:

Table I
Conditions of Co ion exchange for CoNH$_4$- and CoNaK-ferrierites (Si/Al 8.4)

Zeolite	Co/Al	Solution type	Molarity mol l^{-1}	Co solution/zeolite ml/g	Time (h)/ repetition	Temperature °C
CoNH$_4$-FER	0.05	Co(OCOCH$_3$)$_2$	0.05	8.0	10	70
CoNH$_4$-FER	0.09	Co(OCOCH$_3$)$_2$	0.05	20.0	10	70
CoNH$_4$-FER	0.23	Co(OCOCH$_3$)$_2$	0.05	19.2	10/3	70
CoNH$_4$-FER	0.25	Co(OCOCH$_3$)$_2$	0.1	16.0	10/2	70
CoNH$_4$-FER	0.42	Co(OCOCH$_3$)$_2$	0.1	16.0	10/5	70
CoNa-FER	0.01	Co(NO$_3$)$_2$	0.001	18.0	3	28
CoNa-FER	0.03	Co(NO$_3$)$_2$	0.001	54.0	3	28
CoNa-FER	0.06	Co(NO$_3$)$_2$	0.01	73.2	3	28
CoNa-FER	0.07	Co(NO$_3$)$_2$	0.01	296.0	3	28
CoNa-FER	0.12	Co(NO$_3$)$_2$	0.026	125.0	8	28
CoNa-FER	0.18	Co(NO$_3$)$_2$	0.05	125.0	8	28
CoNa-FER	0.28	Co(NO$_3$)$_2$	0.05	125.0	8/3	28
					8/2	70
CoNa-FER	0.310	Co(NO$_3$)$_2$	0.05	150.0	8/5	70

$$x_i, \% = \frac{c_i^0 - c_i}{c_i^0} \, 100 \ , \tag{1}$$

where c_i^0 and c_i are concentrations of NO or CH_4 in the inlet and outlet of the reactor, respectively. Conversion of NO to N_2 (yield of N_2, y_{N_2}, %) and NO_2 (yield of NO_2, y_{NO_2}, %) were expressed as:

$$y_i, \% = \frac{c_j}{c_i^0} \, 100 \ , \tag{2}$$

where c_j is concentration of 2 N_2 or NO_2 in the outlet of the reactor.

RESULTS AND DISCUSSION

Co ions exchanged in ferrierite exhibit three different coordinations as suggested from VIS spectra of the Co ions monitored by diffuse reflectance spectroscopy of zeolites with different Co loadings, and simultaneous presence or absence of non-transition metal ions at exchangeable sites[11]. For illustration, characteristic spectral components reflecting three types of the Co ion coordinations in ferrierite are depicted in Fig. 1. Based on the preferential sites of non-transition metal ions (Na, K, Ca, Ba) at various cationic sites of the ferrierite framework, the known framework topology, local arrangement of framework oxygens adjacent to the cationic sites, and similarities in the

TABLE II
Chemical composition of $CoNH_4$- and CoNaK-ferrierites (Si/Al 8.4)

Zeolite	Co, wt.%	Co/Al	Na/Al	K/Al	H^+/Al^a
$CoNH_4$-FER	0.40	0.05	0.00	0.00	0.94
$CoNH_4$-FER	0.81	0.09	0.00	0.00	0.88
$CoNH_4$-FER	2.08	0.23	0.00	0.00	b
$CoNH_4$-FER	2.16	0.25	0.00	0.00	0.71
$CoNH_4$-FER	3.62	0.42	0.00	0.00	0.42
CoNaK-FER	0.12	0.01	0.28	0.76	0
CoNaK-FER	0.27	0.03	0.23	0.74	0
CoNaK-FER	0.52	0.06	b	b	0
CoNaK-FER	0.64	0.07	0.11	0.75	0
CoNaK-FER	1.01	0.12	0.27	0.47	0
CoNaK-FER	1.52	0.18	0.08	0.46	0.06
CoNaK-FER	2.47	0.28	0.01	0.30	0.17
CoNaK-FER	2.60	0.310	0.01	0.27	0.25

^{a} From the intensity of Si–OH–Al IR band at 3 604 cm^{-1}; ^{b} not determined.

local framework arrangements in pentasil-ring zeolites of mordenite, ferrierite and ZSM-5 (ref.[9]), the Co ion coordinations in ferrierite were suggested[11]. Figure 2 depicts the ferrierite alumosilicate framework with indicated three types of the Co ions coordinated to framework oxygens. Co ions of the type α are located in a main channel, attached to four framework oxygens of the channel wall. Co ions of the type β are placed in deformed six ring of ferrierite cavity, coordinated to six oxygens. Co ions of the type γ are also in ferrierite cavity, in the most packed site, but the detailed geometry
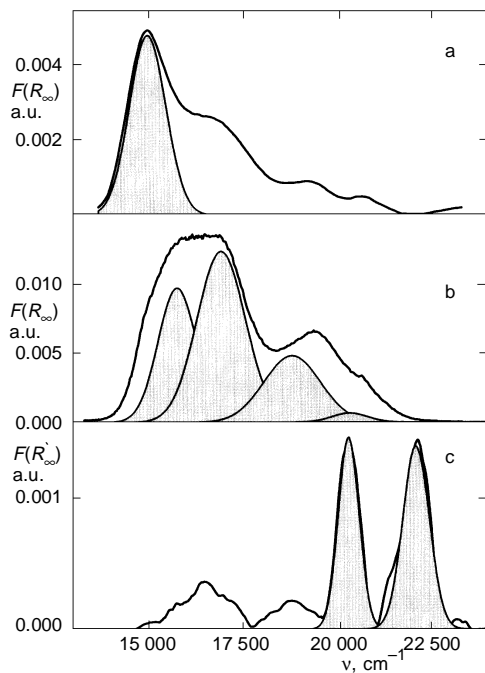

FIG. 1
Characteristic components of VIS spectrum of the Co^{2+} ions in Co-FERs corresponding to the Co ions of the types α (a), β (b) and γ (c)
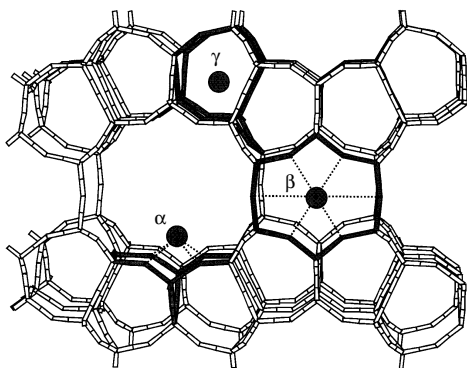

FIG. 2
Schematic representation of the ferrierite framework with indicated Co ion positions (shaded stick intersections are T (Si or Al) atoms, black stick intersections are oxygen atoms and shaded balls are Co ions)

and number of coordinated oxygens is not known. All the Co sites are accessible to NO molecules as follows from the geometry of the ferrierite framework (*cf.* Fig. 2).

Occupation of the cationic sites α, β and γ by the corresponding Co ions in CoNaK- and CoH-ferrierites with different Co loadings was estimated by using extinction coefficients for the Co ions of the types α, β and γ, and intensity of absorption of corresponding spectral components as given elsewhere[11]. The dependence of relative population of the individual Co ions on the concentration of Co in CoNaK- and CoH-ferrierites is depicted in Figs 3 and 4, respectively. Concentrations of protonic sites as determined from intensities of the IR band of Si–OH–Al groups at 3 604 cm^{-1} are also given. It can be seen that in CoH-ferrierites with increasing Co loading, the concentration of protonic sites decreses due to ion exchange of NH$_4^+$ ions by Co^{2+} ions. However, the stoichiometry of the H$^+$ *vs* Co^{2+} exchange is not attained in the whole concentration range. This can be explained by the exchange of some (Co^{2+}L$^-$)$^+$ complexes (where L stands for OH$^-$ or acetate ligand), or formation of undefined hydrolytic Co$_x$O$_y$(OH)$_z$ products at higher Co loadings[13]. With CoNaK-ferrierites, no protons are exchanged

Fig. 3

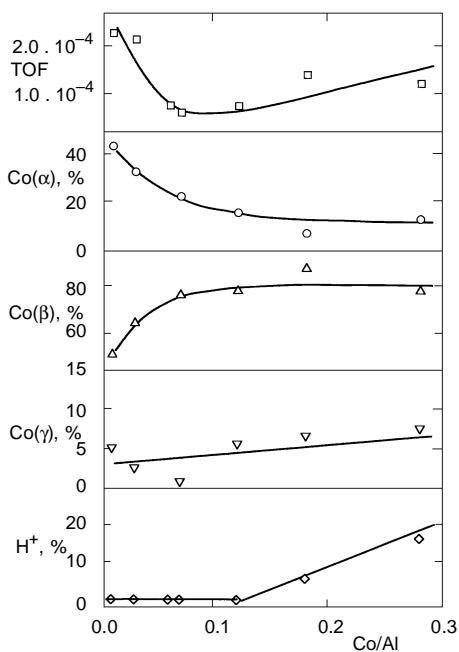Dependence of TOF values (per Co ion) in SCR of NO with methane to N$_2$, relative concentrations of the α-, β- and γ-type Co ions Co, and H$^+$ concentration on Co loading in CoNaK-FER

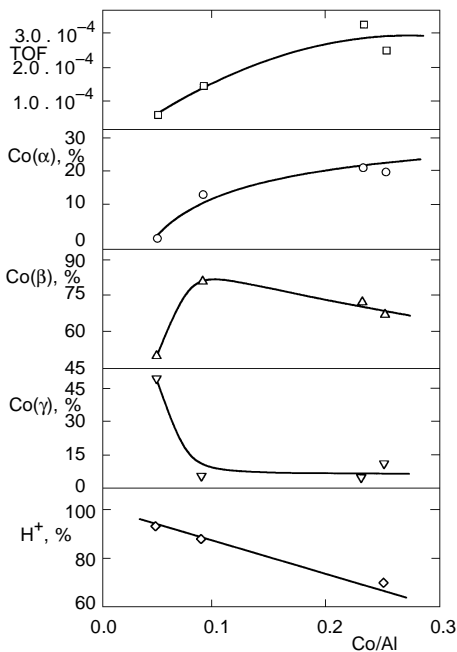Fig. 4

Dependence of TOF values (per Co ion) in SCR of NO with methane to N$_2$, relative concentrations of the α-, β- and γ-type Co ions, and H$^+$ concentration on Co loading in CoH-FER

from Co nitrate solution at low Co loadings, however, a part of Na and K ions is replaced by protons at high Co loadings.

Figure 5 presents an example of overall conversion of NO, conversion of NO to nitrogen and NO_2 and conversion of methane to CO_2 for CoNaK-ferrierite (Co/Al 0.18). Figures 6 and 7 depict conversion of NO to nitrogen in SCR, depending on temperature over CoNaK- and CoH-ferrierites, respectively. N_2O was not detected in the products in any catalyst, and methane was converted to CO (up to 10%) only at temperatures
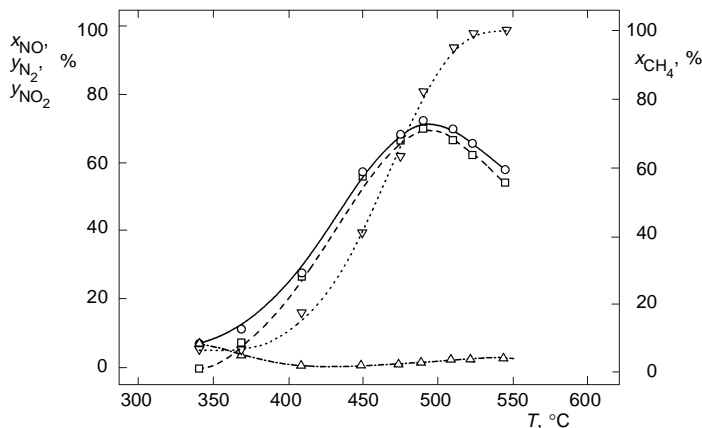

FIG. 5

Effect of temperature on conversion of NO (x_{NO}) (——), conversion of NO to nitrogen (y_{N_2}) (– – – –), and to NO_2 (y_{NO_2}) ($\cdots$), and conversion of methane to CO_2 (x_{CH_4}) (– · – · –) in SCR of NO with methane on CoNaK-FER, Co/Al 0.18, Si/Al 8.4

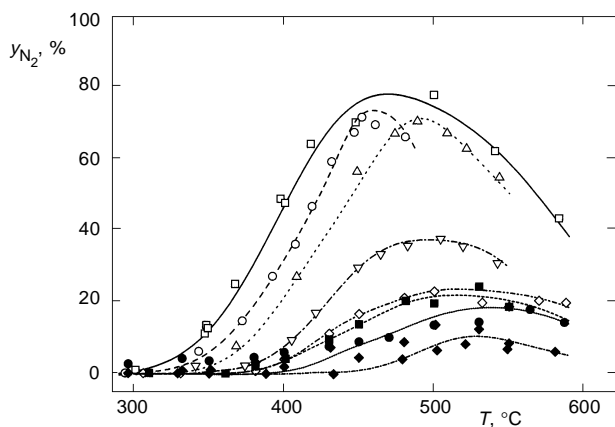

FIG. 6

Effect of temperature on NO conversion to nitrogen (y_{N_2}) in SCR of NO with methane on CoNaK-FER, Si/Al 8.4: ◆ 0.01, ● 0.03, ■ 0.06, ◇ 0.07, ▽ 0.12, △ 0.18, ○ 0.28, ▢ 0.31

above 500 °C on Co-ferrierites with the lowest Co loading. At the reaction conditions of SCR of NO the parent NaK-ferrierite did not exhibit any activity, while parent H-ferrierite converted NO to NO_2 at low-temperature range (150–350 °C); at temperature above 200 °C a significant, but still low compared to Co-zeolites, conversion of NO to nitrogen was detected (Fig. 8). However, conversion of NO to N_2 obtained over all Co ferrierites was much higher.

For both series of Co-ferrierites (CoH- and CoNaK-) the temperature dependence of NO conversion to nitrogen exhibited bell-shaped character. It exponentially increased with increasing temperature, reached a maximum and decreased at high temperatures
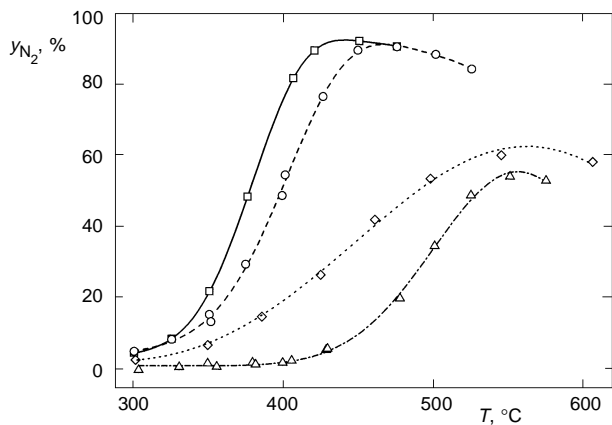

FIG. 7

Effect of temperature on NO conversion to nitrogen (y_{N_2}) in SCR of NO with methane on CoH-FER, Si/Al 8.4: △ 0.05, ◇ 0.07, ○ 0.25, ❑ 0.42
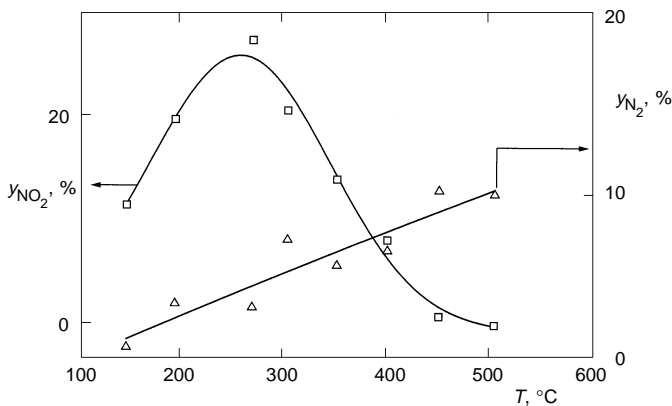

FIG. 8

Conversion of NO to NO_2 (y_{NO_2}) and to N_2 (y_{N_2}) over H-FER depending on temperature

(conversion of NO to NO_2 was low in the whole temperature range and represented only a small fraction of total amount of converted NO), see Figs 6 and 7. On the other hand, conversion of methane increased in the whole temperature range. This shows that at high temperatures oxygen successfully competes with NO_x for oxidation of methane, and that there exists only a "temperature window", where Co ions are able to catalyze selective reduction of NO_x by methane instead of methane oxidation.

From Figs 6 and 7 it is seen that with increasing Co loadings conversion of NO to nitrogen increases, but this is not proportional to the Co content. This indicates that zeolites contain Co ions of different activity. Moreover, the presence of protons, although their activity is low, can affect the overall activity of the zeolite catalyst. The Co ions in CoH-ferrierites are more active compared to those in CoNaK-ferrierites. For evaluation of the Co ion activity, it was necessary to consider the temperature range, where NO conversions exhibit an exponential dependence on temperature and, moreover, the conversion values are sufficiently low. Turnover frequency values per Co ion (TOF) were calculated for conversions below 50% obtained at temperature of 400 °C. The dependences of TOF on Co loading calculated from the NO conversion to nitrogen at 400 °C are given in Figs 3 and 4, where are also given relative concentrations of the Co ions of the types α, β and γ, and of the protonic sites in CoNaK- and CoH-ferrierites.

For CoNaK-ferrierites up to Co/Al loadings of 0.12, there are no protonic sites present in the zeolite; moreover, at such low loadings, formation of some Co_xO_y species during ion exchange and subsequent calcination can be excluded. Accordingly, the active sites are exclusively single Co ions at exchangeable sites. Therefore, this concentration range is suitable for differentiation of the activity of the Co ions of different coordinations. TOF values for CoNaK-ferrierites at low Co concentrations sharply decreased with increasing Co content, then remained constant and slowly increased at higher Co/Al ratios (Fig. 3). If we suggest that both the Co ions of the types α and β are active sites (the α-type Co ions being more active) then an increase in TOF at Co/Al values above 0.15 in CoNaK-ferrierite might indicate the effect of the proton sites on the rate of SCR of NO. This suggestion is also supported by observation that the Co ions in H-ferrierites exhibit higher TOF values compared to those in NaK-ferrierites (*cf*. Figs 3 and 4, and 6 and 7). As the SCR activity of protonic sites in a parent H-ferrierite was very low, some synergetic effect between the Co ions and protons should be considered to explain a higher activity of the Co ions in CoNaK-ferrierites with higher Co loadings and presence of proton sites.

The dependence of TOF values on Co concentration in CoH-ferrierite indicates low activity of the γ-type Co ions predominating at low Co loadings. With increasing Co concentration in CoH-ferrierites, relative concentration of the β-type Co ions followed by population of the α-type Co ions increases accompanied by an increase in catalytic activity. The presence of Co_xO_y species in the zeolites of Co concentration near to

stoichiometric exchange level was indicated by a quantitative analysis of the intensities of IR bands of antisymmetric T–O–T framework vibrations affected by the Co ions at cationic sites depending on the Co content in the zeolite[13].

From the analysis of the dependence of TOF values of SCR of NO on population of the α-, β- and γ-type Co ions in Co-ferrierites, in which there are no conditions for Co_xO_y species formation (CoH-ferrierites with Co/Al < 0.1) and in which protonic sites are absent (CoNaK-ferrierite with Co/Al < 0.12), the following sequence of the catalytic activity of the individual Co ions in SCR of NO with methane results for the individual Co ions:

$$\text{α-type Co ion} \gg \text{β-type Co ion} \geq \text{γ-type Co ion} .$$

The highest activity of the α-type Co ions corresponds to the most open coordination of these ions and easy access of reactants to them as they are located in main channels of the ferrierite framework.

CONCLUSIONS

Single Co ions at exchangeable sites are active centers for SCR of NO to nitrogen with methane. These ions are coordinated to framework oxygens at different cationic sites exhibiting different local geometry. All the Co ions are accessible to NO molecules, but they exhibit different catalytic activity. The Co ions in the most open coordination bound to four framework oxygens of the wall of the main channels of the ferrierite structure possess the highest activity. The lowest activity is found with the Co ions strongly bound in the most packed γ-site in ferrierite pocket. Synergetic effect of protonic and Co sites is documented, but the nature of this effect remains still open.

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