FTIR STUDY OF METAL ZEOLITES. DETERMINATION OF Co(II) CATION IN Co-BETA ZEOLITE BY DEUTERATED ACETONITRILE ADSORPTION

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FTIR spectra of deuterated acetonitrile (ACD) adsorbed on Co-Beta zeolite were investigated. By analysing the IR region of zeolite framework perturbation, the conditions for the prevailing presence of the Co–ACD complex with 1 : 1 stochiometry were established. Analysis of the C≡N region with overlapping bands OH···ACD ($2\ 297\ cm^{-1}$), and Lewis(Al)···ACD ($2\ 325\ cm^{-1}$), provided a value of molar absorption coefficient for a band of Co–ACD complex in Co-Beta at $2\ 310\ cm^{-1}$ equal to $7.12 \pm 0.3\ cm\ \mu mol^{-1}$.
Keywords: Deuterated acetonitrile; Cobalt; Zeolites; Co-Beta; FTIR spectroscopy, Cationic sites; Heterogeneous catalysis.

Recent progress in application of metal ion and metal-oxo species planted in high-silica zeolites and their exceptional activity and selectivity in reactions of NOx abatement and selective oxidation of hydrocarbons[1] stress the importance of detail understanding of such systems. The high potential of these materials is given by a great variety of zeolite matrices with different framework compositions as well as of metal ion structures, which can be stabilised inside the void volume of zeolites. This provides for an exceptionally high range of cation-zeolite combinations and offers a promising tool for fine tailoring of unique catalysts for their application in highly demanding redox systems.

Generally, depending on the preparation conditions, metal ions can be located in zeolites in the form of well-defined cationic species, coordinated

exclusively to the framework oxygens, or less specifically bonded as oxidic species to the zeolite matrice. While the redox properties of the oxide-like entities mostly approximate the supported metal oxides, the cationic species are controlled exclusively by the guest–host interactions and thus could be tuned to suit the specific demands of a specified redox reaction. Obviously, analysis of such systems with potential for exploitation in redox catalysis is of basic importance. Due to the complexity of the host–guest interaction in zeolites a cluster of several methods would be preferred.

The research carried out recently in our laboratory, employing a complementary set of spectroscopic techniques, FTIR, UV-VIS-NIR, emission VIS, ESR, and EXAFS, provided an access to the systematic analysis of relationship between structure and reactivity of cations in zeolitic matrices[2–12]. These studies established the structure sites and bonding of several divalent transition metal ions exchanged in pentasil ring high-silica zeolites.

This contribution is an attempt to complete the FTIR analysis of Al-related (L(Al)) Lewis and Brønsted acid functions of Co-exchanged zeolite by a method providing for easy determination of occupation of cationic sites and capable of supporting previous methods by distinguishing between metal ion present in cationic positions and in a form of unspecified oxidic species.

EXPERIMENTAL

Co-Beta zeolite (Co/Al 0.02–0.16) were prepared by ion exchange of β-zeolite (Si/Al 12.5–15; PQ Corporation), using 0.001–0.033 M $Co(NO_3)_2$ solution, and analysed by XRF method. Deuterated acetonitrile (ACD) provided by Aldrich was degassed by repeated freeze-pump-thaw cycles before use. ACD was adsorbed at 1.33 kPa and room temperature on zeolite samples formed into self-supported pellets ($\approx$ 5 mg cm^{-2}) pre-evacuated (750 K, vacuum 10^{-3} Pa) in a vacuum cell with NaCl windows and a six-position sample holder. Acetonitrile desorption was followed by FTIR at temperatures between room temperature and 720 K. An FTIR spectrometer Nicolet Magna-550 with MCT-B low-temperature detector was used. Spectra were recorded at room temperature, at 2 cm^{-1} resolution collecting 200 scans for a single spectrum, and normalised on the sample thickness of 5.5 mg cm^{-2}. For this, a plot of integral area of the zeolite skeletal bands in the region between 1 750–2 100 cm^{-1} was employed as an internal intensity standard.

RESULTS AND DISCUSSION

A typical experiment showing the spectral changes in the C≡N region (2 350–2 250 cm^{-1}) and region of zeolite framework perturbation (980–900 cm^{-1}) during deuterated acetonitrile adsorption and subsequent desorption for Co-Beta zeolite is illustrated in Fig. 1. As shown previously,

ACD interacts with all types of present OH groups as well as with Lewis acid sites.

While the band intensity of the weakly acidic terminal SiOH group is already restored after evacuation at room temperature (not shown in Fig. 1), the desorption temperatures for the other two OH bands (bridging OH structure at 3 610 cm^{-1} and the Al-bonded OH at about 3 660 cm^{-1}) are restored after evacuation at temperatures above 520 K. The spectral region at 2 350–2 250 cm^{-1} displayed characteristic bands of the C≡N group of a free
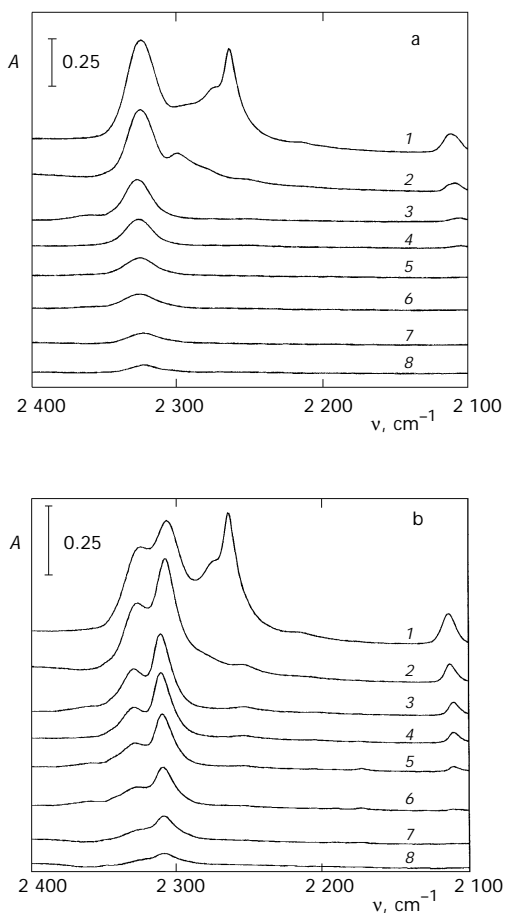

FIG. 1
FTIR spectra in the C≡N region of Beta zeolite (a) and Co-Beta zeolite (Co/Al 0.16) (b), after 2 h evacuation at 750 K followed by deuterated acetonitrile adsorption (*1*) and evacuation at 300 (*2*), 375 (*3*), 425 (*4*), 475 (*5*), 525 (*6*), 625 (*7*), and 725 K (*8*)

CD$_3$CN molecule or interacting with electron acceptor or proton donor sites.

As shown already in the previous studies[8,10], these spectra could be analysed quantitatively for Al-bonded Lewis centers (band at 2 325 cm^{-1}, ε_L = 3.6 ± 0.2 cm μmol^{-1}) or Brønsted acid sites (2 297 cm^{-1}, ε_B = 2.05 ± 0.1 cm μmol^{-1}). A band at about 2 310 cm^{-1} evidenced formation of the Co–ACD complex. The 1 : 1 stoichiometry is generally assumed for ACD interaction with B and L(Al) acidic sites. On the other hand ACD interaction with the Co cation in zeolite displays features typical of formation of a sequence of complexes with increasing the number of ligands with the ACD coverage (see also refs[3,11]).

Accordingly, conditions providing for a specified stoichiometry of the Co–ACD complex were established using the analysis of the zeolite transmission window region at 980–900 cm^{-1}. As shown previously[11], this region provides information on zeolite-framework perturbation by bonding either bare cation or its complex with extra-framework ligands. The sequence of the spectra in the transmission window region with increasing evacuation temperature is illustrated in Fig. 2. With the parent zeolite (Fig. 2a), no new spectral features were found. A new band due to framework perturbation by Co(II) cation (ν_{BM} = 916 cm^{-1}) (see Fig. 2) appeared after full zeolite evacuation. Formation of the Co–ACD complex (ν_{B-ML} = 940 cm^{-1}) and additional spectral features at high ACD coverage indicated the existence of Co–(ACD)$_2$ or higher complexes (ν_{B-ML2} = 960 cm^{-1}). Inspection of the sequence of spectra reflecting the equilibrium between Co ion and Co–(ACD)$_n$, indicated the prevailing presence of the 1 : 1 complex on Co-Beta zeolite after evacuation at about 420 K, where the band at 940 cm^{-1} clearly predominates and the band at 916 cm^{-1} induced by the presence of the bare Co cation is negligible. Accordingly, the spectrum after desorption at this temperature was chosen as representing the state of maximum abundance of the Co–ACD complex and the spectra were chosen for further quantitative analysis.

The C≡N spectral region of complexes evacuated under the conditions of the prevailing presence of Co–ACD complex was analysed using the fitting parameters summarised in Table I (see Fig. 3). These parameters combined the values previously identified for determination of L(Al)-ACD and B-ACD species[10], and the values for Co–ACD complex evaluation averaging the optimum parameters obtained for the complete set of analysed Co-Beta zeolite samples.

The integral areas of the 2 310 cm^{-1} band of Co–ACD complex in Co-Beta zeolite samples of various Co contents are summarised in Fig. 4. From the

slope of the linear correlation of the band area of the complex, and the cation content, the absorption coefficient was calculated according to Eq. (*1*)

$$\varepsilon(\text{Co–ACD}) = A_i/10\ c_i\ , \tag{1}$$

where $\varepsilon(\text{Co–ACD})$ is the absorption coefficient of the Co–ACD complex (cm μmol^{-1}), A_i is the integral band area of the characteristic band at
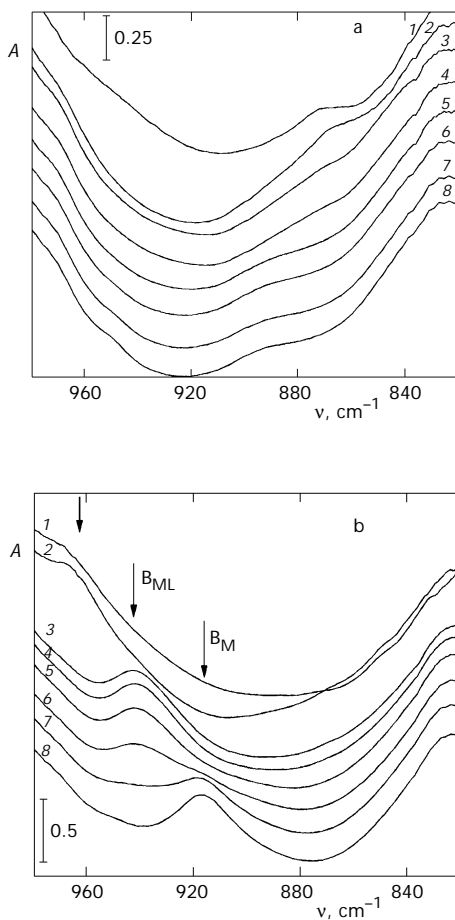

FIG. 2

FTIR spectra in the skeletal vibration region of Beta zeolite (a) and Co-Beta zeolite (Co/Al 0.16) (b), after 2 h evacuation at 750 K followed by deuterated acetonitrile adsorption (*1*) and evacuation at 300 (*2*), 375 (*3*), 425 (*4*), 475 (*5*), 525 (*6*), 625 (*7*), and 725 K (*8*)

2 310 cm^{-1} for the sample thickness of 10 mg cm^{-2}, and c_i is molar concentration of Co cation in zeolite (mmol g^{-1}). Thus the absorption coefficient for Co(II) ion in Beta zeolite ($\nu_{(C\equiv N)\text{-Co(II)}}$ at 2 310 cm^{-1}) was established equal to ε_{Co} = 7.12 ± 0.35 cm μmol^{-1}.

Thus by combining the parallel FTIR evidence in the OH spectral region, providing indication of the OH–ACD complex formation, the T–O–T region (giving direct evidence of equilibrium between the bare Co(II) cation and

TABLE I
Peak fitting parameters for FTIR spectra of deuterated acetonitrile adsorbed on Co-Beta zeolite

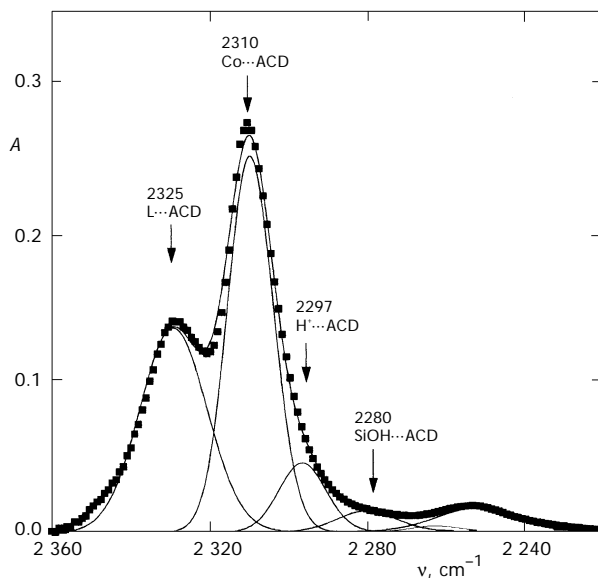| Parameter	L(Al)···ACD	B–OH···ACD	Co···ACD	Si–OH
Band position, cm^{-1}	2323–2330	2295–2301	2307–2310	2274–2284
FWHM, cm^{-1}	14–24	14–18	9–14	14–24

FIG. 3
Deconvoluted IR spectrum in the C≡N region of Co-Beta zeolite (Si/Al 13.5, Co/Al 0.13) after deuterated acetonitrile adsorption and evacuation at 425 K for 30 min

ACD ligands) and the analytical region at 2 350–2 250 cm^{-1} of the –C≡N band could be fully analysed, providing quantitative data on all types of acid sites in the Co-Beta zeolite system.

The analysis of samples of low metal-ion exchange (Co/Al molar ratio up to 0.16) is consistent with the prevailing presence of Co(II) ion in the ion exchange position of zeolite and balanced by two negative charges[9,12]. By analysis of samples with higher Co/Al ratios, approaching or exceeding the theoretical value of Co/Al 0.5, evidenced deviation from the integral intensity of the 2 310 cm^{-1} band with increasing Co content.

Establishing relationship between the structure and catalytic activity of the metal-ion-exchanged zeolites demands a multispectroscopic approach, providing also identification determination of individual potentially active sites. The relatively simple technique of FTIR analysis of adsorbed ACD molecules could thus supplement other methods by providing the possibility to follow the state and content of metal ions exchanged in zeolite systems.

The presented methodology can be generalised for other metal-ion-exchanged systems including other M(II) cations and zeolites with medium Si/Al values.

Complete quantitative analysis of Brønsted, Al-Lewis, and metal-ion-exchanged cation sites has been shown feasible by deuterated acetonitrile adsorption-desorption experiment followed by FTIR spectroscopy measure-
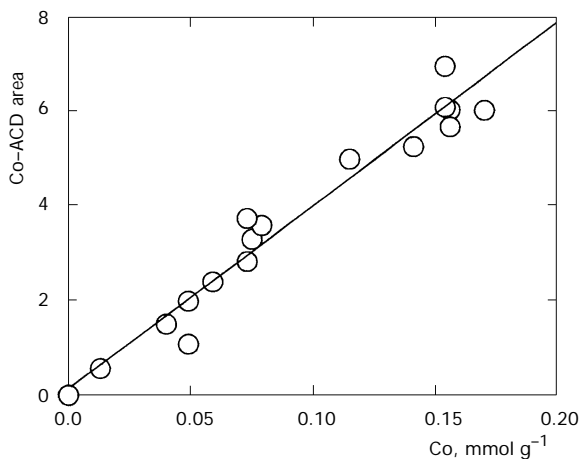

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Dependence of integral intensity of the 2 310 cm^{-1} band on the cobalt content in Co-Beta zeolites

ments. By establishing conditions for optimum separation of individual deuterated acetonitrile complexes, absorption coefficients for deuterated acetonitrile adsorbed on bridging OH groups, Al-Lewis acid sites, and Co(II) ion in Co-Beta zeolite were calculated.

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