NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Technical Progress Report for the Period
June 1995-August 1995

Kamil Klier and Richard G. Herman

with

Jiří Dědeček

Zettlemoyer Center for Surface Studies
and Department of Chemistry
Lehigh University
Bethlehem, PA 18015

September 1995

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY-Pittsburgh Energy Technology Center

Under Contract No. DE-FG22-93PC93222

MASTER

U.S.-DOE Patent Clearance is not required prior to
publication of this document.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *www*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RECEIVED
USDOE/PETC
95 OCT 12 AM 11:09
ACQUISITION & ASSISTANCE DIV.

NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Disclaimer

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

SUMMARY OF TECHNICAL PROGRESS

Samples of Mn(II) Nafion, Mn(II)-A zeolite, and various Co(II)-ZSM-5 zeolites were prepared by aqueous ion exchange techniques. Co(II)- and Mn(II)-containing ZSM-5, erionite, and mordenite were obtained from other sources. Co(II)-containing samples were studied by diffuse reflectance spectroscopy in the dehydrated state and after exposure to NO atmosphere. In addition, the magnetic susceptibilities of these samples were determined. It was shown that two NO molecules were adsorbed onto each Co(II) ion in ZSM-5 and erionite. The visible spectrum of these materials was complex and contained absorption bands corresponding to Co(II) ions in different coordination states. NO desorbed from Co(II) high silica zeolites at temperatures under 190°C, while it completely desorbed from Co(II) Nafion below 160°C. The catalytic activity of Co, Cu, and Mn Nafion samples for NO decomposition was probed, but no activity was observed. Optical absorption and luminescence studies are being initiated with Mn(II)-containing samples.

TECHNICAL PROGRESS

The research during this quarter was centered on the study of the interaction of NO with Co(II) in different zeolitic matrices and in Nafion resin and on the identification of Co(II) siting in high silica zeolites. Optical spectroscopy in the UV-VIS-NIR region and measurement of magnetic susceptibility were used to analyze these Co-based catalysts. Several Co-containing zeolites were obtained from other sources (Co-ZSM-5, Co-erionite, Co-mordenite) or prepared here (various Co-ZSM-5 zeolites).

Two molecules of NO could be adsorbed on each Co(II) ion in Co-ZSM-5 and Co-erionite, and the magnetic moment of Co with adsorbed NO in ZSM-5 and erionite differed dramatically from the magnetic moment of Co in A zeolite. The NO molecule was desorbed from Co-ZSM-5 and Co-erionite at temperatures lower than 190°C, and a significant portion was desorbed at temperatures near 100°C. In the case of Co-Nafion, NO was desorbed completely under 160°C, with the major part of NO being desorbed below 100°C.

The UV-VIS spectra of Co in ZSM-5, erionite, and mordenite were different from the spectra of Co-A and X zeolites and were also different from the spectra of cobalt(II) cations with tetrahedral coordination. These spectra were complex, with the spectrum of Co-ZSM-5 depending mainly on the Si/Al ratio and on the conditions of the ion exchange. At a minimum, two different Co(II) sites are present in ZSM-5. The identification of spectral bands corresponding to the different coordination sites of Co in this zeolite requires further investigation.

To resolve the question of the number of sites of divalent cations in ZSM-5 and erionite, the study of Mn(II)-containing high silica zeolites was started. The Mn(II) ion

exhibits a narrow absorption band near $25,000\text{ cm}^{-1}$ and a luminescence band in the red region of the spectrum. Since one luminescence band represents one specific ion coordination, the analysis of the Mn(II) spectrum in zeolites will probably be simpler than for Co(II) exchanged zeolites. Moreover, the Mn(II) ion (d^5) is half isoelectronic to the Cu(I) ion (d^{10}), and the behavior of these two ions in high silica zeolites and their catalytic activity for NO decomposition will be compared.

1. EXPERIMENTAL

1.1. Ion Exchanged Samples

1.1.1. Co(II)-zeolites. Three high silica Co-zeolites were obtained from Dr. B. Wichterlova, Institute of Physical Chemistry, Prague, Czech Republic, and these consisted of CoH-erionite (Si/Al = 3.5, 3.21 wt% of Co), CoNa-ZSM-5 (Si/Al = 22.6, 0.75 wt% of Co) and CoH-mordenite (Si/Al = 8.5, 2.09 wt% of Co). All samples were prepared by ion exchange from aqueous Co(II) acetate solution.

Three Co-ZSM-5 (Si/Al = 10) samples with different Co concentrations were prepared by ion exchange for 2 hr at 60°C from $\text{Co}(\text{NO}_3)_2$ solution with different molarity. CoNH_4 -ZSM-5 (predicted Co concentration 3-4% of Co) was prepared from 0.01 M solution using 70 ml of solution per gram of zeolite, while a lower Co sample (maximum predicted concentration lower than 0.6% of Co) was prepared from 0.0017 M solution using 70 ml of solution per gram of zeolite. A CoNa-ZSM-5 (ca. 4-6% of Co) was prepared from 0.01 M solution using 120 ml of solution per gram of zeolite.

1.1.2. Mn(II)-zeolites. MnH-ZSM-5 (Si/Al = 22.6, 0.58 wt% of Mn) and MnH-mordenite (Si/Al = 8.5, 1.41 wt% of Mn) were prepared by the group of Dr. B. Wichterlova. These zeolites were prepared by ion exchange from aqueous solutions of Mn

acetate.

MnNa-A zeolite was prepared by ion exchange from 0.01 M aqueous solution of $\text{Mn}(\text{NO}_3)_2$ for 3 hr at 80°C (pH 7.8, where the pH was controlled by addition of a small amount of 0.01 M HNO_3), and 100 ml of solution per gram of zeolite was used.

1.1.3. Mn(II)-Nafion. Mn-Nafion was prepared by ion exchange of 1 g H-Nafion with 12.5 ml 0.2 M solution of $\text{Mn}(\text{NO}_3)_2$ for 2 hr at room temperature. This exchange was repeated three times with decantation between each step.

1.2. Measurement of Magnetic Susceptibility

The paramagnetic moments of bare Co(II) ions in the dehydrated samples and Co(II) ions with adsorbed NO were measured using the Gouy method. The magnetic field was 4200 Gauss, the internal diameter of the sample tube was 6 mm, and the sample tube length was 12-14 cm. The sample weight was from 1.1 to 1.7 g. Pure $\text{HgCo}(\text{NCS})_4$ was used for calibration. The measurements were carried out at room temperature. Each measurement was repeated 5 or 10 times to obtain error of measurement smaller than 5%.

1.2.1. Zeolites. Co-ZSM-5 (Si/Al = 10, 4.4 wt% of Co), Co-erionite (Si/Al = 3.5, 2.47 wt% Co) and Co-A zeolite (2.57 wt% Co) were investigated. The following procedure was used to carry out the susceptibility measurement.

- A. The magnetic susceptibility of the hydrated sample was measured using a 11 cm high column of zeolite in the sample tube.
- B. The sample tube was sealed to a flask that was also connected to a quartz cuvette for diffuse reflectance spectral (DRS) measurements, and the zeolite was quantitatively transferred to the flask. Samples were dehydrated under dynamic

vacuum at 300°C (Co-ZSM-5 and Co-erionite) or at 360°C (Co-A zeolite). The dehydration of the zeolite was checked *via* DRS spectroscopy in the NIR spectral region. The sample was quantitatively transferred to the sample tube, which was then sealed and the magnetic susceptibility was measured.

- C. The sample tube was opened, sealed again to the flask and dehydrated as described in Step B. After this, the zeolite was exposed to excess NO at atmospheric pressure for 30 min. The flask was degassed *via* connecting with a large evacuated flask for 5 sec. This degassing was repeated 2 or 3 times to obtain a residual pressure lower than 1.5×10^{-1} torr. Then, the sample was transferred to the tube as described in Step B, and the magnetic susceptibility was measured.
- D. NO was adsorbed as described in Step C. Then, the zeolite was evacuated at room temperature under dynamic vacuum for 30 min. and the magnetic susceptibility was measured.
- E. The magnetic susceptibility of the calibration sample was measured.

Using this same procedure, magnetic susceptibilities of the parent Na-A zeolite, Na-ZSM-5, and H-erionite were measured. Magnetic susceptibility of Co(II) related per gram of zeolite (x_{Co}) was determined by using the following equation:

$$x_{Co} = x_{CoZ} - x_p - x_{cor},$$

where x_{CoZ} is the magnetic susceptibility of Co in zeolite per gram of zeolite, x_p is the magnetic susceptibility of the parent zeolite per gram, and x_{cor} is the diamagnetic susceptibility of Na or OH ions replaced by ion exchange per grams of zeolite. The molar magnetic moment and paramagnetic moment of Co(II) were calculated according to the Curie law.

1.2.2. Co-Nafion. Because of the problem of quantitatively transferring dehydrated Nafion from the flask to the sample tube due to electrostatic charging, all procedures were done in the same sample tube. To obtain homogeneous temperature conditions of sample preparation, a 7 cm high column of Nafion was used. The procedures of carrying out the measurements and data processing were the same as for Co-zeolites.

1.3. DRS in the UV-VIS-NIR Region

The optical measurements were carried out as described earlier (1). The analytical system has been updated, and now data are collected by a Zenith 386 computer with Spectracalc software. The spectra are now processed using Origin software *via* the Kubelka-Munk function.

1.3.1. Zeolites. Three dehydrated CoNH_4 -ZSM-5 zeolites ($\text{Si/Al} = 10$) with different Co concentrations (4.4 to ca 0.6 wt% of Co), CoNa-ZSM-5 ($\text{Si/Al} = 10$, ca 4% of Co), CoNa-ZSM-5 ($\text{Si/Al} = 22$, 0.75 wt% of Co), Co-erionite, Co-mordenite and Mn-mordenite were investigated using DRS. The spectra of the parent dehydrated zeolites were recorded, too. All zeolites were dehydrated at 350°C under dynamic vacuum as described in (1). The conditions of measurement of Co-zeolites with adsorbed NO are described in Section 1.2.1. The desorption of NO from Co-ZSM-5 ($\text{Si/Al} = 10$, 4.4% of Co) and Co-erionite was investigated. After adsorption and desorption of NO at room temperature, NO was desorbed at 90, 140, and 190°C and spectra were recorded after each desorption step.

1.3.2. Co-Nafion. The conditions employed for NO adsorption and desorption are given in Section 1.2.2. The desorption of NO at 95, 130, and 160°C was investigated by the same method as described for Co-zeolites.

1.4. Photoluminescence

Mn(II)-mordenite and Mn(II)-Nafion samples were excited by 254 nm light from a high intensity UV lamp (UVG-54, UVP Inc.), and the luminescence was observed at room temperature.

1.5. Catalytic Testing of NO Decomposition

The catalytic testing was done by the research group of Dr. B. Wichterlova, and this included the catalytic activity of Co-, Mn-, and Cu-Nafion samples. Samples were dehydrated in a stream of helium (temperature ramp = 2°C per min from room temperature to 160°C, which was then maintained for 2 hr). Conditions of each catalytic test were: 1 g of sample, temperature of 160°C, 100 ml of 4000 ppm of NO in helium per min, and NO and NO_x were detected by chemiluminescence using the apparatus described in detail elsewhere (2).

2. RESULTS

2.1. Co-Zeolites

2.1.1. Magnetic moment of Co(II). The paramagnetic moments (given in Bohr Magnetons) of Co(II) in different zeolitic matrices and the effect of NO adsorption on the paramagnetic moments are given in the Table 1. The value of the paramagnetic moment of cobalt in hydrated zeolites (5.0 BM) is in good agreement with the magnetic moment of Co(II) in [Co(H₂O)₆]²⁺ (5.1 BM (3)), and the value of the magnetic moment of Co(II) in dehydrated A zeolite (5.6 BM) agrees with a value given in the literature (5.65 BM (4)). Magnetic moments of Co in dehydrated samples are significantly higher than the values of magnetic moment of tetrahedral cobalt (4.4-4.8 BM (5)). The high value of the magnetic moment of Co(II) in dehydrated Co-A zeolite is given by high orbital contribution because

Co(II) ions are located in sites with planar symmetry (4). The high values of Co magnetic moment in dehydrated ZSM-5 and mordenite are probably also given by the high orbital contribution. The two different lower magnetic moments of Co(II) after NO adsorption and after desorption of NO at room temperature indicate that two NO molecules could be adsorbed on each Co(II) ion in Co-ZSM-5 and Co-erionite.

Table 1. Paramagnetic moments of Co(II) ion in zeolites and the effect of NO adsorption on the magnetic moments.

Zeolite	Paramagnetic Moment of Co(II) (BM)			
	Hydrated Sample	Dehydrated Sample	NO Desorbed at RT	Exposed to Excess NO
Co-A	5.0	5.6	4.7	3.8
Co-Erionite	5.0	5.2	3.6	2.2
Co-ZSM-5	5.0	5.4	3.2	1.3

2.1.2. DRS of dehydrated Co-zeolites. The UV-VIS spectra of Co-zeolites are shown in Figures 1-14. The NIR spectra are very complex, and they will be discussed in the next report. The absorption of these Co-zeolites in the VIS region is significantly weaker than absorption of partially dehydrated Co-A zeolite containing tetrahedrally coordinated cobalt (dehydrated Co-containing ZSM-5, erionite, and mordenite are light blue, and partially dehydrated Co-A zeolite with a Co content corresponding to these high silica zeolites is dark blue). This weak absorption indicates a higher degree of symmetry and corresponds to the results obtained by measurement of the magnetic moment of Co(II) in these matrices.

The UV-VIS spectrum of Co-mordenite (Figures 1 and 8) is quite complex. It is possible to distinguish the band at $25,000\text{ cm}^{-1}$, characteristic for sites with C_{3v} symmetry,

and a complex of bands ranging from *ca* 14,000 to 22,000 cm^{-1} . This corresponds with a greater number of cation sites in mordenite. The detailed explanation of the Co-erionite spectrum needs further studies.

To-date, spectral analysis has concentrated on Co-ZSM-5 (Figures 3-7 and 10-15) and Co-erionite (Figures 2 and 9), where simpler Co(II) ion localization could be expected. The complex band ranging from 13,000 to 23,000 cm^{-1} is characteristic for these Co-zeolites. This spectrum is different from the spectra of Co(II) in dehydrated A and X zeolites, but the spectrum of CoNH_4 -ZSM-5 (Si/Al = 10) exhibits a similarity with the spectrum of Co-A zeolite with adsorbed N_2O (6).

It is clearly seen (Figure 14) that the spectrum of Co-ZSM-5 depends on Co concentration and mainly on the Si/Al ratio and conditions of sample preparation. It indicates that there are a minimum of two different Co(II) sites in Co-ZSM-5. The number of Co(II) ions located in the site with a characteristic band around 14,500 cm^{-1} increases in zeolites exchanged at higher pH and, probably, in zeolites with a lower Al content. This is in agreement with the results of a study of Cu-containing high silica zeolites, where three different Cu(I) sites were observed (7), and with the XRD study of Ni-ZSM-5, where two Ni(II) sites were identified (8). The confirmation of this preliminary conclusion, and the identification of bands corresponding to the individual sites, requires further detailed study.

2.1.3. DRS of Co-zeolite with adsorbed NO. The adsorption of NO strongly influences the UV-VIS spectra of Co-zeolites. The spectra of Co-ZSM-5 (Si/Al = 10, 4.4% of Co and Si/Al = 22.6, 0.75% of Co) and Co-erionite with adsorbed NO and after NO desorbed at room temperature are given in Figures 16-18. The characteristic bands of bare Co(II) disappear, and new bands centered at 13,500, 22,000, 26,000, and 39,000 cm^{-1} appear

after NO adsorption. The interaction of NO with Co-zeolites will be discussed in detail later.

The dependence of NO desorption from Co-erionite and Co-ZSM-5 at different temperatures was investigated. It was observed that NO was completely desorbed at temperatures under 190°C, and partial desorption was observed at temperatures lower than 130°C.

2.2. Mn-Mordenite

The spectrum of dehydrated Mn-mordenite is shown in Figure 19. The absorption of Mn(II) ions is very weak, but the characteristic band near 24,000 cm^{-1} was evident. The red luminescence of dehydrated Mn-mordenite was observed at room temperature under UV irradiation. The spectrum of this Mn(II) luminescence will be measured at the Institute of Physical Chemistry in Prague.

2.3. Co, Cu, and Mn Nafion

2.3.1. Mn-Nafion. In the spectrum of dehydrated Mn-Nafion, a low intensity narrow band at 24,400 cm^{-1} and an intense band at 38,500 cm^{-1} were observed. The band at 24,000 cm^{-1} was attributed to the absorption of the Mn(II) ion (5). The band in the UV region reflects charge transfer between the Mn(II) ion and the Nafion polymer matrix.

The dehydrated Mn-Nafion exhibited pink luminescence under UV irradiation at room temperature. This luminescence is composed of shorter lifetime "white" luminescence (broad band in the visible region with a decay time in the range of nanoseconds (ns)), which is probably the luminescence of the Nafion matrix, and of a luminescence band with a maximum at 16,000 cm^{-1} , that can be attributed to Co(II). The 308 nm laser-induced luminescence spectra were measured at the Institute of Physical Chemistry, Prague, using

the laser luminescence spectrometer and the measurement procedure described in (7).

It was observed that adsorbed NO was desorbed from the Mn-Nafion at temperatures lower than 160°C. The Mn-Nafion UV-VIS spectrum after NO desorption at 160°C was similar to the spectrum before adsorption of NO.

2.3.2. Co-Nafion. The adsorption and desorption of NO on Co in Nafion was investigated after the sample was dehydrated. The magnetic moment of Co in hydrated and dehydrated Nafion and the effect of NO adsorption is given in Table 2.

Table 2. Paramagnetic moments of Co(II) in Nafion after various treatments.

Sample	Paramagnetic Moment of Co(II) (BM)			
	Hydrated Sample	Dehydrated Sample	NO Desorbed at RT	Exposed to Excess NO
Co-Nafion	5.0	6.4	6.7	5.3

The paramagnetic moment of the Co(II) ion in hydrated Nafion is as expected (5.0 BM), but the values for dehydrated Nafion and the sample after NO adsorption are surprisingly high. The UV-VIS spectra of Co-Nafion with adsorbed NO and with NO desorbed at various temperatures are shown in Figure 20. It is seen that NO was desorbed at temperature lower than 160°C and that a substantial portion of NO was desorbed at temperature lower than 100°C.

2.3.3. Activity of ion-exchanged Nafion in catalytic NO decomposition. The catalytic activity of Co-, Cu-, and Mn-Nafion samples was probed. However, activity was not demonstrated because a decrease of NO concentration in the output of the catalytic reactor

with Cu-Nafion was not observed within experimental error.

3. REFERENCES

1. Klier, K., Herman, R.G., and Dedecek, J., Technical Progress Report DOE/PC/93222-7 (June 1995).
2. Wichterlova, B., Dedecek J., and Vondrova A., J. Phys. Chem., **99**, 1065 (1995).
3. Young, R.S., "Cobalt," ACS Monogr. Ser., NY, **149**, 130 (1960).
4. Klier, K., Langmuir, **4**, 13 (1988).
5. Lever, A.B.P., "Inorganic Electronic Spectroscopy," Elsevier, NY, 324-326 (1968).
6. Klier, K., Herman, R.G., and Hou, S., Final Technical Progress Report DOE/PC/89784-F (Feb. 1993).
7. Dedecek, J., J. Phys. Chem., in press.
8. Zhenyi, L., Proc. 7th Jpn. Zeol. Conf., Tokyo, 415 (1987).

Figure 1

Co-mordenite: Si/Al 8.5, Co 2.1 wt%
dehydration: 350 °C, 3h

Figure 2

DRS of Co(II)-erionite

Co-erionite, Si/Al 3.5, Co 3.21 wt%
dehydration: 350 °C, 3h

Figure 3

DRS of Co(II)- ZSM-5, Si/Al 10, Co 4.4 %

CoNH₄-ZSM-5, Si/Al 10, Co 4.4 wt%

dehydration: 350 °C, 3h

Figure 4

DRS of Co(II)- ZSM-5, Si/Al 10, Co cca 4 %

CoNH₄-ZSM-5, Si/Al 10, Co cca 4%, exchange from Co(NO₃)₂
dehydration: 350 °C, 3h

Figure 5

DRS of Co(II)- ZSM-5, Si/Al 10, Co <0.6 %

CoNH₄-ZSM-5, Si/Al 10, Co <0.6 %, exchange from Co(NO₃)₂
dehydration: 350 °C, 3h

Figure 6

DRS of Co(II)- ZSM-5, Si/Al 10, Co cca 4%

CoNa-ZSM-5, Si/Al 10, Co cca 4%

dehydration: 350 °C, 2h

Figure 7

DRS of Co(II)- ZSM-5, Si/Al 22.5, Co 0.75 %

CoNa-ZSM-5, Si/Al 22.5, Co 0.75 %

dehydration: 350 °C, 3h

Figure 8

DRS of Co(II) in mordenite, visible region

Co-mordenite: Si/Al 8.5, Co 2.1 wt%
dehydration: 350 °C, 3h
spectrum of parent zeolite was subtracted

Figure 9

DRS of Co(II) in erionite, visible region

Co-erionite, Si/Al 3.5, Co 3.21 wt%
dehydration: 350 °C, 3h
spectrum of parent zeolite was subtracted

Figure 10

DRS of Co(II) in ZSM-5, Si/Al 10, Co 4.4 %

CoNH₄-ZSM-5, Si/Al 10, Co 4.4 wt%

dehydration: 350 °C, 3h

spectrum of parent zeolite was subtracted

Figure 11

DRS of Co(II) in ZSM-5, Si/Al 10, Co cca 4 %

CoNH₄-ZSM-5, Si/Al 10, Co cca 4%, exchange from Co(NO₃)₂

dehydration: 350 °C, 3h

spectrum of parent zeolite was subtracted

Figure 12

CoNH₄-ZSM-5, Si/Al 10, Co <0.6 %, exchange from Co(NO₃)₂
dehydration: 350 °C, 3h
spectrum of parent zeolite was subtracted

Figure 13

DRS of Co(II) in ZSM-5, Si/Al 10, Co cca 4%

CoNa-ZSM-5, Si/Al 10, Co cca 4%

dehydration: 350 °C, 2h

spectrum of parent zeolite was subtracted

Figure 14

DRS of Co(II) in ZSM-5, Si/Al 22.5, Co 0.75 %

CoNa-ZSM-5, Si/Al 22.5, Co 0.75 %

dehydration: 350 °C, 3h

spectrum of parent zeolite was subtracted

Figure 15

DRS of Co(II) in ZSM-5 with different Si/Al and Co content and prepared at different conditions of ion exchange

- CoNH₄-ZSM-5; Si/Al 10, Co 4.4 %
- - - CoNH₄-ZSM-5; Si/Al 10, Co cca 4 %
- CoNH₄-ZSM-5; Si/Al 10, Co <0.6 %
- · - · - CoNa-ZSM-5; Si/Al 10, Co cca 4 %
- - - - - CoNa-ZSM-5; Si/Al 22.5, Co 0.75 %

each spectrum was separately normalized to 1 at maximum,
samples are described in Figures 1 - 14, spectra of parent zeolites were subtracted

Figure 16

Effect of NO adsorption on DRS spectrum of Co-erionite

Figure 17

Effect of NO adsorption on DRS spectrum of Co-ZSM-5, Si/Al 10

Figure 18

Effect of NO adsorption on DRS spectrum of Co-ZSM-5, Si/Al 22.5

Figure 19

DRS of Mn(II)-mordenite

— Mn-mordenite; Si/Al 8.5, Mn 1.4 %

---- parent H-mordenite

dehydration: 350 °C, 3h

Figure 20

DRS of Co(II)-Nafion with adsorbed NO
and with NO desorbed at different temperature

- Co-nafion dehydrated at 160 °C
- Co-nafion with NO adsorbed at RT
- Co-nafion, NO desorbed at RT
- Co-nafion, NO desorbed at 95 °C
- Co-nafion, NO desorbed at 130 °C
- Co-nafion, NO desorbed at 160 °C