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NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Technical Progress Report for the Period
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Kamil Klier and Richard G. Herman

with

Jiří Dědeček

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

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SUMMARY OF TECHNICAL PROGRESS

The preparation of Co(II) ion exchanged zeolites was described in the previous quarterly progress report, and NO adsorption/desorption studies with these zeolites have now been carried out, especially with ZSM-5 and erionite zeolites. Diffuse reflectance spectroscopy was utilized to monitor the spectral changes that occurred during adsorption of NO on the Co(II) cations, which was observed to occur after dehydration treatments at 350°C and 525°C. Absorption bands in the charge transfer spectral region of NO-Co intrazeolitic complexes depended mainly on Co siting in the zeolites. Catalytic testing of NO decomposition and NO reduction by methane was carried out. It was observed that Co-mordenite and Co-A zeolite exhibited low, but stable, activity in NO decomposition. For NO reduction by methane in the presence of excess oxygen, Co-mordenite and Co-ferrierite exhibited the highest %NO converted to products and selectivity toward N_2 formation, but Co-A zeolite and Co-erionite yielded the highest selectivities to NO_2 formation. Co-ZSM-5 zeolite exhibited an intermediate behavior.

TECHNICAL PROGRESS

The research during this quarter was centered on (i) investigating the adsorption of NO on Co(II) zeolites, (ii) determining the effect of NO adsorption on the diffuse reflectance spectral (DRS) features of Co(II) in zeolite sites, (iii) degree of NO decomposition over the Co(II) zeolites, and (iv) catalytic activity of the Co(II) zeolites for NO reduction by methane in the presence of excess O_2 in a flowing gas stream. In particular, the catalytic activity of Co-ZSM-5, Co-erionite, Co-mordenite, and Co-ferrierite was investigated for NO decomposition and for the selective reduction of NO by methane.

In general, the spectral features of the Co(II) zeolites were presented in the previous quarterly progress report as increasing dehydration temperatures were utilized [1]. It was shown that strong ligands such as water adsorb onto Co(II) sites after dehydration at 350°C and 500°C, but weak ligands such as CO and C_2H_4 only exhibit adsorption after the high temperature dehydration treatment. It is shown in the present report that NO adsorption after both treatments and that strong absorption bands in the UV-VIS spectral region corresponding to charge transfer spectra that are characteristic of the formation of NO-Co intrazeolitic complexes. These bands exhibit strong dependence on the zeolite matrix. The dependence of these on the cobalt siting in erionite indicates that the NO-Co complex is affected mainly by Co siting in zeolite. Co-A zeolite and Co-mordenite exhibit low, but stable, catalytic activity in NO decomposition. Moreover, Co-mordenite, along with Co-ferrierite exhibits high catalytic activity in the selective reduction of NO by methane.

1. EXPERIMENTAL

1.1. Ion Exchanged Samples

The Co(II) exchanged zeolites were prepared under acidic conditions by ion exchange, generally from aqueous $Co(NO_3)_2$ solutions with molarities of 0.01 or 0.02 at room temperature. The detailed conditions of the preparations utilized for the Co(II)-ZSM-5 zeolites were given in the previous report [1], and a wide range of Co-ZSM-5 have been prepared [2,3].

1.2. Diffuse Reflectance Spectroscopy (DRS)

Procedures used for the optical measurements at room temperature were described earlier [1-3]. Spectra were evaluated by the Schuster-Kubelka-Munk theory; $F(R) = (1-R)^2/(2R)$. Samples were dehydrated at 350°C [2] or at higher temperatures such as 500 or 525°C [1,2].

Adsorption and desorption of NO with the dehydrated Co-containing zeolites was carried while simultaneously monitoring the samples by DRS in the UV-VIS-NIR spectral regions. Typically, after the zeolite was dehydrated at 350 or 525°C, the amount of gas adsorbed by *ca.* 0.8 g of dry sample was regulated by adsorption of gas at pressures of 0.5-700 Torr from 40, 180, and 1400 ml volumes at atmospheric pressure. Nitric oxide (98.5%, Aldrich Chemical Company, Inc.) was purified by freezing liquid nitrogen and then thawing. After adsorption at room temperature, desorption of gas was studied at temperatures ranging from room temperature to 440°C. Samples were evacuated from 30 min to 3 h.

1.3. Catalytic Testing of NO Selective Reduction by Methane

The NO decomposition activity of $Co(NH_4)$-erionite (Co 3.2 wt%), $Co(NH_4)$-ZSM-5 (Si/Al = 10, Co 4.4 wt%, prepared at Air Products and Chemicals, Inc., see [2]), CoH-

mordenite (Co 2.1 wt%), and Co-A zeolite (Co 2.6 wt%) was tested first, as described previously [3]. Samples were dehydrated in a stream of helium using a temperature ramp of 5°C per min from room temperature to 500°C, which was then maintained for 1 h. Weights of samples used were 300 mg of Co-A zeolite, 240 mg of Co-erionite, and 360 mg of all other zeolites. After the NO decomposition activity measurement, selective reduction of NO by methane in an oxidative atmosphere was tested at 400°C using a reaction mixture of 1000 ppm of NO, 1000 ppm of CH_4, and 2.5 vol% of O_2 in helium flowing at a rate of 100 ml/min. NO and NO_x were detected by chemiluminescence.

2. RESULTS

2.1. Adsorption of NO on Co-Containing Zeolites

The spectra of Co-erionite and various Co-ZSM-5 zeolites with adsorbed NO were given previously [3]. A very intensive charge transfer band was observed around 40,000 cm^{-1} in these spectra and it was accompanied by three absorption bands of medium or low intensity. The positions of the charge transfer (CT) bands are given in Table 1. Data corresponding to Co-A zeolite were obtained by analysis of spectra contained in Ref. [4]. It is evident that CT bands of NO-Co complexes depends on the zeolite matrix. This dependence can be explained by different Co(II) siting in different zeolite matrices or by the influence of framework acidity (different Si/Al) to the charge transfer spectra of the NO-Co-zeolite complex.

TABLE 1. Charge transfer bands of NO-Co(II) complexes in zeolites.

Matrix		CT Bands			
Zeolite	Si/Al	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})
Co-A	1.0	37,000	24,000	21,000	13,000
Co-erionite	3.6	41,000	26,700	22,000	13,000
Co-ZSM-5	10	40,000	27,500	22,500	13,500
Co-ZSM-5	22.5	39,000	-	23,000	12,500

It is very interesting that no significant differences between spectra of Co-zeolites with NO adsorbed at atmospheric pressure and the ones evacuated for 30 min in dymanic vacuum were observed. The magnetic measurements reported earlier [3] exhibited significant differences between these two preparations of the Co-NO complex. Calculation of the distribution of electrons in the molecular orbitals of the NO-Co complex in zeolite matrices (*via* Extended Huckel computations) is necessary for interpretation of the CT spectra of this complex.

The influence of adsorption and desorption of NO on the optical characteristics of Co-erionite was studied in detail. The resulting spectra are shown in Figures 1-3. Maxima of CT bands of the NO-Co complex in erionite dehydrated at 525°C are shifted to lower frequencies (40,000, 25,000 and 21,000 cm^{-1}) in comparison to bands corresponding to the complex in erionite dehydrated at 350°C. This result indicates that the charge transfer complex of cobalt(II) in zeolites is mainly affected by siting of Co ions in the zeolite matrix.

FIGURE 1

Adsorption of NO on Co-Erionite dehydrated at 350°C at increasing NO pressure.

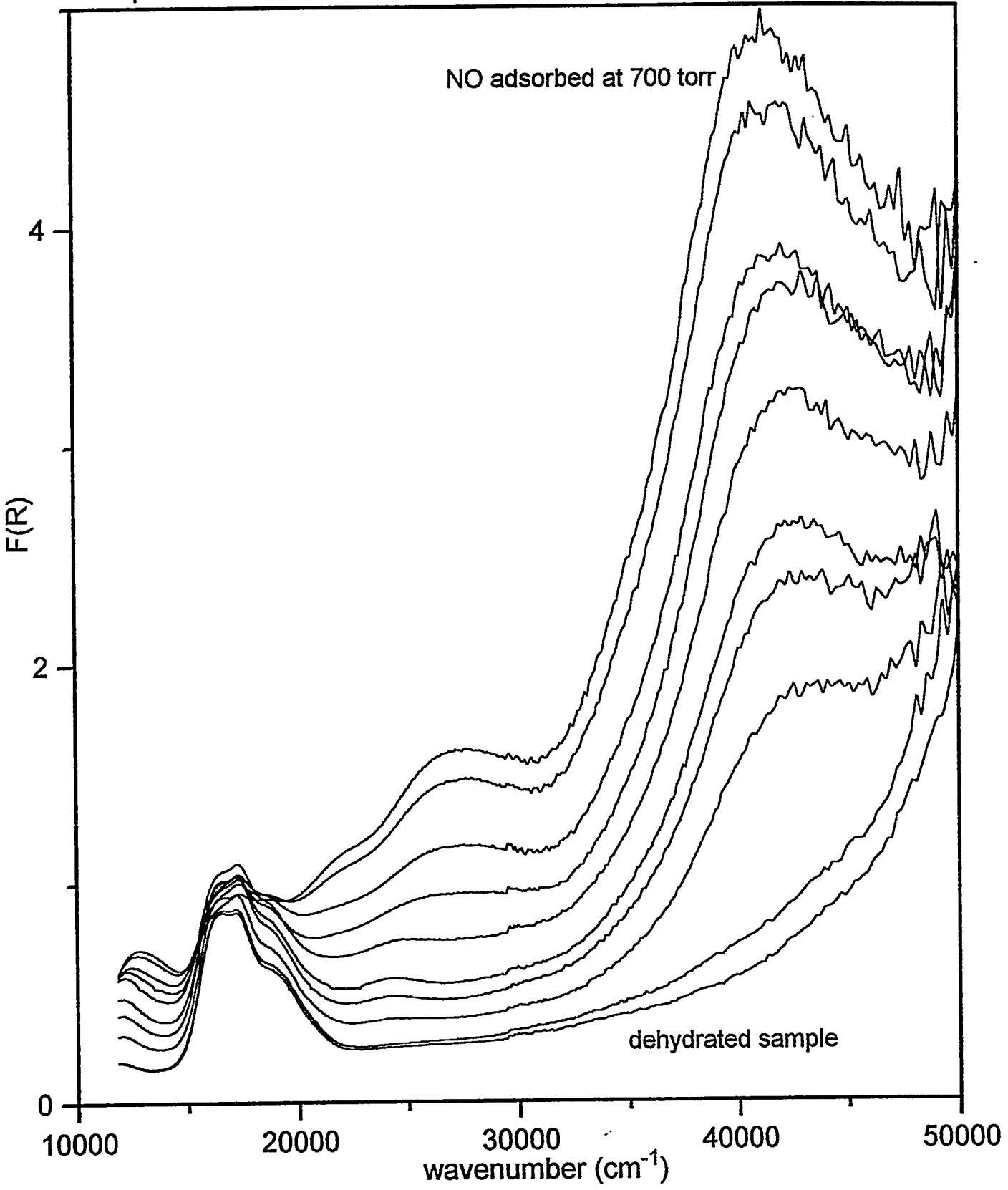


FIGURE 2

Adsorption of NO on Co-Erionite dehydrated at 525 °C at increasing NO pressure.

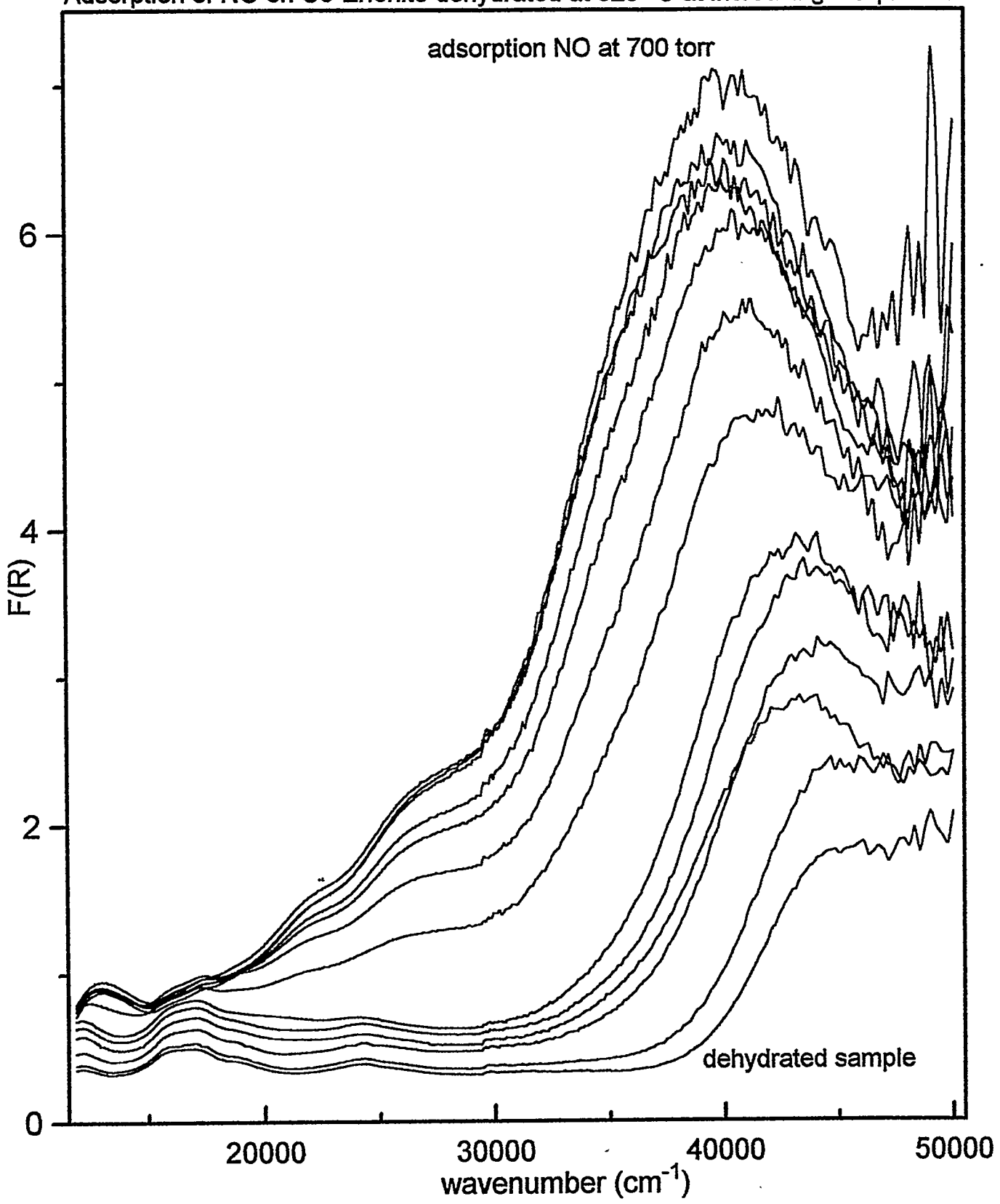
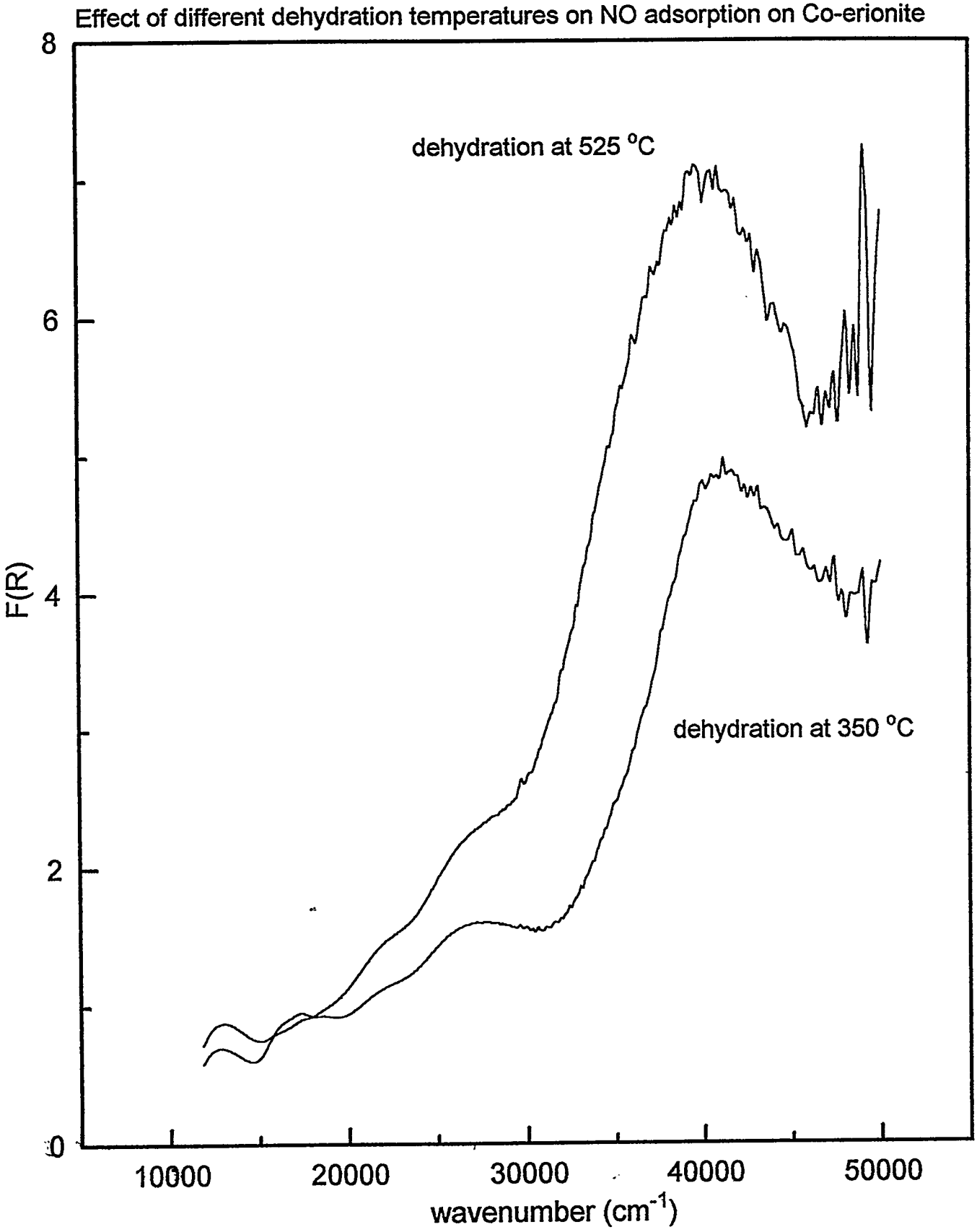


FIGURE 3


Effect of different dehydration temperatures on NO adsorption on Co-erionite
dehydration at 525 °C
dehydration at 350 °C
F(R)
0
2
4
6
8
10000
20000
30000
40000
50000
wavenumber (cm-1)

2.2. Catalytic NO Decomposition Over Co-Containing Zeolites

Catalytic activities for NO decomposition over cobalt(II)-containing ferrierite, mordenite, ZSM-5, and A zeolites are given in Table 2. Catalytic activities of copper(II)-containing ZSM-5, Y, erionite, and mordenite zeolites (from Ref. [5] and [6]) are given for comparison.

TABLE 2. Catalytic activity of Co(II)-zeolites in NO decomposition.

Zeolite Matrix	Co-Containing Zeolites		Cu-Containing Zeolites	
	Co Content (wt%)	Conversion of NO (%)	Cu Content (wt%)	Conversion of NO (%)
A	2.6	1	-	-
Y	-	-	3.7	1
Erionite	-	-	3.1	1.5
Mordenite	2.1	1	3.7	2.5
Ferrierite	5.1	0	-	-
ZSM-5	4.4	0	2	4-20

These results are the first evidence of time stable NO decomposition activity of Co-A and Co-mordenite zeolites under continuous flow reactor conditions at ambient pressure. This catalytic activity is low, but comparison to corresponding copper-containing zeolites (also shown in Table 2) is promising. It is known [7-10] that activity for NO decomposition over Cu-ZSM-5 depends on Cu concentration, on silicon to aluminum ratio, on the form of the original zeolite (Na or H form), and on the method of catalyst preparation. These parameters have not yet been studied with the Co(II)-ZSM-5 zeolite, nor with the other Co(II) zeolites.

2.3. Selective Reduction of NO by Methane

Catalytic activity of cobalt(II)-containing erionite, ferrierite, mordenite, ZSM-5, and A zeolites for the selective reduction of NO in an oxidative atmosphere is given in Table 3. These results were obtained under steady state conditions that were maintained for at least 30 min. All of the Co(II) zeolite catalysts exhibited some activity for the reduction of NO under these reaction conditions.

TABLE 3. Catalytic activity of cobalt(II)-containing zeolites for selective reduction of NO in an oxidative atmosphere at 400°C using a reactant mixture of 1000 ppm NO + 1000 ppm CH_4 + 2.5 vol% O_2 in He flowing at 100 ml/min at ambient pressure.

Zeolite	NO Converted (mol%)	NO Converted to NO_2 (mol%)	Co Content in zeolite (wt%)	Wt of Catalyst in Reactor (g)
Co-A	16	58	2.6	0.30
Co-erionite	25	47	3.2	0.24
Co-mordenite	44	14	2.1	0.36
Co-ferrierite	70	8	5.1	0.36
Co-ZSM-5	39	20	4.4	0.36

Due to varying contents of Co(II) in the catalysts and the different masses of catalysts that were used in the reactor, the conversion of NO was recalculated on the basis of the weight of catalyst and also on the basis of only the cobalt content of the zeolites contained in the reactor. These results are given in Table 4 in terms of rates of NO converted and N_2 formed.

TABLE 4. Catalytic activity of cobalt(II)-containing zeolites for selective reduction of NO by methane in an oxidative atmosphere related to the weight of catalyst and to cobalt(II) content.

Zeolite	mol of NO converted /g of zeolite per second	mol of NO converted to N_2/g of zeolite per second	mol of NO converted /mol of Co per second	mol of NO converted to N_2/mol of Co per second
Co-A	$0.44 \cdot 10^{-7}$	$0.18 \cdot 10^{-7}$	$0.27 \cdot 10^{-3}$	$0.11 \cdot 10^{-3}$
Co-erionite	0.87	0.46	0.46	0.24
Co-mordenite	1.00	0.86	0.78	0.67
Co-ferrierite	1.60	1.47	0.52	0.48
Co-ZSM-5	0.90	0.72	0.33	0.26

Large differences in conversion of NO relative to the cobalt(II) content in zeolites indicate the presence of different catalytic centers in these zeolite matrices. Very interesting is the high conversion of NO to NO_2 by Co-erionite and Co-A zeolite. This behavior might coorelate with the fact that erionite and A zeolite contain Co(II) ions in a similar site (regular six-ring windows). The high catalytic activity of cobalt(II) ions in Co-mordenite is also of interest, and determination of cobalt sites in this zeolite and population of cobalt(II) ions in these sites is of a great importance in optimizing these catalysts for the selective reduction of NO.

3. REFERENCES

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