Time-Resolved FT-IR Study on Isotopic Exchange of Dinitrosyl Species Strongly Adsorbed on a Co-MFI Zeolite

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Very rapid exchange of NO molecules between the strongly adsorbed dinitrosyl species and NO in gas phase has been found at room temperature on a Co-MFI zeolite. The formation of (^{14}NO)(^{15}NO) species during the reaction indicates that the NO ligands are exchanged one by one.

Cobalt ion-exchanged zeolites have attracted much attention in the fields of selective catalytic reduction of NOx by hydrocarbons (SCR-HC)[1-7] and pressure swing adsorption of NOx.[8] In the former the unusual high activity of Co-ZSM-5 (MFI) and -ferrierite(FER) for the SCR by methane[1-4] has widely been recognized. In the latter Co-zeolites show a superior ability for the NO adsorption; they irreversibly adsorb the largest amount of NO at 273 K among a variety of metal ion-exchanged zeolites[8] and the dominant irreversible adsorbate is in a dinitrosyl form.[8-12] To characterize the state and reactivity of the dinitrosyl species is essentially significant to clarify the reaction mechanism of the SCR-HC and the characteristics of Co-zeolites as adsorbents for NO. We wish here to report very rapid exchange of NO molecules between the strongly adsorbed dinitrosyl species and NO in gas phase. The exchange reaction has been followed by a time-resolved FT-IR technique combined with an isotopic tracer method.

Co-MFI used was the same as that reported previously.[8] The exchange level of Co^{2+} ions was 110%. IR absorption spectra were recorded by using Parkin Elmer System 2000 spectrometer. A quartz IR cell with KBr windows was used. A self-supporting wafer (ca. 4mg cm^{-2}) of Co-MFI was heated in the cell at 773 K for 2 h, and then cooled down to ambient temperature under a vacuum (< 10^{-2} Torr, 1 Torr=133 Pa) as a pretreatment. The IR spectra of adsorbed species were obtained by subtracting the spectrum of wafer.

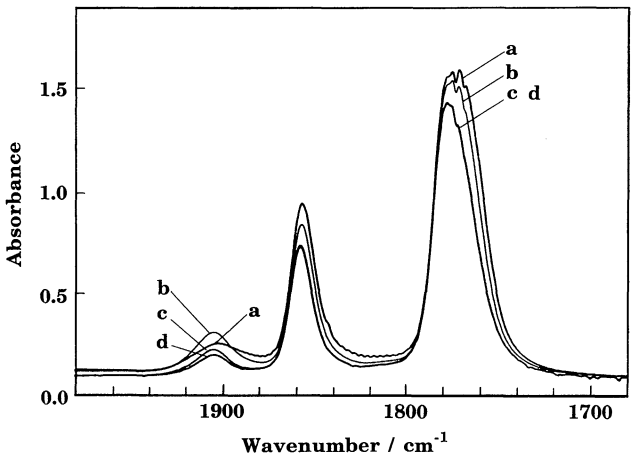

Figure 1. Change in IR spectra with the evacuation time at ambient temperature after introduction of ^{15}NO on Co-MFI.
(a) adsorption of ^{15}NO at 13 Torr for 120 min, (b) evacuation for 5 min at ambient temperature, (c) for 300 min, (d) 500 min.

Figure 1 shows the IR spectra of NO adsorbed on Co-MFI in the region 1980 - 1680 cm^{-1}. Figure 1a was measured after 13 Torr of ^{15}NO was introduced into the cell for 120 min. The absorption bands at 1858 and 1776 cm^{-1} can be assigned to symmetric and asymmetric stretching modes of a dinitrosyl adsorbate, $[Co(^{15}NO)_2]^{2+}$, on the basis of the literature reported.[10-12] The peak at 1904 cm^{-1} is attributable to a mononitrosyl species.[10-12] Upon evacuation of ^{15}NO at ambient temperature, the peak areas of the $[Co(^{15}NO)_2]^{2+}$ species decreased a little and the area of $[Co^{15}NO]^{2+}$ species transiently increased and then gradually decreased. The former is in good agreement with the results of Lunsford et al.[10, 11] and Li et al.[9] that the species responsible for the shoulders of the asymmetric stretching band of $[Co(^{15}NO)_2]^{2+}$ was removed by evacuation at room temperature. The results confirm that most of the dinitrosyl species adsorb strongly on Co-MFI at ambient temperature under a vacuum, and that the weakly adsorbed dinitrosyl species desorb *via* the transient formation of mononitrosyl species.

After the sufficient evacuation of gaseous ^{15}NO, ^{14}NO of 13 Torr was admitted onto the ^{15}NO-preadsorbed Co-MFI at ambient temperature. The change in the IR bands is depicted in Figure 2. One can see the very rapid change in the spectra: The transition was almost completed within 1 sec. The band at 1776

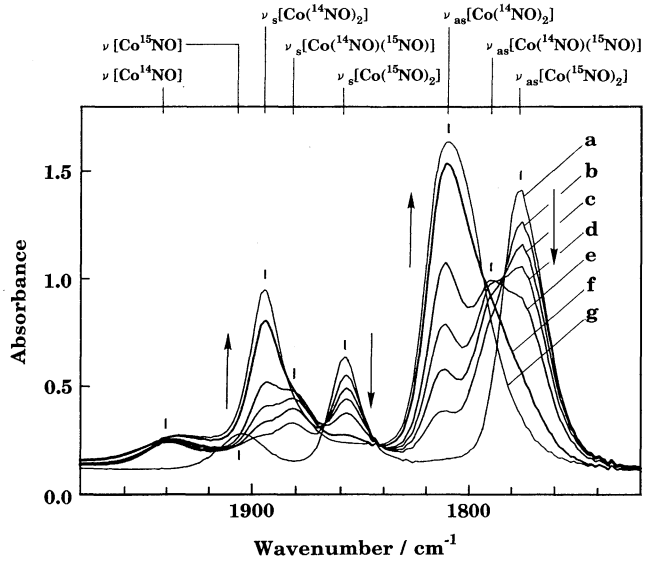

Figure 2. Change in IR spectra by admission of ^{14}NO of 13 Torr at ambient temperature onto ^{15}NO-preadsorbed Co-MFI.
(a) ^{15}NO was introduced at 13 Torr for 120 min and then removed by evacuation at ambient temperature for 30 min, (b) after 0.3 sec from admission of ^{14}NO of 13 Torr, (c) 0.4 sec, (d) 0.5 sec, (e) 0.7 sec, (f) 5.0 sec, (g) 3.0 min.

cm^{-1} decreased with the time, the 1790 cm^{-1} band transiently appeared and then decreased, and the 1810 cm^{-1} band monotonically increased. The identical conversion was observed among the absorption bands at 1858, 1882, and 1894 cm^{-1}. On the basis of the assignment of each band summarized in Figure 2, it follows that the ^{15}NO molecules in the strongly adsorbed dinitrosyl species on Co-MFI can quickly be replaced by ^{14}NO molecules in gas phase: In other words, the $[Co(NO)_2]^{2+}$ adsorbates on the surface come to equilibrium with the gaseous NO.

The exchange of the mononitrosyl adsorbates from ^{15}NO to ^{14}NO (1904 $\rightarrow$ 1942 cm^{-1}) was more rapid than that of the dinitrosyl adsorbates. The transition was completed within 0.3 sec as shown in Figure 2. This is consistent with the observation in Figure 1 that the mononitrosyl species was more labile than the dinitrosyl species.

The respective areas of the absorption bands corresponding to the asymmetric stretching frequencies of the $[Co(NO)_2]^{2+}$ species were evaluated by deconvolution of the spectra. The values are plotted as a function of the elapse of time in Figure 3. It is clear that, with decreasing of the $[Co(^{15}NO)_2]^{2+}$ species, the $[Co(^{14}NO)(^{15}NO)]^{2+}$ species first appeared and then the $[Co(^{14}NO)_2]^{2+}$ species grew up. At equilibrium the sum of peak areas of the three species was greater than the initial value of the $[Co(^{15}NO)_2]^{2+}$ species, which is evidently due to the presence of weakly adsorbed dinitrosyl species as has been pointed out in Figure 1. Figure 3 concludes that the NO ligands are exchanged one by one.

It was confirmed in separate experiments that the admission of N_2 or CO onto the NO-preadsorbed Co-MFI did not give any change in the IR spectrum. This suggests that the dinitrosyl species is stable even in the presence of CO and the exchange reaction of NO found in the present work is not attributed to a collision-substitution mechanism. The reaction perhaps proceeds *via* formation of a short-lived trinitrosyl species. It might be useful to take into consideration that the desorption of CO on Ni is enhanced under gas phase CO due to the repulsive interaction.[13] More detailed exchange mechanism of NO on the Co-MFI zeolite is under investigation.

This is the first evidence for the exchange reaction of NO between the strongly adsorbed species and the gas phase molecules. The similar exchange reaction of weakly adsorbed NO species has already been reported.[14] The reactions should be included in the discussion of the decomposition/reduction mechanisms or adsorption phenomena of NO.

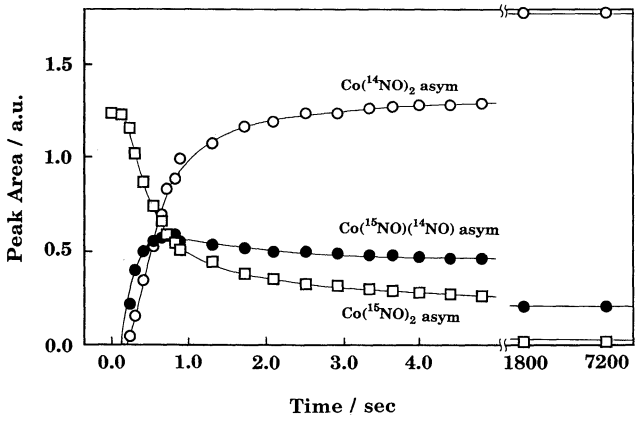

Figure 3. Peak areas of the absorption bands corresponding to the asymmetric stretching frequencies of the $[Co(NO)_2]^{2+}$ species as a function of the elapse of time from the introduction of ^{14}NO. The experimental conditions were the same as those in Figure 2.

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