

Effect of Coexchanging with a Second Metal upon the Interaction of Nitric Oxide with Cu-ZSM-5

V. I. Pârvulescu

University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis,
B-dul Republicii 13, 70346 Bucharest, Romania

P. Grange and B. Delmon*

Universite Catholique de Louvain, Unite de Catalyse et Chimie des Materiaux Divises, Place Croix du Sud,
2/17, 1348 Louvain-la-Neuve, Belgium

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The effect of coexchanging of Cu-M-ZSM-5 zeolites (M = Ce, Sn, Sm) upon the interaction with nitric oxide was investigated by FT-IR. Spectra recorded on Cu-ZSM-5, in the presence of NO and at room temperature, exhibit typical features, very well reported in the literature. During NO decomposition at 673 K in the presence of 50 mbar NO, the band assigned to $(\text{NO})^{\delta+}$ species exhibits both a splitting and a shift. This behavior was attributed both to some modification in the copper(II) state during the reaction and to the formation of N_2O_3 species, active in NO decomposition. The presence of a second metal influences this process, and the intensity of the effect depends both on the chemical nature of the second metal and on its loading. It was also found that in the presence of Ce or Sm, the bands assigned to *gem*-dinitrosyl and to Cu^+-NO as well as those of the N_2O_3 species are more intense. These effects were correlated with a more intense activity of Ce or Sm-promoted zeolites compared to pure Cu-ZSM-5. It is noteworthy that this increase occurs simultaneously with a diminution of the intensity of the nitrate–nitrite species bands.

Introduction

During the last decade, research concerning NO decomposition has concentrated on the investigation of Cu-ZSM-5, as very important conversions are obtained on this catalyst. As a consequence numerous papers and patents have been published.^{1–10} Almost all these catalysts were prepared using the “exchange technique” and the published data present the experimental conditions and the properties of the zeolites that have been used.

One of the more investigated and intriguing problems is the mechanism of this reaction and, in order to solve this question, infrared studies of NO adsorbed on these catalysts have been widely reported.^{11–15} Iwamoto et al. proposed that NO is adsorbed only on metallic centers because no adsorption bands of NO were evidenced on the pure MFI structure.¹¹ However, very recently Szanyi and Pfafet¹⁶ reported that this occurs to a very small extent, but in the presence of copper the effect of the lattice is negligible. At room temperature, the investigations on Cu-ZSM-5 catalysts evidenced seven intense bands, which were assigned to N_2O , $(\text{NO}_2)^{\delta+}$, $(\text{NO})^{\delta+}$ adsorbed on multi-metallic centers, $(\text{NO})^{\delta+}$, $(\text{NO}_2)^{\delta-}$ symmetric, $(\text{NO})^{\delta-}$ and $(\text{NO}_2)^{\delta-}$ asymmetric stretches. A very good agreement appears in the assignment of these bands.^{11,17–19} Iwamoto et al. suggested that NO decomposition could be directly correlated with the presence of *gem*-dinitrosyl species and showed that these are generated through the interaction between $\text{Cu}^{2+}-\text{NO}^-$ and NO .¹¹ This explanation generally supposes the presence of two neighbor atoms of copper in a $\text{Cu}^{(2-\delta)+}$ state. The main argument of this assumption is the absence of $(\text{NO})^{\delta-}$ species on Cu-ZSM-5 pretreated in oxygen, whereas $(\text{NO})^{\delta+}$ bands were very well identified. Generation of active centers was considered to take place in successive steps in which the presence of

gem-dinitrosyl species, as intermediate, is also determinant. Generally, this process is considered to occur on neighbor copper atoms bonded on aluminium. Yashima's group²⁰ also supports this model. However this pattern is surprising because the distance between two aluminium atoms is too large to allow a close proximity of two copper atoms. Therefore, Iwamoto⁷ reconsidered this model and suggested that $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ species are formed during the ion exchange procedure, when water molecules coordinated near Cu^{2+} ions are easily ionized and dissociated because of the strong electrostatic fields, with generation of $\text{Cu}(\text{OH})^+$ and a Bronsted acid site. During dehydration at elevated temperatures, dimerization or polymerization could occur to form $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$ species. Infrared studies made by Valyon and Hall^{21,22} showed that the extralattice oxygen (ELO) bridging the two divalent cations produces a band near 910 cm^{-1} . In the presence of NO, on the overexchanged catalysts, they assigned the bands located at 2130, 1634, and 1562 cm^{-1} to species formed by interaction of NO with ELO. The presence of these species was also reported by other authors. Very recently Sachtleer's group²³ gave supplementary arguments that, in overexchanged Cu-ZSM-5, a significant fraction of copper is present as dimeric species. They found that internal zeolite stretching vibrations are perturbed by the presence of Cu^+ and Cu^{2+} ions.

Another attempt to explain the *gem*-dinitrosyl formation was proposed by Shelef, who considers that this intermediate could be associated with the sequence $\text{Cu}^{2+}:\text{NO} + \text{NO}_{\text{gas}} \rightarrow \text{Cu}^{2+}(\text{gem-dinitrosyl})$.²⁴ Using this model, Shelef tried to explain both variation of the reaction with temperature and the co-existence of mono and *gem*-dinitrosyl species in the IR absorption spectra. Previous studies of Gandhi and Shelef about adsorption of NO on copper oxides indicated that surface cupric ions chemisorb NO much faster than the cuprous ions.²⁵ Using the same model of isolated copper atoms, Anpo's group^{12,26} suggested that the *gem*-dinitrosyls do not occur via Cu^{2+} but

* To whom correspondence should be addressed.

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via Cu^+NO (that is paramagnetic and exhibits an EPR spectrum) following the sequence: $\text{Cu}^+\text{NO} + \text{NO} \rightarrow \text{Cu}^+$ (*gem*-dinitrosyl). Wichterlova's group^{27–29} also agrees with the isolated copper atoms model. Both these groups brought arguments showing that different Cu ions in defined cationic sites of the ZSM-5 could occur. Moreover, Wichterlova et al.²⁹ attributed the redox behaviour of Cu in overexchanged Cu-ZSM-5 only to copper sites adjacent to a single framework Al. With a similar model Centi et al.^{30,31} also agree. Very recently, Bell's group^{15,32} reinvestigated the interaction of NO with Cu-ZSM-5. Infrared spectra recorded at high temperatures led them to suggest that N_2 is formed via N_2O and that O_2 release occurs in two steps: first O atoms resulting from NO decomposition desorb from Cu^{2+}O^- and second react with additional Cu^{2+}O^- to produce $\text{Cu}^{2+}\text{O}_2^-$.

Introduction of a second metal was reported to have a positive effect upon the activity of Cu-ZSM-5. Kagawa et al.³³ and Zhang and Flytzani-Stephanopoulos^{34,35} indicated that Ce or Mg increases the Cu-zeolite activity. The authors claimed that the effect of cerium was to hinder the sintering of the catalytically active components rather than to degrade the metastable zeolite support. Other studies were performed by Eranen et al.³⁶ who used bicomponent catalysts prepared using two techniques: exchange of zeolites in which metals (Co, Ni, Ga) were introduced during synthesis and impregnation of copper-exchanged zeolites with a second metal (Co, Ni, Ag). However, up to now there is no evidence on the mechanism through which transitional cocations such as Ce promote the copper activity. Very recently, Centi and Perathoner³⁷ suggested some factors that contribute to this effect: modification of the electrostatic field and surface potential within pores/cavities of the zeolite, change of local softness around copper ions, or change in the diffusional properties of NO. Soon after that, Budi et al.³⁸ and Kuchеров et al.³⁹ reported a noticeable influence of lanthanum on Cu-ZSM-5. They interpreted this behaviour in terms of a treatment-induced bonding change between the isolated Cu^{2+} cations and the framework oxygens of ZSM-5 linked, in turn, to the Al^{3+} ions.

The aim of this study was to investigate the influence of a second metal like tin, cerium, or samarium upon the chemisorption of NO on Cu-ZSM-5 zeolite and to obtain some information about the modifications caused by the introduction of the second metal. The following properties were considered in the choice of these metals: cerium and samarium exhibit high values of the redox potential $\text{M}^{4+}/\text{M}^{3+}$ and $\text{M}^{3+}/\text{M}^{2+}$ respectively (about 1.50 eV for cerium and 1.61 eV for samarium) and thus are able to easily change from one oxidation state to another. The redox potential $\text{M}^{4+}/\text{M}^{2+}$ of tin oxide has a low value (0.15 eV), but this oxide is very well known as a good carrier for oxygen spillover. It was speculated that perhaps spillover could facilitate the cleaning of the oxygen chemisorbed on copper.

Experimental Section

All catalysts were obtained using the exchange or coexchange technique. The solutions were obtained by dissolving 3.76 mM copper acetate monohydrate (Aldrich Chemical Co.Ltd.) or/and 3.0 mM or 1.0 mM of a second metal salt (in the case of cerium or tin) or/and 0.6 or 0.3 mM (in the case of samarium) in 300 mL of biological purified water. Five grams of ZSM-5 zeolite (Valfor CBV-5020) was then added under vigorous stirring. The suspensions were maintained under these stirring conditions for 24 h at room temperature. Tin chloride (UCB), cerium chloride, and samarium nitrate (Merck) were used. The incipient pH was in the range 5.5–6.0 for copper, cerium, and copper–cerium

TABLE 1: Chemical Composition of Mono- and Coexchanged ZSM-5 Zeolites

catalyst	metal content	
	Cu, wt %	second metal, wt %
Cu-	3.04	
Cu-Ce-1	2.53	4.65
Cu-Ce-2	2.40	1.52
Ce-		4.65
Cu-Sn-1	2.79	4.09
Cu-Sn-2	2.35	2.01
Sn-		4.13
Cu-Sm-1	2.61	0.18
Cu-Sm-2	2.30	0.19
Sm-		1.00

suspension, 4.1–5.1 for samarium and copper–samarium suspension, and 1.5–2.0 for tin and copper–tin suspensions. The pH modification during the exchange process was in the limit of 0.3–0.4 units. After 24 h the pH was modified to around 7.5 by using dilute NH_3 solution. The exchanged zeolites were then washed, centrifugated, and dried at room temperature in a vacuum stove. Metal concentration was analytically determined (Table 1). Different copper concentrations in the samples given in Table 1 are a consequence of the cocation exchange competition.

FTIR spectra were recorded with a Bruker FT-IR 88 spectrometer. The samples were compressed into self-supporting discs ($10\text{--}15\text{ mg/cm}^3$) and placed in a special vacuum cell where they underwent all activation and adsorption treatments. Spectra were recorded at 298 K at a resolution of 1 cm^{-1} using 50 scans for each measurement. A background spectrum was recorded before the determinations. This was automatically subtracted. The reported spectra are the result of this subtraction. Before the measurement, the samples were heated at 673 K under a vacuum of 10^{-6} mbar for 6 h. The increase of temperature was 1 K min^{-1} . The NO-FTIR spectra were measured in the region $1200\text{--}2400\text{ cm}^{-1}$ in four different steps as follows. Fresh catalysts and also Cu-Sn-1R that was previously tested in NO decomposition for 24 h were investigated.

In the first step, the spectra were recorded at room temperature under 50 mbar NO and at different times in the range 15 min–2 h. In the second step, the cell was evacuated at room temperature at 10^{-6} mbar. In the third step, the spectra were recorded after 1 h of reaction under 50 mbar NO at 673 K. In the fourth step, the spectra were recorded after a new cell evacuation at 10^{-6} mbar. The NO pressure was chosen in order to achieve a full saturation of the Cu centers with NO.

The ratio of the area intensities was determined by measuring the area of the decomposed bands. All the bands located in the range $1879\text{--}1912\text{ cm}^{-1}$ were deconvoluted using a Gaussian distribution.

Results

FT-IR Spectra of Cu-ZSM-5 and Cu-M-ZSM-5 Zeolites (M = Sn, Ce, Sm). The FT-IR spectra of Cu, M-, and Cu-M-zeolites in the $400\text{--}1300\text{ cm}^{-1}$ region contain bands characteristic of zeolite framework stretching vibrations²¹, i.e., bands near 550 and 1220 cm^{-1} associated with the structural assembly of the tetrahedra and near 800 and 1087 cm^{-1} associated with both asymmetric and symmetric stretching vibrations of the aluminosilicate lattice.^{40–42} Samples previously treated in helium exhibit a window between the last two frequencies irrespective of the nature of the metallic components or their loading. After treatment in O_2 or in NO, at 773 K for 1 h, an additional band, similar to that found by Valyon and Hall²² and

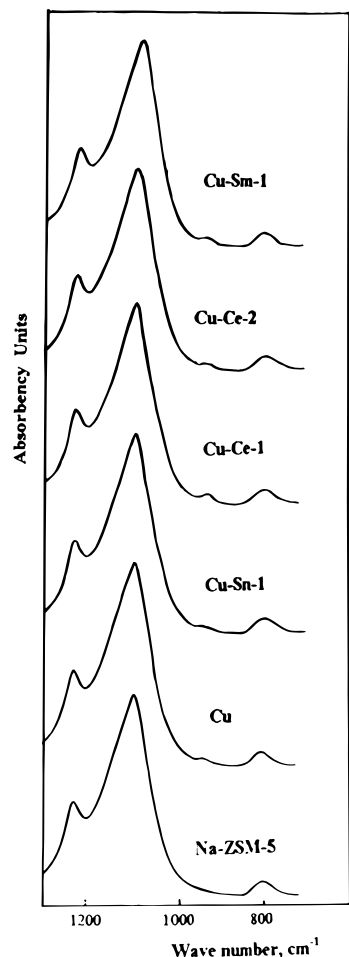


Figure 1. FT-IR spectra of Na-ZSM-5 and metal zeolites after reaction with NO, under 50 mbar at 673 K, for 1 h.

Lei et al.,²³ was also detected (Figure 1). This is located in the region 935–940 cm^{-1} , and its intensity varies in the following order: Cu-Sn-1 < Cu < Cu-Ce-2 < Cu-Ce-1 < Cu-Sm-1. Both groups assigned this band to the existence of ELO, generated by two metallic atoms in a very close proximity. Taking these authors' assumption, one could conclude that the presence of the second metal, except tin, promotes the formation of these species.

Spectra recorded for M-ZSM-5 (M = Sn, Ce, Sm) show a similar band only in the case of cerium, but its intensity was comparable with that recorded on Cu-Sn-1.

Interaction of NO with Cu-ZSM-5. Figure 2 presents the infrared spectra in the four steps of NO adsorption on Cu-ZSM-5 catalyst. The location of the observed bands and their assignments are summarized in Table 2. In both the first and second steps, a typical spectrum for Cu-ZSM-5 zeolites in the presence of NO was recorded. The asymmetry of the band assigned to $\text{Cu}^{2+}(\text{NO})^{\delta+}$, in the first step, suggested the existence of different species. Indeed, its deconvolution indicates as dominant the species located at 1897 cm^{-1} and a low contribution of the other two bands corresponding to 1912 and 1905 cm^{-1} , respectively (Figure 3). The first species is generally accepted as corresponding to copper in square planar coordination. Concerning the other two, Wichterlova's group,²⁸ on the basis of the combined photoluminescence and NO-FT-IR spectra, attributed the band located at 1912 cm^{-1} to Cu sites in a square pyramidal environment while that at 1906 cm^{-1} was attributed to Cu^{2+} sites in the vicinity of framework Al pairing arrangements belonging to zeolites with higher framework Al content. This band is generally detected in the case of overexchanged zeolites



Figure 2. NO-FT-IR spectra on Cu-ZSM-5 zeolite. (1) 50 mbar NO, room temperature; (2) after evacuation of the cell at 10^{-6} mbar; (3) after heating 1 h at 673 K in the presence of 50 mbar; (4) after reevacuation of the cell.

TABLE 2: NO Absorption Bands and Their Assignment on Cu-ZSM-5 Zeolite

assignment	room temp, 50 mbar NO	room temp, evacuated 10^{-5} Torr	723 K	room temp, evacuated 10^{-5} Torr
$\nu(\text{N}_2\text{O})$				
$\nu(\text{NO}_2)$	2169	2170 ^a		
		2159		
$\nu(\text{NO})^-$	1991 ^a	1993 ^a	1993 ^a	
$\nu(\text{NO})^{\delta+}$	1897	1898	1906	
$\nu(\text{N}_2\text{O}_3)^{\delta-}$			1879	1882
asymmetric				
$\nu(\text{NO})_2^{\delta-}$	1827			
$\nu(\text{NO})^{\delta-}$	1813	1812		
symmetric				
$\nu(\text{NO})_2^{\delta-}$	1735			
$\nu(\text{NO}_2)_2$	1700 ^a			
νNO_2	1646	1655	1621	1615
$\nu(\text{N}_2\text{O}_3)$			1584	1584
νNO_2^- , νNO_3^-	1613	1558	1635	1635

^a Shoulder.

at high Cu loading. In addition, both Valyon and Hall²¹ and Bell et al.^{15,32} consider that the band located at 1905 cm^{-1} corresponds to isolated Cu^{2+} , whereas the one located at around 1895 cm^{-1} would correspond to Cu^{2+}O^- species. Valyon and Hall²¹ suggested that in fact this O is an ELO species. For the band located at 1912 cm^{-1} , Lei et al.²³ suggested the possibility that it indicates the existence of $\text{Cu}^{(2-\delta)+}$ species, which could result from decomposition of the $\text{Cu}^{2+}\text{OCu}^{2+}$ dimer. Summarizing, the spectra recorded at room temperature indicated mainly a Cu^{2+} species in a square planar configuration, also containing an extralattice oxygen, and two other species in a low content, one inactive located at 1912 cm^{-1} and another one at 1906 cm^{-1} , indicating an overexchanged zeolite. Evolution of the spectrum shape in time was the same as that presented in the literature.^{11,17-19} At the same time, one could notice the presence of the bands, even having low intensity, in the region 1600–1700 cm^{-1} at room temperature. By analogy with the recent results of Hadjiivanov et al.⁴³ indicating that the bands located at 1630, 1613 and 1577 cm^{-1} describe different kinds of nitrate species, namely the higher-frequency components of

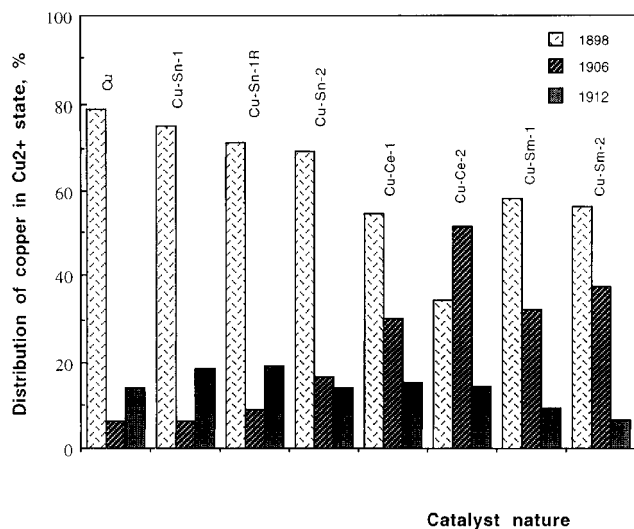


Figure 3. Distribution of species assigned to different states of copper after deconvolution of the band located in the range 1898–1912 cm^{-1} .

ν_3 split vibrations, we assigned these to adsorbed nitrate species. After treatment at 673 K in presence of NO, the $(\text{NO})^{\delta-}$ and $(\text{NO})_2^{\delta-}$ species completely disappear, but the intensities of the bands in the region 1600–1700 cm^{-1} increase very much. Under these conditions the band assigned to the $(\text{NO})^{\delta+}$ species is split and shifted to 1906 and 1879 cm^{-1} . Deconvolution of this band shows that in these conditions the band located at 1906 cm^{-1} becomes dominant but the contribution of those located at 1898 and 1912 cm^{-1} is still present (Figure 3). This behaviour could indicate that in conditions of reactions both a migration of copper (taking the assumption of Wichterlova's group²⁸ about the significance of the band located at 1906 cm^{-1}) and a modification of coordination^{15,21,23,28} occur. The frequency of the band located at 1879 cm^{-1} is lower than that generally reported for $(\text{NO})^{\delta+}$. Its time modification as well as its position make us attribute this band to stretching modes of N_2O_3 . This is in total agreement with previous data reported by Bell et al.^{15,32} and Hadjiivanov et al.⁴³ According to Bell et al.^{15,32} the concomitant presence of the band located 1584 cm^{-1} , which is very close to those of solid phase N_2O_3 ,⁴⁴ is a supplementary argument to sustain the existence of N_2O_3 species. In addition, Hadjiivanov et al. presented some arguments indicating that the presence of this band in this position could provide evidence for the existence of a Cu–O adsorbent species. After the cell evacuation, only the shifted band remains and the bands located at 1635, 1615, and 1584 cm^{-1} become significant.

Summarizing, FT-IR spectra recorded at 673 K indicate that in these conditions both a migration and a modification of copper coordination occurs. The presence of N_2O_3 species could indicate their direct contribution in NO decomposition, as already mentioned.^{15,32}

Interaction of NO with M-ZSM-5 Zeolites (M = Ce, Sn, Sm). Interaction of NO with these zeolites leads to a different behaviour than that determined for Cu-ZSM-5 (Figure 4, Table 3). For all these monocomponent zeolites, dinitrosyl species were not evidenced, thus indicating a different interaction than that previously reported for Co,⁴⁵ Cr,⁴⁶ or Fe,⁴⁷ although implanted on different supports.

In the first step, few bands exhibit important intensities irrespective of the metal nature: 1811, 1885, and 2136 cm^{-1} (Figure 4, Table 3). Supplementary intense bands at 1585 cm^{-1} for Ce, at 1649 cm^{-1} for Sn and Sm, at 1705–1718 cm^{-1} for Sn and Ce and at 1985 cm^{-1} for Ce and Sm, respectively, were also recorded.

The band located at 2136 cm^{-1} , assigned to $(\text{NO}_2)^+$ species,

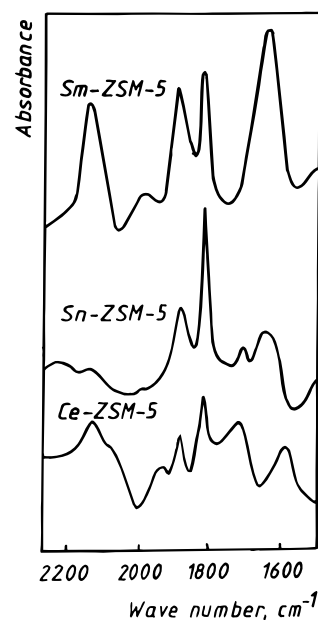
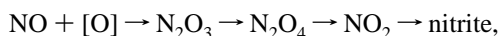


Figure 4. NO-FT-IR spectra on M-ZSM-5 zeolites at room temperature and in the presence of 50 mbar NO.

is more important than the similar band recorded on Cu-ZSM-5 or on the investigated Cu-M-ZSM-5. Near-zero catalytic activity of these zeolites as well as the time variation of this band excludes the hypothesis that it could be due to N_2 .¹⁵ This band slowly decreases in intensity with time while the band located in the range 1880–1890 cm^{-1} increases. These spectra allowed us to attribute the band located in the range 1880–1890 cm^{-1} to stretching modes of N_2O_3 . Taking the assumption of Hadjiivanov et al.,⁴³ its presence could also provide evidence for the existence of an extralattice oxygen ion due to these metals. However, the existence of these species was also reported by Grunert et al.⁴⁸ for lanthanum in faujasite-type zeolites. Another intense band located at 1811 cm^{-1} could also be assigned to some M–O₂–N–N=O complexes such as proposed by Larsen et al.³² and Lane and Ohlsen.⁴⁹ We suppose that it is more probably this species than another OONO species suggested by Smith and Guillory⁵⁰ or Hadjiivanov et al.,⁴³ because catalytic tests⁵¹ indicated a very low tendency of these to decompose NO to O₂ even at high temperatures. One can conclude that on these metals the presence of *gem*-dinitrosyl species was not detected, but the formation of another bidentate species such as N_2O_3 is possible due to the oxidation properties of ELO belonging to these implanted metals.

Concerning the supplementary bands, only the one located at 1985 cm^{-1} could be assigned to $(\text{NO})^+$ species. The bands located at 1705–1718 cm^{-1} as well as those at 1637–1649 cm^{-1} characterize different frequency modes of NO_2 , first²² as $(\text{NO}_2)_2$ and second as an individual NO_2 species.^{43,52} These assumptions also agree with recent data recorded on CeNaMOR by Ito et al.⁵³

Summarizing this data, the interaction of NO with M-ZSM-5 (M = Sn, Ce, Sm) is consistent with a rapid oxidation of this molecule by some extralattice oxygen. It is therefore very probable that even in absence of free oxygen, adsorbed NO undergoes successive oxidation steps:



nitrate species, using ELO belonging on these metals

However, as already mentioned, the NO adsorption is low on these zeolites.

TABLE 3: NO Absorption Bands and Their Assignment on M-ZSM-5 Zeolites

assignment	room temp, 50 mbar NO			room temp, evacuated 10^{-5} Torr			723 K			room temp, evacuated 10^{-5} Torr		
	Sn	Ce	Sm	Sn	Ce	Sm	Sn	Ce	Sm	Sn	Ce	Sm
$\nu(\text{N}_2\text{O})$	2228								2185			
$\nu(\text{NO}_2)$	2137	2136 ^a 2078 ^a	2136	2100 ^a	2138 ^a	2136		2132	2136	2138	2137	2139
$\nu(\text{NO})^-$	1989 ^a	1937	1986	1942 ^a	1988 ^a	1978	1998	1952 ^a				
$\nu(\text{NO})^{\delta+}$												
$\nu(\text{N}_2\text{O}_3)^{\delta-}$	1883	1885	1887	1884	1878	1868	1881	1875	1888+ 1862	1874 ^a	1878 ^a	1875 ^a
asymmetric												
$\nu(\text{NO})_2^{\delta-}$												
$\nu(\text{N}_2\text{O}_3)$	1812	1811	1811	1811	1811	1811	1810 ^a					
$\nu(\text{NO}_2)_2$								1742	1746	1738	1742	1747
symmetric												
$\nu(\text{NO})_2^{\delta-}$												
$\nu(\text{NO}_2)_2$	1705	1718		1696 ^a	1685		1704 ^a	1686		1680	1682	
νNO_2	1649		1649	1644	1660	1638	1643				1660 ^a	1638
					1618	1610						
$\nu(\text{N}_2\text{O}_3)$		1589			1580	1576		1579	1584		1565	1572
νNO_2^- , νNO_3^-				1602	1598			1622		1624	1623	1616 1541

^a Shoulder. ^b Shoulder of N_2O_3 vibration.

Evacuation of the cell, in the second step, causes an important decrease in the intensity of the bands assigned to $(\text{NO}_2)^+$ and $(\text{NO})^+$ species. These remain as typical bands only in the case of Sm-ZSM-5. In other cases, these bands were observed as shoulders (Table 3). On the contrary, both bands assigned to N_2O_3 species were still present, and a shift to lower frequencies was evidenced for the band located at 1885 cm^{-1} . The presence of the bands due to NO_2 and NO_3^- species even after evacuation clearly indicates the oxidation of the NO molecule on these catalysts at ambient temperature.

The interaction of NO with these zeolites at high temperature is consistent with a modification of the spectra shape. In this sense, one can note that the band located at 1811 cm^{-1} disappeared irrespective of M (Table 3). However, the band located at 1885 cm^{-1} refinds the initial position. At this temperature, the band assigned to nitrate–nitrite species increases in intensity while those of N_2O_3 and $(\text{NO}_2)_2$ decrease in time. For Sm-ZSM-5, a supplementary band located at 1862 cm^{-1} was determined, which could indicate the differentiation of two different Sm sites during the oxidation of NO.

Summarizing, the increase of the temperature causes an increase of the oxidation rate of NO due to the extralattice oxygen, merely associated with the presence of the second metal.

In the fourth step, the species located at $1738\text{--}1747\text{ cm}^{-1}$, indicating the presence of $(\text{NO}_2)_2$ species, are again found, but the predominant bands are those assigned to nitrite and nitrate species.

Interaction of NO with Cu-Sn-ZSM-5. Figure 5 shows the FTIR spectra for the Cu-Sn-2 catalyst. The bands recorded during the investigated stages and their assignments are given in Table 4. The modification of the tin concentration changes the ratio of the band intensity, but the shape of the spectra recorded for these catalysts is close to that of the parent Cu-ZSM-5 catalyst (see Figures 8–10). In the first step, a small shift (3 cm^{-1}) and splitting of the band located at 1897 cm^{-1} were evidenced only for the sample previously tested in NO decomposition. Evacuation of the cell evidences a remarkable increased intensity of the bands due to NO_2 and nitrate species. In the third step, the shift and the splitting of the band located at 1897 cm^{-1} occur for all the investigated Cu-Sn-ZSM-5 catalysts, but important values were only recorded in the case of the low tin concentration (Cu-Sn-2). A supplementary band located at 1747 cm^{-1} , indicating $(\text{NO}_2)_2$ species,⁴⁴ was also evidenced for the low concentration of tin only.

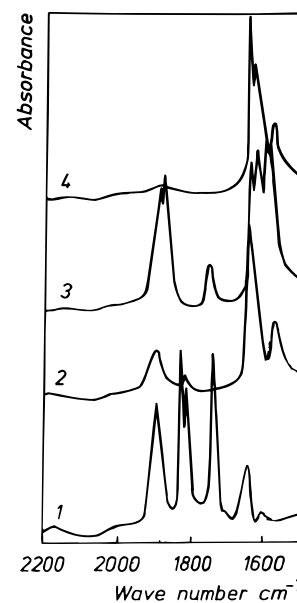


Figure 5. NO-FT-IR spectra on Cu-Sn-2. (1) 50 mbar NO, room temperature; (2) after evacuation of the cell at 10^{-6} mbar; (3) after heating 1 h at 673 K in the presence of 50 mbar; (4) after reevacuation of the cell.

Interaction of NO with Cu-Ce-ZSM-5. Cerium introduction (Figure 6) does not modify spectra shape, but differences in the intensity ratios of the bands could be observed both with the parent Cu-ZSM-5 and between the two investigated Cu-Ce-ZSM-5. The assignment of the bands is given in Table 5. It is noteworthy that cerium introduction leads to an important oxidation of NO even at room temperature, as one can observe from the intensity of the band due to $(\text{NO}_2)^+$ species. The intensity of these bands increases in time while the bands due to dinitrosyl species decrease, indicating that NO oxidation is merely due to the oxygen released because of NO decomposition. On the other hand, cerium introduction determines in the first step an important shift in the band located at 1898 cm^{-1} (Figure 2). Considering the assumption given by Wichterlova's group,²⁹ this shift could not be due to an enhancement in copper concentration, since both Cu–Ce zeolites contain lower copper than the investigated Cu-ZSM-5. Moreover, for Cu-Ce-1, this shift (1901 cm^{-1}) is lower than that recorded for Cu-Ce-2 (1908 cm^{-1}). It appears that in the presence of cerium, for the same

TABLE 4: NO Absorption Bands and Their Assignment on Cu-Sn-ZSM-5 Zeolites

assignment	room temp, 50 mbar NO			room temp, evacuated 10 ⁻⁵ Torr			723 K			room temp, evacuated 10 ⁻⁵ Torr		
	Cu-Sn-1	Cu-Sn-1R ^b	Cu-Sn-2	Cu-Sn-1	Cu-Sn-1R	Cu-Sn-2	Cu-Sn-1	Cu-Sn-1R	Cu-Sn-2	Cu-Sn-1	Cu-Sn-1R	Cu-Sn-2
$\nu_{(\text{N}_2\text{O})}$	2222	2224				2225	2224					
$\nu_{(\text{NO}_2)}$	2169	2133	2165	2169	2159 2137 ^a	2180	2134 ^a	2139 ^a	2136 ^a	2162 ^a		2136 ^a
$\nu_{(\text{NO})}^-$	2005 ^a	1991 ^a	1999 ^a	1988		2003 ^a	2001 ^a	1990 ^a	1997 ^a	2017 ^a	1951 ^a	1997 ^a
$\nu_{(\text{NO})}^{\delta+}$	1897	1901+ 1899	1897	1897	1900	1897	1892	1891		1902	1894	
$\nu_{(\text{N}_2\text{O}_3)}^{\delta-}$							1874	1874	1887+ 1881			1889
asymmetric												
$\nu_{(\text{NO})_2}^{\delta-}$	1827	1827	1827									
$\nu_{(\text{NO})}^{\delta-}$	1812	1812	1813	1812	1813	1814						
$\nu_{(\text{NO}_2)_2}$									1747			
symmetric												
$\nu_{(\text{NO})_2}^{\delta-}$	1733	1734	1735									
$\nu_{(\text{NO}_2)_2}$			1706 ^a									
ν_{NO_2}	1644 ^a	1644 ^a	1648 ^a	1643 ^a	1668		1619	1629	1630		1629	1629
$\nu_{\text{NO}_2^-}, \nu_{\text{NO}_3^-}$			1601		1608	1633	1608	1616	1615	1602	1619	1615
	1442 ^a	1442 ^a				1563	1576	1576	1585	1577	1519 ^a	1571
	1362 ^a	1362 ^a					1508	1505 ^a	1574			

^a Shoulder. ^b R, previously tested in NO decomposition for 3 h at 773 K.

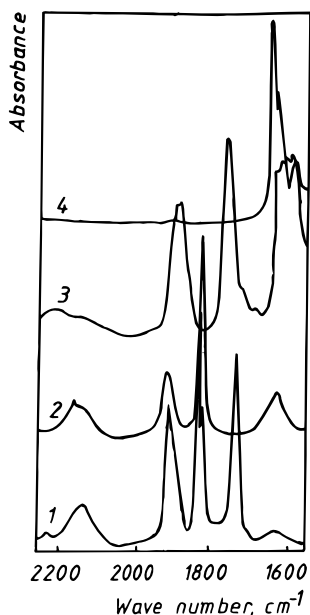


Figure 6. NO-FT-IR spectra on Cu-Ce-2. (1) 50 mbar NO, room temperature; (2) after evacuation of the cell at 10⁻⁶ mbar; (3) after heating 1 h at 673 K in the presence of 50 mbar; (4) after reevacuation of the cell.

aluminium content and even for low copper loading, the bands assigned to copper species directly connected to framework Al are more evident. The other main absorption bands were located at positions similar to those in the parent Cu-ZSM-5. The shift of the band located at 1897 cm⁻¹ is slightly accentuated in the second step (under vacuum). Deconvolution of this band also showed the contribution of the band located at 1912 cm⁻¹, indicating the presence of the square pyramidal species.²⁹ The spectra recorded at high temperature (673 K) in presence of NO, in the third step, is consistent with the shift to low wavenumbers of the bands located at 1901 and 1908 cm⁻¹. This behaviour is more evident for low cerium content. Also, the splitting of this band is more evident for the low concentration of copper and cerium, where three bands were determined instead of two (Cu-Ce-1). Two of these are directly related to the presence of N₂O₃ species. In the third step a supplementary band located at 1748 cm⁻¹, indicating the existence of bidentate

(NO₂)₂ species, was also evidenced but is more intense for the low concentration of cerium.

Interaction of NO with Cu-Sm-ZSM-5. Figure 7 shows the typical spectra of Cu-Sm-ZSM-5 catalysts. As for cerium, in the presence of samarium, deconvolution of the band located at 1897 cm⁻¹ shows another band located at a high wavenumber. Moreover, for the Cu-Sm-1, the maximum of this band is located at 1906 cm⁻¹, indicating that the new species is the most important. This shift is still evident in the second step when the contribution of the band located at 1898 cm⁻¹ becomes very low (Table 6). In the third step, concomitantly with an evident splitting, a very important shift to 1878 and 1871 cm⁻¹, respectively, occurs in the position of this band. It is quite difficult to suppose the existence of (NO)^{δ+} species at these lower frequencies. Therefore it is more probable that these bands reveal the existence of N₂O₃ species adsorbed on the two different copper sites observed in the previous steps. A supplementary band located at 1747 and 1749 cm⁻¹, respectively, was evidenced for both catalysts.

Influence of the Presence of the Second Metal upon Different NO Species at Room Temperature and at 673 K.

Figure 8 presents the variation of the arbitrary intensity ratios of the main bands to the intensity of the band located at 1898 cm⁻¹ (including also the contribution of the other bands previously discussed), as these were evidenced in the first step. One can observe that the presence of the second component determines an increase of the Cu⁺ species, indicating an increased population of copper implanted in the vicinity of the framework Al. Moreover, the diminution of the content in this second metal is consistent with a supplementary increase. This behaviour is more clear after evacuation of the cell, when the presence of Cu⁺ species appears to be more evident for Cu-Ce-ZSM-5 and Cu-Sm-ZSM-5, even though the copper content in these is lower than that in Cu-ZSM-5 (Figure 9).

In the third step the presence of the second metal reduces the intensity of the nitrate bands and increases the intensity of the N₂O₃ and both (NO₂)₂ and NO₂ bands (Figure 10).

Discussion

The detailed study of the spectra seems to indicate that it is the analysis of the bands located at 1813 and 1897 cm⁻¹ that give the most important information. The first band gives information about the different kinds of Cu⁺ and the second

TABLE 5: NO Absorption Bands and Their Assignment on Cu-Ce-ZSM-5 Zeolites

assignment	room temp, 50 mbar NO		room temp, evacuated 10^{-5} Torr		723 K		room temp, evacuated 10^{-5} Torr	
	Cu-Ce-1	Cu-Ce-2	Cu-Ce-1	Cu-Ce-2	Cu-Ce-1	Cu-Ce-2	Cu-Ce-1	Cu-Ce-2
$\nu(\text{N}_2\text{O})$	2224	2224			2225	2212		
$\nu(\text{NO}_2)$	2165	2135	2159	2155+ 2135 ^a	2141 ^a	2135	2132 ^a	
$\nu(\text{NO})^-$	2083 ^a	2000 ^a	2084	2000 ^a	2007 ^a	1962 ^a		
$\nu(\text{NO})^{\delta+}$	1901	1908	1905	1913	1900		1895	
$\nu(\text{N}_2\text{O}_3)^{\delta-}$					1874	1887+ 1881+ 1869		1890
asymmetric								
$\nu(\text{NO})_2^{\delta-}$	1827	1827	1812	1814				
$\nu(\text{NO})^{\delta-}$	1812	1814						
$\nu(\text{NO}_2)_2$					1746	1748		
symmetric								
$\nu(\text{NO})_2^{\delta-}$	1734	1737						
$\nu(\text{NO}_2)_2$		1703 ^a		1712 ^a + 1679 ^a				
νNO_2	1644 ^a	1634		1628	1629	1625	1629	1636
	1613 ^a	1617			1618	1615	1618	1622
νNO_2^- , νNO_3^-	1442 ^a				1576	1595	1576	
					1511		1522	

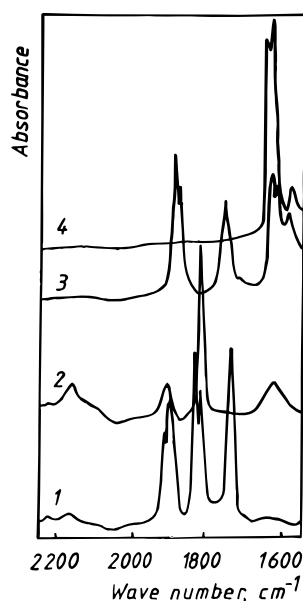
^a Shoulder.

Figure 7. NO-FT-IR spectra on Cu-Sm-2. (1) 50 mbar NO, room temperature; (2) after evacuation of the cell at 10^{-6} mbar; (3) after heating 1 h at 723 K in the presence of 50 mbar; (4) after reevacuation of the cell.

one about the Cu^{2+} -NO species that also seem to be determinant in NO decomposition.

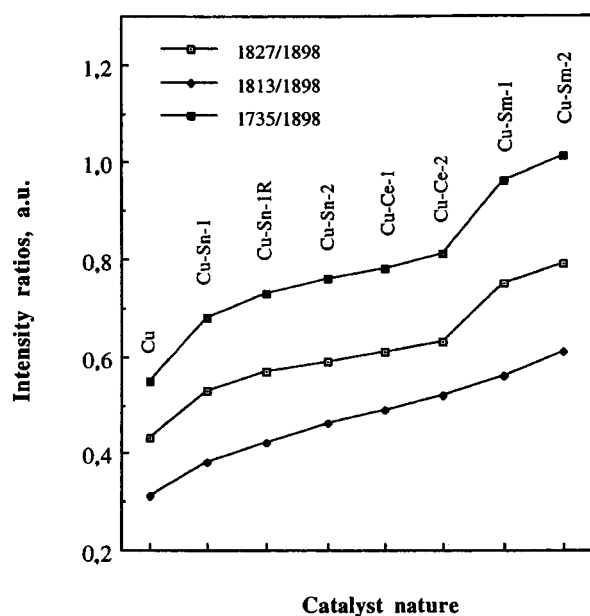
Interaction of NO with Cu-ZSM-5. At room temperature, the spectrum recorded for Cu-ZSM-5 in the presence of 50 mbar NO exhibits typical bands, well evidenced and discussed in the literature.^{13–15} It is generally accepted that the copper adjacent single-framework Al could exhibit redox behaviour^{9,29,36,54} and that these species could be found by NO-FT-IR at room temperature at 1895 cm^{-1} . Also, it is generally agreed that the species giving bands at 1912 cm^{-1} correspond to square pyramidal Cu^{2+} that is not active in NO decomposition. However, up to now the contribution of the species located at 1905 cm^{-1} was not well defined. Both Bell et al.^{15,32} and Wichterlova et al.²⁹ suggested that this band corresponds to NO adsorbed species on monoatomic Cu^{2+} in the vicinity of Al pairing arrangements. The spectrum recorded after NO evacuation also concurs with the reported data and evidences only the presence of monoadsorbed species. Dinitrosyl bands

disappear, thus evidencing the weak bonds implied in their formation. The NO decomposition on the Cu-ZSM-5 (step three) is consistent with an important splitting and shift of the band assigned to $(\text{NO})^{\delta+}$ species. The new band located at 1879 cm^{-1} indicates the presence of N_2O_3 species. It is noteworthy that the shifted band has a certain asymmetry and its deconvolution showed different Cu^{2+} species. The increase of the population of the species giving the 1906 cm^{-1} band could be correlated with superficial migration of copper in positions close to the Al framework, while the increase of the population of the species giving the 1912 cm^{-1} band could be correlated with a modification of Cu coordination, this copper species being inactive. The new distribution appears mainly during the reaction in the presence of NO, and therefore, one can suppose that NO, at least at the beginning of the reaction, also induces some superficial Cu rearrangements. In such conditions the population of species existing in square pyramidal coordination increases, indicating that a part of the metal there is in inactive positions. This data agrees with in situ TG-DTA measurements performed in the presence of NO using these catalysts⁵⁵ and also with XPS measurements performed on fresh and tested catalysts.⁵⁶ This behaviour is not surprising and has been largely reported in the literature. For example, a rapid sintering of nanometric sized Pt particles on $\gamma\text{-Al}_2\text{O}_3$ in the presence of NO was also recently reported by Loof.⁵⁷ Particularly, in the case of copper, the acceleration of the migration of the ions was also evidenced by Maxwell et al.⁵⁸ and Strome and Klier.⁵⁹ Computer simulation made by Miyamoto et al.⁶⁰ reached the same conclusions, indicating that copper ions always migrate toward the neighborhood of a T12 site where Al is substituted. The presence of the different oxidized N_xO_y also agrees with data previously reported in the literature.^{9,15,32,36,43}

Interaction of NO with M-ZSM-5 (M = Sn, Ce, Sm). The spectra recorded for monocomponent Sn, Ce, or Sm-ZSM-5 indicated poor and not very well-resolved bands irrespective of the investigated step. For these catalysts, at room temperature, dinitrosyl species have not been evidenced, which clearly indicates a different interaction with NO than that observed in the case of copper. Even the adsorption of NO occurs to a low extent, its oxidation also takes place very quickly at room temperature and the relative ratios of the determined bands show that oxidation occurs to a different extent onto these metals. The shift recorded for the band located at about 1885 cm^{-1}

TABLE 6: NO Absorption Bands and Their Assignment on Cu-Sm-ZSM-5 Zeolites

assignment	room temp, 50 mbar NO		room temp, evacuated 10^{-5} Torr		623 K		room temp, evacuated 10^{-5} Torr	
	Cu-Sm-1	Cu-Sm-2	Cu-Sm-1	Cu-Sm-2	Cu-Sm-1	Cu-Sm-2	Cu-Sm-1	Cu-Sm-2
$\nu(\text{N}_2\text{O})$	2222	2223		2216 ^a	2220 ^a			
$\nu(\text{NO}_2)$	2159	2161	2159	2169	2132 ^a	2132 ^a		
$\nu(\text{NO})^-$	1999 ^a	2014 ^a	1999 ^a	2003 ^a				
$\nu(\text{NO})^{\delta+}$	1908	1905	1910	1906				
		1898						
$\nu(\text{N}_2\text{O}_3)^{\delta-}$					1887+ 1871	1887+ 1874	1884 ^a	1884 ^a
asymmetric								
$\nu(\text{NO}_2)^{\delta-}$	1827	1829						
$\nu(\text{NO})^{\delta-}$	1813	1814	1813	1813				
$\nu(\text{NO}_2)_2$					1747	1747		
symmetric								
$\nu(\text{NO}_2)^{\delta-}$	1735	1738						
$\nu(\text{NO}_2)_2$	1705					1712 ^a		
νNO_2	1636	1637	1626	1622	1628	1632	1628	1641
	1616	1610 ^a			1613	1616		1625
νNO_2^- , νNO_3^-					1582	1584	1573	1571

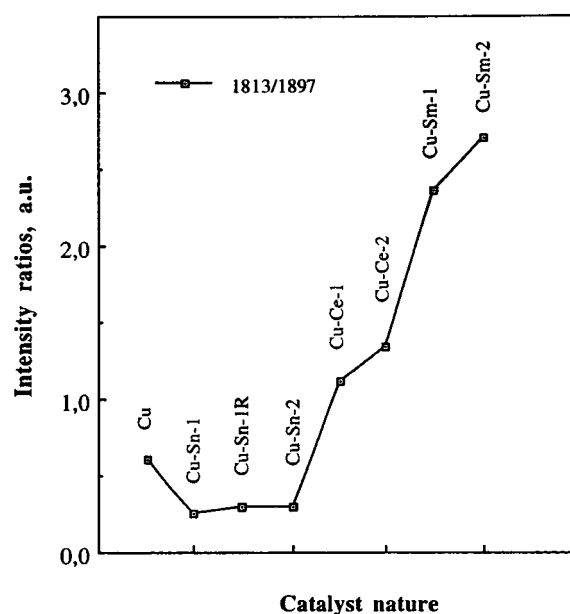
^a Shoulder.Figure 8. Variation of the intensity ratio of the bands located at 1827, 1813, and 1735 cm^{-1} to that located at 1897 cm^{-1} , in the first step of investigation: (\square) 1827/1897, (\blacklozenge) 1813/1897, and (\blacksquare) 1735/1897.

during the third step could suggest that, except for tin, at high temperature and in the presence of NO a certain superficial modification (maybe reorganization) could occur.

Interaction of NO with Cu-M-ZSM-5 (M = Sn, Ce, Sm).

(i) *Influence of the Oxidation State of Copper.* Simultaneous deposition of Sn, Ce, or Sm and copper on the ZSM-5 surface influences the interaction of the latter with NO. The effect of the second metal in bicomponent Cu-M-ZSM-5 is different as a function of its nature and concentration. Because the interaction of NO with these individual metals is very weak, it is difficult to assign their direct contribution. Therefore, the shapes of the spectra recorded for bicomponent Cu-M-ZSM-5 are close to those recorded for monocomponent Cu-ZSM-5 and very different to those recorded for monocomponent Sn, Ce, or Sm-ZSM-5. The differences are related to the presence of N_xO_y species, which is more important on these catalysts.

In the first step, introduction of the second metal generates an increase of the intensity of the bands assigned to dinitrosyl and $(\text{NO})^{\delta-}$ species, and as one can observe from Figure 8, this increase seems to depend both on the chemical nature and on the content of these metals. The evolution of the chemi-

Figure 9. Variation of the intensity ratio of the band located at 1813 cm^{-1} to that located at 1897 cm^{-1} , in the second step of investigation.

sorption bands of the *gem*-dinitrosyl species on copper, in steps 1 and 2, suggests that the presence of the second metal does not modify the strength of the adsorption of these species but only the population of species able to coordinate them.⁸⁻¹³ For Cu-Ce-ZSM-5 as well as Cu-Sm-ZSM-5 zeolites, one can note the increased intensities of the bands due to NO_2 species, meaning that in the presence of these metals the NO decomposition is more accentuated than that on Cu-ZSM-5, even if the copper loading is lower than that in the latter.

The increased population of Cu^+ species is also described by the data presented in Figure 9, which show that after the evacuation of the cell, the change in the intensity ratio of the bands located at 1813 and 1897 cm^{-1} respectively, is more accentuated for these zeolites comparatively with the ratio determined in the first step. No shift of the band located at 1813 cm^{-1} was observed for any of the investigated catalysts. This data could be associated with an increased number of Cu sites that could play a redox role. One can also note the different situation in the case of zeolites containing Sn.

(ii) *Influence of the Coordination of Copper.* It is very important to note that the presence of metals with high redox potential determines, in the first step, the shift to high wave-

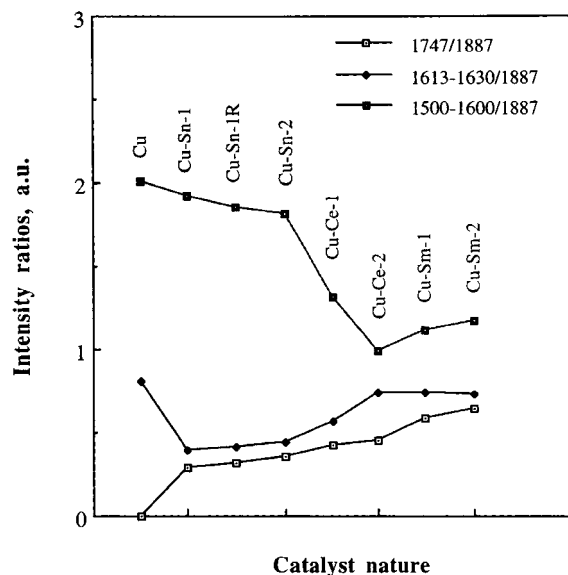


Figure 10. Variation of the intensity ratio of the bands located at 1747, 1613–1630, and 1500–1600 cm^{-1} to that located at 1887 cm^{-1} , in the third step of investigation: (□) 1747/1887, (◆) 1613–1630/1887, and (■) 1500–1600/1887.

numbers values of the band located at 1897 cm^{-1} (Figure 2). Moreover, in the presence of Cu-Sm-2, a splitting of this band and shift was evidenced. We can suppose that in the presence of cerium and samarium, but not of tin, copper takes other positions than in pure Cu-ZSM-5. This behaviour was already mentioned in the literature. For example, Sass and Kevan^{61,62} showed that Cu^{2+} in ZSM-5 interacted with framework Al only when Ca^{2+} was the cocation. Very recently, Keane,⁶³ investigating equilibrium properties of the Ni/CuY system, showed that thermodynamic data obtained for the binary system indicate that copper is more efficient in neutralizing the framework charge of zeolite Y. Investigation of the Cu-Sm-ZSM-5 system led us to the same conclusion.⁵¹ Furthermore, comparative data of Cu-Ni/ZSM-5 with Cu-Sm/ZSM-5 shows that the trivalent cocation is more efficient in this aspect.⁶⁴

In such conditions, the increased intensity of the band located at around 1905 cm^{-1} appears as an effect of the occupation of the positions in the close vicinity of framework Al, and this behaviour is due to the presence of the second metal. Therefore, the increased intensity of the bands indicating the presence of a high percentage of Cu^+ species becomes logical. A direct redox influence of the second metal is very difficult to suppose and even a structure like that proposed by Tomoshige et al.⁶⁵ for Rh-Sn-SiO₂, containing an increased population of extralattice oxygen, could exhibit a positive effect. One of the reasons is that the atomic Cu-to-cocations ratio for zeolites that exhibited better NO decomposition activity is very high. Thus, for Cu-Sm-2, which was the best in the series of Cu/Sm zeolites,⁵¹ this ratio is about 28-to-1. However, very recently Hadjiivanov et al.⁴³ concluded that the band located at 1879 cm^{-1} could be directly related to the existence of the extralattice oxygen. There is at present a very large agreement^{3–5,14,23,36} concerning the beneficial effect of these species in NO decomposition. Other authors, such as Bell et al.,^{15,32} consider that it is more probably a superoxide CuO_2^- structure. However, both groups indicate that CuO species have an important contribution to this reaction. In such an assumption, one can suppose that the second metal promotes the formation of the extralattice oxygen but we are not able to indicate in which mode. We are also unable to say if these species are related to

Cu–O–Cu or to Cu–O–M. However, a similar band was detected in the case of Ce-ZSM-5.

In conditions of NO decomposition, it is noteworthy that on bicomponent zeolites the band assigned to $\text{Cu}^+(\text{N}_2\text{O}_3)$ species, located in the range 1870–1879 cm^{-1} , was well developed. Very recently, Szanyi and Paffett,¹⁶ investigating the absorption of NO over Cu-ZSM-5, also observed a similar shift only after introduction of NO. Considering recent data of Host et al.⁶⁶ concerning the adsorption of NO on alumina-supported CuO catalysts, they attributed the new band to vibrations of NO molecules onto CuO, also. All Cu-M-ZSM-5 zeolites also exhibit a band located in the range 1887–1891 cm^{-1} .

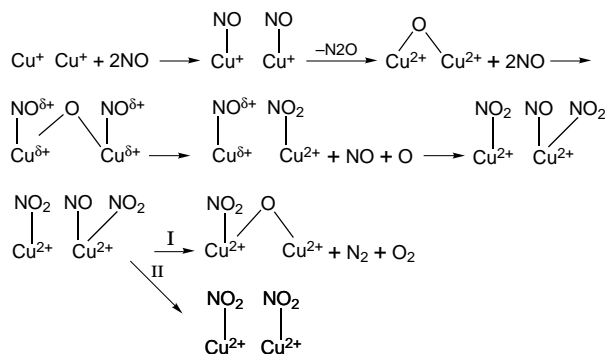
The intensities of the bands recorded for Cu-M-ZSM-5 zeolites, in the reaction conditions, are very well correlated with a more intense activity.⁴⁵ This is also in perfect concordance with data reported by other authors.^{33–35,39} Only the oxygen released could determine such an increase in the intensity of N_xO_y species. Very recent data of Cheung et al.⁶⁷ sustains this idea. They showed that these species are the last step before the oxygen release and indicated the positive effect of the species located at about 1610–1630 cm^{-1} assigned by them to be also a consequence of N_2O_3 existence.

(iii) *Influence of the Stability of Copper.* It is generally accepted that the presence of the nitrite–nitrate species could be correlated with nonactive blocked copper sites. Spectra recorded in the presence of the second metal denote that the intensity of the bands due to nitrate–nitrite species is lower compared to the investigated Cu-ZSM-5 (Figure 10). One must again notice that such behaviour occurs for catalysts containing less copper than the investigated Cu-ZSM-5, being an indirect probe of the presence of more copper in the close vicinity of framework Al in these catalysts.

As we have already shown, the coexchange of Cu/Ce or Cu/Sm leads to these favorable positions only when these second metals are in low amounts. Otherwise, these metals compete with copper in occupying the active positions. In such conditions, copper only remains dispersed on the silicon-containing zeolites and is very sensitive to migration and to sintering.⁶⁸

However, if we suppose that during NO decomposition some modification in the active copper species occurs, the data obtained for the Cu-Sn-ZSM-5 catalyst previously tested for 24 h in catalytic conditions seems to indicate a reversible process. So under the conditions of cleaning the surface before FTIR measurements (10^{-6} mbar vacuum and 673 K), almost all the copper is in the initial state.

(iv) *Influence of the Reaction Mechanism.* The positive effect of cerium or samarium as promoter for copper in NO decomposition could be considered irrespective of the mechanism proposed in the literature. In the mechanism proposed by Giamello et al.¹³ the formation of $(\text{NO})^-$ species is the determinant step in NO decomposition. We observed that the presence of Ce or Sm improves the concentration of this species. Also, if we consider the mechanism proposed by Iwamoto et al.^{11,69} as correct for generating active centers in NO decomposition on Cu-ZSM-5 catalysts, the important intensities of the dinitrosyl bands could be associated with a high number of the promoted catalytic active centers (first step in the scheme proposed by Iwamoto¹²). Our data also agree with the mechanisms recently proposed by Bell et al.¹⁵ and Cheung et al.,⁶² which consider the positive effect of the N_2O_3 species. However, we are tempted to sustain this latter version more considering that the NO decomposition occurs as follows:



The presence of the second metal seems to favor route I.

Conclusions

FTIR spectra recorded at room temperature and in the presence of 50 mbar NO evidenced different kinds of implanted copper. On Cu-ZSM-5 the band located at 1897 cm^{-1} was mainly found. Introduction of a second metal has different effects. Thus, Sn does not modify the position of the Cu^{2+}NO band, a change occurring only for the catalysts used before in catalytic reactions. Ce and Sm determine important shifts of this band, indicating the modification of the copper implantation compared with monocomponent Cu-ZSM-5. Moreover, Ce and Sm also cause an important increase of the intensity of the bands attributed to Cu^+ state, i.e., of the dinitrosyl species and of Cu^+NO^- . This behaviour could be a first evidence of the fact that their presence determines an implantation of copper in positions in which it could easily have a redox behaviour.

FTIR spectra recorded in the reaction conditions show that the presence of Ce or Sm leads to an increased activity of Cu-ZSM-5, evidenced by the increased intensity of the bands attributed to N_xO_y species. At the same time, the intensity of the nitrite–nitrate species on these zeolites is lower compared with monocomponent Cu-ZSM-5.

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