

FTIR study of carbon monoxide adsorption on ion-exchanged X, Y and mordenite type zeolites*

V. RAKIĆ^{1,**}, V. DONDUR^{2,#} and R. HERCIGONJA²

¹Faculty of Agriculture, Institute of Food Technology, University of Belgrade, Nemanjina 6, 11081 Belgrade - Zemun, P. O. Box 127 and ²Faculty of Physical Chemistry, University of Belgrade, Akademski trg 12, 11000 Belgrade, P. O. Box 137, Serbia and Montenegro

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Abstract: In this work Fourier transform infrared (FTIR) study has been applied to study the adsorption of carbon monoxide on transition metal (Mn^{+} , Co^{2+} , Ni^{2+}) ion-exchanged zeolites type Y, X and mordenites. The adsorption of CO at room temperature produces overlapping IR absorption bands in the 2120–2200 cm^{-1} region. The frequency of the band around 2200 cm^{-1} is found to be dependent not only on the charge-balancing transition metal cation, but also on the framework composition. The frequencies of the band near 1600 cm^{-1} was found to be dependent on the Si/Al ratio of the investigated zeolites.

Keywords: FTIR, zeolites, carbon monoxide.

INTRODUCTION

The catalytic properties of synthetic zeolites are related to the framework composition and the nature of the charge-balancing cation, situated in the void internal space of zeolites. The role of these extraframework cations as catalytically active sites has been widely considered – being electron acceptors, they are able to act as Lewis acid centers. Their electrostatic fields are thought to be responsible for the activation and reactivity of adsorbed guest molecules,^{1,2} which is of special importance in catalytic processes. Several techniques have been developed in order to characterize the surface acidity, most of them are based on the adsorption of typical probe molecules.^{3,4} As a result of its possibility to monitor the perturbation of probe molecules in the adsorbed state, IR spectroscopy is a widely used technique for the study of these adsorption phenomena.³⁻⁵

Among the probe molecules which can be used to characterize surface acidity, carbon monoxide meets many criteria which have promoted its extensive use during the last years: apart from its small molecular size, this molecule has a small dipole moment (0.1 D), but, a

* Dedicated to Professor Miroslav J. Gašić on the occasion of his 70th birthday.

** Author to whom correspondence should be addressed, e-mail: vrakic@ffh.bg.ac.yu.

Serbian Chemical Society active member.

rather high polarizability. Therefore, the adsorption of CO has been widely used to study surface acidity of many different materials, particularly at low temperatures.⁵⁻⁷ In zeolitic systems, as a result of the sensitivity of CO molecule to the strong electrostatic fields surrounding coordinatively unsaturated cations, the stretching frequency of CO adsorbed of these types of Lewis acid centers exhibits hypsochromic shifts.⁷⁻¹⁰

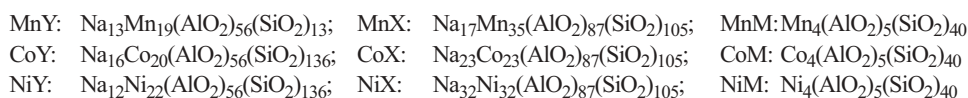
Zeolites can be considered to be constructed of tetrahedra, with oxygen atoms as apices and cations in their center. The tetrahedra form a three-dimensional system by sharing one oxygen atom between each two tetrahedra. With Si⁴⁺ cations, the zeolitic framework is a polymorph of quartz and has a SiO₂ stoichiometry. However, zeolitic framework loses neutrality when lattice Si⁴⁺ cations are replaced with lattice Al³⁺ cations. Built in this way, the lattice possesses an excess negative charge, which has to be compensated by positively charged cations. The total negative charge per unit cell depends on the Si/Al ratio. Therefore, it could be expected that the polarization of a carbon monoxide molecule could come from the influence of the electrostatic field of the zeolite framework.

The objective of this work was an IR investigation of CO adsorption on Mn²⁺, Co²⁺ and Ni²⁺ ion-exchanged zeolites. In order to elucidate the influence of the total negative charge of the zeolite framework on the stretching frequency of adsorbed CO, this probe was adsorbed on zeolites with different Si/Al ratios: X, Y and mordenite.

EXPERIMENTAL

Samples

The samples used in this work were prepared from synthetic NaX (13X, Union Carbide, Si/Al = 1,2), NaY (SK-40, Union Carbide, Si/Al = 2,45) and mordenite (Zeolon, Norton, Si/Al = 5). The transition metal (Co²⁺, Ni²⁺ and Mn²⁺) cation-exchanged samples were obtained by conventional ion-exchanged procedures,¹ and are denoted according to the corresponding cation:



Infrared spectroscopic studies

A Nicolet 740 FTIR spectrometer equipped with a DRIFT (diffuse reflectance infrared Fourier transform) cell was used. The cell, containing ZnSi windows which were cooled by water circulating through blocks in thermal contact with the windows, allowed collection of spectra over the temperature range 20 °C – 500 °C. During the FTIR experiments, the external optics were continuously purged with dry nitrogen. For all spectra reported, 100 scan data accumulation was carried out at a resolution of 2.0 cm⁻¹. The sample holder was connected to the temperature controller (Spectra Tech). Pretreatment of the sample, the adsorption of CO and the collection of the spectra were done *in situ*, at atmospheric pressure. The gas inlet was at the bottom of the sample holder, the thermocouple was placed in its middle. About 50 mg of the sample (previously finely powdered) was placed in the sample holder; its surface was carefully flattened in order to obtain high IR reflectivity.

The samples were activated in dry argon atmosphere, at 400 °C, during 4 h. The IR spectra were collected during the adsorption of flowing CO, at 20 °C. This adsorption temperature was chosen in order to realize interaction with very strong active sites, exclusively. Subsequently, the sample was purged for 15 min with argon, after which it was heated up to the chosen temperature. The corresponding background spectrum (collected from the activated sample obtained at the corresponding temperature was subtracted from each IR spectrum under Ar flow. The spectrum of CO on α -alumina (Alfa-Products, particle size 20 μm) was re-

corded with 500 scans, and was denoted as the CO gas-phase spectrum, because it is known that α -alumina is inert concerning CO adsorption.¹²

Gases

The gases used in this work (Ar and CO, 99.995 % purity) were supplied by L'Air Liquide and passed through 5 A molecular sieve traps before entering the switching system. The flow rates of both the inert and reactive gas were $30 \text{ cm}^3 \text{ min}^{-1}$ in all experiments.

RESULTS AND DISCUSSION

It is well known that the C–O stretch bands of CO molecules adsorbed on a zeolite surface occur in the same spectral region as the CO gas-phase (2143 cm^{-1}) appears^{8,9,13}: between 2000 and 2250 cm^{-1} . As a typical example, Fig. 1 presents a spectrum recorded during the adsorption of CO on the NiY sample (spectrum a). In the same Figure the spectrum denoted as (b) is CO gas-phase spectrum; while the spectrum denoted as (c) is obtained by subtraction of spectra (b) from (a), and is denoted as the difference spectra. As a result of the adsorption of carbon monoxide on the NiY sample, three overlapping bands appear in the $2000 - 2200 \text{ cm}^{-1}$ region: bands at 2200 cm^{-1} , at 2170 and at 2120 cm^{-1} .

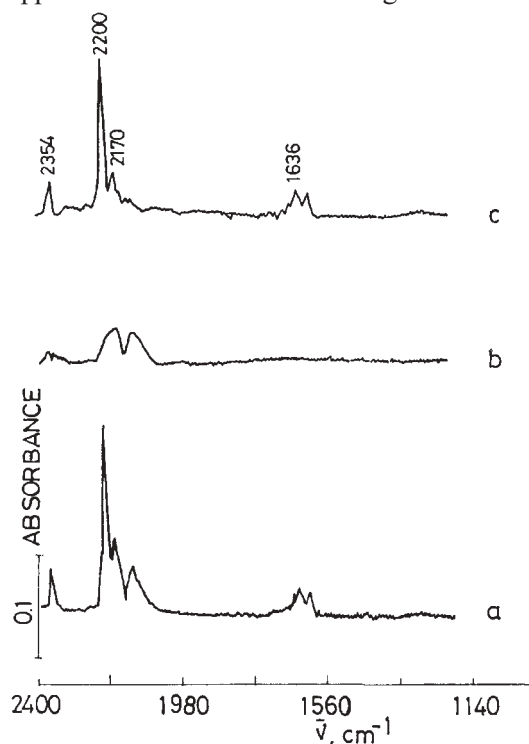


Fig. 1. FTIR spectra collected during the adsorption of CO on NiY zeolite: (a) – spectrum obtained during the purge of CO through the sample; (b) – CO gas-phase spectrum; (c) – difference spectra obtained by the subtraction of spectrum (b) from spectrum (a).

During the adsorption of CO on all the other investigated samples, IR bands in the same region were found. Therefore, the CO gas-phase spectrum was subtracted from all FTIR spectra collected during adsorption at $20 \text{ }^\circ\text{C}$. Figure 2 presents these difference IR spectra collected during CO adsorption on the samples of X, Y and mordenite.

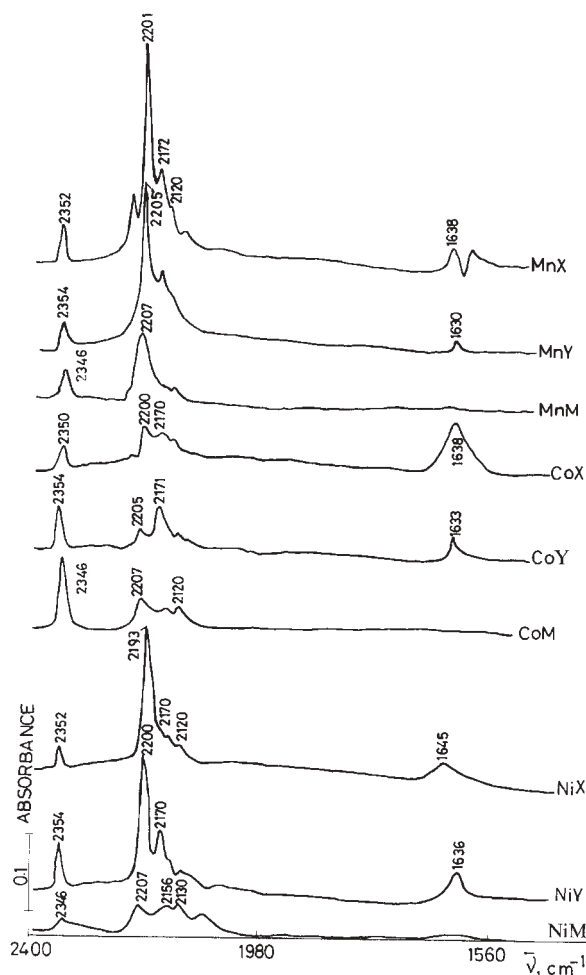


Fig. 2. Difference FTIR spectra collected during the adsorption of CO on the samples of X, Y and mordenite type zeolites.

Evidently, as a result of the adsorption of CO on the ion-exchanged zeolites, overlapping bands in the C–O stretch region appeared. Two bands at a frequency higher than the gas-phase CO frequency are found: a band around 2200 cm^{-1} and a band near 2170 cm^{-1} , for most samples exactly at this frequency. A band at a frequency lower than the CO gas-phase frequency band (at 2120 cm^{-1}) is also noticed. IR bands at higher frequency than the gas-phase CO frequency have been reported in the adsorption of CO over various materials.^{5–8,13} In the case of FAU type zeolites, previous workers assigned these bands to CO bound to coordinatively unsaturated cations (2200 cm^{-1} band) and to CO bound to tri-coordinated aluminum atoms through the carbon (band at 2170 cm^{-1}).⁹ The band at a frequency lower than the CO gas-phase frequency was assigned to CO bound at tri-coordinated aluminum atoms through the oxygen.⁹

In their pioneering work, Angel and Schaffer⁸ attributed the band near 2200 cm^{-1} to CO attached to a cation. They reported that when CO was adsorbed on X and Y zeolites containing different charge-balancing cations, the stretching vibration frequencies shifted by amounts dependent upon the nature of the cation to values higher than that for gaseous carbon monoxide. The first theoretical explanation was given by Hush and Williams⁹ who used an approximate finite self-consistent field (SCF) method, and concluded that the positive field of the cation stabilize the $^{-}\text{C}\equiv\text{O}^{+}$ canonical form of the carbon monoxide molecule.

The analysis of the results presented by Fig. 2 confirm that the frequency of the band found near 2200 cm^{-1} is dependent on the nature of the transition metal cation. However, it is worth noticing that the results obtained in this work clearly show that the position of the band near 2200 cm^{-1} is also dependent on the type of the investigated zeolite. The frequencies of these bands, in the literature often called "cation-sensitive", are presented in Table I. As can be seen from this Table, the frequency of this band, considered for the same charge-balancing cation, is higher in the case of the more siliceous zeolite. This result clearly show that the polarization of the CO molecule is greater in the case of zeolites with a higher Si/Al ratio.

For a CO molecule adsorbed at an isolated cation site, the polarization effect depends on the local positive electrostatic field. However, the strength of this electrostatic field is influenced not only by the cation, but also by the surroundings oxygen, which provide a compensating negative charge. Neighbouring basic oxygens decrease the positive electric field around the cation. This effect is more evident in the case of a more "ionic" zeolite lattice¹⁴ – which is the case with zeolites with a higher extent of AlO_2^{-} units.

TABLE I. The position of the IR absorption band near 2200 cm^{-1}

Sample	Wavenumber/ cm^{-1}	Si/Al ratio
MnX	2201	1.2
MnY	2205	2.45
MnM	2207	5
CoX	2200	1.2
CoY	2205	2.45
CoM	2207	5
NiX	2193	1.2
NiY	2200	2.45
NiM	2207	5

Therefore, the lower stretching frequencies of the "cation-sensitive" bands observed for X zeolite samples, as compared with Y zeolite or mordenite samples (Table I) can be explained as being the consequence of the smaller polarization of the CO molecule in the case of zeolites with a higher aluminum content (lower Si/Al ratio).

The insight into the results presented in Table I enables the conclusion to be reached that an increased polarizing power for adsorbed CO molecule can be correlated with a

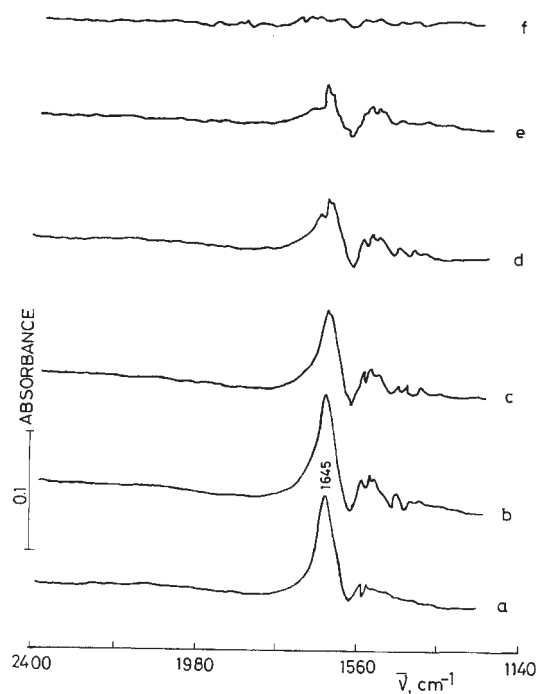


Fig. 3. FTIR spectra collected during heating of NiX, after adsorption of CO and purging of the sample with pure dry argon. Spectra (a) to (f) were collected at 30 °C, 60 °C, 100 °C, 150 °C, 200 °C and 300 °C, respectively. The desorption was finished at 300 °C.

higher Si/Al ratio of the zeolite lattice, or with a lower basicity of the whole zeolite framework in the mordenite samples, as compared with X-zeolite or Y-zeolite samples.

TABLE II. The position of the IR absorption band near 1600 cm^{-1}

Sample	Wavenumber/ cm^{-1}	Si/Al ratio
MnX	1638 (500 °C)	12
MnY	1630 (300 °C)	2.45
MnM	1618 (400 °C)	5
CoX	1638 (400 °C)	1.2
CoY	1633 (300 °C)	2.45
CoM	1620 (200 °C)	5
NiX	1645 (300 °C)	1.2
NiY	1636 (400 °C)	2.45
NiM	1627 (200 °C)	5

We reported in a previous paper that during adsorption of CO on transition-metal ion exchanged zeolites of the FAU type at room temperature, a disproportionation of CO into C and CO_2 occurred.¹⁵ During adsorption of CO on the Mn^{2+} and Co^{2+} exchanged mordenites investigated in this work, a band at 2350 cm^{-1} (attributed to the ν_3 asymmetric

stretching vibration of physisorbed CO₂, linearly bound to the cation by ion-induced dipole interaction¹⁶) is also observed, confirming the formation of CO₂ on the Lewis acid centers of mordenites.

As was already reported,¹⁵ changing the feed from CO-containing to pure argon led to the quick removal (in less than 2 min) of the bands in the CO stretch region, as well as the band near 2350 cm⁻¹; the same holds for ion-exchanged mordenites. At elevated temperatures, only the bands around 1600 cm⁻¹ were found. A typical set of spectra, collected for the case of NiX, is presented in Fig. 3. The frequencies of these bands are given in Table II, the temperatures at which the bands disappear are given in parenthesis. In a previous paper, we attributed the bands near 1600 cm⁻¹ to some strongly bound species on the surfaces.¹⁵ The very high temperatures at which these bands disappear confirm that their origin really lies in some very strongly bound species. The analysis of the data given in Table II shows that the frequencies of these bands are dependent on the Si/Al ratio: in the case of more siliceous zeolites the frequencies are lower, which is a clear indication of the influence of the zeolite framework on the CO species bound at these strong active sites.

CONCLUSION

During the adsorption of carbon monoxide as a probe molecule on zeolites, its molecules interact with active centers which have dual acid-base characteristics. The results obtained in this work show that the frequencies of the IR absorption bands in the C–O stretching region exhibit not only a dependence on the nature of extra-framework cation but also on the total negative charge of the zeolite lattice. This influence of aluminosilicate framework on the characteristics of the charge-balancing cation (Lewis acid site) can be recognized and considered by IR spectroscopy of the adsorbed CO. The results presented in this work, demonstrate that not only the different extra-framework cations sites but also their environment can be investigated by the adsorption of CO.

ИЗВОД

FTIR СТУДИЈА АДСОРПЦИЈЕ УГЉЕН-МОНОКСИДА НА ИЗМЕЊЕНИМ ЗЕОЛИТИМА ТИПА X, Y И МОРДЕНИТА

В. РАКИЋ¹, В. ДОНДУР² и Р. ХЕРЦИГОЊА²

¹Пољопривредни факултет, Институт за технологију хране, Универзитет у Београду, бр. 127, Немањина 6, 11081 Београд - Земун и ²Факултет за физичку хемију, Универзитет у Београду, бр. 137, Академски брз 12, Београд

У овом раду испитивана је адсорпција угљен-моноксида на измењеним зеолитима (Mn²⁺, Co²⁺, Ni²⁺) типа X, Y и морденита применом инфрацрвене спектроскопије са Фуријеовом анализом (FTIR). Адсорпцијом CO на собној температури настају сложене траке у спектралној области од 2120 до 2200 cm⁻¹. Уочено је да фреквенција траке на око 2200 cm⁻¹ зависи и од катјона присутног у структури, и од састава саме зеолитске решетке. Уочено је такође да фреквенције траке на око 1600 cm⁻¹ зависе од структуре, односно од Si/Al односа испитиваних зеолита.

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