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Thermochimica Acta 379 (2001) 77–84

thermochimica acta

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Thermal effects of the interactions of carbon monoxide with zeolites

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Abstract

The interactions of carbon monoxide with Lewis acid sites of zeolites were investigated using microcalorimetric and temperature programmed desorption (TPD) techniques. Carbon monoxide was adsorbed at 25°C on transition-metal ion-exchanged FAU (Y and X) and MOR type zeolites. The differential heats of adsorption (Q_{dif}) indicate the heterogeneity of the acid sites, in all the investigated systems. The specific interactions of CO with the strongest acid sites were recognized. The results of TPD confirm that CO molecules were adsorbed on the sites of different strength. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; Carbon monoxide; Acid site; Adsorption; Differential heat

1. Introduction

The zeolites are well known as substances that are extensively used as catalysts or adsorbents in a variety of catalytic reactions, therefore, they have attracted big attention for the last few decades. Fundamental approach to the understanding of their catalytic abilities involves the characterization of the active centers which they possess [1–3]. Many physicochemical methods for the determination of the nature, number and strength of active centers are based on the adsorption of gas-phase probe molecules such as pyridine, ammonia and acetonitrile [1–3]. Among the other methods, temperature programmed desorption (TPD) [1,3,4] and calorimetric measurements [5] enable direct determination of the distribution of the strength of active centers, while infrared spectroscopy has been used extensively with probe molecules to identify their nature [1].

Carbon monoxide is very often used probe in the spectroscopic investigation [6–10]. The molecule has an asymmetric charge and is easily polarized, it is therefore sensitive to the electrostatic fields surrounding cations. As a result of the polarization by the metal cation of the zeolitic lattice, its stretching frequency increases relative to the gas phase. There are many data showing a correlation between the carbonyl frequency and the polarizing power of the cation, that, being electron acceptor, acts as a Lewis acid site in the zeolite framework. Besides the strength of the Lewis acid sites, the adsorption of CO also provides the information about their location, aluminum distribution in the surroundings [11], etc. There is a number of literature data about IR investigation of CO adsorption on various catalysts, however, there are only a few about TPD of CO [9,12–14]. Also, on the contrary to the numerous literature data presenting the differential heats of adsorption (Q_{dif}) of ammonia or pyridine as probe molecules on zeolites [15–20], there are only several reported results about the Q_{dif} of CO on the zeolites in the newest literature [9,10].

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PII: S0040-6031(01)00605-0

In this work, the differential heats of the adsorption of carbon monoxide on transition-metal ion-exchanged FAU and MOR type zeolites were measured.

2. Experimental

The samples used in this work were prepared from synthetic FAU and MOR type zeolites: NaY (SK-40, $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$), NaX (13X, $Na_{87}(AlO_2)_{87}(SiO_2)_{105}$) (Union Carbide) and NaM ($Na_8(AlO_2)_8(SiO_2)_{40}$ (Zeolon, Norton). The cation exchanged (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) samples were obtained by conventional ion-exchange procedures [21], and are denoted according to the compensating cation. The following formulae were derived:

MnY: $Na_{13}Mn_{19}(AlO_2)_{56}(SiO_2)_{136}$
CoY: $Na_{16}Co_{20}(AlO_2)_{56}(SiO_2)_{136}$
NiY: $Na_{12}Ni_{22}(AlO_2)_{56}(SiO_2)_{136}$
CuY: $Na_{14}Cu_{21}(AlO_2)_{56}(SiO_2)_{136}$
CoM: $Co_4(AlO_2)_8(SiO_2)_{40}$
NiM: $Ni_4(AlO_2)_8(SiO_2)_{40}$
MnM: $Mn_4(AlO_2)_8(SiO_2)_{40}$
MnX: $Na_{17}Mn_{35}(AlO_2)_{87}(SiO_2)_{105}$
CoX: $Na_{23}Co_{32}(AlO_2)_{87}(SiO_2)_{105}$
NiX: $Na_{23}Ni_{12}(AlO_2)_{87}(SiO_2)_{105}$

The Q_{dif} were determined using a SETARAM differential scanning calorimeter DSC 111. The experiments were done in the flow system (Scheme is done on Fig. 1), which is equipped with pressure regulators, high precision rotameters and valves. Gases can be introduced to the DCS cell in either the continuous flow mode or the pulse mode. Before adsorption, the samples were activated in the DSC cell at 400°C under an inert gas flow for 4 h and then cooled to 25°C in the same atmosphere. Subsequently, carbon monoxide (diluted in helium) was adsorbed using regular gas mixture injection (the volume of injection loop is 0.2 ml), in situ. After the injection, the sample was again in helium stream. The adsorption was done at 25°C, the employed mass of the sample was 0.15 g. The DSC 111 calorimeter was connected with mass spectrometer (Sensorlab 200D-VG Quadrupoles) which signal was properly calibrated using diluted gas streams. The masses corresponding to CO ($m/e = 28$) and CO_2 ($m/e = 44$) were monitored. In the cases where mass spectrometer did not record any signal, this was the clear indication that all injected amount of CO was adsorbed. In the cases where mass spectrometer recorded a signal of CO, it was possible to calculate the amount which was adsorbed, owing to the calibrated MAS signal. The quantitative measurements of DSC and MAS signals allowed precise association of Q_{dif} to the quantitative amounts of

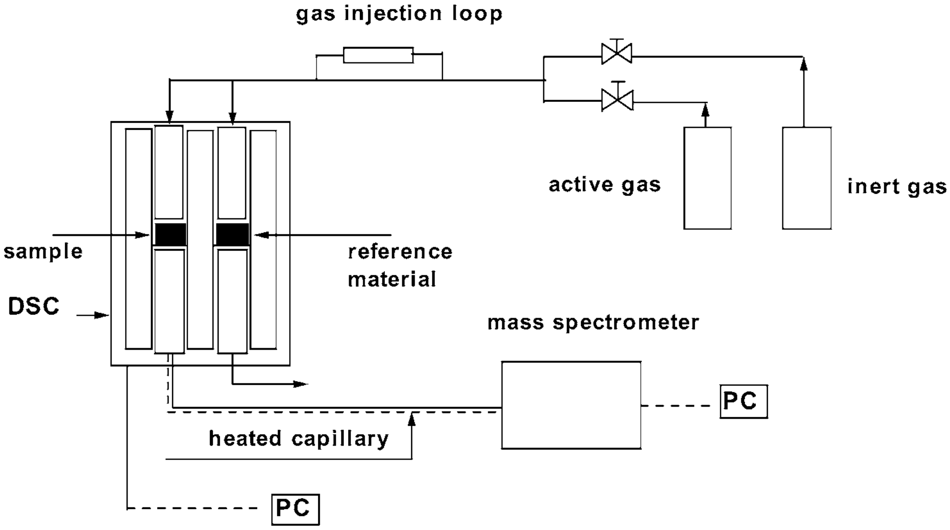

Fig. 1. Schematic presentation of experimental equipment for the measurements of differential heat of adsorption.

CO adsorbed. Carbon monoxide was adsorbed until all active sites for adsorption were occupied (which is indicated with the appearance of first endothermic DSC peak).

The desorption of CO was monitored by TPD technique, with a mass spectrometer as a detector. The experimental set-up for the TPD measurements and experimental details have been described

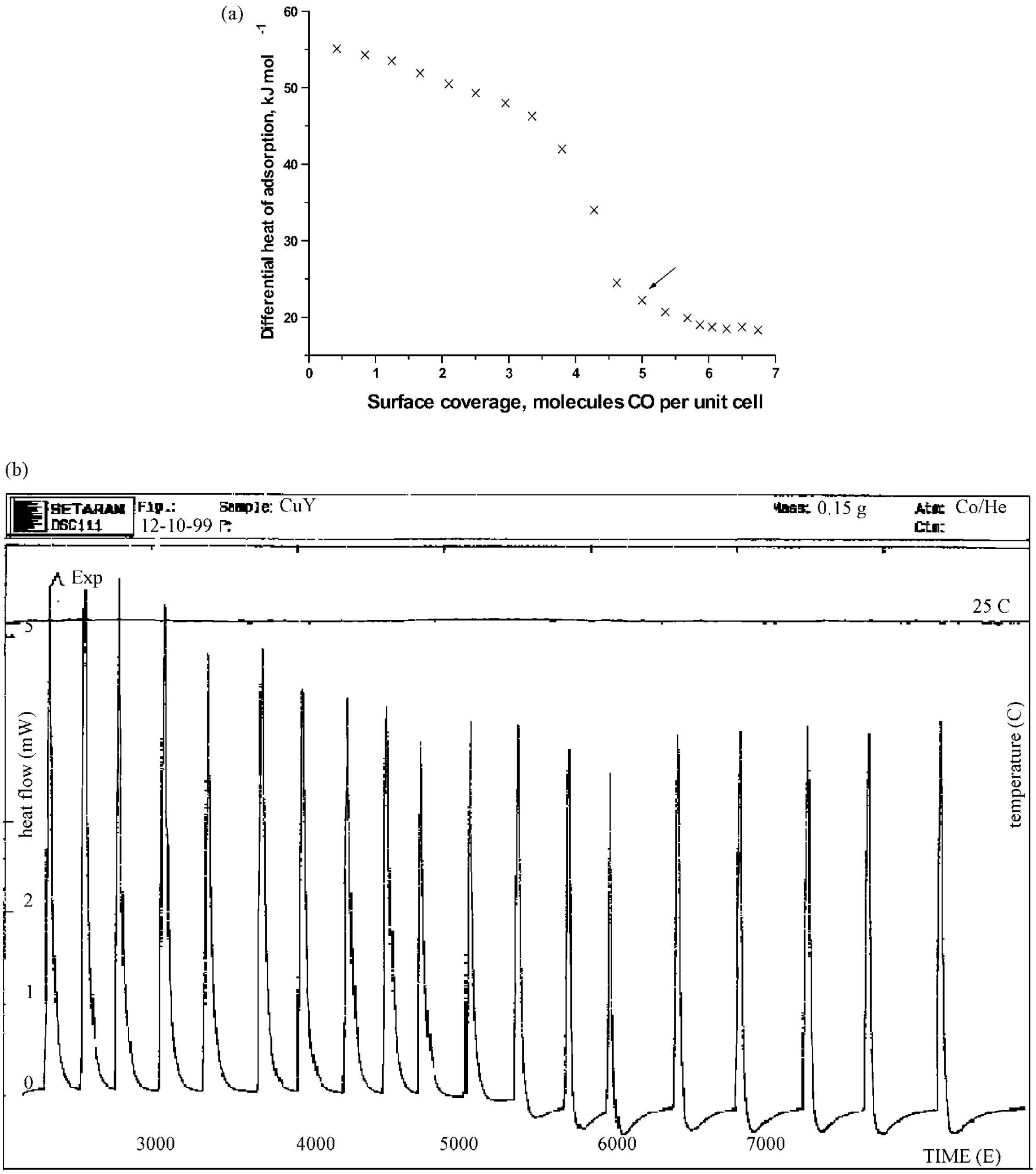

Fig. 2. (a) The differential heats of adsorption of CO on CuY as a function of surface coverage. The arrow denotes the value obtained for the first endothermic peak. (b) A set of DSC peaks obtained as a result of pulse adsorption of CO on CuY zeolite.

elsewhere [14]. Briefly, TPD experiments were done using the equipment which consists of a flow measuring and switching system, a cylindrical furnace (controlled by a linear temperature programmer, Omega CN 2010) and an on line mass spectrometer (Sensorlab 200D-VG Quadrupoles). The construction of this flow system enables to switch from one to another gas using the same flow rate and keeping all the other conditions of the sample the same. In all TPD experiments, carried out in the temperature range from 25 to 800°C, the heating rate was 20°/min, and the same masses of the samples (0.15 g) were employed.

The gases used in this work (helium and carbon monoxide, both 99.995% purity) were supplied by L'Air Liquide. In addition, the gases were passed through molecular sieve 5 A traps before entering in the switching system. The flows of either inert or reactive gas were 30 ml/min in all experiments.

3. Results

Fig. 2a presents the values of Q_{dif} of carbon monoxide on CuY. CO has an initial heat of adsorption of 55 kJ mol^{-1}, and the Q_{dif} decrease with increasing CO coverage. After adsorption of five molecules of CO per unit zeolite cell, the values of Q_{dif} decrease from 55 to 20 kJ mol^{-1}. The presented results suggest that the surface of CuY contains a distribution of strengths of active sites. Fig. 2b presents a set of DSC peaks obtained as a result of pulse adsorption of carbon monoxide. Evidently, for the first 11 injections, the exothermic DSC peaks show the irreversible adsorption of CO on the sample, after that, the endothermic peaks appear. For the first injections, the whole amount of CO from the injection loop is adsorbed by the CuY zeolite; the mass spectrometer detected the CO signal after the eleventh injection.

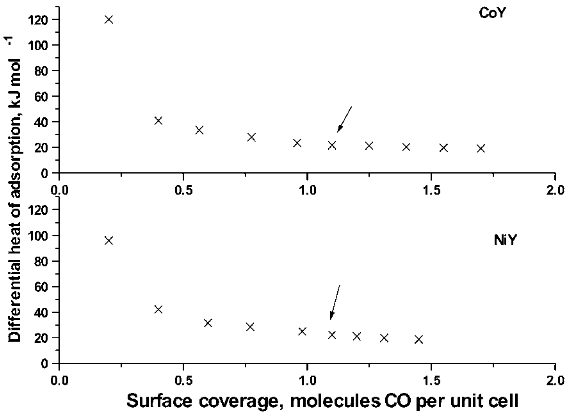

Fig. 3. The differential heats of adsorption of CO on CoY and NiY zeolites as a function of surface coverage. The arrows denote the values obtained for the first endothermic peaks.

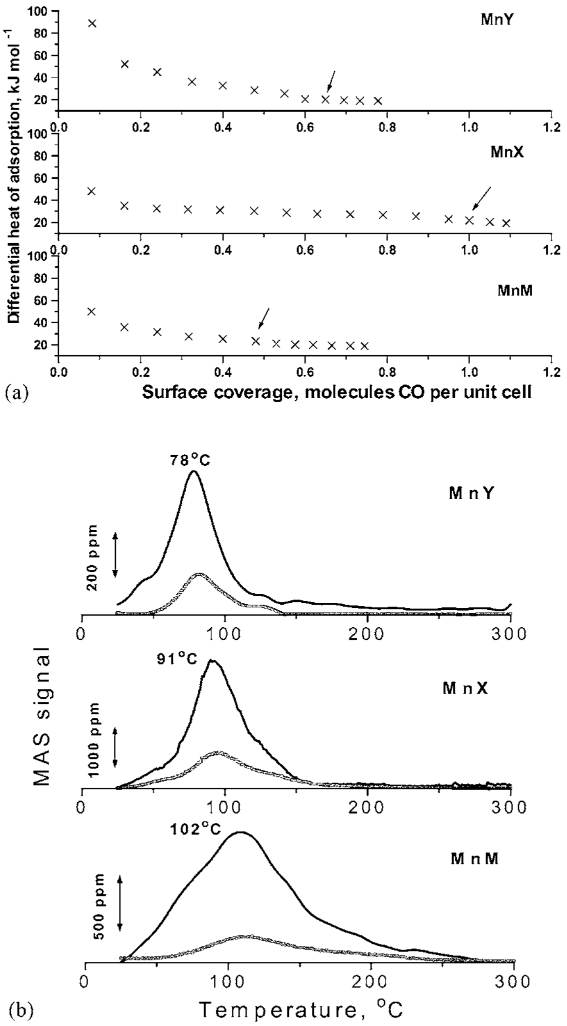

Fig. 4. (a) The differential heats of adsorption of CO on Mn^{2+}-exchanged zeolites, as a function of surface coverage. The arrows denote the values obtained for the first endothermic peaks. (b) TPD profiles of CO obtained for Mn^{2+}-exchanged zeolites.

Fig. 3 presents the values of Q_{dif} obtained as a result of CO adsorption on Co^{2+}- and Ni^{2+}-exchanged Y zeolites. In both cases, the initial heat of adsorption is much higher than the second one, this decrease is sharp. These results indicate again the existence of distribution of strengths of active sites. However, in contrast with CuY sample, the amounts of CO adsorbed before the appearance of first endothermic peak is lower.

The results obtained on Mn-exchanged samples are presented in Fig. 4a. It is evident that the highest initial value of differential heat of adsorption is found in the case of MnY zeolite. The initial value of Q_{dif}, found for MnY (88.9 kJ mol^{-1}) indicates the strong interaction of CO with the active sites. Fig. 4b shows the profiles of CO desorption spectra obtained in TPD experiments, for the Mn^{2+}-exchanged zeolites. The desorption in the temperature region between room temperature and 250°C confirms that CO was strongly bonded in that systems.

The value of differential heat of adsorption evolved as a result of first CO injection can be comprehended as a measure of the strength of the strongest active sites in the structure. As it can be seen from Table 1, these values are dependent on the zeolite lattice as well as on the structure cation. The amounts of carbon monoxide adsorbed before the appearance of first endothermic peak are also presented. For the sake of comparison, the amounts of CO desorbed during TPD experiments are also shown in Table 1.

Table 1
The values of initial heats of CO adsorption on the investigated zeolites

Sample	Initial value, Q_{dif} (kJ mol^{-1})	n_1, CO[a]	n_2, CO[b]
MnY	88.9	0.6	0.5
CoY	120.0	0.9	0.7
NiY	96.0	1.1	1.2
CuY	55.1	4.5	4.1
MnX	48.0	1.0	1.4
CoX	72.0	0.6	0.5
NiX	61.2	0.8	0.7
MnM	47.0	0.4	0.3
CoM	45.0	0.5	0.2
NiM	50.0	0.5	0.6

[a] n_1: number of CO molecules adsorbed per unit cell, before the appearance of first endothermic peak.

[b] n_2: number of CO molecules desorbed per unit cell during TPD procedure.

4. Discussion

It is likely that carbon monoxide meets the requirements defined by Dumesic and coworkers [17] about the use as a probe molecule in the microcalorimetric measurements at a given temperature, but also those proposed by Zecchina et al. [22].

We reported in the previous paper the results of TPD and FTIR investigation of CO interactions with transition-metal ion-exchanged FAU-type zeolites [14]. It was demonstrated that, at 25°C, carbon monoxide interacted with charge-balancing cations. Being coordinatively unsaturated, these cations act as a source of Lewis acidity, which is known in the literature [6,22]. It is worth noticing that, during the adsorption at 25°C from the gas stream, the low surface coverage of CO (between two and seven molecules per unit cell) was achieved for all investigated samples. Accordingly to the consideration published by Zecchina, carbon monoxide seems to be the best choice for probe Lewis acid sites [22]. One of the conditions that must be fulfilled is that the probing process must involve only a minimum fraction of the surface sites, in order to avoid so-called lateral interactions. The fact that the low surface coverage was achieved on FAU-type zeolites [14] means that the interaction of one CO molecule with one cationic active site can be considered.

It is evident from Fig. 1 that in the case of CuY, the differential heat of adsorption is approximately 55 kJ mol^{-1} in the initial adsorption (the reported value for isosteric heat of CO adsorption on CuY is 61.5 kJ mol^{-1} [23]). With increasing coverage up to five molecules per unit cell, the values of Q_{dif} decrease monotonously to about 20 kJ mol^{-1}, it is a clear indication that there are active sites of different strength on the surface. This result is in accordance with this one obtained from TPD experiment: the desorption takes place in the temperature interval from 25 to 300°C, TPD profile is complex, composed of four overlapping peaks indicating different binding states of adsorbed CO. The data presented in Table 1 show that the amount of CO adsorbed before the appearance of first endothermic DSC peak and the number of CO molecules desorbed during TPD measurement are close in values. The appearance of endothermic peak is usually interpreted as a sign of adsorption which is immediately followed by desorption, i.e. it is comprehended as a sign of the interaction with weak active sites. Indeed, we concluded from both FTIR and TPD results published in the previous paper, that there is a part of weakly adsorbed (or physisorbed) CO which can be easily "swept out" from the surface by the inert gas flow, at room temperature. Therefore, the correspondence in the number of CO molecule adsorbed before the first endothermic peak in the microcalorimetric measurements, and in the number desorbed in TPD, indicates the amount of strong active sites for the interaction with CO molecules at 25°C.

The results presented here indicate energetic heterogeneity of all the other investigated zeolites, both FAU and MOR type. However, in contrast to the results obtained for CuY sample, after the initial differential heat of adsorption (which is, owing to the sample, between 45 and 120 kJ mol^{-1}, see Table 1) the values for Q_{dif} decrease sharply with increasing surface coverage. The high values for Q_{dif} were obtained only in the initial adsorption steps, i.e. only for very small amounts of adsorbed CO. From this it can be inferred that there is only very small number of active sites strong enough to realize chemisorption with CO molecule, on the investigated systems (for example, the value of $Q_{\text{dif}} = 120\,\text{kJ}\,\text{mol}^{-1}$ can be revealed as a result of adsorption on only one very strong active center in eleven unit cells of CoY zeolite). As already mentioned for the case of CuY, it should be emphasized again that this is in accordance with the TPD results — TPD profiles (complex desorption curves in the broad temperature region) confirm the existence of different binding states of carbon monoxide.

The results of FTIR investigation of CO interaction with the same zeolite systems were presented and discussed in detail in a previous paper [14]. It was shown that the position of the IR band found in the C–O stretch region near 2200 cm^{-1}, assigned to CO bound to coordinatively unsaturated cations, was dependent on the nature of the transition metal cation present "cation-sensitive" band, and on the Si/Al ratio of the zeolite. In the case of CuY zeolite, the appearance of the spectral bands in the region around 2140–2160 cm^{-1} was interpreted as evidence for the possible reduction of Cu^{2+} ions to Cu^{+}, which could occur during the adsorption of CO on this sample. Strongly bound species were investigated by collecting FTIR spectra in the temperature range from 20 to 500°C. Only the CuY exhibits IR bands characteristic for the C–O symmetric stretch vibration at elevated temperatures, the stability of these bands at high temperatures clearly indicates that CO molecules were held strongly by the copper cation. The results of microcalorimetry are in accordance with those obtained from FTIR experiments: only CuY zeolite has a significant number of strong active sites for the interaction with CO molecules, while this number is very small in the case of other investigated zeolites (see Figs. 1 and 2, and Table 1).

The results obtained from TPD and FTIR experiments suggest that disproportionation of CO occurs on the transition-metal ion-exchanged FAU-type zeolites, except on the CuY [14]. As a result, carbon dioxide was formed and a deposition of carbon on the surface took place, also. Therefore, it was necessary to check whether this reaction happened during microcalorimetric experiments. For this purpose, the mass spectrometric signal of CO_2 was also recorded, together with this one for CO. During the microcalorimetric experiments, there were not CO_2 signal monitored in the effluent after the pulse adsorption, even in the cases where the signal of CO appeared. In the TPD experiments, the adsorption of CO was carried out from the continuous gas stream, and the sample was exposed to the high partial pressure of CO during the adsorption. Under these conditions, the reaction of disproportionation of two CO molecule was possible. On the contrary, during the pulse adsorption in the microcalorimetric experiment, the surface is exposed to very small amount of CO. As a consequence, it seems that the direct reaction of two molecules of CO is not possible.

It is evident from the results presented in Table 1, that the initial heat of CO adsorption increases with the polarizing power of the cation. It was found that the heats of adsorption of CO are dependent on the electronic configuration in the case of CO adsorption on metals [24]. Higher value of initial Q_{dif} obtained in the case of CoY, compared to those obtained for NiY and CuY, can be explained with electronic configurations of these cations, which have some half empty d-orbitals. The same effect was noticed in the case of *n*-hexane adsorption on ion-exchanged X zeolite [25]. It is important to emphasize that the value of initial Q_{dif} obtained for CuY is lower than the values obtained for the other samples of the same zeolite. Contrary to the other transition-metal atoms, copper has completely full 3d-orbital, consequently, its polarizing power is the lowest. The surface coverage which is achieved in the case of CuY is higher then those obtained for the other investigated zeolites. This behavior can explain the fact that Cu^{2+}-exchanged zeolites are good catalysts in a number of catalytic reactions involving carbon monoxide.

However, the analysis of results presented in this work indicates the influence of cation surroundings, also. It is evident that the value of initial Q_{dif} is lower in the case of ion-exchanged X zeolite, compared to that obtained on ion-exchanged Y zeolite.

It was shown from the FTIR results [14] that for the same charge-balancing cation, the frequency of "cation-sensitive" band is higher for more siliceous zeolite. From this, it is evident that the polarization of CO molecule is higher in the case of adsorption on zeolites with higher Si/Al ratio. For CO molecule adsorbed at an isolated cation site, the polarization effect depends on the local positive electrostatic field. Evidently, 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. Half-empty d-orbitals of transition metal cations can be filled by electron pairs of oxygen atoms of the zeolite framework. Hence, structure cations can coordinate oxygen atoms in their coordination sphere, which weakens the electrostatic field around those cations. In other words, neighboring basic oxygen atoms decrease the positive electric field around the cation. This effect is more evident in the case of more "ionic" zeolite lattice what is the case of zeolites with higher extent of AlO_2^- units such as X zeolite. Therefore, the decrease of the heat of adsorption of CO can be comprehended as a result of this net effect of the cation and its surroundings on the electrostatic interaction CO molecule — active site.

5. Conclusion

It is noticeable from all the results presented so far that energetic heterogeneity can be recognized in the CO adsorption on the investigated zeolites. Importantly, these microcalorimetric results are in agreement with TPD results obtained on the same systems. At 25°C, very low surface coverage of adsorbed CO molecules was achieved, and therefore, the specific interaction with the strongest Lewis acid sites was realized. The differential heats of CO adsorption on the investigated zeolites give useful insight into the state of adsorbed molecules on the surface, especially in the chemisorption region.

Acknowledgements

All DSC and TPD experiments were done in the Laboratory for Heterogeneous Catalysis, Institute of Chemical Engineering and High Temperature Chemical Processes, University of Patras, Greece. The authors greatly thank Prof. Xenophon Verykios, who enabled this investigation.

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