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Calorimetric study of room temperature adsorption of N_2O and CO on Cu(II)-exchanged ZSM5 zeolites

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Abstract

Copper ion-exchanged ZSM5 zeolites have been prepared with different cooper loadings from under- to over-exchanged levels. The adsorptions of N_2O and CO at 303 K have been studied using calorimetric method and infrared spectroscopy. The samples were additionally characterised by ammonia adsorption at 423 K. The active sites for both N_2O and CO are Cu(I) ions, which were formed as a result of pre-treatment in vacuum at 673 K.

Room temperature adsorption of nitrous oxide at low equilibrium pressures (up to 66.7 Pa) resulted in small amounts of chemisorbed N_2O ($<$0.2 molecule per one Cu ion). Differential heats of N_2O adsorption between 80 and 30 kJ/mol were obtained. Differential heats of CO adsorption between 140 and 40 kJ/mol were obtained. The obtained amounts of chemisorbed species in the investigated systems and the values of differential heats of both nitrous oxide and carbon monoxide demonstrate the dependence on the copper content.

Keywords: Calorimetry; ZSM5; N_2O; CO; FTIR of N_2O

1. Introduction

Copper-exchanged zeolites are active catalysts in industrially important reactions. Many scientific contributions concerning their activity in the reactions of catalytic de-NO_x processes [1–5], in the reactions of selective catalytic reduction of NO_x by hydrocarbons [6,7], as well as in photocatalytic decomposition of NO [8] have been published. It is generally accepted that Cu-ZSM5 zeolite prepared by the so-called excess ion-exchanged procedure from aquatic solution of Cu(II) salts are the most efficient catalysts for NO decomposition. In that case, so-called over-exchanged samples with the concentration of Cu(II) ions that exceeds the value necessary to achieve 100% exchanged level (defined to occur when one Cu(II) substitutes two monovalent cations) were obtained. In over-exchanged zeolites, copper species with different aggregation and oxidation states appear. Big efforts and a multitechnical approach to the elucidation of subjects such are: location, coordination state, adsorptive capacity, reactivity and mobility of Cu ions in the frame of different zeolites, particularly ZSM5 zeolite, resulted in a number of scientific contributions [7,9–15].

Among other nitrogen oxides, nitrous oxide (N_2O) attracted a big interest during the last years, because it has been identified as a greenhouse gas [16]. The long-lived N_2O molecules, which have both global warming and ozone destruction effect, are generated from artificial fertilizers and aquatic systems, as well as in combustion processes. However, it is worth noticing that N_2O can be produced also in the de-NO_x processes, based on the use of heterogeneous catalysts [2,4]. N_2O can be either catalytically decomposed or selectively reduced by adding a reductant (usually, hydrocarbons such as propane or methane, or ammonia) [17,18]. Catalytic decomposition of N_2O on metal particles supported on oxides has been studied [6,19]; however, high activities for N_2O decomposition are found on Cu-ZSM5

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zeolites. Several reports are devoted to infrared spectroscopic investigations of high temperature decomposition of nitrous oxide on these zeolites [2,4,20]. Also, room temperature adsorption of N_2O was investigated by means of FTIR [21]. In both cases, the interaction of nitrous oxide molecule with copper ions was observed. In the experiments of temperature programmed desorption (TPD) [22] high-temperature decomposition (above 673 K) has been shown. Besides, several theoretical considerations have been devoted to N_2O interactions with Cu ions on Cu-ZSM5 structure [23–25]. The N-down adsorption is estimated as preferable on Cu^+ ions in the ZSM5 structure, compared with O-down adsorption; the adsorption energies calculated on MP2 level are estimated as "relatively strong" (∼40 kJ/mol) [23]. However, there is no experimental evidence about thermal effects of N_2O adsorption on ZSM5 zeolites.

As it is already well known, experimentally obtained differential heats of adsorption provide information about the strength and strength distribution of the sites active for adsorption, which is of the crucial interest in the catalytic behaviour of investigated material. Therefore, the interest of present study is to investigate adsorption of N_2O on copper ion-exchanged ZSM5 zeolites. Taking into account that the majority of N_2O emission happens at near room temperature (RT), the adsorption of this gas is investigated at 303 K. The main goals are to determine the amounts of adsorbed N_2O and the heats of its adsorption. In addition, the same parameters were determined for RT adsorption of carbon monoxide on the same samples. CO is known as a reducing agent; therefore, thermal effect of its adsorption on Cu-ZSM5 is important information in design of possible catalytic reduction of N_2O by carbon monoxide.

2. Experimental

2.1. Materials

The parent Na-ZSM5 zeolite (Si/Al = 50) was home synthesized and its crystalinity was confirmed by XRD technique. Ion exchange was performed following the procedure described in detail [26]: aqueous Cu(II) acetate solution (0.01 M, pH = 5.5–5.6) was stirred with Na-ZSM5 for 24 h at room temperature. Subsequently, zeolite was filtered, washed with deionised water and dried overnight at 383 K. For higher ion-exchange levels, the procedure was repeated: wet cake obtained after filtration was again ion-exchanged with a fresh copper acetate solution. The degree of ion exchange was determined after the samples were treated with solutions of $HClO_4$ and HF; the liberated copper was measured by using atomic absorption spectrometry. The samples were denoted as CuZ-*x*, where *x* represents the % of ion exchange. The results of chemical analysis are presented in Table 1.

Table 1
Chemical composition of investigated samples

Sample	Si/Al	Cu/Al	Ion-exchange (%)
CuZ-79	50	0.395	79
CuZ-128	50	0.64	128
CuZ-150	50	0.75	150

2.2. Methods

2.2.1. Microcalorimetry

A well-established stepwise procedure, previously fully described elsewhere [27] was followed. The heats of adsorption were measured in a heat-flow microcalorimeter of the Tian-Calvet type (C80 Setaram) linked to a glass volumetric line that permits the introduction of successive small doses of adsorbed gas. Before the adsorption, the samples were pre-treated in vacuum (10^{-3} Pa) overnight, at 673 K. The adsorption temperature for N_2O and CO was maintained at 303 K, while ammonia adsorption was done at 423 K. The equilibrium pressure corresponding to each adsorbed amount was measured by means of a differential pressure gauge from Datametrics. Successive known doses of any gas were sent on the investigated sample until a final equilibrium pressure of 66 Pa was obtained. Subsequently, the sample was pumped, desorption peak was recorded and a readsoprtion was performed at the same temperature. The irreversibly adsorbed amount of a chemisorbed gas was calculated from the difference between primary and secondary isotherms. The calorimetric and volumetric data were stored and analysed by microcomputer processing.

2.2.2. FTIR measurements

FTIR spectra were recorded using an FTIR Brucker IFS-48 Vector 22 spectrometer equipped with OPUS 22 software. A self-supported pellet (40–50 mg, $d = 18$ mm) was placed in a sample holder placed in an IR cell with CaF_2 windows. Thus prepared sample was activated in situ in the oxygen flow from room temperature up to 673 K, with a heating rate of 0.5 K/min and the sample was held at 673 K for 4 h in the same atmosphere. Subsequently, the sample was evacuated in vacuum (10^{-3} Pa) during additional 2 h. The adsorption of N_2O and CO was done after cooling up to room temperature and the collections of 200 scans spectra at a 4 cm^{-1} resolution were recorded.

3. Results and discussion

Quantitative data (volumetric isotherms) of the adsorption of N_2O on Cu-ZSM5-*x* zeolites are presented in Fig. 1. Differences in the N_2O uptake at a given pressure are noticed for the samples with different copper loadings. Not shown in the figure are the secondary isotherms obtained after the first adsorption isotherm followed by degassing in vacuum at 303 K. By subtracting the adsorbed volume of the

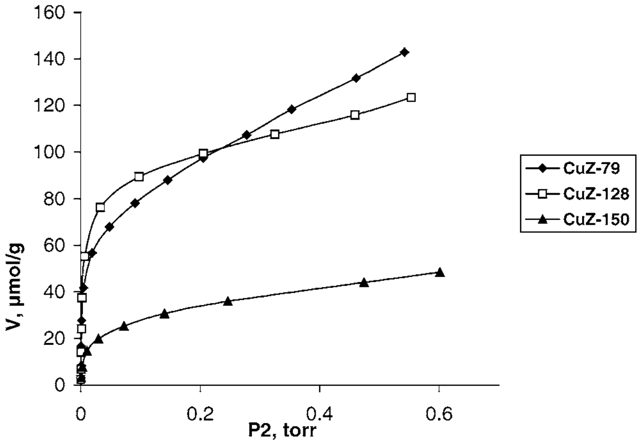

Fig. 1. Volumetric isotherms of N_2O adsorbed at 303 K on the samples with different copper content, activated at 673 in vacuum.

secondary isotherm from that of the primary isotherm at the same equilibrium pressure ($p = 26.7$ Pa), the volume of irreversibly adsorbed N_2O (chemisorbed, denoted as V_{irr}) is calculated. Also, the correspondent calorimetric isotherms (integral heat Q_{int} versus equilibrium pressure) are not reported for the sake of brevity. Both V_{irr} and Q_{int} are presented in Table 2.

It is evident from the results presented in Fig. 1 and Table 2 that small amounts of N_2O are irreversibly adsorbed at 303 K, on the investigated systems. These results clearly indicate the existence of a small number of strong active sites for the adsorption of N_2O on the investigated samples. The influence of copper addition to ZSM5 structure is visible: both V_{irr} and Q_{int} have similar values for the samples with lower copper contents (CuZ-79 and CuZ-150) while in the case of over-exchanged sample (CuZ-150), these values are considerably lower. It could be inferred that the sites active for adsorption are not accessible for N_2O molecules in the case of CuZ-150 sample.

As it was already mentioned in the Section 2, the investigated samples were pre-treated at 673 K overnight in vacuum before the adsorption procedure. The changing of oxidation state of Cu(II)ions as a result of evacuation procedure at elevated temperatures has been the subject of a big scientific interest. The reduction of Cu^{2+} to Cu^{+} in dynamic vacuum has been proven using multi-spectroscopic approach involving VIS-NIR diffuse reflectance spectroscopy, Cu^{+} photoluminescence, EPR and IR spectroscopy [11–14]. In addition, it has been shown that CO adsorption takes place on Cu^{+} species in the zeolitic systems [28]. CO molecule is selectively adsorbed on the Cu^{+} but very weakly on the Cu(0) and Cu^{2+} species [29]. Therefore, the adsorption of CO could be comprehended as a test interaction that can prove the existence of Cu^{+} ions in the system.

Table 2
Quantitative (number of moles per gram of zeolite; number of molecules per cation) and energetic data (integral heat of adsorption per gram of zeolite and initial differential heat of adsorption) on the adsorption of N_2O on CuZ-*x* zeolites

Sample	V_{irr} (µmol N_2O/g)	N_2O molecules/ Cu ion	Q_{int} (J/g zeolite)	Q_{diff} (kJ/mol)
CuZ-79	41.3	0.16	7.9	79
CuZ-128	41.8	0.10	7.3	81
CuZ-150	7.3	0.015	2.3	63

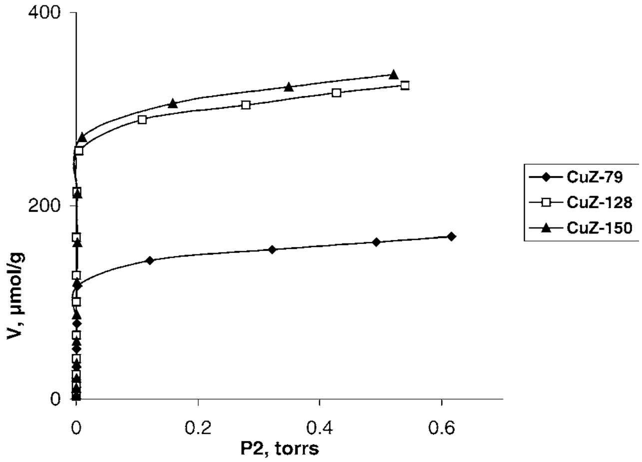

Fig. 2. Volumetric isotherms of CO adsorbed at 303 K on the samples with different copper content, activated at 673 in vacuum.

In this work the adsorption of CO at 303 K was performed in order to elucidate the nature and the strength of the active sites in the investigated samples. Adsorption isotherms of CO adsorption on the samples under study are presented in Fig. 2. Table 3 compiles the values of irreversibly adsorbed CO at the 26.7 Pa equilibrium pressure, integral heat evolved as a result of adsorption and the initial values of differential heats of adsorption for the samples of interest. The analysis of the presented results reveals that mono-carbonyl species are formed as a result of CO adsorption at the pressures applied in this work: less than 1 CO molecule was strongly adsorbed per one Cu ion. Even though, these numbers of adsorbed CO molecules are higher than in the case of N_2O adsorption, indicating higher affinity of the active sites for CO adsorption at a given temperature. Thermal effects of CO adsorption confirm this affinity towards CO adsorption: both integral heats of adsorption and initial differential heats are higher then in the case of N_2O adsorption.

The influence of ion-exchange level is evidenced in the experiments of CO adsorption. The increase of irreversibly adsorbed amount of CO, V_{irr}, in the case of CuZ-128 compared with that for CuZ-79 is proportional to the increase of copper content. However, it can be seen from Fig. 2 and Table 2 that there is no significant increase of V_{irr} in the case CO adsorption on CuZ-150 sample.

To clarify completely the nature of active sites for N_2O and CO adsorption, an FTIR investigation designed in a similar way as volumetric adsorption experiments, was performed. As it was described in Section 2, self-supported zeolite (CuZ-79) pellet was treated in vacuum, prior the room temperature adsorption of either N_2O or CO. Successive

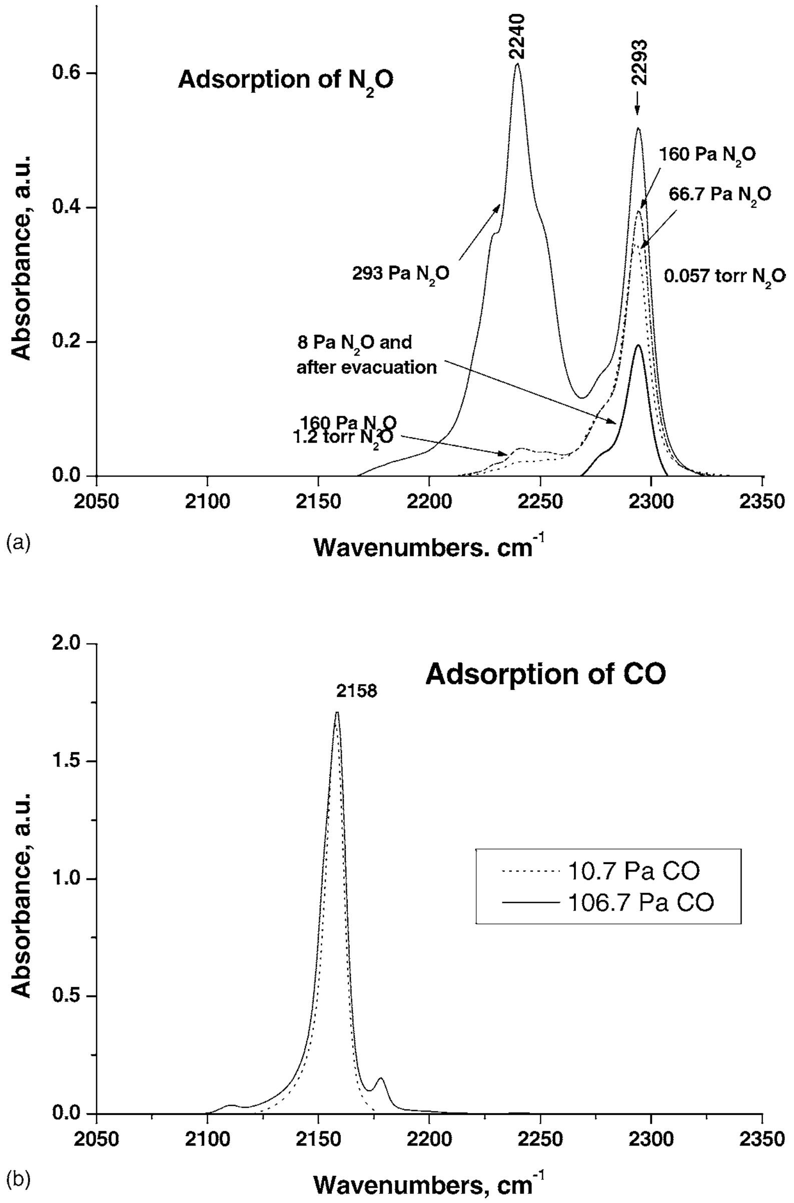

Fig. 3. FTIR investigation of room temperature adsorption of: (a) N_2O; (b) CO. The doses of different pressures were sent to the self-supported zeolite pellet placed in the IR cell. After the adsorption, the sample was evacuated and an IR spectrum was collected.

increasing doses of a given gas were admitted to the sample, and FTIR spectrum was collected after each dose. The doses similar to those applied in the experiments of calorimetry were applied. In Fig. 3(a), it is possible to notice the progressive increase of the band at 2293 cm^{-1} with increasing doses up to ~267 Pa. This band is assigned to N–N stretch of N_2O molecule bound to Cu^+ ion [22,30]. A band at 2293 cm^{-1} is a clear confirmation that a reduction of Cu^{2+} ions happened in dynamic vacuum before the contact of zeolite with N_2O was achieved. Also, the appearance of a broad complex band in the region 2250–2218 cm^{-1} is noticeable. This band is assigned to the interaction of N_2O with ZSM5 framework [22]. It is worth noticing that this band appears at the pressures higher then 0.5 Torr, which is the last equilibrium pressure in the calorimetric experiments. Therefore, it could be taken into account that only the interaction of N_2O with Cu(I) species takes place during the room temperature calorimetric experiments. The FTIR experiment was fully parallel to calorimetric one: after the adsorption of N_2O up to the final pressure of interest (~267 Pa), the sample was degassed at room temperature. It is evident from the Fig. 3(a) that a band at 2293 cm^{-1} still exists after the evacuation. It can be therefore concluded that one small part of N_2O molecules is really strongly held to Cu(I) ions in the ZSM5 structure, what is in accordance with the results obtained in the calorimetric measurements, and presented in Fig. 1 and Table 2.

FTIR experiment confirmed also the interaction of one CO molecule CO with one Cu^+ ion: a band at 2158 cm^{-1} is specific for monocarbonyl species found in the ZSM5 structure [10,29]. For the sake of brevity, Fig. 3(b) presents only

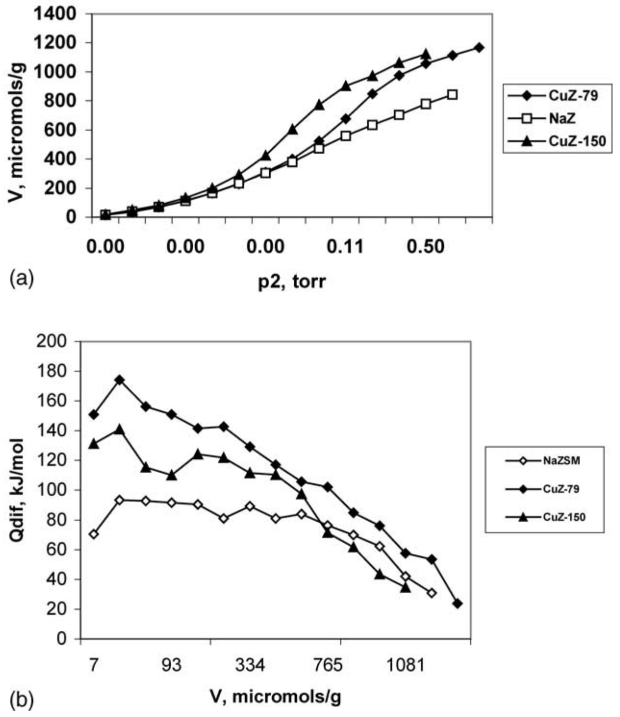

Fig. 4. The adsorption of ammonia on the parent Na-ZSM5 and two Cu(II) ion-exchanged samples CuZ-79 (under-exchanged) and CuZ-150 (over-exchanged), activated at 673 in vacuum; (a) volumetric isotherm of NH_3 adsorbed at 423 K, (b) differential heats of adsorption of NH_3.

two spectra obtained for the adsorption of two considerably different doses of CO: 0.08 and 0.8 Torr. It is evident that the bands noticed for those two pressures are of similar intensities. Also, this band is stable upon the room temperature degassing, proving in that way the existence of irreversibly bound CO.

In order to better describe the nature and strength of active sites that reveal as a result of ion exchange with Cu(II), the adsorption experiments of ammonia were performed in this work, also. The adsorption of ammonia was done at 423 K, because the value of irreversibly adsorbed ammonia at this temperature is believed to correlate with the number of strong active sites present [31]. Fig. 4(a) presents the volumetric isotherms of NH_3 adsorption on Na-ZSM5 and two ion-exchanged samples: one under-exchanged (CuZ-79) and the other, over-exchanged (CuZ-150) (Table 3). Fig. 4(b) presents the differential heats of adsorption on the same samples, while Table 4 compiles the values of irreversibly adsorbed NH_3 molecules and the data concerning the thermal effects of adsorption. The analysis of all these data reveals that, as a consequence of ion exchange of sodium with copper ions, a whole number of active sites for ammonia adsorption increase, while the values of V_{irr} are quite similar. Importantly, as a result of adsorption up to 26.7 Pa equilibrium pressure, di-amino complex with Cu(I) was produced on CuZ-79 sample and strongly bound. This results is in accordance with that one reported in Ref. [10], where the adsorption of ammonia was investigated on pure Cu(I)ZSM5 obtained by gas phase exchange with CuCl. Although in that case ammonia was adsorbed at room temperature, this accordance prove again that a reduction of Cu^{2+} to Cu^{+} happened in the case of the samples investigated in this work.

Table 3
Quantitative (number of moles per gram of zeolite; number of molecules per cation) and energetic data (integral heat of adsorption per gram of zeolite and initial differential heat of adsorption) on the adsorption of CO on CuZ-*x* zeolites

Sample	V_{irr} (μmol CO/g)	CO molecules/ Cu ion	Q_{int} (J/g zeolite)	Q_{diff} (kJ/mol)
CuZ-79	130.4	0.50	18	125
CuZ-128	268.8	0.66	38	130
CuZ-150	243.2	0.49	33.2	120

Table 4
Quantitative (number of moles per gram of zeolite; number of molecules per cation) and energetic data (integral heat of adsorption per gram of zeolite and initial differential heat of adsorption) on the adsorption of NH_3 on CuZ-*x* zeolites

Sample	V_{irr} (μmol NH_3/g)	NH_3 molecules/ Cu ion	Q_{int} (J/g zeolite)	Q_{diff} (kJ/mol)
Na-ZSM5	571	–	62	90
CuZ-79	542.8	$2.1 \approx 2$	117.4	160
CuZ-150	555.5	$1.1 \approx 1$	106	135

It is noticeable that ion exchange produced stronger active sites for ammonia adsorption: differential heat profiles obtained for Na-ZSM5 and CuZ-79 clearly show a significant increase of Q_{diff} in the case of later zeolite. However, it has to be noticed here that there is also the decrease of both V_{irr} value and initial differential heat of NH_3 adsorption in the case of CuZ-150 (see Fig. 4(b) and Table 4), as it was found in the case of N_2O adsorption. Instead of di-amino complexes formed between two ammonia molecules strongly bonded to the Cu ion in the CuZ-79 sample, in the case of CuZ-150, only one ammonia molecule is chemisorbed per one Cu ion. Similarly to nitrous oxide adsorption it could be concluded that ammonia molecules cannot access all copper ions in the structure. All these data can be comprehended as an indication of possible coexistence of Cu(I) ions produced during the evacuation and the other possible copper species, such as agglomerates of copper oxides, for example.

The profiles of differential heats versus gas uptake (μmol/g), for both N_2O and CO adsorption on all CuZ-*x* samples are presented in Fig. 5(a) and (b). The profiles and the initial values of Q_{diff} obtained in the case of CO adsorption are similar to those already published [10,29]. It is evident that differential heats of adsorption of N_2O are lower than those of CO, indicating a weaker interaction. Differential heats of N_2O adsorption between 80 and 30 kJ/mol were determined. Taking into account the amounts of irreversibly adsorbed N_2O, it can be inferred that only those N_2O molecules bonded with a differential heats higher that 60 kJ/mol are chemisorbed ones. It is

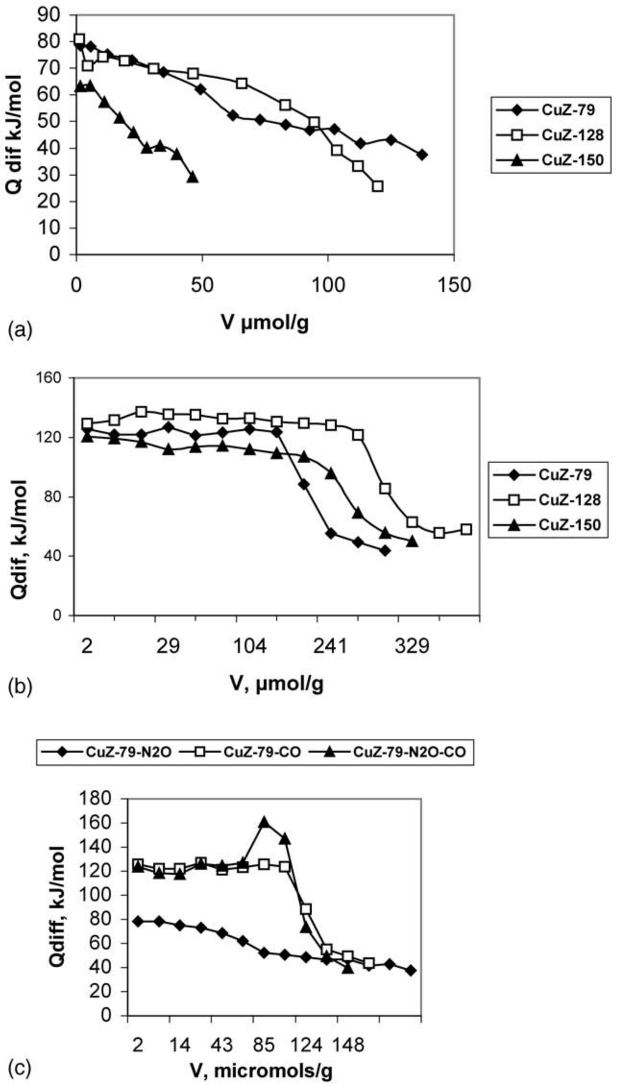

Fig. 5. Differential heats of adsorption on CuZ-*x* at 303 K: (a) adsorption of N_2O, (b) adsorption of CO, (c) adsorption of CO on CuZ-79 previously contacted with N_2O. In all cases, the samples were activated at 673 K in vacuum.

evident from Fig. 5(a) that insignificant number of such strong sites exists on CuZ-150 sample. On the contrary, the highest amount of the strongest sites for N_2O adsorption is found on CuZ-128 sample that exhibits a different distribution of active sites in comparison with under-exchanged sample CuZ-79 (see Fig. 5(a)).

The results presented so far are a clear indication that Cu^+ ions, produced by reduction of Cu^{2+} ions in ion-exchanged zeolite samples, are stronger active sites in CO adsorption that in N_2O adsorption. Therefore, it could be concluded that CO would be adsorbed primarily in the case of possible competitive co-adsorption of these two gases. Here, the experiment of CO adsorption on the CuZ-79 sample previously contacted with N_2O was performed. Before the CO adsorption, N_2O was adsorbed at RT and subsequently, pumped at the same temperature. After that, the adsorption of CO was completed. In that way, carbon monoxide was adsorbed on the surface partly covered with strongly bonded N_2O molecules. Fig. 5(c) shows the obtained differential heats of CO adsorption. The profiles Q_{diff} versus gas uptake (µmol/g) obtained for single adsorption (of CO or N_2O) are presented on the same figure for the comparison. It is important to notice that the profile obtained for CO adsorption on the surface previously contacted with N_2O is almost identical to that one obtained for the adsorption of CO on one empty surface, but only in the first part of adsorption procedure. It is evident from all presented results that the investigated sample posses a bigger number of sites active for CO adsorption, in comparison with those active in N_2O adsorption. A first part of profile Q_{diff} versus CO uptake, identical to that one found in the adsorption of CO on one empty surface could be considered as a result of CO adsorption on unoccupied active sites. After the adsorption on these unoccupied sites, the increase of differential heats of CO adsorption, compared with those obtained in the case of CO adsorption on an "empty" surface, was obtained. This result could be comprehended as an indication of possible reaction between adsorbed nitrous oxide and carbon monoxide from the gas phase.

4. Conclusions

The adsorption behaviour of Cu(II) ion exchanged ZSM5 samples with different copper loadings was investigated. Room temperature adsorptions of nitrous oxide and carbon monoxide were performed by means of microcalorimetry. Nitrous oxide was chosen for this investigation mainly because of increasing interest on this long-lived atmospheric pollutant which emission happens at near room temperature.

The adsorption of N_2O takes place at Cu^+ ions formed by reduction in dynamic vacuum during the activation procedure before adsorption. The interactions of both N_2O and CO with monovalent copper ions are confirmed by FTIR spectroscopy investigation.

The quantitative amounts of gas phase molecules adsorbed per one copper ion were determined from the volumetric isotherms. This study demonstrated that in the applied experimental conditions only the interactions between one gas phase molecule and one active Cu^+ site take place, in both cases of N_2O and CO adsorptions. Only mono carbonyl species were formed during the adsorption of CO. The investigated samples were additionally characterised by the ammonia adsorption at 423 K. Forming of strongly adsorbed di-amino complexes with Cu^+ ions was observed.

The values of differential heats of N_2O adsorption in the investigated systems have shown that this interaction is weaker than that with CO. Small amounts of N_2O are chemisorbed in the investigated systems. For the room temperature adsorption of N_2O, the strongest active sites for the interaction with copper ions in the ZSM5 structure were identified.

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