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Competitive adsorption of N_2O and CO on CuZSM-5, FeZSM-5, CoZSM-5 and bimetallic forms of ZSM-5 zeolite

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Abstract

The behavior of copper-, iron- and cobalt-exchanged ZSM-5 (Si/Al = 20) and bimetallic forms of the same zeolite was investigated with reference to the adsorption of N_2O and CO at 303 K. The interactions of both gases with investigated zeolites have been studied using microcalorimetry and infrared spectroscopy. The values of differential heats of adsorption and the amounts of adsorbed gases were determined. Both gases react with the charge-balancing cations as active sites for adsorption. CuZSM-5 shows significantly better performances than FeZSM-5 and CoZSM-5, toward both gases; additionally, nitrous oxide can be chemisorbed on CuZSM-5. Adsorption capabilities of FeZSM-5 and CoZSM-5 are increased with the addition of copper ions. The heats of CO interaction with copper-containing samples have been found to be higher then the heats of N_2O interaction, while for FeZSM-5 and CoZSM-5 samples similar heats were detected for both gases. In the case of CuZSM-5, as a result of competitive adsorption between previously adsorbed N_2O and incoming CO from the gas phase, a surface reaction is found.

Keywords: Nitrous oxide; Carbon monoxide; Competitive adsorption; ZSM-5

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1. Introduction

Copper-, iron- and cobalt-exchanged zeolites with MFI topology have been identified as potential catalysts in the decomposition of NO_x and their selective catalytic reduction (SCR) by hydrocarbons or ammonia [1–20]. Particularly, CuZSM-5 has been widely investigated for its ability in decomposition and selective catalytic reduction of NO in the presence of oxygen [10,21–24]. SCR of NO with hydrocarbons or ammonia over FeZSM-5 catalysts is currently extensively studied due to their superior stability and high activity [1–9,25,26]. Besides, FeZSM-5 zeolites express high selectivity to phenol in the selective oxidation of benzene using nitrous oxide as oxidant [20,27–31], while CoZSM-5 has been found to posses a unique ability for SCR of NO by methane [14–19]. Evidently, Cu-, Fe- and Co-exchanged ZSM-5 zeolites have been identified as potential catalysts for a number of environmentally benign processes.

On the contrary to other nitrogen oxides, nitrous oxide has been long considered as a harmless gas, what caused a lack of scientific interest. However, in the past decades, N_2O has been recognized as a notorious pollutant exhibiting 300 times more powerful greenhouse effect than CO_2. Moreover, N_2O reacts with the ozone layer in the stratosphere, causing its destruction. Due to potentially disastrous environmental effects, the control and reduction of N_2O emissions have been claimed in Kyoto, 1997 (The United Nations Framework Protocol on Climate Change). Main options examined and proposed for the abatement of this pollutant are: direct decomposition catalyzed by heterogeneous catalysts, SCR by hydrocarbons or other known reductans, or the usage of N_2O as an oxidant in selective catalytic oxidation reactions. Among the other solid catalysts, such are transition (Cu, Co and Ni) and noble metal-based catalysts (Rh, Ru, Pd and Pt) on different supports, Cu-, Fe- and Co-exchanged ZSM-5 zeolites have been widely investigated and recognized as promising materials which might provide a technologies for N_2O abatement.

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Direct catalytic decomposition of N_2O into N_2 and O_2 on iron-containing ZSM-5 zeolites has been widely investigated [20,32–40]. Since Panov et al. [28] suggested that only the oxygen atoms deposited from N_2O (so-called α-oxygen atoms) take part in the forming of O_2, the mechanism of N_2O decomposition on iron-containing zeolites and the properties of the oxygen species involved in the surface reaction remained a topic of big interest and discussion [39,41–43]. In addition, simultaneous catalytic reduction of nitrous oxide and nitric oxide with hydrocarbons in the presence of excess oxygen and water vapor was carried out over FeZSM-5 [7,33,34,36,40]. Although CuZSM-5 and CoZSM-5 zeolites exhibit higher activities than FeZSM-5 for N_2O decomposition it seems that in the presence of O_2, NO and H_2O, iron-containing catalysts are superior because of higher stability and resistance to poison [17,36,37]. Therefore, recent literature sources report on developing multimetallic zeolite systems, which intend to combine the properties of single metallic catalysts: the high activity of Cu and Co zeolites in N_2O decomposition, with the stability and resistance to poison of Fe-containing zeolites [44,45].

The major industrial sources of N_2O are the productions of nitric and adipic acids. Besides, N_2O can be produced at low temperatures—in the low temperature oxidation of NH_3 or amines, and in the agricultural sector. All previously mentioned catalytic processes for the reduction of N_2O emissions take part at high temperatures (>573 K), and can be used for N_2O abatement in tail-gases. Evidently, the direct decomposition of N_2O, SCR of N_2O with hydrocarbons or selective oxidation reaction involving N_2O as an oxidant still attract a great scientific interest. However, the possibility of N_2O adsorption on ion-exchanged zeolites at near room temperature has not been still widely discussed. It has been shown that, at low temperatures (between 303 and 393 K) different forms of ion-exchanged ZSM-5 can be used to remove low concentrations of N_2O from the flow [46]. Infrared spectroscopy has been applied for the investigation of NO_x with various zeolitic systems [38,47–53]. IR data concerning N_2O interaction with zeolitic systems containing strong Lewis acid sites [48], Fe or Cu charge-balancing cations [43,49–53] have been reported. Several theoretical considerations have been devoted to N_2O interactions with ion-exchanged ZSM-5, the adsorption energies between N_2O and charge-balancing cation, calculated on MP2 level were estimated as "relatively strong" [54–56]. However, the experimental evidence of thermal effects of N_2O interactions with active sites in zeolite structure is also very important.

In this work, we investigated the room temperature adsorption of N_2O and CO on Cu^{2+}, Fe^{2+} and Co^{2+} ion-exchanged ZSM-5, and bimetallic forms of ZSM-5 containing copper, iron and cobalt with the main intention to determine the amounts of adsorbed N_2O and the heats of interaction. Besides, this manuscript refers the results concerning CO adsorption on the same zeolites, in order to judge about the possibility of competition in the adsorption of N_2O and CO in the mixtures containing both gases. It is known that in the case of under-exchanged zeolitic samples, all of the exchanged cations are present as isolated cations. In addition, in our previous work [57] done on CuZSM-5 containing different copper loadings, it was noticed that the highest amounts of adsorbed N_2O were obtained in the case of under-exchanged samples. It was inferred that the sites active for adsorption are not accessible for N_2O molecules in the case of over-exchanged samples. Besides, it is known that at low loadings, metal cations are present as mononuclear species [58–60]. For that reasons, all investigated samples investigated in this work were prepared as under-exchanged.

2. Experimental

2.1. Materials

NaZSM-5 (Si/Al = 20) zeolite was synthesized hydrothermally as a starting material, after synthesis zeolite was calcined in air at 793 K, for 12 h. NH_4ZSM-5 was derived by three-fold ion-exchange with 0.5 M ammonium chloride at 363 K. As prepared material was filtered, washed with de-ionized water and dried in an oven at 393 K. The resulting NH_4ZSM-5 was calcined in air at 793 K, for 5 h, to produce HZSM-5.

Under-exchanged samples containing Cu^{2+}, Fe^{2+} or Co^{2+} were obtained from HZSM-5 using usual ion-exchange procedures: HZSM-5 was suspended in 0.01 M solution of corresponding divalent salt and stirred for 24 h, followed by filtering, washing with de-ionized water and drying. Cu^{2+} ions were introduced at 298 K using an aqueous solution of copper acetate, as described previously [57]. Fe^{2+}-containing samples were obtained by aqueous ion exchange with $FeCl_2\cdot 4H_2O$, at 298 K, in the flow of nitrogen. CoZSM-5 samples were prepared at 353 K, using a solution of $CoCl_2\cdot 6H_2O$, at pH 6.4. The obtained samples were denoted as MZSM-5, where M denotes cation. Consecutive ion exchange method was applied in order to obtain the bimetallic samples. These samples were denoted as M,NZSM-5, both M and N denote cations, cation N was exchanged firstly.

The crystallinity of parent NaZSM-5, HZSM-5 and ion-exchanged forms was checked by X-ray diffraction, powder X-ray diffraction patterns were recorded on a Bruker (Siemens) D5005 diffractometer at room temperature using Cu Kα (radiation, 0.154 nm) from 3° to 80° 2θ in a 0.02° steps with 1 s. The structure of ZSM-5 zeolite remains unaffected by ion-exchange procedure. Surface areas were determined by the BET method from the adsorption of nitrogen at 77 K after pre-treatment for 4.0 h at 673 K under vacuum. The cations contents were determined by AES-ICP in a Spectroflame-ICP instrument. The results of chemical analysis and the values of BET surface areas are presented in Table 1.

Table 1
Chemical composition and BET surface areas of investigated samples

Sample	Cu content (wt%)	Fe content (wt%)	Co content (wt%)	BET surface area (m^2/g)
CuZSM-5	1.50			310
FeZSM-5		0.30		335
CoZSM-5			0.37	284
Cu,FeZSM-5	1.25	0.20		342
Fe,CuZSM-5	0.48	0.87		340
Cu,CoZSM-5	1.22		0.10	345

2.2. Methods

2.2.1. Microcalorimetry

A well-established stepwise procedure, previously fully described elsewhere [61], 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. The adsorption takes place by repeatedly sending small doses of gas onto the initially pre-treated solid (in vacuum, 10^{-3} Pa overnight, at 673 K) while recording the heat flow signal and the concomitant pressure evolution. The equilibrium pressure corresponding to each adsorbed amount was measured by means of a differential pressure gauge from Datametrics. The adsorption temperature for N_2O and CO was maintained at 303 K. In a particular case of copper-exchanged sample, N_2O and CO adsorption were studied at 303, 353 and 423 K. 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 re-adsorption was performed at the same temperature. The irreversibly adsorbed amount of a chemisorbed gas was calculated from the difference between primary and secondary isotherms (adsorbed volume as a function of equilibrium pressure over the sample). By subtracting the adsorbed volume of the secondary isotherm from that of the primary isotherm at the same equilibrium pressure (26.7 Pa), the volume of irreversibly adsorbed gas (chemisorbed, denoted as V_{irr}) is calculated.

2.2.2. FTIR and UV–vis measurements

FTIR spectra were recorded using an FTIR Brucker IFS-48 Vector 22 spectrometer with a DTGS detector, equipped with OPUS 2 software. A self-supported pellet (~25 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 673K for 4 h in the same atmosphere. Subsequently, the sample was evacuated in vacuum (10^{-3} Pa) during additional 2 h. The adsorption of dried gases: N_2O or CO was done after cooling up to room temperature and the collections of 100 scans spectra at a 2 cm^{-1} resolution were recorded. N_2O or CO was adsorbed on the surface, then, the cell was evacuated, and the adsorption of other gas was performed. The background for each spectrum was the state of a solid after pre-treatment and before any adsorption, which means, a spectrum collected from self-supported zeolite pellet.

UV–vis spectra were measured using a Perkin-Elmer Lambda 9 spectrometer equipped with diffuse reflectance attachment with an integrating sphere coated with $BaSO_4$. The spectra were recorded in a differential mode with a parent HZSM-5 as reference. Accordingly to the literature sources [58–60], the obtained results indicate the presence of mono-nuclear, isolated cations, in the case of all investigated samples, except for Fe,CuZSM-5, where one part of iron seems to be present in form of multinuclear iron clusters [64].

3. Results and discussions

In a particular case of copper-containing ZSM-5, the microcalorimetric studies of N_2O and CO adsorptions were performed at two different temperatures—at 303 and 423 K. The profiles: differential heats of adsorption versus gas uptake are presented in Fig. 1. The quantitative amounts of chemisorbed gases obtained for all investigated samples, are summarized in Table 2. The influence of adsorption temperature on the initial values of differential heats of N_2O adsorption on CuZSM-5 and on the amounts of chemisorbed gas is evident: at higher temperature, the evolved initial differential heats are somewhat higher then those obtained at 303 K, however, the chemisorbed amount of nitrous oxide is importantly lower. CO adsorption was not found to be dependent on the temperature in this way: similar amounts of this gas are chemisorbed at 303 and 423 K. Differential heats evolved as a result of CO adsorption are importantly higher (the value of initial differential heat ~130 kJ/mol) in comparison with those evolved during N_2O adsorption (the value of initial differential heat ~70 kJ/mol). Evidently, the interaction of N_2O with CuZSM-5 is not strong enough, and at 423 K, only very small number of N_2O molecules can remain adsorbed on the surface, by contrast with the case of CO adsorption. It is widely

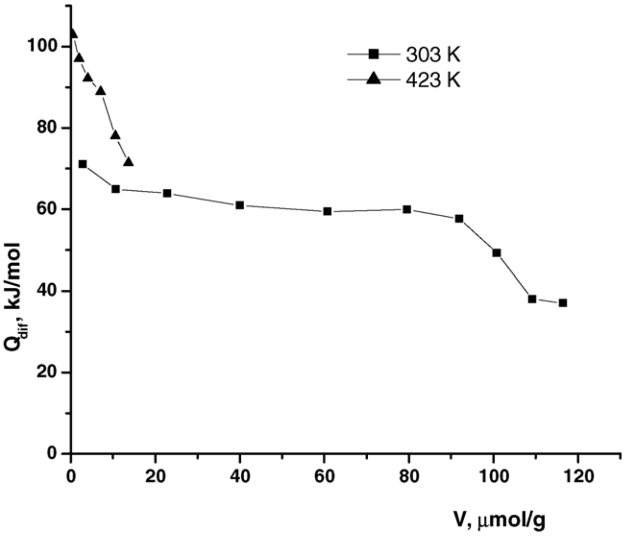

Fig. 1. Differential heats of adsorption of N_2O on CuZSM-5. The effect of adsorption temperature.

Table 2
Quantitative data on the adsorption of N_2O and CO on the investigated samples

Sample	Irreversibly adsorbed N_2O (μmol/g)	Irreversibly adsorbed CO (μmol/g)
CuZSM-5, $T_{ads} = 303$ K	40.0	110
CuZSM-5, $T_{ads} = 423$ K	2.7	100.1
FeZSM-5	5.5	7.1
CoZSM-5	5.0	4.5
Cu,FeZSM-5	15.0	120.0
Fe,CuZSM-5	5.5	53.0
Cu,CoZSM-5	17.0	60.0

accepted that copper ions are active sites for N_2O or CO adsorption [49,63]. Evidently, very small number of these sites is strong enough to adsorb N_2O molecules at the temperatures higher than room temperatures. Therefore, in the case of other samples investigated in this work, only room temperature adsorptions were studied.

Fig. 2 shows microcalorimetric results of N_2O and CO adsorptions performed at 303 K on CuZSM-5. It is worth noticing that differential heats for CO adsorption are significantly higher then those found during N_2O adsorption, indicating that CO would be adsorbed primarily in the case of possible competitive co-adsorption of these two gases. In addition, it can be seen from Table 2 that chemisorbed amount of CO is higher than the amount of chemisorbed N_2O, what means that the investigated sample has a bigger number of sites active for CO adsorption, in comparison with those active in N_2O adsorption. The same results are presented in a form of adsorption isotherm, in Fig. 2b.

Here, one additional experiment was performed with reference to the adsorption of N_2O and CO on CuZSM-5 sample. Carbon monoxide was adsorbed on the same sample, which was previously contacted with N_2O. Before the CO adsorption, N_2O was adsorbed and subsequently evacuated at 303 K. Thus, CO was adsorbed on the surface partly covered with strongly bonded N_2O molecules. The result is also presented in Fig. 2. It is important to notice that initial differential heats obtained for CO adsorption on a surface which possesses residual chemisorbed N_2O are similar to those obtained for the adsorption of CO on the empty surface. This first part of a profile: Q_{dif} versus CO uptake, 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 values was noticed, in comparison with differential heats obtained in the case of CO adsorption on an "empty" surface. This increase of differential heats is a clear indication of some spontaneous event, which takes part during CO adsorption over chemisorbed N_2O. This event can be a surface reaction between previously adsorbed nitrous oxide and carbon monoxide from the gas phase. Besides, the increase of pressure detected in a corresponding part of microcalorimetric experiment indicates the forming of a gas in a volumetric line. In Fig. 2b, adsorption isotherm is shown. Its complex shape (two superimposed adsorption isotherms) indicates again a possible surface reaction between N_2O and CO. A possibility of reaction between pre-adsorbed N_2O and CO has been already reported in the case of zeolites containing strong Lewis acid sites (ZnO/HZSM-5, dehydroxylated HZSM-5, HGaZSM-5). In that case, heating to 400–450 K leads to the forming of CO_2 [48].

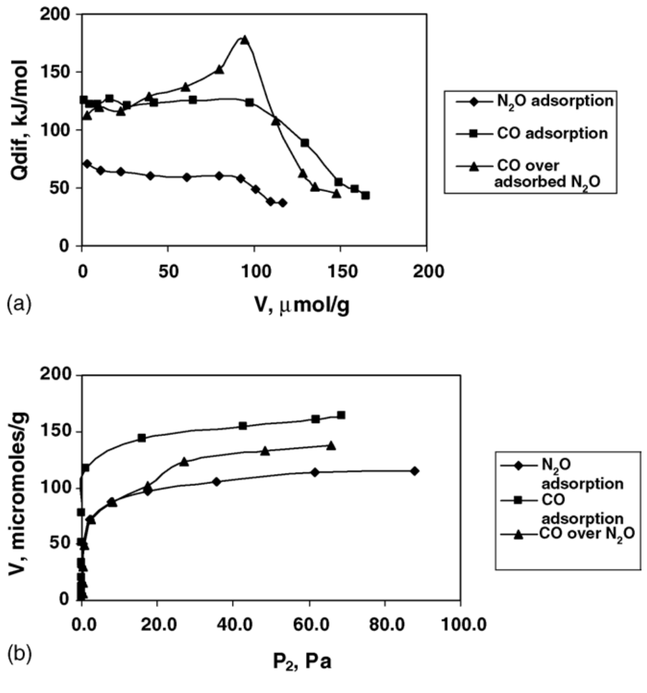

Fig. 2. Differential heats of N_2O and CO adsorption on CuZSM-5 at 303 K: (a) differential heats vs. gas uptake and (b) adsorption isotherms.

The adsorption of N_2O and CO on CuZSM-5 was studied by FTIR spectroscopy, in one experiment designed in a similar way as a volumetric adsorption experiment. As it was described in Section 2, self-supported zeolite pellet was treated in a flow of oxygen and then in vacuum, prior to the room temperature adsorption of either N_2O or CO. Successive increasing doses of a given gas were admitted to the sample and FTIR spectrum was collected after each dose. In the case of CuZSM-5 sample, the doses similar to those applied in the calorimetric experiment were applied.

The N_2O molecule has a linear N–N–O structure with the respective N–N stretching vibrations at 2224 cm^{-1} and N–O stretches at 1285 cm^{-1}, in the gas phase [42]. Here, as a result of N_2O adsorption on CuZSM-5, well resolved IR absorption bands at 2293 and 1327 cm^{-1} were detected. In Fig. 3a, it is possible to notice the progressive increase of the band at 2293 cm^{-1} with increasing doses up to 270 Pa. It should also be noted that the intensity of a peak found at 1327 cm^{-1} seems to be proportional to the intensity of a former peak. The IR investigations of N_2O adsorption on CuZSM-5 have been already reported [49–53]. The peak at 2293 cm^{-1} has been assigned to the N–N stretch of N_2O bonded to Cu^+, while a band found at 1327 cm^{-1} has been assigned to N–O stretch of N_2O bonded to Cu^+ [49,51]. It is worth noticing that both bands found in this work are stable upon evacuation at 298 K (30 min, 10^{-3} Pa; see Fig. 3a). The obtained result is consistent with that one obtained from microcalorimetric experiment, and it can be finally inferred that one part of N_2O molecules is strongly held to copper ions in the ZSM-5 structure. Also, the appearance of a broad complex band in the spectral region 2250–2210 cm^{-1} is noticeable. In this work, it was found that this band can be removed by evacuation. This result is consistent with microcalorimetric experiment and confirms that one part of N_2O is physisorbed on CuZSM-5, but also, this result is in accordance with already published statement that this band can be assigned to the N–N stretch of weakly bonded N_2O, most likely associated with the zeolite framework [49,51].

The room temperature adsorption of CO over chemisorbed N_2O was also performed, and studied by FTIR spectroscopy. The increasing doses of CO were admitted to the pellet with

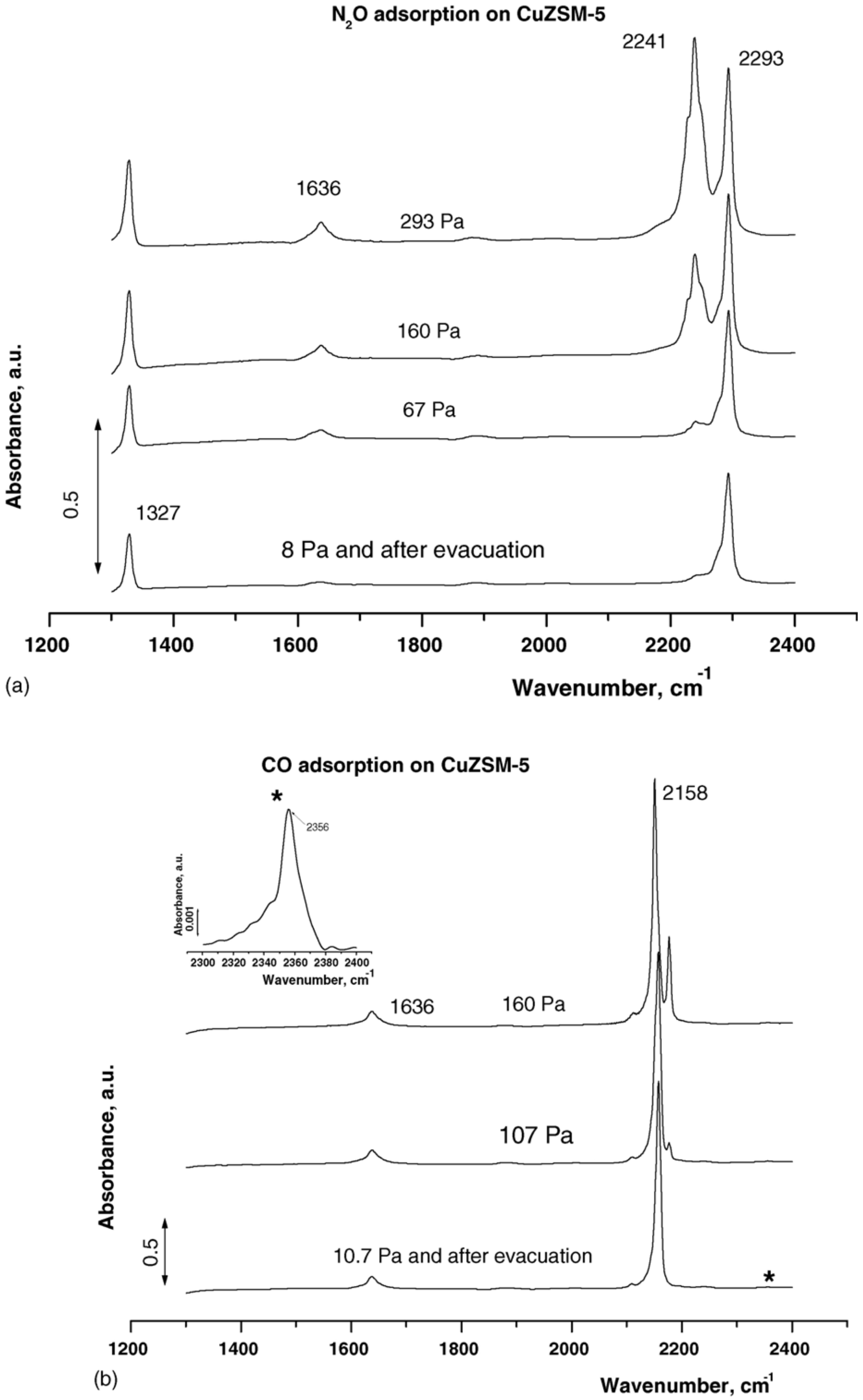

Fig. 3. FTIR investigation of room temperature adsorption of: (a) N_2O and (b) CO. The doses of different pressures were sent to the self-supported zeolite pellet placed in the IR cell.

residual chemisorbed nitrous oxide and FTIR spectrum was collected after each dose. The obtained spectra are presented in Fig. 3b. A band at 2158 cm^{-1}, specific for monocarbonyl species adsorbed on Cu^+ ions in ZSM-5 structure is found [62,63]. The appearance of this band is a clear proof that a reduction of Cu^{2+} to Cu^+ happened as a result of pre-treatment in vacuum. In the case of CuZSM-5 investigated in this work, the appearance of a band centered at 2158 cm^{-1} (as a result of CO adsorption) and a band at 2293 cm^{-1} (collected during N_2O adsorption) are clear indication that Cu^+ ions are active sites for adsorption of both gases. Therefore, a competition for the same active sites should be expected between these two gases. It can be seen that both bands specific for the interaction of N_2O molecule with copper ions disappear with the admission of a very small CO pressure. Evidently, CO can easily expel the adsorbed N_2O from the surface, what is consistent with the result obtained from microcalorimetry: CO interaction with CuZSM-5 is stronger then that one of N_2O. A band centered at 2158 cm^{-1} is stable upon the room temperature evacuation, proving in that way the existence of chemisorbed carbon monoxide.

Importantly, as a result of CO admission over chemisorbed N_2O, on CuZSM-5, a weak band centered at 2356 cm^{-1} appeared. This band, which disappears with the evacuation, is typical for physisorbed CO_2, and could be another indication of surface reaction between CO and N_2O.

In order to check whether CO_2 could be formed as a result of CO admission to CuZSM-5 zeolite, one additional IR experiment was performed. CO was adsorbed after common pre-treatment procedure, without any previous contact with N_2O. The obtained IR spectrum is presented in Fig. 4. A weak band at 2356 cm^{-1} indicates again the presence of physisorbed CO_2 on the surface. Evidently, this physisorbed CO_2 appeared as result of CO interaction with the active sites of CuZSM-5.

In spite of this result, it could be stated that in the case of CO adsorption over chemisorbed N_2O, surface reaction happened as a results of competitive adsorption between previously adsorbed N_2O and incoming CO from the gas phase. A plateau like profile: differential heats versus gas uptake is obtained for CO adsorption on an ‘‘empty’’ surface, proving that a forming of weakly bonded CO_2 does not influence importantly on the whole heat effect of the adsorption process. A shape of a corresponding volumetric isotherm also indicates the adsorption as a sole surface event. On the contrary, both differential heats and volumetric isotherm profiles obtained in the case of CO adsorption over chemisorbed N_2O prove a reaction between two gases (see Fig. 2a and b).

The interactions of both nitrous oxide and carbon monoxide with the other samples investigated in this work are visibly weaker then in the case of CuZSM-5. The insight in the data presented in Table 2 gives evidence that very small amounts of both N_2O and CO were irreversibly adsorbed on iron- and cobalt-containing samples. Fig. 5a and b shows the profiles of differential heats as a function of adsorbed amounts for both adsorbed gases. The heats of adsorption of both gases are similar, in the case of CoZSM-5, while in the case of FeZSM-5 the initial heat of N_2O adsorption is slightly higher then the initial heat of CO adsorption. Importantly, both gases were mainly physisorbed on these two samples. Consequently, a competitive adsorption between N_2O and CO could not be expected. For this reason, IR spectra were recorded after a single dose of around 300 Pa (of either N_2O or CO) was admitted to the sample of interest. The obtained results confirm that N_2O and CO were mainly physisorbed on FeZSM-5 and

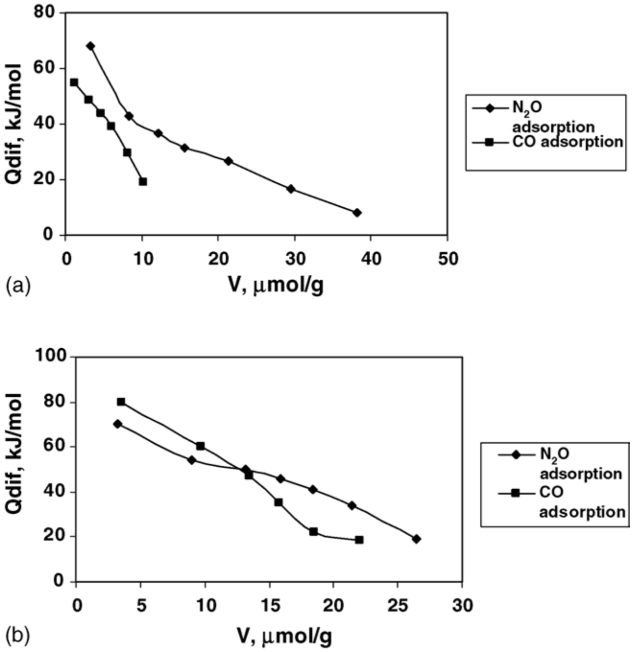

Fig. 5. Differential heats vs. gas uptake, obtained for N_2O or CO adsorption at 303 K on: (a) FeZSM-5 and (b) CoZSM-5.

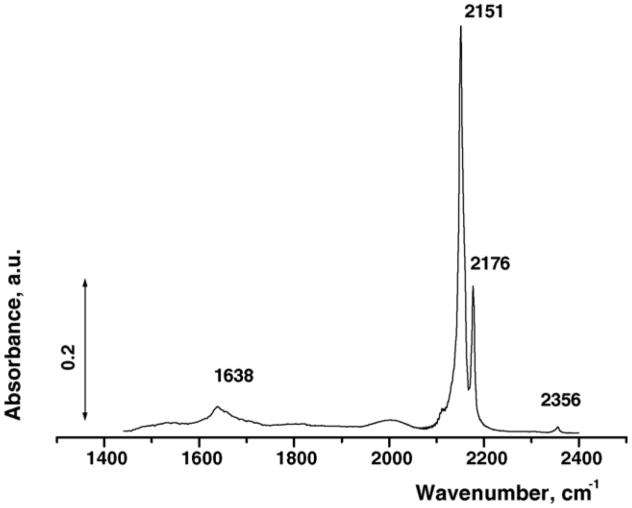

Fig. 4. FTIR spectrum collected after CO was admitted (dose of 200 Pa) to CuZSM-5 zeolite.

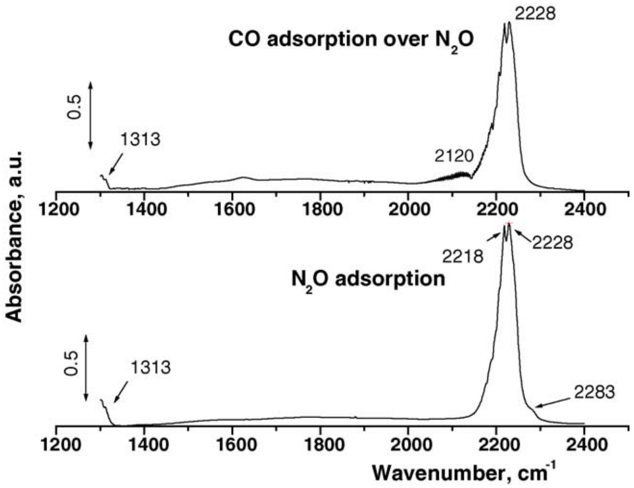

Fig. 6. FTIR spectra collected after N_2O and CO were admitted to FeZSM-5 zeolite.

CoZSM-5. Fig. 6 shows IR spectra collected for FeZSM-5. As a result of nitrous oxide admission on FeZSM-5, weak bands at 2284 and 1313 cm^{-1} were found. In addition, two overlapped peaks at 2218 and 2228 cm^{-1} are evident. Similar results are obtained for N_2O admission on CoZSM-5: overlapped bands at 2216 and 2231 cm^{-1}, and a shoulder around 2286 cm^{-1} have been found. These results, different in comparison with a spectrum obtained for the admission of >100 Pa N_2O on CuZSM-5 (a band centered at 2241 cm^{-1}), could be comprehended as an indication of the influence of charge-balancing ion nature (iron or cobalt) on the interaction N_2O-zeolite.

These results are also consistent with already published literature data. Wood et al. [38] have demonstrated that N_2O adsorbed on HZSM-5 at 298 K exhibits a strong band at 2226 cm^{-1} and a weak band at 1308 cm^{-1}, while in the case of FeZSM-5, N_2O adsorption results with IR bands at 2282 and 1344 cm^{-1}. In addition, the authors reported the calculated heats of N_2O adsorption: the heat of adsorption on HZSM-5 and FeZSM-5 are estimated to be 21 and 67 kJ/mol, respectively. These values are comparable with the experimental data done in this work. It is worth noticing that we report here 68.2 kJ/mol as the initial value of differential heat of N_2O adsorption on FeZSM-5. Evidently, iron cations are the sites active in N_2O adsorption. To the best of our knowledge, the heats of N_2O interactions with FeZSM-5 are quantitatively determined for the first time. Moreover, it is important to notice that only a small part of N_2O is adsorbed on FeZSM-5 with the evolution of this initial heat of adsorption; quantitative value can be seen in Table 2. This amount might be dependent on the iron content in the zeolite, and should be higher for higher iron loadings.

As it could be expected, based on the results obtained from microcalorimetric experiment, N_2O can be easily desorbed: IR spectra collected for both FeZSM-5 and CoZSM-5 exhibit a background profile after a very short evacuation, proving that N_2O was only physisorbed on these samples. Therefore, CO was admitted to these samples over physisorbed N_2O. Fig. 6 presents IR spectrum collected in the case of FeZSM-5: a spectrum very similar to gas-phase CO spectrum is overlapped with this one obtained as a result of N_2O admission; all these bands disappear with a very short evacuation.

In the case of bimetallic samples investigated in this work, it was noticed that the adsorption capabilities of FeZSM-5 and CoZSM-5 toward both gases are enhanced with the addition of copper ion. Fig. 7 presents the results of microcalorimetric experiment performed on two samples containing iron and copper: Fe,CuZSM-5 and Cu,FeZSM-5. Both the differential heats of adsorption and the amounts of chemisorbed N_2O and CO become higher when Cu ions are added on FeZSM-5 zeolite (Fig. 7 and Table 2). Moreover, it is important to notice that the addition of Fe ions on CuZSM-5 (Fe,CuZSM-5 sample) has as a consequence a decrease of differential heats values, and a decrease of chemisorbed amounts of both gases, as well. This result can be interpreted with a possible presence of multinuclear iron clusters, which might be steric hindrance for the adsorption of both gases. The appearance of multinuclear iron clusters is indicated by the result obtained from diffuse reflectance UV–vis spectroscopy [64] (the appearance of sub-band above 400 nm).

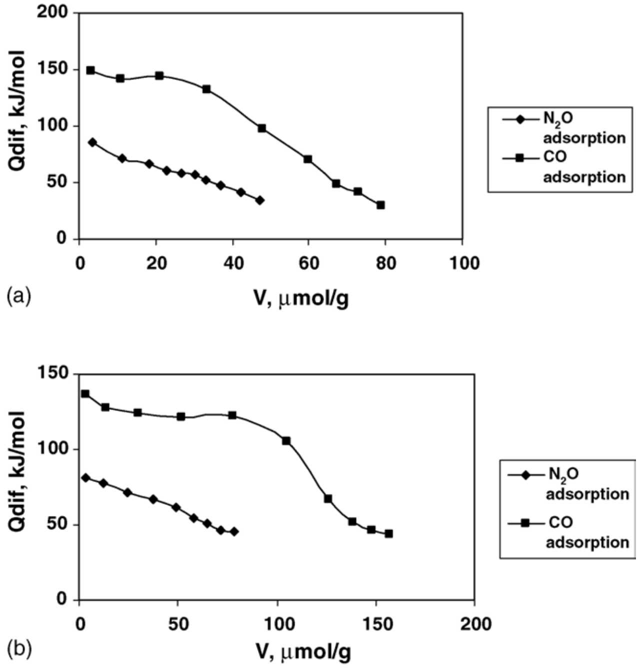

Fig. 7. Differential heats vs. gas uptake, obtained for N_2O or CO adsorption at 303 K on: (a) Fe,CuZSM-5 and (b) Cu,FeZSM-5.

The effect of copper addition on FeZSM-5 and CoZSM-5 was proven by IR spectroscopy. Fig. 8 shows IR spectra collected from Cu,FeZSM-5. In what follows, the design of experiment is explained: N_2O was admitted (300 Pa) to Cu,FeZSM-5 pellet, IR spectrum was collected, then, the pellet was evacuated for 30 min. Spectrum a presented in Fig. 8 shows the result of N_2O admission. In the 2200–2300 cm^{-1} spectral region, two overlapped bands with the peaks at 2215 and 2233 cm^{-1} and a low intensity peak at 2294 cm^{-1} were noticed. A shoulder at 1328 cm^{-1} is also found as a result of N_2O admission. After the evacuation of 30 min, two bands which can originate from a weak N_2O interaction with zeolite framework (2215 and 2233 cm^{-1}) disappeared, while the band at 2294 cm^{-1} remained stable (spectrum b), proving the strong N-down interaction of N_2O with copper cation. When CO was admitted over this strongly bonded N_2O, it was expelled and only the bands typical for CO interaction with a zeolite were collected (spectrum c). A band at 2158 cm^{-1} remained stable after 30 min of evacuation (spectrum d) what is in accordance with the result obtained from microcalorimetry: one part of CO was chemisorbed on Cu,FeZSM-5. It is worth noticing again the importance of copper ion addition over FeZSM-5: as was previously mentioned this can be assigned to monocarbonyls adsorbed on CuZSM-5. All results concerning this sample are quite different in comparison with those obtained for FeZSM-5, indicating the importance of copper ion presence in the bimetallic form of ZSM-5. Fig. 9 shows the results of IR experiment performed on Cu,CoZSM-5. Here, only a weak interaction of N_2O with the investigated sample was found: a

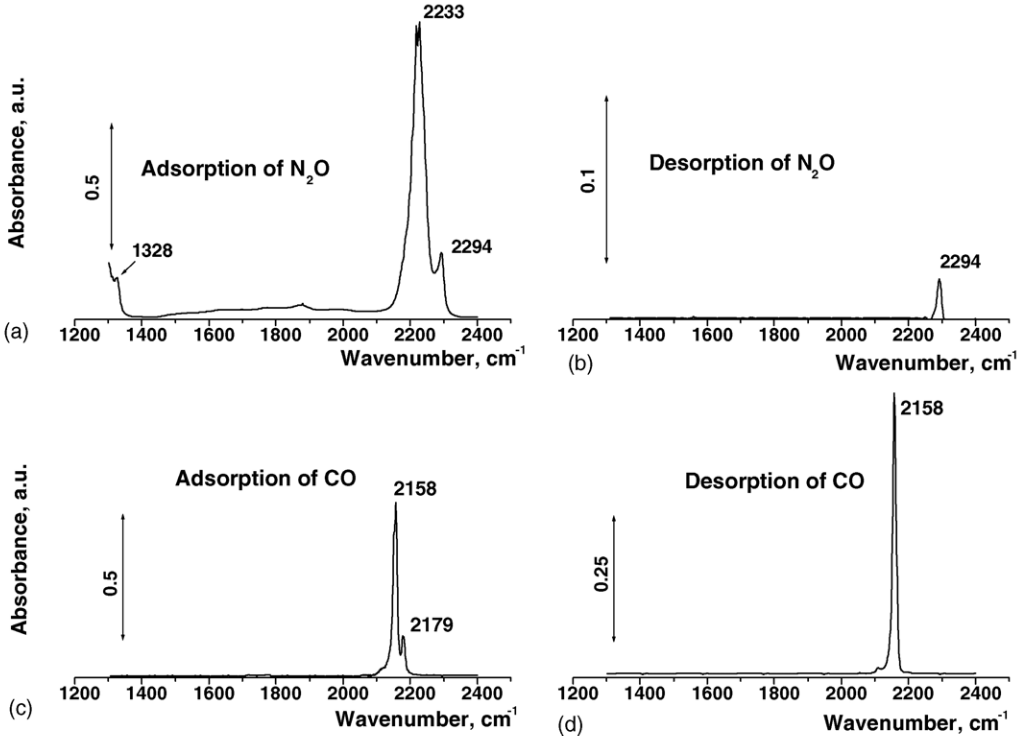

Fig. 8. FTIR spectra collected for the adsorption on Cu,FeZSM-5. N_2O was admitted (spectrum a), subsequently, the cell was evacuated during 30 min (spectrum b). CO was adsorbed over chemisorbed N_2O (spectrum c) and the sample was evacuated during 30 min (spectrum d).

spectrum collected after N_2O admission has one peak in a 2200–2300 cm^{-1} spectral region (2225 cm^{-1}, spectrum a) which disappears with a short evacuation. However, when CO is admitted over this physisorbed N_2O, a band at 2159 cm^{-1} remained stable upon 30 min long evacuation (spectra b and c), indicating again the influence of copper ion on the possibility of this bimetallic sample to adsorb CO.

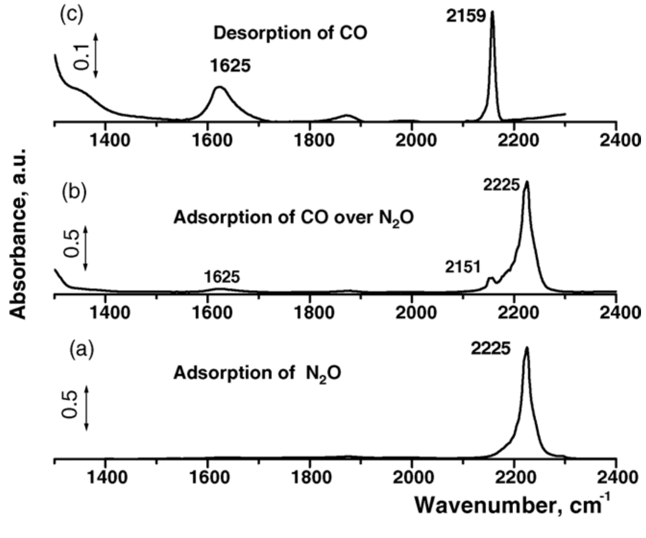

Fig. 9. (a–c) FTIR spectra collected for the adsorption on Cu,CoZSM-5. N_2O was admitted, CO was adsorbed over N_2O, without evacuation. Subsequently, the evacuation was performed 30 min.

4. Conclusions

In this work, the properties of Cu-, Fe- and Co-under-exchanged ZSM-5 samples toward N_2O and CO adsorptions are investigated. It is shown that both N_2O and CO can be chemisorbed on the investigated samples. CuZSM-5 exhibited higher differential heats of carbon monoxide in comparison with nitrous oxide adsorption. A reaction between pre-adsorbed N_2O and CO from the gas phase happened on CuZSM-5 as a result of competitive adsorption, and it was proven by microcalorimetric and FTIR experiments. In the case of FeZSM-5 and CoZSM-5 zeolites, similar thermal effects were detected for the adsorption of both gases. Initial differential heats of N_2O adsorption, which are indicative for the interaction with the strongest sites in the investigated systems are similar for all investigated samples ($\sim$70 kJ/mol), while in the case of CO adsorption these values are: 125, 58 and 80 kJ/mol for CuZSM-5, FeZSM-5 and CoZSM-5, respectively. The amounts of chemisorbed gases are higher for copper-containing ZSM-5 then for iron and cobalt containing samples. The addition of copper ion in FeZSM-5 and CoZSM-5 causes the increase of differential heats of N_2O and CO adsorption, as well as the increase of the adsorbed amounts of both gases.

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