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Quantitative IR studies of the concentration of different nickel sites in NiZSM-5 zeolites

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A B S T R A C T

Quantitative IR studies were realized in order to determine the concentration of Ni^{2+} and Ni^{+} in two zeolites NiZSM-5 differing in Si/Al and nickel content. The NiZSM-5 zeolite of Si/Al = 11.5 contained most of Ni^{2+} in exchange positions whereas another one, of Si/Al = 40 contained most of Ni^{2+} in the form of oxides. Also the Ni^{+} ions in NiZSM-5 reduced by CO were investigated. The experimental procedure of quantitative studies was elaborated and the condition of stoichiometric reaction between probe molecule (CO or NO) and sorption site (Ni^{2+} or Ni^{+}) was fulfilled: each CO or NO molecule introduced into the IR cell reacted with one Ni^{2+} forming $Ni^{2+}(CO)$ or $Ni^{2+}(NO)$ adducts. The procedure was also elaborated for quantitative studies of concentration of Ni^{+} in zeolite reduced. The absorption coefficients of IR bands of $Ni^{2+}(CO)$, $Ni^{2+}(NO)$ and $Ni^{+}(CO)$ at 2212, 1898, and 2109 cm^{-1}, respectively were determined, and finally the concentrations of Ni^{2+} and Ni^{+} were calculated. In the zeolite of Si/Al = 11.5 the concentration of Ni^{2+} in exchange positions determined by our IR studies was nearly the same as that determined by chemical analysis. The values of the absorption coefficients turned out to be independent on the probe molecule (CO or NO). In the zeolite of Si/Al = 40, containing the most of Ni^{2+} in the form of oxides, the concentration of Ni^{2+} found by IR was 66% of concentration of Ni determined by chemical analysis demonstrating that dispersion of Ni^{2+} was low and some of Ni^{2+} was hidden inside oxide clusters being inaccessible to probe molecules. In reduced NiZSM-5 of Si/Al = 11.5 and 40 the concentration of Ni^{+} determined by IR studies was nearly the same as concentration of Ni determined by chemical analysis. In NiZSM-5 of Si/Al = 40 the dispersion of Ni increased distinctly upon the reduction, and all Ni^{+} cations became accessible to probe molecules or reactants.

1. Introduction

Among many materials showing promising activity in selective catalytic reduction of NOx with hydrocarbons (HC-SCR), metal exchanged ZSM-5 zeolites remain still the most interesting catalysts. In this context zeolite CuZSM-5 is reported as potential catalyst for HC-SCR [1,2]. It works with alkenes and alkanes (C3+), however, it loses its activity in the presence of water. Therefore, many efforts are concentrated on Fe [3], Co [4,5], and Ni [6,7] cations hosted in ZSM-5 zeolite as they are highly active, even in the presence of large H_2O amounts. The excellent properties of transitions metal ions (TMI) in HC-SCR consequences in a high number of accessible coordinative vacancies; therefore they are able to coordinate various reactant molecules.

One of the most useful methods of characterization of TMI in zeolites is IR study with the use of probe molecules such as carbon monoxide or nitrogen monoxide.

The present research concerns the Ni^{2+} and Ni^{+} hosted in zeolites followed with CO and NO as probe molecules. Many studies of CO adsorption on different nickel containing systems have been done. As reported in the literature, the ligation of carbon monoxide to Ni^{2+} cations, consequences in the appearance of the IR bands of $Ni^{2+}(CO)$ monocarbonyls in two spectral regions: 2220–2180 cm^{-1} [8–11] and 2170–2130 cm^{-1} [12,13]. The latter ones are formed at low temperatures with bulk nickel compounds, e.g. NiO and mixed oxides [12,13]. Dicarbonyl adducts of nickel(II), characterized by low stability, are created at cryogenic temperatures (ca.100 K).

Another very useful probe molecule for the investigation of TMI properties is nitrogen monoxide. The NO stretching frequency in the both mono and dinitrosyls of Ni^{2+} are observed in the region 1890–1810 cm^{-1} [14–23]. These frequencies are close to the frequency of gaseous NO (1876 cm^{-1}), hence the weakening of N=O bond in the both type nitrosyl complexes is only slightly influenced by π-backdonation.

The previous IR studies provided only qualitative data. Information on the amount of Ni^{2+} and Ni^{+} usually obtained by comparing the intensities of Ni^{2+}–CO and Ni^{+}–CO bands provided semi-quantitative data only, because the absolute values of concentration of Ni sites have not been available.

The aim of the present work was to estimate the absolute values of the concentrations of Ni^{2+} and Ni^{+} cations in quantitative IR

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experiments. The main step of our study was to elaborate the experimental conditions in which used probe molecules (carbon monoxide or nitrogen monoxide), interacted selectively with each type of Ni sites. The values of absorption coefficients of Ni^{2+}–CO and Ni^{+}–CO bands, as well as of Ni^{2+}–NO band were determined. Subsequently, the concentration of Ni^{2+} both in the exchange positions and in the oxo-forms as well as the concentration of Ni^{+} ions were calculated and compared with the amount of Ni determined by chemical analysis.

Two zeolites of different aluminum content have been studied: NiZSM-5 (Si/Al = 11.55 and Ni/Al = 0.22) hosting Ni^{2+} cations mostly in the exchange positions and NiZSM-5 (Si/Al = 40, Ni/Al = 0.43) where the Ni^{2+} cations were mostly in the form of oxides.

2. Experimental

The NiZSM-5 samples were obtained by the standard ion exchange procedure from the parent ammonium forms (Si/Al = 11.5 and 40, Zeolyst, Inc.). The mixture of 100 cm^3 0.2 M $Ni(NO_3)_2$ and 1.5 g zeolite was stirred for 24 h at 340 K. After the ion exchange procedure samples were washed with water and dried at 373 K. The NiZSM-5/11.5/0.22 and NiZSM-5/40/0.43 samples were characterized by ICP method, revealing Ni/Al = 0.22 and Ni/Al = 0.43, respectively. The composition of these zeolites denoted as NiZSM-5/11.5/0.22 and NiZSM-5/40/0.43 can be represented by following formula: $Ni_{1.7}(NH_4)_{4.3}[(SiO_2)_{88.3}(AlO_2)_{7.7}]$ and $Ni_{1.0}(NH_4)_{0.3}[(SiO_2)_{93.6}(AlO_2)_{2.4}]$, respectively.

Prior to IR studies both zeolites were pressed into thin wafers and activated in vacuum in the quartz cell. First, sample was evacuated at ambient temperature for 10 min, and then temperature was elevated to 820 K and kept for 1 h.

Carbon monoxide (Linde Gas Polska 99.95%), and nitrogen monoxide (Linde Gas Polska 99.5%), were used as adsorbates. Before adsorption nitrogen monoxide was purified by the freeze–pump–thaw technique. Carbon monoxide was used without previous purification.

The reduction of Ni^{2+} species in NiZSM-5/11.5/0.22 and NiZSM-5/40/0.43 was performed at 650 K for in CO atmosphere (60 Trr in gas phase) for 1 h.

IR spectra were recorded with a Bruker Tensor 27 FTIR spectrometer equipped with an MCT detector, the spectral resolution was 2 cm^{-1}.

3. Results and discussion

3.1. Interaction of CO with Ni^{2+} and Ni^{+}

3.1.1. Assignment of $Ni^{2+}(CO)$ and $Ni^{+}(CO)$ bands

The spectra of CO sorbed in NiZSM-5/11.5/0.22 and NiZSM-5/40/0.43 zeolites up to saturation of all the cationic sites (the maximum intensities bands in the spectral region 2220–2180 cm^{-1}) are presented in Fig. 1. Sorption of CO at room temperature (spectrum a) results in the ligation of CO to Ni^{2+} in cationic exchange positions in NiZSM-5/11.5/0.22, which is manifested by the appearance of the complex band at 2212 cm^{-1} of the $Ni^{2+}(CO)$ monocarbonyls. This band shows a submaximum at 2220 cm^{-1} which is better seen in the spectrum of CO sorbed in NiZSM-5/11.5/0.22 at 170 K (Fig. 1 spectrum b) and also in the difference spectrum (spectrum c). The presence of two $Ni^{2+}(CO)$ bands (2212 and 2220 cm^{-1}) points to the occurrence of two Ni^{2+} sites differing in electron acceptor properties, however the less electron accepting cations (CO band at 2212 cm^{-1}) are much more populated. Many authors [8–13] offered the same interpretation of the bands around 2220 and 2212 cm^{-1} developed upon CO sorption in Ni-containing zeolites.

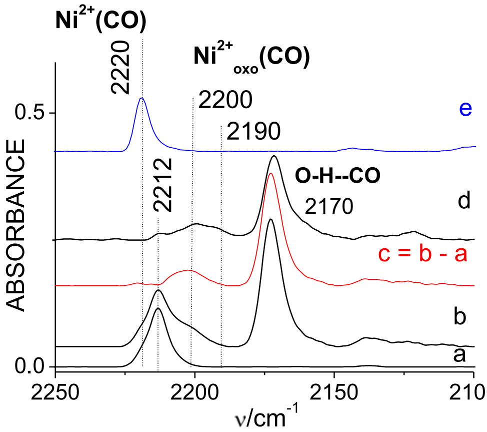

Fig. 1. IR spectra of CO sorbed in zeolites: (a) NiZSM-5/11.5/0.22 at room temperature (b) NiZSM-5/11.5/0.22 at 170 K (c) difference spectrum c = b – a (d) NiZSM-5/40/0.43 at 170 K (e) zeolite NiY at room temperature.

Additionally, the 2172 cm^{-1} band of CO interacting with Si–OH–Al (B–CO) can be distinguished in the spectrum of CO sorbed in NiZSM-5/11.5/0.22 at low temperature (170 K) – Fig. 1, spectrum b.

Low temperature sorption of CO in NiZSM-5/11.5/0.22 reveals also the existence of the additional band at ca. 2200 cm^{-1} which may be ascribed to CO bonded to Ni^{2+} in the oxo-forms (Fig. 1 spectra b and c). The lower frequency of the monocarbonyl band $Ni^{2+}_{oxo}(CO)$ in comparison to the band of CO bonded to Ni^{2+} in exchange positions point out less electron accepting properties of Ni^{2+} in the oxo-forms due to the partial neutralization of positive charge of Ni^{2+} by framework oxygens. Similar situation was already observed for Co^{2+} hosted in CoZSM-5: the frequency of the band of CO bonded to Co^{2+} both in the oxo-forms and in bulk CoO was lower than Co^{2+} in exchange positions (2179–2195 and 2206–2210 cm^{-1}, respectively) [25].

In NiZSM-5/40/0.43 zeolite of lower aluminium content (Si/Al = 40), the isolated Ni^{2+} in cationic exchange positions are present in negligible amount (small CO band at 2212 cm^{-1}) and main Ni^{2+} species are in the oxo-forms – Fig. 1, spectrum d. These oxo-forms are believed to originate from hydrolysis: $Ni^{2+} + H_2O = NiOH^{+} + H^{+}$. The condensation of $NiOH^{+}$ species leads to the formation of the oxo-forms. Such hydrolysis takes place upon activation of TMI-zeolites at elevated temperatures and it is governed by the density of AlO_4^{-} tetrahedra. In zeolite NiZSM-5/11.5/0.22 high density of AlO_4^{-} stabilizes the divalent Ni^{2+} cations, whereas in zeolite NiZSM-5/40/0.43 large distances between AlO_4^{-} favour the splitting of a "double-positive" charge of Ni^{2+} into two "mono-positive" charges of H^{+} and $NiOH^{+}$. Hence, in highly siliceous zeolites most of the AlO_4^{-} is neutralized by protons and nickel takes form of an oxides.

The difference in the temperature of binding CO between Ni^{2+} in exchange positions (CO bonded at RT) and Ni^{2+} in the oxo-forms (CO bonded at 170 K) points also to the differences in the strength of CO interaction with the respective adsorption sites: CO is more strongly bonded to Ni^{2+} in the exchange positions than to Ni^{2+} in oxo-forms. Similar situation was already observed for Co^{2+} [24,25].

Interaction of CO with Ni^{2+} hosted in zeolite NiY results only in the formation of the band of $Ni^{2+}(CO)$ adducts at 2220 cm^{-1} (Fig. 1, spectrum e). Higher frequency of $Ni^{2+}(CO)$ band in NiY in comparison to NiZSM-5 points to stronger electron acceptor properties of Ni^{2+} cations in NiY than in NiZSM-5. Therefore not only the electrical charge of framework oxygens, but mainly the geometry of environment of Ni^{2+} site is supposed to affect the extend of neutralization of cation by framework oxygens.