THE INVESTIGATION OF STRONG ACTIVE SITES OF DEALUMINATED Y-TYPE ZEOLITE BY TPD OF CARBON MONOXIDE

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Abstract

The active sites of hydrogen-exchanged Y zeolite (HY) and dealuminated (HDY) zeolites are investigated by TPD of carbon monoxide. Only the high temperature TPD spectra of CO ($T_M \approx 620$–690°C) were observed, meaning that CO molecules interact with very strong acid sites. The amounts of CO bonded on these sites are small (less than 1 molecule per unit cell). The strong influence of dealumination on the coverage degree is found. The calculated values for kinetic parameters indicate chemisorption of CO in the investigated systems ($E_{des} \approx 240$ kJ mol^{-1}, $A \approx 10^{11}$ s^{-1}).

Keywords: CO, dealuminated Y zeolite, TPD

Introduction

Zeolites are known to be important catalysts for a number of industrially important reactions. The applicability of these materials as catalysts requires a detailed characterisation of the active sites, including their nature, number, strength and strength distribution. A question of basic interest is to determine the correlation between these properties and the promotion of catalytic activity. Therefore, the investigation of very strong acid sites, both Lewis and Brønsted type, is very important subject.

Adsorption of bases, investigated by IR and NMR spectroscopies [1, 2] as well as temperature programmed desorption (TPD) [3, 4] or microcalorimetry (MC) [5–7], is established method for the characterisation of zeolitic acidity. Some adsorbates such as ammonia and pyridine, being strong bases, have become conventional probe molecules to study the surface acidity. Besides, carbon monoxide meets many criteria that have promoted its extensive use as a surface probe for the study of Lewis as well as Brønsted sites particularly by IR and NMR spectroscopy [1, 8, 9].

We reported in the previous papers that CO could be suitable probe for the TPD and MC investigations of Lewis acid sites. Very strong Lewis acid sites were identified and characterised on the transition-metal ion-exchanged FAU and MOR type zeolites [10–12].

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The Brønsted acidity of Y-type zeolites is a subject of permanent interest, owing to the important role of these zeolites in the catalytic behaviour of cracking (FCC) catalysts [2]. The heterogeneity of their Brønsted acid sites is well known and widely investigated [13–15]. Besides, it is known that the dealumination of Y zeolite may influence its acidic characteristics [15, 16].

Of fundamental interest is to identify and characterise very strong Brønsted acid sites in HY and dealuminated HY zeolites. The objective of this contribution is the study of carbon monoxide interaction with dealuminated HY zeolites. TPD investigation is performed in order to obtain a new insight concerning very strong Brønsted acid sites. Also, kinetic parameters (activation energy and pre-exponential factor) for desorption of CO are calculated and compared with those obtained for CO desorption from transition-metal ion-exchanged FAU-type zeolites.

Experimental

The samples were prepared from SK-40, $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$ (Union Carbide). The dealumination procedure was performed following the procedure described in [17]. Either Na_2H_2EDTA or H_4EDTA were added directly to slurry of initial NaY zeolite in water and stirred at 90°C. The concentration of dealumination agent and the contact time were varied. Thereafter, the samples were washed with distilled water, dried and ion-exchanged with 10% NH_4Cl. The samples treated with Na_2H_2EDTA are denoted as HDY-a while the samples treated with H_4EDTA are denoted as HDY-b.

The samples were activated at 520°C under the helium flow for 4 h and then cooled to 25°C in the same atmosphere. The adsorption was performed from the mixture of 10% CO in He until the saturation of the sample and during additional 30 min. Subsequently, the sample was purged with He until the constant base line value for CO signal was reached, then the desorption was started. He and CO (99.995% purity) were supplied by L'Air Liquide, both gases were admitted at a constant flow rate (30 mL min^{-1}).

The experimental setup for the TPD measurements has been described in detail elsewhere [10]. The equipment consists of a flow measuring and switching system, a cylindrical furnace in which the sample is placed, and the analysis system: on line mass spectrometer Sensorlab 200D-VG Quadrupoles, connected with the outlet of the TPD cell via a heated silica capillary tube 2 m length with a fast response at 1 atmosphere sampling pressure. In all TPD experiments the heating rate was 20°C min^{-1} and the same masses of the samples (0.15 g) were employed. The masses 28 (CO) and 44 (CO_2) were recorded.

Temperature programmed heating procedure was also done, without previous activation of the samples. In that case, the masses corresponding to NH_3 (m/e=15) and H_2O (m/e=18) were monitored. The MAS signals were properly calibrated using dilute gas streams of known concentrations (0.5% CO in He, 1% CO_2 in He and 0.5% NH_3 in He) except the signal for m/e=18, which one is presented in arbitrary units. The area difference between the CO responses in the detector obtained when the gas is passed through the sample and that one obtained when CO passes through the empty reactor pro-

vides the true adsorbed amount of CO at given temperature. The integration of the area under TPD profile provides the amount of CO evolved during desorption.

Kinetic parameters – activation energy for desorption (E_{des}) and pre-exponential factor (A) were calculated using well-known equation that presents the thermodesorption as a first-order non-associative process:

$$\frac{d\Theta}{dT} = f(\Theta) \frac{A}{\beta} \exp\left(-\frac{E_{des}}{RT}\right)$$

(1)

where $f(\Theta)$ is a function of surface coverage (Θ). In the case of first-order reaction, $f(\Theta)=\Theta$. After the rearrangement of Eq. (1) a linear relationship:

$$\ln\left[\frac{d\Theta/dT}{\Theta}\right] = \ln\frac{A}{\beta} - \frac{E_{des}}{RT}$$

(2)

is obtained. Evidently, E_{des} can be obtained from the slope of a straight line.

Results and discussion

Figure 1 presents the profiles of CO desorption spectra obtained in TPD experiments, for HY and dealuminated HDY samples. Only the high-temperature desorption peaks of CO were found ($T_M \approx 620–690°C$).

The high-temperature desorption of CO molecules indicate their interaction with some very strong acid sites. As it can be seen from Fig. 1, the temperature of maximum are only slightly changed with the dealumination.

However, quantitative analysis of TPD results presented here indicate that dealuminated samples possess different amounts of these very strong active sites, in comparison with the parent HY zeolite. The amounts of CO adsorbed at room temperature and the amounts desorbed during TPD procedure are done in Table 1. De-
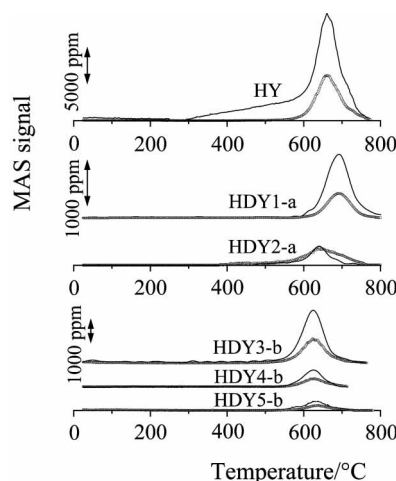

Fig. 1 TPD signals of — – CO and ∘∘∘ – CO_2 obtained from HY and HDY

tailed insight in these values reveal that low surface coverage of adsorbed CO was achieved. The amounts of CO preadsorbed at room temperature are higher than the amounts desorbed during TPD, for all investigated samples. Obviously, weakly bonded CO was desorbed from the surface by the inert gas flow, at 25°C, before the start of TPD procedure. By contrast, strongly bonded molecules were desorbed during TPD in the high-temperature region. In addition, it is important to notice that in HY sample the amount of strongly bonded CO (5.3 molecules per unit cell) is much higher than for dealuminated samples (<1 molecule per unit cell). Evidently, one part of very strong active sites is removed from the zeolite as a result of dealumination.

Table 1 The quantitative amounts of gases obtained from the adsorption/desorption experiments

Sample	Si/Al	n_1, NH$_3$[a]	n_2, NH$_3$[b]	n_3, CO[c]	n_4, CO[d]
HY	2.4	46	2.7	15.6	5.3
HDY1-a	2.6	37	2.6	2.4	0.5
HDY2-a	2.7	35	1.4	2.0	0.2
HDY3-b	3.1	31	2.3	1.6	0.7
HDY4-b	4.0	25	<1	2.1	0.4
HDY5-b	4.5	22	<1	2.4	0.2

[a]n_1 – number of NH$_3$ molecules desorbed per unit cell in the experiment of temperature programmed heating of NH$_4^+$ forms of zeolites
[b]n_2 – number of NH$_3$ molecules desorbed per unit cell in the high-temperature desorption process
[c]n_3 – number of CO molecules adsorbed per unit cell at 25°C
[d]n_4 – number of CO molecules desorbed per unit cell during TPD procedure

The calculated kinetic parameters confirm the interaction with the active sites of similar strength, for all investigated samples. The activation energies and pre-exponential factors calculated for desorption of CO from HY and HDY are presented in Table 2. High values of activation energies and pre-exponential factors for desorption, almost the same for all samples ($E \approx 240$ kJ mol^{-1}, $A \approx 10^{11}$ s^{-1}) point out on the unexpected, strong chemisorption of CO on the investigated systems.

In the previous papers [10–12], the results of TPD, FTIR and MC investigations of CO interactions with transition metal cation-exchanged FAU and MOR type zeolites were presented and discussed in details. It was demonstrated that, at 25°C, carbon monoxide interacted with charge-balancing cations, which act as a source of Lewis acidity. High-temperature TPD peaks of CO have been found and interpreted as the indication of the existence of very strong Lewis acidity.

Here, the kinetic parameters for CO desorption from transition-metal cation-exchanged FAU and MOR type zeolites are evolved from previously reported TPD spectra [10], using Eq. (2). For the sake of comparison, these values are also shown in Table 2. Very high values for activation energies confirm the existence of acid sites strong enough to realise chemisorption with CO molecule.

All previously published results, as well as kinetic parameters given in Table 2, clearly show that CO is very useful probe, particularly in the recognition of very

strong Lewis acid sites. The results presented in this work indicate that CO could be suitable probe in the recognition of very strong acid sites in the case of HY and HDY zeolites, too. However, additional experimental evidences are necessary, in order to obtain the information about the nature of these active sites.

Table 2 Kinetic parameters obtained for HY, HDY and transition-metal ion-exchanged zeolites

Sample	E_{des}/kJ mol^{-1}	A/s^{-1}
HY	242	$6.7 \cdot 10^{11}$
HDY1-a	266	$4.4 \cdot 10^{12}$
HDY2-a	237	$8.8 \cdot 10^{11}$
HDY3-b	232	$4.2 \cdot 10^{11}$
HDY4-b	224	$1.6 \cdot 10^{11}$
HDY5-b	225	$2.6 \cdot 10^{11}$
NiX	296	$3 \cdot 10^{16}$
NiM	180	$7 \cdot 10^{8}$
	232	$8 \cdot 10^{10}$

For that purpose, mass spectrometric signals of ammonia were recorded during temperature programmed heating of NH_4^+ forms of all investigated Y zeolites. In that way, TPD spectra of ammonia were monitored in the course of deammoniation process. The results are presented in Fig. 2. Quantitative amounts of NH_3 evolved as a result of temperature programmed heating up to 800°C are presented in Table 1. In the same time, the signals for water (m/e=18) were monitored. As a typical one, a spectrum of water desorption obtained for HY zeolite is shown in Fig. 2, also.
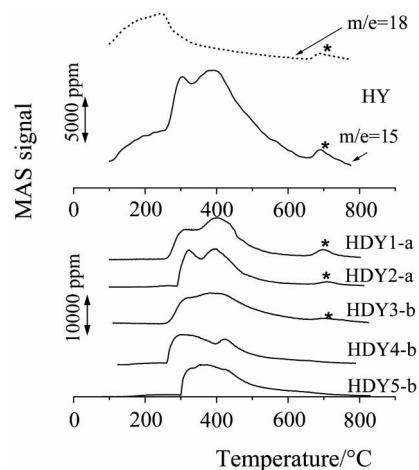

Fig. 2 TPD signals for ammonia (m/e=15) and water (m/e=18) obtained during the temperature programmed heating of NH_4^+ forms of zeolites

All TPD profiles of ammonia presented in Fig. 2 are complex, consisting of at least four overlapped peaks, what is a clear indication of energetic heterogeneity of investigated samples. TPD spectrum of ammonia obtained for parent NH_4Y zeolite is very similar to already reported [3]. However, in the present study, a high-temperature TPD peak ($T_M \approx 700°C$) is noticed. It was not noticed before because the ammonia was monitored as $m/e=17$, what is the mutual signal for NH_3 and H_2O.

It is worth noticing that, although only slight dealumination degrees were achieved, the dealumination caused the changes in TPD spectra of ammonia. The desorption starts at higher temperature and the amounts of desorbed NH_3 become lower, for dealuminated samples (Fig. 2 and Table 1). However, the high-temperature desorption process of ammonia around 700°C was found for dealuminated samples, also, and it could be clearly assigned to the desorption from the strongest acid sites. In order to estimate quantitatively the population of these strongest sites, the deconvolution of TPD spectra was performed. PeakFit 4 software was used for deconvolution, with Gaussian line shapes chosen for fitting. The results are presented in Table 1. The analysis of the results presented in Fig. 2 and Table 1 shows that the population of the strongest acid sites is diminished with the increasing dealumination degree. Obviously, the number of ammonia molecules desorbed in the high-temperature desorption process is similar to the number of CO molecules adsorbed on the corresponding samples.

It is worth noticing that the position of high-temperature desorption peak of NH_3 is the same as the position of the dehydroxylation peak ($m/e=18$, Fig. 2). Two parallel desorption processes: dehydroxylation and deammoniation take part from the strongest acid sites. The high-temperature desorption process of mass 18 has been noticed in the case of HY and HDY zeolites, and it has been assigned to the dehydroxylation [3]. IR spectroscopy of adsorbed pyridine has shown that the number of Brønsted acid sites is diminishing with the process of dehydroxylation [18]. In addition, it has been shown that the amount of the strongest Brønsted acid sites is lower at higher dealumination degrees [18].

As already mentioned, the activation of the samples investigated in this work was performed at 520°C. Evidently, the deammoniation process is not completed during the process of activation. From the results presented so far, it could be inferred that, in the case of systems investigated in this work, CO was adsorbed on the zeolites partially covered with ammonia, bonded on the strongest Brønsted acid sites.

It has been already reported that disproportionation of CO occurs when it was admitted to transition-cation-exchanged Y and X zeolites [10]. It was shown that, during the adsorption at 25°C from the gas flow, this reaction takes place as a result of CO adsorption on Lewis acid sites. Therefore, it was interesting to check whether this reaction happened in case of CO adsorption on HY and HDY zeolites. For that purpose, the signal of CO_2 was monitored in the course of temperature programmed desorption of CO. TPD signals of CO are followed by lower intensity CO_2 signals, for all investigated samples.

The appearance of CO_2 signals in TPD spectra is the indication of disproportionation or oxidation of CO. Both CO and CO_2 are desorbed in the same high-temperature region in which the dehydroxylation and deammoniation were found. Evidently, CO adsorption (done at 25°C from the flow) leads to the catalytic reaction.

Conclusions

It is noticeable from the results presented in this work that, in the case of HY and HDY zeolites, very strong acid sites could be recognised using TPD of carbon monoxide. Importantly, it is shown that, after the activation of NH_4^+ forms of Y zeolite at 520°C, one part of Brønsted acid sites is still covered with ammonia. At 25°C, specific interaction of CO with these strongest acid sites was realised, as a result, low surface coverage of adsorbed CO molecules was achieved. The influence of dealumination on the population of the strongest sites was recognised. The presented results suggest that a complex interaction of CO with zeolite acid sites could be expected, in the investigated systems.

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