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The influence of the initial acidity of HFER on the status of Co species and catalytic performance of CoFER and InCoFER in CH_4-SCR-NO

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Abstract

The role of the initial acidity of ferrierite type zeolite on the status of cobalt and the catalytic activity of CoFER and InCoFER was investigated. Two FER zeolites were used: NH_4FER without any pretreatment (FER-1) and the same zeolite, dehydroxylated at 825 K (FER-2). Dehydroxylation removed most of the Si–OH–Al groups, therefore the resulting zeolite revealed practically no ion exchange capacity. The status of cobalt was followed by IR spectroscopy with probe molecules: CO (a probe for Co^{2+}) and NO (a probe for Co^{3+}). The introduction of cobalt by solid-state ion exchange produced divalent cobalt in exchange positions and in the form of oxide-like clusters, their respective concentration was determined by quantitative IR experiments of CO sorption. The amount of Co^{3+}, present in CoFER-1 and InCoFER-1, was also determined. All these forms of cobalt were practically absent from CoFER-2 and InCoFER-2. The NO conversion and selectivity to N_2 of CoFER-2 in CH_4-SCR-NO was poor, indicating the essential role of the initial acidity of the ferrierite matrix on the formation of catalytically active Co species. The introduction of indium into CoFER only slightly increased the NO conversion and shifted the reaction path from NO_2 towards N_2 formation for FER-1, while greatly improved the catalytic performance of the FER-2 series.

Keywords: Acidity; Cobalt species; CoFER; CH_4-SCR-NO

1. Introduction

Cobalt-containing zeolites have gathered a lot of attention since the discovery of Li and Armor [1] that over those zeolites the process of CH_4-SCR can be performed. For many years Co^{2+} bare ions have been supposed to play the key role in SCR, recently however, the new findings of Montanari et al. [2] and Čapek et al. [3] shifted the attention towards altervalent states of cobalt, i.e. Co^{3+} and Co^{2+} present in zeolites in the form of oxide-like clusters. This fact opened again the discussion on the assignment of IR band resulting from the interaction of CO and NO, probes and partakers of the SCR, with the specific cobalt sites.

Especially the assignment of the band at 1939 cm^{-1}, arising after NO admission, has been for a long time the matter of discussion, its attribution to weakly bonded Co^{2+}–NO mononitrosyls was based on the works of Lunsford and co-workers [4,5] and later supported by other groups [6,7]. Hadjiivanov et al. [8] presented the evidence that all the bands in the 1935–1955 cm^{-1} region should be credited to Co^{3+}–NO complexes. There is a general agreement, supported by data from other than FTIR techniques [9,10] that 2204–2208 cm^{-1} band is characteristic of CO sitting at the low-coordinated Co^{2+} cations in exchange positions. The assignment of 2184–2186 and 2194–2196 cm^{-1} bands is more complicated. On the basis of CO sorption on cobalt supported on silica [11] these bands were attributed to Co^{2+} sitting at the internal defects of the lattice [6] or even CO–Co_3O_4 or CO–$CoAl_2O_4$ [12,13] and for zeolites to oxide-like clusters [14]. In addition, the problem of location of oxide-like species, containing Co on different valence states, was recently addressed and not yet resolved [15].

The aim of this work is to characterize the immediate influence of the initial acidity of the zeolite matrix on the final form of cobalt species and thus the catalytic performance of the

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resulting HC-SCR catalyst. Two samples of CoFER, and consecutively also two samples of InCoFER, were prepared from one parent zeolite by the same procedure of contact-induced ion exchange. Different pre-treatment conditions ensured, before cobalt introduction, the preservation of its full acidity for the first sample, and for the second one its total destruction. Such pre-treatment combined with the manner the cobalt was introduced (solid-state exchange), should direct cobalt towards exchangeable or other positions in the zeolite.

The introduction of indium into the zeolites is known to improve the stability of catalysts against water vapour, and some improvement of catalytic properties was observed in our case. The properties of indium centres will not be discussed here, as our data seem to agree with the results already published by other authors [16,17].

2. Experimental

The parent NH_4FER (Si/Al = 9.2) from Tosoh Inc., Japan was transformed into cobalt form from acetate, using contact-induced ion exchange in the helium flow at 825 K for 2 h. The first sample (CoFER-1) was transformed into CoFER directly from the NH_4FER, whereas the second one (CoFER-2) was calcined at 825 K for 16 h prior to incorporation of cobalt. Subsequently, both cobalt-containing samples were transformed into InCo-forms, by contact-induced ion exchange with In_2O_3 in the helium flow at 825 K for 2 h and H_2 flow for 8 h. The amount of cobalt determined by AAS (PerkinElmer) was 4% for both FER, which correspond to Co/Al = 0.45 (mol/mol). The crystallinity of the hydrated zeolites was determined by powder X-ray diffraction patterns (XRD), measured using a Siemens D5005 automatic diffractometer with Cu Kα radiation. Silicon powder was used as the internal standard. ^{27}Al MAS NMR spectra were acquired on a home-made pulse NMR spectrometer at the magnetic field of 7.05 T, using a Bruker HP-WB high-speed MAS probe with the 4 mm zirconia rotor. Status of the cobalt sites was investigated by adsorption of CO and NO (Linde Gas, Polska 99.9%) followed by FTIR spectroscopy. For IR all samples were activated in a form of self-supporting wafers (ca. 5 mg/cm^2) at 825 K under vacuum for 1 h. CO was adsorbed at 175 K and NO at ambient temperature. Spectra were recorded on a Bruker Equinox 55 spectrometer with a resolution of 2 cm^{-1} and an MCT detector. The catalytic tests were performed in a continuous flow, fixed bed reactor at atmospheric pressure. The standard reaction conditions were: NO = 1000 ppm, CH_4 = 2000 ppm, O_2 = 4%, H_2O = 2500 ppm in He, GHSV = 10 000 h^{-1}. For tests 0.2–0.5 mm fraction was used. All the catalytic data are related to steady-state conditions, which were established usually after 2 h time-on-stream.

3. Results and discussion

The integrity of the sample after prolonged calcination was carefully checked as there was extremely important not to damage the crystallinity and the channel system of FER zeolite and only eliminate its acidity. Diffractogram of the parent ferrierite sample (ammonium form) exhibited good crystallinity and characteristic diffraction lines were consistent with the reported data for FER [18]. No important changes were observed after prolonged calcination thus allowing a conclusion that the crystalline structure of the sample was indeed preserved. The status of aluminium in ferrierite before and after prolonged calcination was followed by ^{27}Al MAS NMR on the re-hydrated samples. In the spectrum (Fig. 1A, bottom line) a substantial decrease of tetrahedral aluminium sites in HFER-2 (dehydroxylated sample), comparing to NH_4FER could be observed (60 ppm peak decreased by 90%). At the same time, however, peaks of octahedrally (at 0 ppm) or pentahedrally coordinated (30 ppm) aluminium species were absent. Such changes in the NMR spectrum could be explained by the presence of NMR-silent extraframework aluminium, resulting from very strong quadrupole interactions, as showed by Man et al. [19].

IR spectra in the OH region also characterize changes, consistent with these observed in NMR spectra. The amount of bridging Si–OH–Al represented by a band at 3605 cm^{-1} decreased significantly (Fig. 1B) in HFER-2 comparing to HFER-1, the sample resulting from the *in situ* activation of NH_4FER zeolite. At the same instant a broad maximum at 3650 cm^{-1} appeared, characteristic of non-acidic, faulting Al–OH groups, showing that at least a part of the aluminium ions was relocated from the original positions in the framework.

On the basis of all above data it was possible to ascertain that two zeolite matrices were prepared: NH_4FER with preserved acidity (an ammonium form of zeolite will be *in situ* transformed into the acidic form during ion exchange) and almost non-acidic HFER-2. Introduction of cobalt into zeolite in a form of exchange cations requires the presence of available exchangeable positions, present in NH_4FER and absent (the most probably taken by positively charged AlO_x species) in HFER-2. It can be assumed that it would be possible to prepare samples containing different amount of Co^{2+} species at the cationic sites. The fact that Co was introduced by contact-induced ion exchange, ensured firstly that the whole Co will be present in the resulting samples and secondly, reduced the hydrolysis to the absolute minimum. The latter process seem to be very important as it can transform aquacomplexes of cobalt into $[CoOH(H_2O)_5]^+$ which can lead to further hydrolysis and oxides formation [20]. In a case of contact-induced ion exchange, no aquacomplexes are present, although the use of air-stored zeolite and hydrated acetate cannot exclude their formation.

Introduction of cobalt into parent zeolite resulted in a decrease of the OH band for FER-1 sample by ~60% (Fig. 1B), suggesting exchange of acidic protons for cobalt, whereas the ionic exchange did not change the spectrum of OH groups of FER-2 sample implying that cobalt occupied other than exchangeable positions in the resulting catalyst. The status of cobalt was monitored in this study by the sorption of CO (a probe for divalent cobalt in a form of exchange cations and oxide-like clusters) and NO (a probe for trivalent cobalt).

Depending on the sorption temperature, CO interacts with different species inside the zeolite. Room temperature sorption

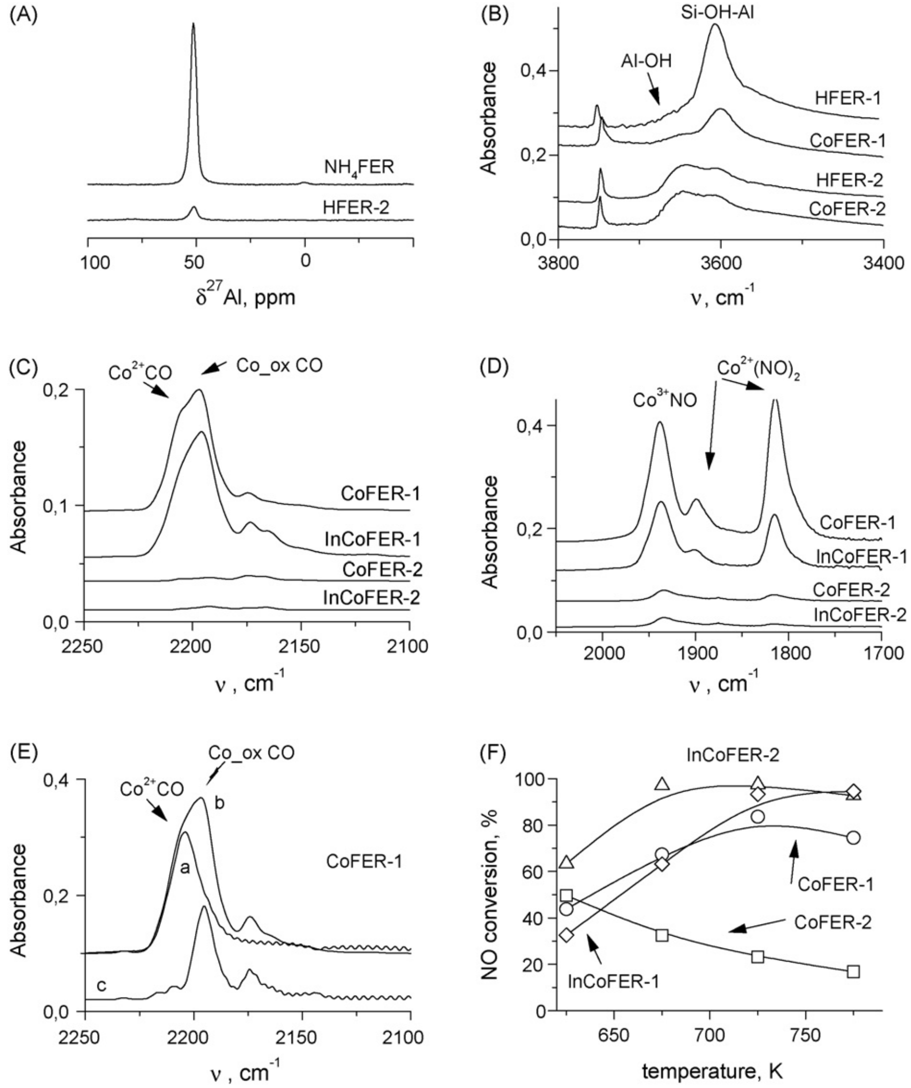

Fig. 1. (A) ^{27}Al MAS NMR spectra of FER; (B) IR spectra of the OH region of activated FER samples; (C) IR spectra of CO excess adsorbed at 170 K in FER; (D) IR spectra of NO excess adsorbed at RT in FER; (E) IR spectra of CO adsorbed in CoFER-1: (a) CO excess at RT, (b) CO sorption at 170 K, (c) difference spectrum (b–a); (F) NO conversion in CH_4-SCR-NO reaction. All IR spectra normalized to 10 mg samples.

results in the appearance of one band only (2207 cm^{-1}) of CO interacting with divalent cobalt in exchange positions (denoted here as Co^{2+}). At 175 K carbon monoxide interacts with the same Co^{2+} (the band at 2207 cm^{-1}), with divalent cobalt in a form of oxide-like clusters (denoted as Co_ox) with IR band at 2197 cm^{-1} and with residual acidic hydroxyls (2174 cm^{-1}) together with non-acidic Al–OH groups (2160 cm^{-1}).

From the analysis of CO spectra, presented in Fig. 1C, it is evident that for CoFER-1 sample cobalt was introduced, in substantial amounts, both in a form of Co^{2+} in the exchangeable positions (2207 cm^{-1}) and in a form of oxide-like clusters (2197 cm^{-1}), contrary to CoFER-2 for which the corresponding IR maxima of adsorbed CO are considerably lower. Therefore, the presence of both types of cobalt requires the availability of exchangeable positions. As it was proposed before [21] Co^{2+} in a form of low-coordinated bare cations can be present in zeolite only when its charge can be neutralized by two, neighbouring AlO_4^- tetrahedra, when these tetrahedra are too distant, the charge must be split between cobalt, this time bearing an additional oxygen, and proton. For CoFER-1 the amount of both types of cobalt was calculated, using intensity of the proper IR bands and their extinction coefficient, determined in our laboratory [22] and equal 0.12 and 0.13 cm^2/μmol for Co^{2+}–CO and Co_ox–CO, respectively. For that purpose, CO was adsorbed firstly at the ambient temperature in excess to ensure that all Co^{2+} were saturated. The maximum intensity is achieved only in the presence of the gas phase, so when the rotational spectrum of gaseous CO is visible, as presented in Fig. 1E, spectrum a. Afterward, the sample was cooled down to 175 K and CO was again adsorbed, in small doses, up to the point of maximum coverage of all cobalt sites but before massif reaction with acidic OH groups, to avoid the interference from the ''tail'' of 2175 cm^{-1} band (Fig. 1E, spectrum b). To calculate the amount of Co_ox form, the intensity of 2197 cm^{-1} band was estimated from the difference spectrum (Fig. 1E, spectrum c). The same procedure

Table 1
Concentration (Co/unit cell) of cobalt species in FER-1 series, determined from AAS and IR spectroscopy

Sample	Cobalt concentration			
	AAS (total)	IR		
		Co^{2+}	Co^{2+}_ox	Co^{3+}
CoFER-1	1.60	0.66	0.47	0.47
InCoFER-1	1.59	0.47	0.49	0.30

Table 2
Conversion (%) of NO and CH_4 and selectivity (%) to N_2 and NO_2 in CH_4-SCR-NO tests of FER zeolites

Sample	$T_{reaction}$ (K)	Conversion (%)		Selectivity (%)	
		NO	CH_4	N_2	NO_2
CoFER-1	625	43.8	4.0	44.0	56.0
	675	67.3	30.3	87.0	13.0
	725	83.6	73.0	96.0	4.0
	775	74.5	96.7	95.0	5.0
InCoFER-1	625	32.5	4.8	51.5	48.2
	675	63.2	20.2	87.0	12.5
	725	93.3	60.4	99.0	0.7
	775	94.6	92.2	99.5	0.2
CoFER-2	625	49.6	2.0	3.3	96.7
	675	32.4	4.8	3.6	96.4
	725	23.2	9.2	3.9	96.1
	775	16.8	23.6	32.6	67.4
InCoFER-2	625	63.3	22.1	72.4	18
	675	97.0	54.9	86.5	0
	725	97.5	84.6	91.2	0
	775	92.7	98.8	100	0

was repeated for InCoFER-1 zeolite (Table 1). The amount of cobalt for the FER-2 series was not estimated, as the experimental error, resulting from extremely low intensities of IR bands, was supposed to be too high.

The role of altervalent cobalt cations in HC-SCR is still an open issue. Recently, Montanari et al. [2] pointed at the possible role of trivalent cobalt ions which is most probably present in a form of oxides as the presence of three aluminium cations, located so near to each other that they would be able to neutralize trivalent cation, is virtually impossible. Such Co^{3+} is detectable after NO sorption, giving the band at 1939 cm^{-1}. Again, the amount of Co^{3+} is much lower for the FER-2 sample. As the CoFER samples were not washed after ionic exchange, cobalt was not removed in any way, so it is still present in CoFER-2 but in a form not discernible by IR with any of probe molecules used. The absence of any cobalt species from the FER-2 series on one hand supports the hypothesis that for their occurrence, the presence of initial acidity is required, on the other hand it raises the question what is the form of the cobalt in it. Unfortunately, at present we cannot answer this question.

According to Trombetta et al. [23], the sorption of pivalonitrile, of kinetic diameter higher than the critical diameter of the FER channels, can detect the presence of cobalt in any of its form on the external surfaces of the crystals. For neither FER-1 nor FER-2 series, no additional bands of pivalonitrile bonded to external cobalt sites were detected (spectra not shown). The only reasonable explanation is the proposal that cobalt is present as the separate phase, the most possibly amorphous. XRD patterns showed the presence of only very small amounts of CoO and $CoAl_2O_4$. On the other hand, the size of the majority of their crystals could be under the limit of detection for XRD method.

Apart from spectroscopic studies, SCR tests with the use of the methane as the reductor demonstrated (Table 2) relatively high activity of CoFER-1 and much worse performance of CoFER-2. The more, the main product (for temperatures higher than 560 K) of CH_4-SCR for CoFER-1 was N_2, while for CoFER-2 mainly NO_2 was produced. It seems that only those cobalt species which are directly associated with the zeolite structure (are actually coordinated to the zeolite framework) are able to act as active species in HC-SCR.

The introduction of indium into the zeolite changed the catalytic performance of the resulting catalysts not only by means of NO conversion but also changed the reaction path from the formation of NO_2 towards N_2, in much higher extend for the FER-2 zeolite. The activity of InCoFER-1 zeolite was comparable to InCoFER-2 (especially at higher temperature) but for InCoFER-1 the selectivity toward N_2 was slightly better and no N_2O was formed, the product which was observed for InCoFER-2.

From the presented data, for cobalt-exchanged ferrierites, it seems evident that the initial acidity of the zeolite matrix has the vast impact on the final form of cobalt species and so the catalytic performance of the resultant catalyst. Dehydroxylation did not destroy the zeolite but suppressed the number of tetracoordinated Al, so the number of acidic hydroxyls and as a result the exchange capacity of the zeolite which consequently greatly reduced its catalytic feature. This catalytic performance could be improved by the addition of indium.

4. Conclusions

1. Dehydroxylation of ferrierite removed most of the tetrahedral aluminium, so nearly all of the OH groups, therefore the resulting zeolite had practically no ion exchange capacity.
2. The introduction of cobalt by contact-induced ion exchange into FER-1 produced Co(II) in exchange positions and in the form of oxide-like clusters. Concentration of Co(II) and Co(III) was determined in quantitative IR experiments of CO and NO sorption, respectively.
3. The introduction of cobalt to dehydroxylated FER-2 produced only very small amount of Co^{3+} and Co^{2+}, the status of majority of Co in this zeolite remains unknown.
4. The catalytic activity in the reduction of NO with methane was significantly lower for CoFER-2 than for CoFER-1 indicating the importance of the initial acidity of zeolite in the formation of the cobalt species, active in reduction of NO.
5. The introduction of In improved the catalytic performance of both series and shifted the reaction path from NO_2 towards formation of N_2.

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