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MÖSSBAUER AND EPR STUDY OF ZEOLITE Fe^{3+}/USY[1]

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The incorporation of Fe ions in structural and cationic positions of zeolite NH_4Na-Y has been investigated by ^{57}Fe transmission Mössbauer and EPR spectroscopy. The effects of preparation conditions including heat treatment and hydrogenation are discussed. Ionic exchange at elevated temperature leads to an occurrence of magnetic particles. Their presence can be avoided by proper heat treatment. Reduction by hydrogen decreases the amount of Fe(III) on account of Fe(II) and, simultaneously, helps with the identification of different occupation sites of Fe ions.

Zeolites are widely used in chemical industries as adsorbents, ion exchangers and catalysts. Their chemical properties, especially the content and power of acidic centres, which are important for their application as catalysts in several reactions, can be modified by the Si/Al ratio and the insertion of iron [1]. Presence of Fe^{3+} ions incorporated into zeolites by ion-exchange or impregnation increased the activity and time stability of hydrocracking catalysts [2]. In the last years, the possibility of ion exchange of zeolites with metal chlorides at elevated temperatures (up to 300-500° C) was described [3].

In our work, we incorporated the Fe cations into Y-type zeolite in one step during deep-bed (DB) treatment by solid-state ion exchange of ammonium Y zeolite with iron(II) chloride. DB process consists of a treatment of ammonium-form of Y zeolite in closed space at a temperature up to 800° C. In the presence of ammonium and steam which are released by thermal decomposition and dehydration of the NH_4Y zeolite the structure is stabilised [4]. Such treated Y zeolite is called an ultra stable Y zeolite (USY). Identification of the nature and positions of Fe ions was carried out by transmission Mšsbauer effect measurements and EPR spectroscopy.

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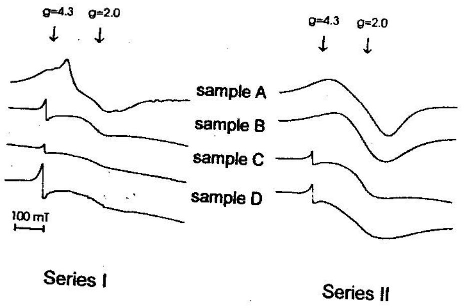

Fig. 1 Room temperature EPR spectra of Series I and II samples.

Table 1. Hyperfine parameters as derived from the Mössbauer spectra.

	Series I					Series II				
	form of Fe	A_{rel} (%)	IS (mm/s)	QS (mm/s)	H (T)	form of Fe	A_{rel} (%)	IS (mm/s)	QS (mm/s)	H (T)
A	Fe(III)	61	0.36	0.55	-	Fe(III)	24	0.34	0.86	-
	Fe(III)	39	0.37	0.93	-	Fe(III)	11	0.32	1.39	-
						Fe(II)	50	0.84	0.66	-
						$(Fe,Al)_3O_4$	6	0.32	0.04	47.5
						$(Fe,Al)_3O_4$	9	0.58	-0.02	42.5
B	Fe(III)	16	0.36	0.55	-	Fe(III)	12	0.36	0.55	-
	Fe(III)	23	0.37	0.93	-	Fe(III)	16	0.37	0.92	-
	Fe(II)	32	0.93	2.41	-	Fe(II)	42	0.96	2.37	-
	α-Fe_2O_3	29	0.38	0.19	51.6	$(Fe,Al)_3O_4$	12	0.31	0.06	49.4
						$(Fe,Al)_3O_4$	5	0.80	0.04	44.0
						α-Fe	13	0.00	0.00	33.0
C	Fe(III)	37	0.36	0.55	-	Fe(III)	15	0.36	0.56	-
	Fe(III)	37	0.37	1.00	-	Fe(III)	15	0.38	0.95	-
	Fe(II)	26	0.97	2.55	-	Fe(II)	70	0.97	2.25	-
D	Fe(III)	11	0.33	0.87	-	Fe(III)	10	0.34	0.86	-
	Fe(III)	66	0.32	1.40	-	Fe(III)	36	0.32	1.39	-
						Fe(II)	30	1.06	2.14	-
	Fe_2O_3	23	0.38	0.14	51.7	Fe_2O_3	24	0.34	0.21	51.6

Two types of samples were prepared. Series I consists of the following samples: (A) denoted as Fe^{3+}/USY which was prepared by conventional ion exchange of USY with Fe^{3+} ions from $FeCl_3$; (B) Y-15/8 - prepared by heating a mechanical mixture of USY with $FeCl_2.4H_20$ (0.75g / 10g NH_4Y zeolite) at up to 600° C in flow of nitrogen; (C) Y-15/5 - prepared as a mechanical mixture of NH_4Y zeolite (1.65 wt.SiO_2/Al_2O_3 = 5.38) with $FeCl_2.4H_20$ at the same ratio as in (B) with subsequent thermal treatment under DB conditions at 560° C; and (D) Y-15/4 - the same as (C) treated at 780° C. Series II includes the samples A to D after the reduction with hydrogen at 350° C.

Room temperature EPR spectra of all samples are shown in Fig.1. Characteristic features of the Series I spectra are in accordance with those described in [5, 6]. The signals at g=4.3 correspond to Fe^{3+} in cationic sites. Decrease of this signal in sample C with respect to sample D is due to self-reduction of Fe^{3+} in cationic sites to Fe^{2+} [6]. Because EPR spectra do not provide complete identification of Fe sites we have

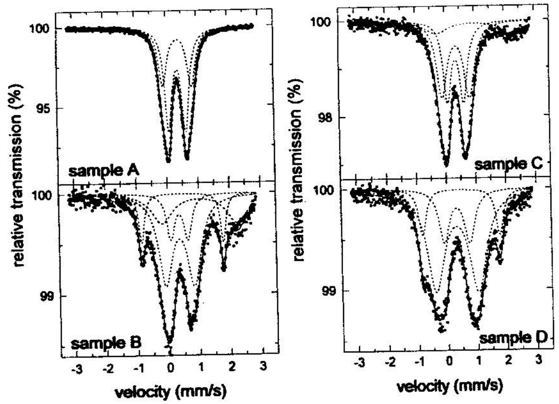

Fig. 2. Room temperature Mössbauer spectra of Series I samples.

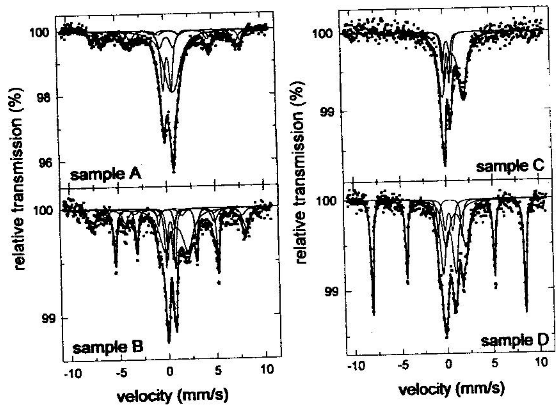

Fig. 3. Room temperature Mössbauer spectra of Series II samples.

employed Mössbauer spectroscopy.

Mössbauer spectra have been recorded at room temperature and those corresponding to Series I samples are illustrated in Fig.2. We have used the velocity ranges of 3 and 10.5 mm/s. The lower velocity range allowed precise determination of the central part of the spectra whereas higher velocities were necessary for unambiguous identification of magnetic components. The relative area of the particular component, A_{rel}, and the hyperfine parameters derived, comprising the isomer shift (with respect to natural iron), IS, the quadrupole splitting, QS, and the magnetic hyperfine field, H, are listed in Table 1 for Series I and II.

Two doublets of almost the same isomer shifts and very slightly different quadrupole splittings can be ascribed to Fe^{3+} which occupy two distinct cationic positions similar to those reported in [5]. They were detected in all samples except in samples A (Series II) and D (Series I and II). In sample A, nearly 2/3 of tri-valent Fe ions have been transformed into di-valent Fe and substituted-magnetite-like oxide (probably $(Fe,Al)_3O_4$) after reduction with hydrogen. The remaining Fe^{3+} ions resumed positions in zeolite cavities characterised by different set of hyperfine parameters. It is noteworthy that the same Fe sites occur in sample D.

Sample D was prepared at high temperature of 780° C in DB conditions. As a result, two forms of Fe are detected: (i) Fe^{3+} localised in zeolite cavities which do not undergo self-reduction but are readily reduced to Fe^{2+} with hydrogen [6], and (ii) hematite (α-Fe_2O_3). High temperature enable the Fe atoms to enter rather stable positions perhaps inside the zeolite frame. Theoretical calculations poited out such possibility [7] and our experimental results support this assumption by practically unchanged amount of Fe_2O_3 after the reduction (see Table 1). This is not the case when the preparation conditions were different (sample B). The parameters of hematite in sample D deviate from those corresponding to pure α-Fe_2O_3 (IS = 0.379 mm/s, QS = 0.194 mm/s, and H = 51.6 T, as from our measurements) which implies that the Fe atoms are affected by the zeolite structure.

Pure hematite was identified in sample B, Series I which means that there is no interaction between the magnetic particles and the zeolite structure. Due to mixing at 600° C and no DB conditions Fe_2O_3 is localised in extraframe positions where it is easily affected by hydrogen. Consequently, Fe_2O_3 changes completely into substituted-magnetite-like oxides and metallic α-Fe characterised by two and one sextuplets, respectively (Table 1, Series II). Formation of magnetite-like oxide phase and metallic α-Fe was reported by Lazar et al. [8]. Fe^{3+} in sample B occupy cationic sites and the presence of Fe^{2+} was established, too. Its relative amount has increased after the reduction at the expense of Fe^{3+}.

Sample C has been prepared in DB conditions at 560° C. The temperature was not high enough, however, to allow the formation of similar Fe sites as those observed in sample D. No magnetic component was revealed. The hyperfine parameters of Fe^{3+} imply cationic sites which are easily self-reducible, viz. the presence of Fe^{2+} in Series I, and are readily reduced to Fe^{2+} with hydrogen (Series II) [6].

The results presented document the feasibility of Mössbauer spectroscopy in the investigation of Fe^{3+}/USY zeolites and further experiments are in progress.

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