Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 561–565

A STUDY OF THE REACTION BETWEEN ZEOLITE H-FERRIERITE AND Cd OR Zn METAL

Gy. Onyestyák[*], *F. Lónyi and J. Valyon*

Institute of Surface Chemistry and Catalysis, Chemical Research Center, Hungarian Academy of Sciences, P. O. Box 17, H-1525 Budapest, Hungary

Cd- and Zn-form ferrierites were obtained by reacting the mixture of zeolite H-ferrierite and the powder of cadmium or zinc metal. Hydrogen was detected as reaction product, suggesting that the metal was oxidized by the zeolite protons. The reaction was characterized by the rate of H_2 evolution using the temperature-programmed reaction (TPRc) method. The H_2-TPRc peak was found to appear at lower temperature for the more volatile Cd metal and for the H-ferrierite, having higher Si-to-Al ratio and containing less extra-framework aluminum (EFAl) species in the zeolite channels. Results suggested that the diffusion rate of the metal vapor within the micropores governed the rate of the reaction.

Keywords: *Cd,H-ferrierite, H-ferrierite-metal reaction, temperature-programmed reaction (TPRc), Zn,H-ferrierite*

Introduction

The solid-state ion exchange between zeolite and metal salt attracted much attention [1]. Some salt anions were shown to hinder the exchange process [2]. For avoiding any anion effect, cations were introduced into zeolites by reacting the mixture of powdered H-form zeolite and metal (M), such as, Cd [3] or Zn [4]. At elevated temperatures the zeolite protons oxidized the M atoms. The process resulted in hydrogen evolution and in M^{2+} cations, balancing the negative charges on the zeolite framework. The ammonium form zeolites also reacted with the metals giving the same products as the H-zeolites above the temperature of zeolite deammoniation (NH_4-zeolite$\rightarrow$$NH_3$+H-zeolite) [5]. Recently, the solid-state reaction was used to prepare Zn- and Cd-clinoptilolite and Zn-ZSM-5 catalysts [6–9].

The amount of hydrogen evolved from a zeolite/M mixture gives the amount of the reactive OH groups. The temperature and rate of H_2 release was suggested to characterize the reactivity of the hydroxyls and was related to the acid strength of the Brønsted sites [5]. In the present work the method of temperature-programmed reaction (TPRc) was applied for studying the H-ferrierite-metal reaction. The results show that the temperature of the H_2-TPRc peaks reflects rather the diffusion resistance of the zeolite channels against the transport of the metal vapor than the reactivity and acidity of the zeolite OH groups.

Experimental

The zeolite NH_4-ferrierites used in this study were supplied by PQ Co., USA. The main characteristics of the samples are given in Table 1.

The H-forms of the ferrierite samples were obtained from the NH_4-form by thermal deammoniation in nitrogen flow at 550°C. The samples were different regarding both the framework Al content, i.e., the Brønsted acid site concentration, and the EFAl concentration (Table 1). Moreover, scanning electron microscopic (SEM) examinations showed that the crystallite platelets of FER(10) were of about 0.1–0.3 μm size, while the FER(28) platelets were ten times larger.

Table 1 Characterization of the ferrierite samples

Sample designation[a]	Si/Al ratio	CEC[b]/mmol g^{-1}	Al[c]/mmol g^{-1}	EFAl[d]/mmol g^{-1}
FER(10) [CP 914C]	10	0.92	1.56	0.64
FER(28) [CP 914]	28	0.40	0.55	0.15

[a]The designation of the PQ Co., USA, is given in brackets. [b]Cation exchange capacity (CEC). The NH_4-form was thermally deammoniated and the amount of released NH_3 was determined. The CEC was considered to be equivalent with the framework Al content. [c]The total Al content, determined by conventional chemical analysis. [d]Extra-framework aluminum (EFAl), obtained as difference of the total and the framework Al content

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[*] Author for correspondence: ony@chemres.hu

1388–6150/$20.00
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Springer, Dordrecht, The Netherlands

The H-ferrierite powder was mixed with Cd or Zn dust, containing <60 μm size metal particles. The molar ratio of the framework Al to the admixed metal was about two. The hydrogen evolution was monitored while the mixture was heated up at a rate of 10°C min^{-1} in a 20 cc(STP) min^{-1} N_2 stream. The stream was passed through a thermal conductivity detector to follow the composition change of the gas. See experimental details [5].

The H-ferrierite-metal reaction was also studied by high-temperature X-ray diffraction (XRD) measurements in high vacuum and in He flow. The measurements were carried out using an Anton Paar HTK 1200 High Temperature Oven-Camera, equipped with a source of CuK_α (λ=0.15409 nm) radiation.

The intrinsic acid strength of the OH groups of the zeolites was characterized by the adsorption induced shift of the ν_{OH} infrared (IR) absorption band. A more detailed description of the measurement was given in [10]. Briefly, the N_2 adsorption was carried out at room temperature and 9 bar pressure in a DRIFT spectroscopic cell. The $\Delta\nu_{OH}$ band shift was determined from the spectra of the activated zeolite sample, recorded before and after N_2 adsorption using a Nicolet 5PC FTIR spectrometer.

Results

TPRc curves of hydrogen evolution are shown for the reactions of the ferrierites with Cd and Zn in Figs 1a and 1b, respectively. The amount of hydrogen, released from zeolite FER(10), corresponded to the number of protons in the sample (1.05 mmol H_2/mmol applied Cd and 1.10 mmol H_2/mmol Zn). That means that all the M atoms must have been oxidized to the M^{2+} state. In contrast, only about half of the protons were consumed in the same reactions of the high-silica FER(28) sample (0.50 mmol H_2/mmol applied Cd and 0.58 mmol H_2/mmol Zn). All of the applied metal was found in the zeolite after the solid state reaction by chemical analysis (e.g. FER(28) sample admixed with 2.19% (m/m) Cd prior to the reaction preserved 2.14% (m/m) Cd after the hydrogen evolution at elevated temperature).

The peak temperatures, i.e., the temperatures of the highest-rate hydrogen evolution, were significantly different for the metals and also for the different ferrierite samples. In general, the H_2 peak of the H-ferrierite-zinc reaction appeared at higher temperature than that of the H-ferrierite-cadmium reaction. Comparing the ferrierites, the FER(10) oxidized the metals at much higher temperature than the FER(28) (Fig. 1). The FER(28) reacted with Zn close to the 419°C melting point of the metal. In contrast, the protons of the FER(28) sample started to oxidize the Cd metal far below its melting point, i.e., below 321°C.

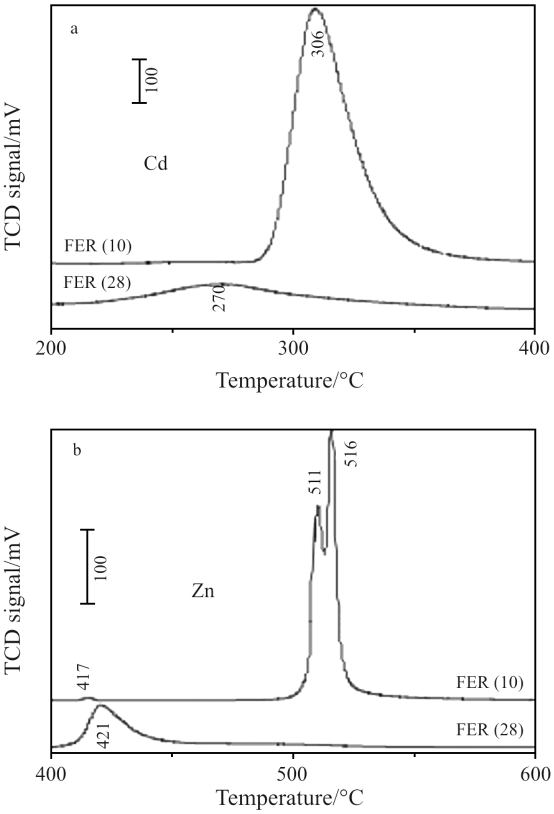

Fig. 1 TPRc curves of H_2 evolution from the reaction of H-ferrierite with a – cadmium and b – zinc metal dust. The zeolite framework Al to metal molar ratio was 2

The XRD patterns of the zinc/H-ferrierite mixtures, determined at elevated temperatures, are shown in Fig. 2. The reflections of the Zn metal disappeared at lower temperature in vacuum than in He flow. Interestingly, the reflections of the metal phase disappeared also in the reaction with the FER(28) sample, substantiating that all the metal participated in the oxidation process. It follows from the amount of evolved H_2 that in the FER(28) sample the zinc was oxidized by one electron and stabilized in the zeolite as Zn^+.

The TPRc results of the present study were interpreted in relation with results of independent acidity measurements. The bands appearing in the DRIFTS spectra of the H-ferrierites at 3748 and 3640 cm^{-1} (shoulder) were assigned to non-acidic silanol groups and OH groups linked to EFAl species, respectively. The band around 3600 cm^{-1} stems from acidic OH groups bridging between framework Al and Si atoms (Fig. 3). The intensity of the EFAl hydroxyls relatively to the acidic hydroxyls was significantly higher for the FER(10) than for the FER(28) sample, in accordance with the EFAl concentrations of the samples. The interaction of the OH groups with N_2 weakened the O–H bonds and,

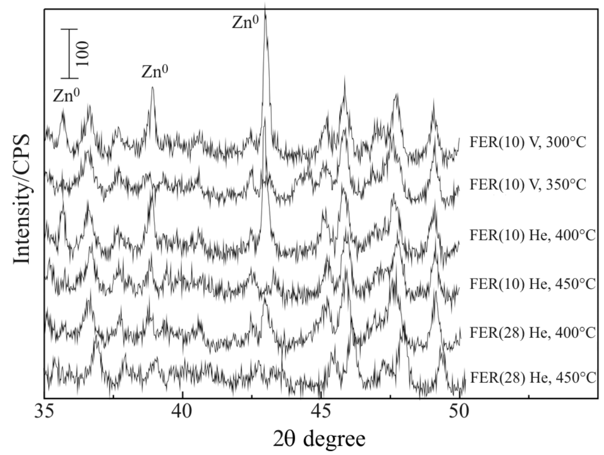

Fig. 2 XRD patterns of zinc/ferrierite mixtures. XRD patterns were recorded *in situ* after exposing the solid mixture to vacuum or He flow at the indicated temperature for 10 min

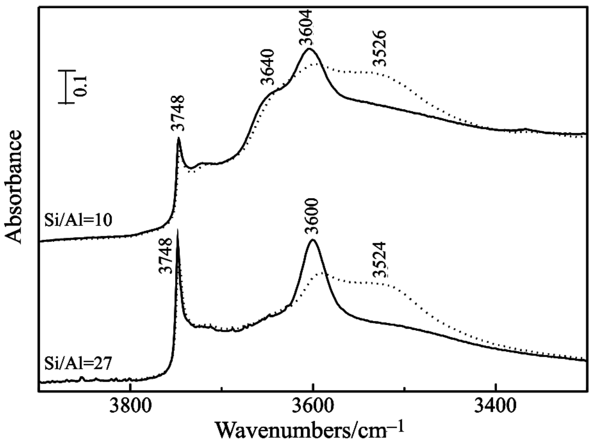

Fig. 3 DRIFT spectra of H-ferrierites in the OH stretching region —– prior to and ···· – after N_2 adsorption. The samples were activated in a flow of 50% O_2/N_2 mixture at 773 K *in situ* in the DRIFTS cell. Spectra were recorded at room temperature while the sample was under He or N_2 at 9 bar pressure

thereby, resulted in the appearance of new ν_{OH} bands shifted to somewhat lower frequencies. The $\Delta\nu_{OH}$ shift parallels the OH·· N_2 bond strength that depends on the acid strength of the hydroxyl groups. The $\Delta\nu_{OH}$ of the bridging OH band was much the same for the two ferrierites. It can be concluded that samples, regardless of their different chemical compositions, contain Brønsted acid sites having nearly the same intrinsic acid strength. The results of the DRIFTS examination suggest that the TPRc characteristics of the H_2 evolution do not correlate with the intrinsic acid strengths of the samples.

Discussion

The controlled preparation of metal nanoparticles or clusters in zeolites is a challenge for the material science [11]. Small transition metal particles can be generated by reducing the metal cations, balancing the negative framework charge, by liquid or gaseous reducing agent. The use of hydrogen is the most common. When an exchange cation is reduced with hydrogen, protons are generated, which are retained by the zeolite to maintain the electrical neutrality of the material. It was found [12] that, at elevated temperature, protons can re-oxidize the metal according to Eq. (1),

$$M + nZO^- H^+ = (ZO^-)nM^{n+} + n/2\ H_2\uparrow \qquad (1)$$

wherein ZO^- represents the aluminum silicate framework of a zeolite. Interestingly, this oxidation process was feasible also for metals, having high positive standard redox potential ($E°$), such as silver ($E°_{Ag/Ag^+}$=0.8 V) [13]. That could happen because the electrochemical potential depends on the size of metal agglomeration. The potential decreases with the metal cluster size and clusters of less than about four Ag atoms do not behave like 'noble' metal. The potential of a single silver atom is –1.8 V, indicating that atomic silver is a strong reductant [14]. These results are suggesting that the standard electrode potential of a M/M^{n+} system is merely a guideline, if the possibility of a H-zeolite-metal reaction is considered.

The thermodynamically favored H-zeolite-metal reactions proceed according to Eq. (1). No Ag-, Cu-, Sn-, or Pb-ferrierites could be obtained in this reaction, because at temperatures, where the zeolite retained its structure the oxidation of these metals were not initiated yet. This can be understood considering that the E^o of these metals are positive (Ag, Cu) or hardly below zero (Pb, Sn).

The comparison of the $E°$ values of Zn and Cd shows that Zn ($E°_{Zn/Zn^{2+}}$= –0.763 V) is a stronger reducing agent than Cd ($E°_{Cd/Cd^{2+}}$= –0.403 V). Accordingly, the reaction of these metals with the H-ferrierites was found feasible. However, the TPRc results show that Cd reduced zeolite protons at lower temperature than Zn (Figs 1 and 2). This finding suggests that the temperature of the H_2-TPRc peak is controlled rather by kinetic than by thermodynamic factors.

The metal vapor pressure below the melting point of the metal is presented in Fig. 4. The Cd reaches a given vapor pressure at lower temperature than the Zn. The H_2-TPRc curves (Fig. 1) show that the oxidation of the metal speeds up at temperatures, where the vapor pressure and, therefore, the rate of metal evaporation becomes significant. This is substantiating that the rate of the reaction is controlled either by the kinetics of metal evaporation or by the rate of metal transport in the zeolite channels.

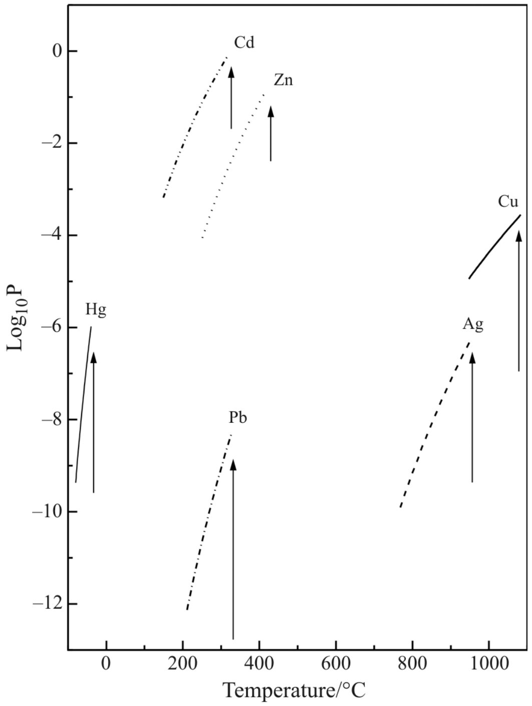

Fig. 4 Vapor pressures (*P*, Torr) of metals below the melting point of the metal, indicated by arrow. The data were taken from [16]

The found low reactivity of the Cu, Ag, Sn and Pb can be either due to the low reducing power of these metals, or due to kinetic reasons, which are related with the low vapor pressure of the metals up to relatively high temperature. In this work the H-zeolite-Hg reaction was not examined, however, the reaction is very unlikely because of the high and positive standard redox potential of the mercury (E^0=0.79V).

The Cd and the Zn reacts with the FER(28) sample close to the melting point of the metal (Fig. 1b) or far below it (Fig. 1a). Moreover, the amount of H_2 produced (Fig. 1) and the full disappearance of the metal phase (Fig. 2) substantiates that the metal was oxidized by one electron only. In the high-silica H-zeolites, such as the FER(28) sample, the framework Al atoms and the bridging OH groups are relatively far from each other. Reaction of a metal atom with a single OH group gives a M^+ species and a H-atom (Eq. (1), n=1). Since charge balancing of far-away negative charges by M^{2+} ions is energetically not favoured the metal atoms seem to be stabilized in the M^+ state while the H-atoms combine to H_2 and are released. It follows from the similar acid strengths of the OH groups in the FER(10) and the FER(28) samples that the reactivity of the zeolites was very similar. Therefore, it must be considered that the significantly different reaction temperatures of the ferrierites with the same metal was due to the different rates of metal transport within the channels of the different zeolites.

In principle, the metal can be oxidized close to the entrance of the zeolite channels and the formed ions can migrate to particular cation positions in the zeolite crystal. Alternately, the atoms of the metal vapor can move along the zeolitic channels wherein they reduce and replace zeolitic protons. It seems probable that jumping of charged cations from site to site is more hindered in the high-silica sample, where the cation sites are further away than in the Al-rich ferrierite. On the contrary, the lower polarity of the high-silica sample promotes the mobility of the neutral metal atoms in the channels. The temperature of H_2-TPRc peak was lower for the high-silica ferrierite than for the Al-rich FER(10) sample, suggesting that the transport rate of the metal vapor in the zeolite channels may govern the reaction rate. The width of the H_2-TPRc peaks can be related with the time constant of the rate controlling kinetic process. Broader peaks were obtained for the FER(28) sample having larger crystallites, i.e., in the larger crystallite a longer time was needed for the completion of the reaction.

It is also to be noted that EFAl species in the channel system can reduce the accessibility of the reacting hydroxyls for the reactant metal atoms. Recent catalytic studies support this notion [15]. The activity of the H-ferrierites, used also in the present study, were compared in the skeletal isomerisation of butene [15]. The selectivity of EFAl-poor FER(28) was found to be very low compared with that of FER(10), containing large amount of EFAl. The catalytic properties could be interpreted as the result of the different mass transport resistances in the micropores of the different H-ferrierite catalysts. Obviously, the different EFAl concentrations can be responsible for the found differences in the transport properties of the samples. Based on the existing data the significance of each factor, affecting the metal transport in the ferrierites, can not be discussed in more detail.

Conclusions

Cd- and Zn-ferrierites can be obtained by reacting the corresponding metal and H-ferrierite in the solid phase. The Al-rich ferrierite can oxidize the metals to the M^{2+} state. The high-silica ferrierite stabilizes the oxidized metal cations in the M^+ state. The dynamics of the metal oxidation process does not show correlation with the acid strength of the Brønsted acid sites but is sensitive to the zeolite composition and to the presence of structural defects, such as EFAl species. These factors are modifying the accessibility of the zeolite protons and the mass transport of the metal in the micropores.

Acknowledgements

The authors say thanks to Prof. D. Kalló for the valuable discussion, to Dr. G. Pál-Borbély for TPRc measurements, and to Mrs. Ágnes Wellisch for the valuable technical assistance. The financial support of the Hungarian Scientific Research Fund (OTKA, Project Nos. T 043552, T 037681 and M036939) is gratefully acknowledged.

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