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Co- and Ni-exchanged ferrierite: The contribution of synchrotron X-ray diffraction data to siting of TMIs

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Abstract

High-silica zeolites exchanged with transition metal ions (TMIs) are the subject of great interest for their unusual catalytic activity and selectivity. Structural information like coordination and accessibility of TMIs in zeolites are important factors for understanding their catalytic activity. Siting of TMIs in zeolites is typically obtained by spectroscopic (EXAFS, EPR, UV–vis and IR) and computational methods, as in the case of Co-ferrierite. However, some controversy exists in the literature concerning the model for incorporation of bare Co ions in ferrierite. We show here that the results of our synchrotron X-ray powder diffraction studies on Co- and Ni-exchanged ferrierite (Si/Al = 8.5) are in a good agreement with the model of Co siting based on an indirect spectroscopic approach and help to validate this model. By direct structural evidences, a possible explanation for the larger catalytic activity of Co sites in the main channels of ferrierite can be inferred. A combination of data from in situ XRD continuous monitoring of the Co ion migration during calcination and crystal-chemical considerations allows to device a strategy for the design of optimised co-cations containing Co-ferrierite catalysts.

Keywords: Ferrierite; Transition metal ions; Synchrotron diffraction; In situ XRD; Catalytic activity

1. Introduction

Transition metal containing zeolites have received increasing attention in academic and industrial fields because of their promising catalytic activity for a wide variety of important reactions [1–2]. The unique catalytic activity of transition metal ions (TMIs) exchanged zeolites is related to the reciprocal interplay between TMIs and the zeolite host. Zeolites exert specific effects upon the coordination of TMIs: inducing a high cation dispersion on multiple crystal sites; stabilizing unusual oxidation states of the exchanged cations; stabilizing coordinatively unsaturated TMIs sites. The catalytic activities attributed to TMIs differ in different types of zeolites and are dependent on the concentration and location of TMIs, their accessibility to and coordination with adsorbate molecules [3] (and references therein). The local structure of metal ion sites, their coordination chemistry, and the specific properties of the surrounding framework are important issues to be addressed for a better understanding of the catalytic mechanism. The principal methods that have been used to elucidate the catalytic function of TMI within zeolites are based on the absorption of typical probe molecules and their interaction with active sites. Most information on the localisation of metal ions in zeolites has been deduced from spectroscopic measurements such as FTIR, DR UV–vis–NIR, EXAFS and XANES, XPS, ESR, Mössbauer, Raman or has been derived from quantum chemical calculations (DFT) or energy minimization techniques.

Besides the large number and variety of spectroscopic studies on TMIs zeolites, very few articles dealing with crystal structure investigations on these systems are present in literature. We believe that important complementary information can be obtained from crystal structure analysis by means of diffraction studies. The Rietveld refinement of synchrotron powder diffraction data collected at high resolution on calcined

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samples or in situ during the heat treatment can give the extraframework location and occupancies of TMIs and their evolution upon interaction with adsorbates or heating. It is worth recalling that TMIs exchanged zeolites usually exhibit their catalytic activity at high temperatures. During the heating treatment and with the proceeding of the dehydration process the zeolite framework may undergo structural modifications and the exchanged cations tend to move into different sites modifying their coordination. Monitoring the continuous structural evolution of extraframework metal ions upon heating (thermal activation process of the zeolite) can provide useful information for optimising the catalytic system.

In the following the attention will be focused on Co- and Ni-exchanged ferrierite addressing the similarities in site distribution of the guest Co^{2+} and Ni^{2+} ions in hydrated and dehydrated forms of ferrierite. For Co-exchanged ferrierite, the results obtained by XRD analysis will be discussed in comparison with the results derived from spectroscopic studies. We must consider that spectroscopic and diffraction techniques can give complementary information and that each method has its own limitations. Spectroscopy is a highly sensitive tool for local scale information (i.e. the local environment around the absorbing TMIs, averaged over crystallographically different structural sites), whereas diffraction can detect long range order structural features (TMIs in distinct crystallographic sites with bond distances around the metal ion averaged on the entire crystal). High TMIs loadings are often necessary for unequivocal recognition of TMIs sites by diffraction whereas spectroscopy applies equally well on very low doping levels. Zeolite structures usually present great complexity and the accurate characterization of the extraframework cations may be a difficult task. Supporting the local information obtainable by spectroscopic techniques with crystal structure information (long range order information) could be highly desirable.

The aim of this paper is two-fold: in the first part we will briefly review the results from literature concerning the spectroscopic and computational studies on the location and characterization of Co ions in ferrierite. This will allow us to highlight the existing controversial issues. In the second part, we will discuss the results of our synchrotron X-ray diffraction studies on Co- and Ni-exchanged ferrierites to illustrate the information obtainable by this technique.

2. Review of studies on the characterization of active sites in ferrierite

2.1. *Structure of active sites of dehydrated Co-ferrierite based on spectroscopic methods*

Co-exchanged ferrierite has been found to be a very active catalyst for selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons as reducing agents in presence of excess oxygen [4]. It was observed that the catalytic activity is not linearly proportional to the concentrations of exchanged cobalt ions in the zeolite, suggesting the presence of different Co ions sites characterized by different activities [5]. An extensive spectroscopic study (FTIR, UV–vis and EXAFS) on Co-exchanged ferrierite (in the activated form) was performed by Wichterlová and co-workers [6–12]. These authors indicated the presence of three types of exchanged Co ions (α-, β- and γ-type) on the basis of the similarities in both the spectral components of the Co ions and the known local framework geometries in mordenite, ferrierite and ZSM-5. The α-type Co ions (corresponding to B site of Mortier's notation [13]) were located in the main 10-membered ring channel of ferrierite four-fold coordinated to framework oxygens of the straight channel. The β-type ions (G site according to Mortier's notation) are sited in the deformed six-membered ring window delimiting the ferrierite cage and the γ-type Co ions (Mortier C site) are in the "boat-shaped" site of ferrierite. The relative population of the α-, β- and γ-type Co ions was estimated by quantitative analysis of the Co^{2+} vis spectra. By simultaneous monitoring the Co^{2+} vis spectra and IR vibrations of the T–O framework bonds, the authors observed a direct perturbation of hosted framework bonds determined by the coordination of Co ions to framework oxygens. They also indicated that the extent of perturbations reflects the strength of Co bonding to framework oxygens. The different catalytic activity of individual α-, β- and γ-type Co ions exchanged in ferrierite was also investigated [7]. A schematic representation of these results found in the literature is reported in Table 1 and Fig. 1.

2.2. *Other results on the nature and location of active sites in Co-ferrierite*

Density functional theory (DFT) calculations have been applied to study extraframework Co ions siting in ferrierite by McMillan et al. [14,15]. Quantum chemical calculations show that a given observed signature in IR spectra may not be an intrinsic property of a specific Co ions site, but could correspond to Co ions in multiple sites. According to these authors, the relative arrangements of aluminium substitutions in addition to the position of Co ions determine the observed cobalt-framework infrared signature. The assignment of the IR signatures to an individual and specific cobalt ions site may not be straightforward.

Montanari et al. [16] investigated the nature and location of the protonic and cationic sites of Co–H–zeolites (FER, MOR and MFI) by UV–vis and IR spectroscopy of adsorbed hindered

Table 1
Properties of Co ions sites in ferrierite as determined by spectroscopic results

Property/site	α (B)	β (G)	γ (C)
Location and coordination	On the walls of the 10-ring channel	Deformed 6-rings of the FER cage	"Boat-shaped" site inside the FER cage
Population	10–30%	50–85%	0–15%
Strength of bonding	Weakest	Medium	Highest
Ability to form dinitrosyls	High	Lower than α	None
Catalytic activity (TOF)	Most active	Lower than α	Very low

From refs. [6–12].

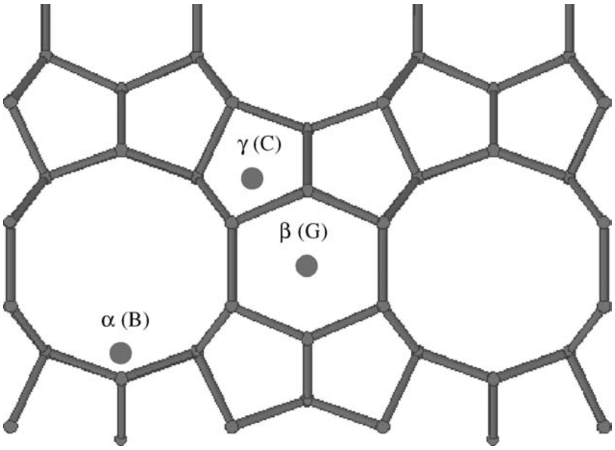

Fig. 1. Schematic representation of ferrierite structure showing the position of three Co ions types indicated by Wichterlová and co-workers.

nitriles. They provided evidence for the location of Co ions on the external open surface of the zeolite, indicating that in exchanged Co–H–FER Co ions are likely distributed between internal and external surface of the zeolite. These authors also evidenced that UV-vis spectra of cobalt in partially exchanged zeolites and on microporous silica-alumina (surface cobalt species) are always very similar. UV–vis spectra of Co species in exchanged zeolites result to be quite insensitive to the nature of the environment where the ions are located.

Concerning previous diffraction studies on transition metal exchanged ferrierite in dehydrated form, Attfield et al. [17] localised one Cu^{2+} site coordinated to two framework oxygens of the eight-membered ring of ferrierite (site F of Mortier). No Cu^{2+} ions were identified corresponding to the extraframework cation sites indicated by Wichterlová end co-workers. Copper oxide was also detected as a second extra-zeolite phase. This dissimilar behaviour could depend on the different exchanged conditions used for the Cu-ferrierite sample.

3. Discussion of results from synchrotron X-ray diffraction studies

3.1. Direct evidence of Co- and Ni-siting in ferrierite by XRD analysis

The locations of cobalt and nickel ions in hydrated and dehydrated ferrierite (Si/Al $\cong$ 8.5, Co/Al and Ni/Al ca. 0.5) have been directly observed by synchrotron XRD. The experimental and data analysis details are described in [18–20]. Four Co^{2+} ions have been recognised in dehydrated ferrierite, three of which correspond to the cation sites inferred from spectroscopic results [10] and confirmed by DFT calculations [14]. The fourth cationic site (Co3b or Ni3 according to our notation, see Fig. 2) closely resembles the Cu^{2+} site identified by Attfiled et al. [17] and corresponds to extraframework site F of Mortier's notation.

An identical distribution of extraframework cation sites was observed in dehydrated Ni-ferrierite [18].

Fig. 2 shows the cobalt and nickel siting as observed by XRD while Table 2 summarises and compares the results from XRD and spectroscopic analysis. In Table 3, the Co ions- and Ni ions-framework oxygens bond distances as derived from XRD results [18,20] are listed. It is worth recalling that the bond distances determined by DFT calculations or EXAFS spectroscopy are not directly comparable with the XRD bond distances. Metal ions coordination to framework oxygens may induce local distortions of the framework around the cationic sites. If the cation sites are only partially occupied, the XRD metal–oxygen bond lengths result longer than the real bond distances. XRD analysis averages the occupied (with framework distortion) and unoccupied sites (without framework distortion).

According to XRD analysis [20], Co1a site is located near the centre of the six-membered ring window of ferrierite (corresponding to β-type or G site of Mortier). The presence of

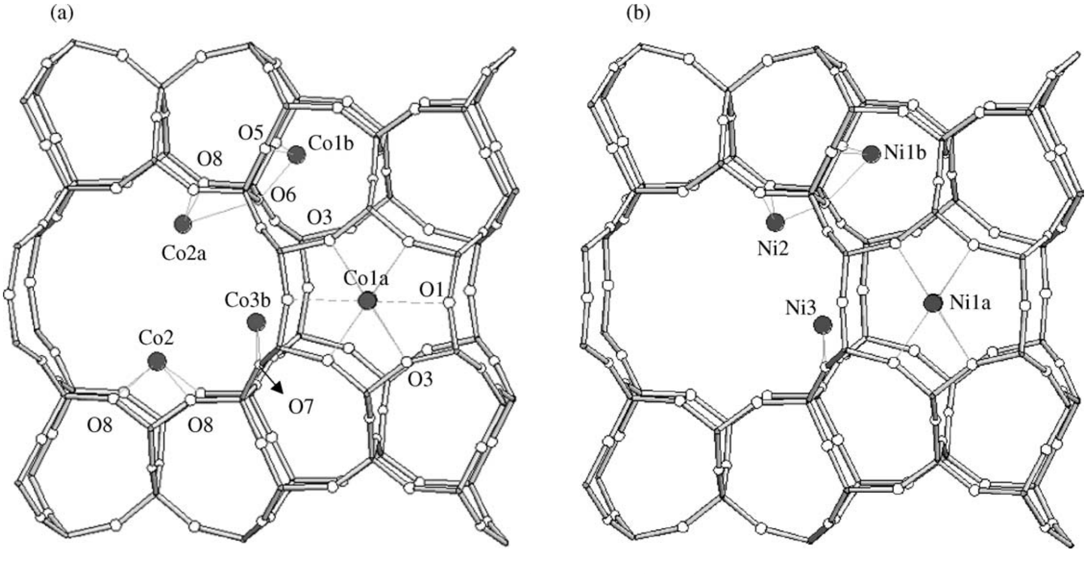

Fig. 2. Cation sites distribution in Co-exchanged (a) and Ni-exchanged ferrierite (b) as determined by XRD data analysis.

Table 2
Transition metal ion sites in ferrierite

Mortier notation	Wichterlová and co-workers (ref. [6,10])	Our study (ref. [20]) Co-ferrierite	Our study (ref. [18]) Ni-ferrierite	Attfiled et al. (ref. [17]) Cu-ferrierite
B	$^{[4]}$Co-α (10–30%)	$^{[3]}$Co2a (∼13%)	$^{[3]}$Ni2 (∼19%)	–
G	$^{[4]}$Co-β (50–85%)	$^{[4+2]}$Co1a (∼49%)	$^{[4]}$Ni1a (∼39%)	–
C	$^{[4]}$Co-γ (0–15%)	$^{[3]}$Co1b (∼15%)	$^{[3]}$Ni1b (∼19%)	–
F	–	$^{[2]}$Co3b (∼23%)	$^{[2]}$Ni3 (∼23%)	$^{[2]}$Cu (∼74%)

[*n*] = coordination number; (*n*%) = Co% (and Ni%) located in the specific site of total Co (and Ni) ions found.

cobalt ions in this site induces a relevant distortion of the framework window determining a ca. 0.6 Å shift of the O1 framework oxygens toward the centre of the window. This suggests that the O1 oxygens are involved by the coordination sphere of cobalt ions. Spectroscopic and DFT results indicated Co^{2+} ions in G site as four-fold coordinated only to O3 framework oxygens [10,14]. In Ni-exchanged ferrierite, no evidence of the O1 oxygen shift toward the Ni1a site was detected [18]. According to our XRD results, there are no evidences that Ni cations reach optimal bond distances from the O1 oxygens of the six-membered ring window.

Co2 site (α-type or B site) was localised near the wall of the 10-membered ring channel coordinating four O8 framework oxygens [20]. At increasing temperatures, we observed a further migrations of Co^{2+} ions to a new position, called Co2a, which approaches the O6 framework oxygen. Co^{2+} ions in this site are likely three-fold coordinated to framework oxygens O8 (×2) and O6. The in situ temperature resolved XRD analysis of Co-exchanged ferrierite allowed the continuous monitoring of the Co cations migration upon heating treatment. Data collection for Ni-exchanged ferrierite was performed at isothermal condition at 600 °C. The Ni^{2+} ions were localised only in the Ni2 site shifted toward the O6 framework oxygen [18].

Co1b (and Ni1b) cation site (γ-type or C site) was located inside the ferrierite cage in the "boat shaped" position bonded to O5 (×2) and O6 framework oxygens [20]. It is also to note that two Brönsted acid sites have been recognised in D-ferrierite [21]. One of them is attached to the framework oxygen O4 and points toward the centre of the ferrierite cage (Fig. 3). The second proton site is localised on framework oxygen O6 not far from the centre of the eight-membered ring window of ferrierite cage and from site Co3b. The tendency of both cations and protons to localise near the O6 oxygen of the eight-membered ring window of the ferrierite cage could be indicative of an Al enrichment in the adjacent/neighbouring tetrahedral sites.

3.2. Contribution of XRD data for a possible interpretation of Co site activity in Co-ferrierite

One of the most addressed questions about Co-exchanged zeolite catalyst regards the parameters which mainly control the catalytic activity of the system and in particular the nature of the most active cation sites. It has been recognised that the presence of protons (CoH-FER) or cobalt oxide species in Co-FER enhances the catalytic activity promoting the NO oxidation to NO_2 which represent the first step of the complex reaction of CH_4-SCR of NO_x [22,23]. The controlling factor of the catalytic rate is generally attributed to the presence o eschanged Co^{2+} in extraframework cation sites. Dědeček et al.

Table 3
Selected distances of Co and Ni ions to framework oxygens as derived from XRD (ref. [20,18])

	Interatomic distances (Å)
Co1a-O3	2.28(1) [×4]
Co1a-O1	2.59(1) [×2]
Co1b-O5	2.07(1) [×2]
Co1b-O6	1.91(4)
Co2a-O6	2.53(6)
Co2a-O8	2.31(3) [×2]
Co3b-O6	2.17(5)
Co3b-O7	2.05(3)
Ni1a-O3	2.34(3) [×4]
Ni1b-O2	2.4(1)
Ni1b-O5	2.20(9) [×2]
Ni1b-O6	2.17(20)
Ni2′-O6	1.77(18)
Ni2′-O8	2.15(8) [×2]
Ni3′-O6	2.51(15)
Ni3′-O7	2.14(14)

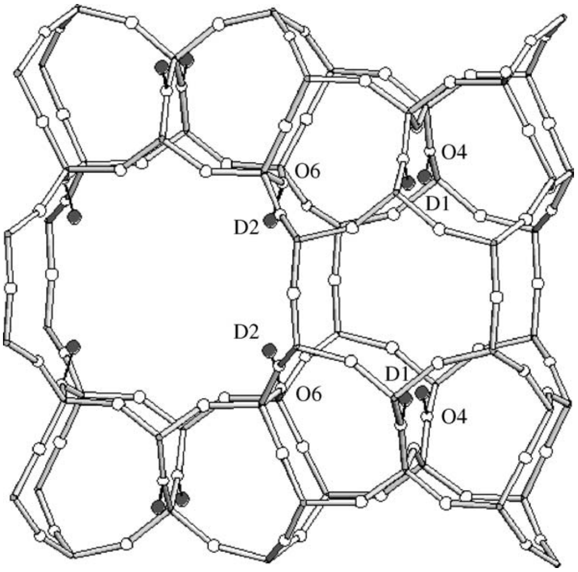

Fig. 3. Location of Brönsted acid sites in the framework of D-FER, from ref. [21].

[24] proposed an estimation of the catalytic activity of the individual types of Co ions (α-, β- and γ-type) in various zeolites (FER, MOR, MFI, BEA, CHA) suggesting that the distance between Co^{2+} sites could be a controlling factor. They observed that the α-type Co ions in ferrierite and β-type Co ions in ZSM-5 exhibit the highest activity. Both these sites are located in accessible position (main zeolite channels) and are four-fold coordinated to framework oxygens. The difference of their activity is not explained as an effect of favoured accessibility of these sites, because other less active cation sites are equally well accessible. The authors noticed some correlation between the catalytic activity and the distance between closest cation sites. From a rough estimate of the distances between the cation sites, they pointed out that the most active sites present the shortest distance between two closest cations. XRD data analysis can provide, in some cases, more accurate structural information on the position of cation sites and their reciprocal distances. Table 4 reports part of the results presented in [24] and the distances between Co^{2+} sites as determined by our XRD data analysis. It is also to be considered the low occupancy of these cation sites. According to XRD results and assuming a statistical distribution of cobalt ions in extraframework sites, the probability of finding cobalt ions occupying simultaneously the Co2a positions at a distance of 4.5 Å is quite low (ca. 0.07%). In Table 4 is also reported the closest distance (ca. 4.3 Å) between the cation sites Co2a and Co3b. Also for these two cation positions the probability of being simultaneously occupied by Co ions is low (<0.07%).

3.3. Application of XRD data for optimising the preparation of new catalysts

Assuming that the Co ions in the main 10-membered ring channel of ferrierite (α-type or Co2a site or B site of Mortier) are the most catalytically active sites for the CH_4-SCR, it would be desirable to minimise the number of Co ions distributed on hardly accessible or less active cation sites inside the ferrierite cage (β- and γ-type or Co1a and Co1b site or G and C site). The distribution of cobalt ions on different sites take place during the cation exchange procedure which is usually carried out via acqueous solutions. In the as-prepared (not activated) Co-exchanged ferrierite in hydrated form, the Co ions are coordinated to water molecules and occupy different cation sites respect to the positions occupied in the dehydrated (or activated) form. In situ time resolved XRD in the 53–810 °C temperature range allowed the continuous monitoring of Co cations migration as a function of the heating treatment (thermal activation) [20]. At low temperature, the Co ions are located at the centre of the ferrierite cage ($Co[H_2O]_6^{2+}$ octahedron) and within the main 10-membered ring channel coordinating water molecules. Co1a and Co1b sites arise from the migration of Co ions from the centre of the ferrierite cage, whereas Co2a and Co3b sites likely originate from the hydrated Co ions within the main channel.

Table 4
Estimated distances of Co ions in zeolites

Co site/matrix	Sites distances (Å) (ref. [24])	Co sites in FER	Sites distances (Å) from XRD (ref. [20])
α/HFER	5.4	Co2a–Co2a	4.3–4.5
β/HFER	6.1	Co1a–Co1a	7.0
		Co2a–Co3b	4.3
α/HZSM-5	7.1		
β/HZSM-5	4.5		

The above behaviour upon heating together with the comparison of Co-exchanged ferrierite to the natural Mg-rich forms might be used to speculate on a possible strategy, among the others, for forcing the α(B)-type population by Co ions. We have found that the refined population of the Co sites at the centre of the ferrierite cage never exceed half the occupancy, even in the overexchanged samples [19], whereas in natural Mg-ferrierite the Mg ions fully occupy the site at the centre of the cage [25]. Such a difference can be simply explained by a partially hindered diffusion of Co ions into the ferrierite cage during cation exchange which clearly does not occur during crystallization of the Mg-rich natural forms. However, we know that hydrated Mg-clusters completely fill not only the ferrierite cage such as in Mg-ferrierite, but also the similar gmelinite cage in mazzite [27] and offretite [28] revealing the structure directing role of small inorganic cations surrounded by water molecules in charged clusters [26]. From this considerations it can be inferred that Mg ions have a particular affinity for the position at the centre of the ferrierite cage and or a larger preference with respect to Co ions. Therefore, it is likely that performing the Co exchange of a Mg-rich ferrierite or the Co–Mg exchange of NH_4-ferrierite would result in Mg ions competitively occupying the sites at the centre of the ferrierite cage and forcing the Co ions to be located into the other (more accessible) sites. The use of Mg as co-cation during direct synthesis or ion exchange could allow some control on the Co ions placement into the most catalytically active cation sites.

4. Conclusions

Synchrotron X-ray powder diffraction and Rietveld refinement can be successfully applied to obtain overall structural information and TMI location in relatively high-silica pentasil zeolites. The long range, average picture from diffraction is of essential importance to complement and validate the crystallographic model derived from spectroscopy data. Furthermore, in situ experiments provide with a unique opportunity to follow the calcination (or the catalytic) reactions in the *operando* conditions allowing a better understanding and optimization of the catalyst behaviour.

Acknowledgments

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