

Chemometric Analysis of Diffuse Reflectance Spectra of CoA Zeolites: Spectroscopic Fingerprinting of Co²⁺-Sites

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1. ABSTRACT

A new method for spectroscopic fingerprinting is proposed for Co²⁺ in zeolite A. The method is based on the use of different mathematical (GRAMS) and chemometrical techniques (PCA and SIMPLISMA) which were applied on series of diffuse reflectance spectra of CoA zeolite as a function of the Co-content and taken after dehydration at 400°C. Two Co²⁺ species could be determined, which were assigned to trigonal and tetrahedral coordination at the hexagonal windows. Their relative concentrations as a function of the Co-loading were determined.

2. INTRODUCTION

The coordination of TMI on surfaces is characterized by low symmetry and incomplete coordination. Different sites can be occupied simultaneously, which can lead to overlapping spectra. This is also the case for zeolites. However, the sites are crystallographically known and therefore well-defined. Here, we present an analysis method of such overlapping spectra with the most simple example Co²⁺A, where according to XRD only one site is present: the oxygen six-ring. Diffuse reflectance spectroscopy is ideally suited for probing the coordination environment *via* d-d transitions measured in the VIS region. The DRS spectra of CoA zeolites as a function of Co-content are unraveled with chemometrical techniques, like Principal Component Analysis (PCA)^{1,2} and SIMPLe-to-use Interactive Self-Modeling Analysis (SIMPLISMA)³⁻⁵. Chemometric analysis is not yet generally used in spectroscopic investigations of catalysts.^{6,7} Here, the results on the number of components and the obtained spectroscopic signatures of the different coordination sites of Co²⁺ will be discussed.

3. EXPERIMENTAL SECTION

3.1. Sample preparation and spectroscopy

Zeolite A (HMV 7) was exchanged with CoCl₂·6H₂O to obtain cobalt zeolites with variable cobalt content.⁶ The Co²⁺ contents of the samples as determined by atomic absorption spectroscopy (AAS) after acid dissolution of the solids were 0.25, 0.5, 0.86, 1.32, 1.85, 2.18, 2.48 and 2.72 Co²⁺/UC. The samples were dried, granulated (0.25-0.40 mm) and calcined at

400°C in a DRS flow cell during 24h in an oxygen stream. Diffuse reflectance spectra were taken on a Varian Cary 5 UV-VIS-NIR spectrophotometer at room temperature in the 200-2500 nm region. The spectra were recorded against a BaSO₄ standard (KODAK). Before applying mathematical/chemometrical techniques, the spectrum of the NaA support after dehydration at 400°C was subtracted from each of the CoA spectra and a baseline correction was performed.

3.2. Mathematical and chemometrical techniques

(i) The spectra were decomposed in Gaussian bands with a Grams 386 software package of Galactic. Industries. Corp.. The band positions were estimated by eye and were kept almost constant when decomposing the series of spectra. Also the bandwidths were kept almost constant.

(ii) PCA^{1,2} is a factor analysis method and the model is:

$$\bar{A} = \bar{T} \cdot \bar{B} + \bar{E}_A$$

\bar{A} (m×n) is the spectral data matrix of m samples taken at n digitized wavelengths. \bar{B} is a h×n matrix with h the number of PCA basis vectors, also called the loading vectors or loading spectra. \bar{T} is a m×h matrix with in the columns the intensities ('scores') of the h loading vectors for the m samples. The columns in \bar{T} are orthogonal. \bar{E}_A is the matrix of the spectral residuals. PCA describes the spectral information *via* principal components. This means that each component maximally describes the spectral variation in \bar{A} . The PCA analysis is performed by using the Chemometric toolbox of MATLAB.

(iii) SIMPLISMA (SIMPLE-to use Interactive Self-Modeling Analysis)³⁻⁵ is a method to resolve the spectral data matrix \bar{A} (m×n) in pure component spectra. The method is based on the principle of the pure variable. This is a variable, in this case a given wavelength, at which the intensity comes from one component only. The model is:

$$\bar{A}^T = \bar{C} \cdot \bar{S}$$

\bar{A}^T is the transpose of the spectral data matrix. \bar{S} is a (k×m) matrix with the unknown pure spectra in the mixture and \bar{C} a (n×k) matrix with in the columns the fractional contributions of the pure spectra. k is the number of pure spectra. When using in \bar{C} the observed intensities of the pure variables, \bar{S} can be resolved by the method of least-squares. The SIMPLISMA software has been developed by Willem Windig of KODAK and runs under MATLAB.

4. RESULTS

In order to gather information on the speciation of cobalt, different techniques have been applied on the DRS spectra of Co²⁺A and the visible region has been selected because of the resolution. A flowchart of the applied methods is shown in figure 1. With the Grams decomposition method the spectra were systematically resolved in Gaussian bands. In addition to the mathematical fitting of spectra, chemometrical techniques were introduced. First PCA was used to obtain the number of components. This number is necessary in the

SIMPLISMA analysis. The latter method results in pure component spectra and intensities of the pure components in the individual spectra, which allows spectroscopic fingerprinting.

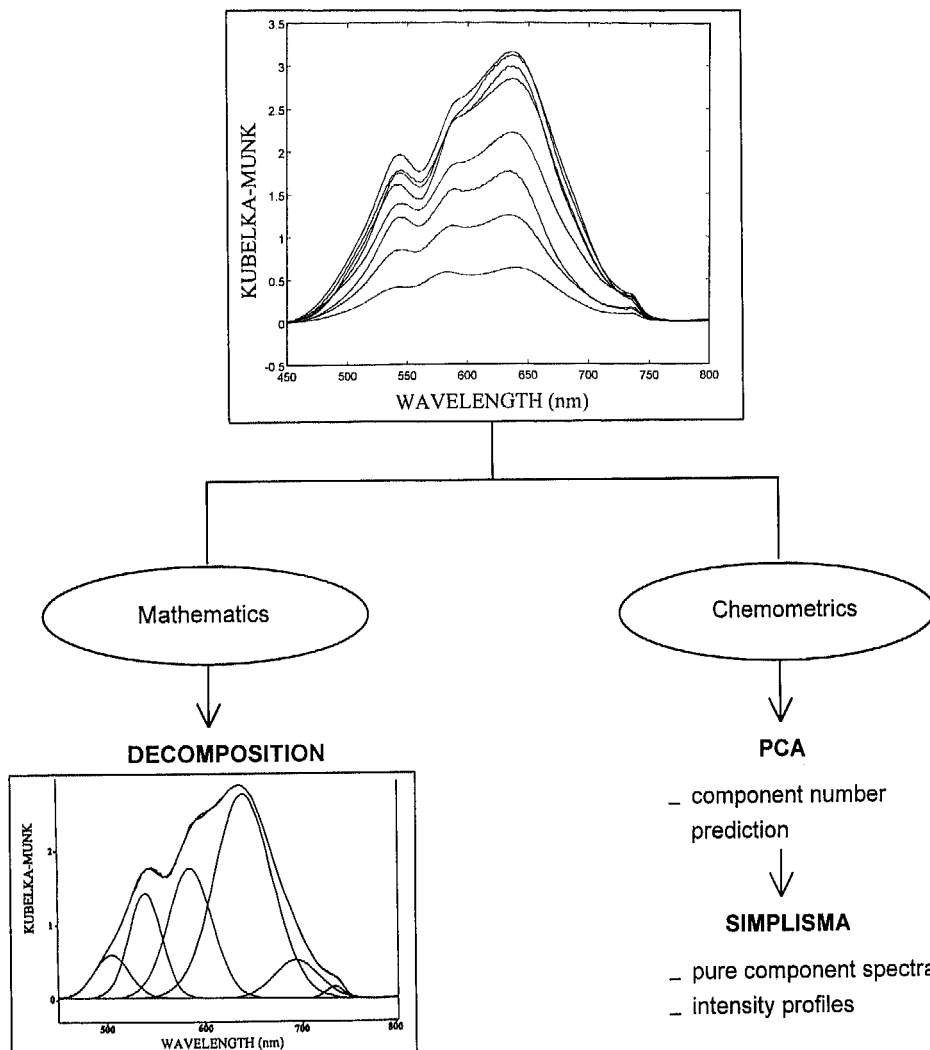


Figure 1. Flowchart for the method followed to obtain information on the speciation of Co^{2+} in zeolites. The upper figure contains the DRS spectra of CoA with increasing Co-content. The figure left below is the decomposed spectrum of $\text{Co}_{2.48}\text{A}$.

Figure 2 gives the overall spectrum of $\text{Co}_{1.85}\text{A}$ after dehydration at 400°C . In the visible region a band is present around 390 nm. A triplet can be observed with maxima around 538, 580 and 637 nm with a shoulder at 733 nm. In the near infrared a broad overlapping region of cobalt exists with at 1385 nm and 2200 nm respectively the overtone and combination bands of hydroxyls.

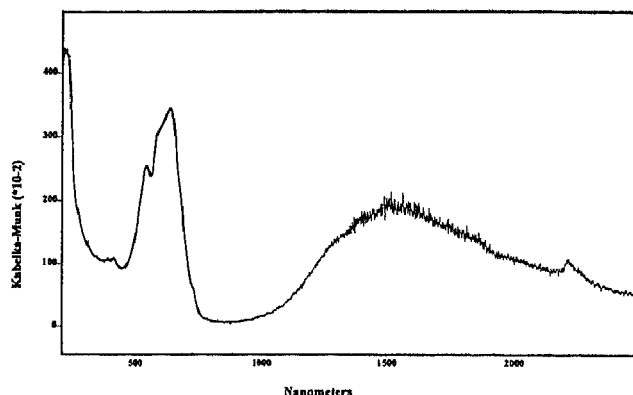


Figure 2. DRS spectrum of $\text{Co}_{1.85}\text{A}$ after dehydration at 400°C .

4.1. Spectral decomposition

The visible region of the CoA spectra was decomposed in Gaussian bands at 505, 538, 580, 637, 692 and 733 nm. The band positions were kept constant with a small variation of ± 3 nm. Figure 3 shows the intensity courses of the band areas of the band decomposition of CoA dehydrated at 400°C . The band evolutions are shown for the separate bands at 505, 692 and 733 nm. A summation of the band areas has been taken for the triplet bands around 538, 580 and 637 nm. There is a global increase of the band areas with increasing Co^{2+} -content, except for the band at 733 nm. The upper curve in figure 3 is the overall intensity of the visible region (sum of the band areas of the six bands). The intensity course is not strictly linear, which is an indication that more than one component contributes.

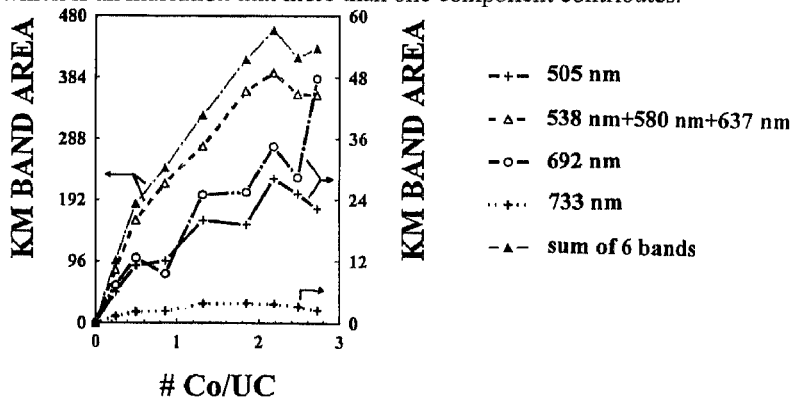


Figure 3. Band areas of the separate bands at 505, 692 and 733 nm; of the sum of the bands at 538, 580 and 637 nm; and of the sum of the six bands, all as a function of Co content for CoA dehydrated at 400°C .

4.2. Principal Component Analysis

PCA is a chemometrical tool for the determination of the number of principal components. It is an explorative technique and can be used as a predictive step before SIMPLISMA analysis. Because normalization of the spectral data in \bar{A} is a necessary step in the SIMPLISMA procedure, the same data pretreatment must be performed for a well

matched PCA analysis. The normalization formula of SIMPLISMA for a set of spectra ($j = 1 \dots m$) taken in a wavelength region with n wavelengths ($i = 1 \dots n$) and equal intervals, is:

$$Z_{ij} = \frac{x_{ij}}{\|x_i\|} = \frac{x_{ij}}{\sqrt{n(\sigma_i^2 + \mu_i^2)}}$$

with σ_i and μ_i respectively the standard deviation and mean at wavelength i of the m spectra. This normalization procedure can be simulated by variance scaling (VARSCALE) the data, which is an optional function of the chemometrics toolbox of MATLAB. Determining how many of the principal components to keep is a crucial step in factor-based techniques like PCA. The indicator function PCAREV calculates the Reduced Eigenvalues (REV) according to the method of Malinowski.⁸ It looks at the eigenvalues associated with each eigenvector and is proportional to the amount of variance in the data. Tabel 2 gives the reduced eigenvalues for the CoA data. From the REV% values in table 2, it is derived that approximately 97% of the variance can be explained with two eigenvectors or PCA components. If more than two factors are kept, one is in danger of overfitting the data and adding noise.

Table 2
Reduced Eigenvalues (REV) of the VARSCALED spectral CoA data

RANK	REV	REV%
1	0.1206	94.88
2	0.0025	1.9669
3	0.0012	0.944
4	0.0012	0.944
5	0.0007	0.0055
6	0.0005	0.0039
7	0.0003	0.0024
8	0.0001	0.0008

4.3. SIMPLISMA

Taking into account the PCA prediction of two components for CoA, SIMPLISMA can highlight the pure spectra and their intensity profile.

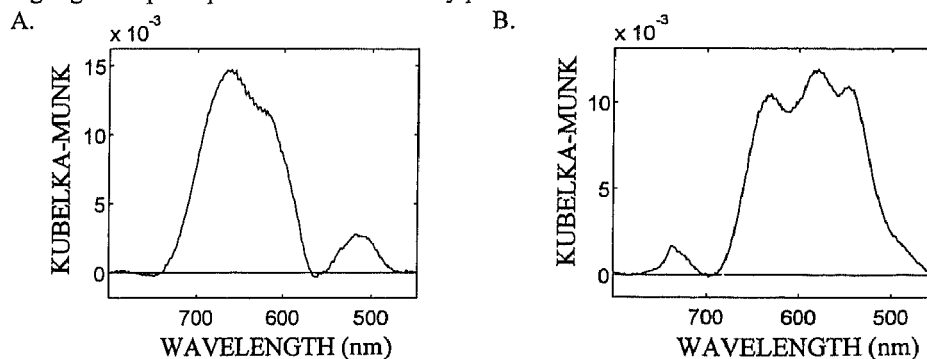


Figure 4. Pure component spectra of component 1 (4A) and component 2 (4B).

Figures 4A-B show the pure spectra. The first component has two main absorption bands at 666 and 616 nm, accompanied by a band at 512 nm. The second component has three bands at 635, 582 and 546 nm and a small band at 738 nm. Figure 5 gives the intensity contributions of the pure spectra to the individual CoA spectra. Both components increase with increasing Co^{2+} content.

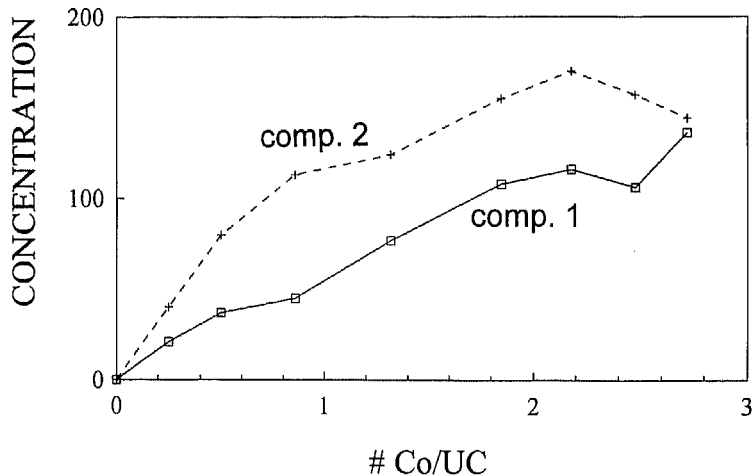


Figure 5. Intensity contributions of component 1 and 2 to the individual DRS spectra of CoA.

Table 3 gives the pure variables and the corresponding weight, purity and purity-corrected standard deviation.³ The values in the third row of table 3 are almost zero, which is an indication that only noise is left after two components were selected.

Table 3

Relative total intensities of the weight, purity and purity-corrected standard deviation.

Pure variable selected	Weight	Purity	Stdev
-	100	100	100
688	1.5371	1.2587	1.2512
552	0.0102	0.0068	0.0030

4.4. Comparison of the different techniques

The best fit decomposition of the CoA spectra gives six Gaussian bands. The band positions and widths are given in the first and second column of table 4. The third and fourth column of table 4 give respectively the absorption maxima of the pure spectra of component 1 and 2, resolved with SIMPLISMA. There is a good agreement between the band positions at 538, 580, 637 and 733 nm decomposed with Grams and the absorption maxima of component 2 of SIMPLISMA. Correspondence also exist between the intensity contributions of the sum of the three bands in figure 3 and component 2 in figure 5.

Table 4

Band positions and widths of the Gaussian bands in which the CoA spectra are decomposed and positions of the absorption maxima of the pure spectra obtained with SIMPLISMA.

Gaussian bands	Gaussian bands	component 1 (SIMPLISMA)	component 2 (SIMPLISMA)
λ/nm	width λ/nm	λ/nm	λ/nm
505 ± 3	40 ± 4	512	
538 ± 3	38 ± 3		546
580 ± 3	46 ± 6		582
		616	
637 ± 3	70		635
		666	
692 ± 3	55 ± 6		
733 ± 3	20		738

5. DISCUSSION

The three spectral analysis techniques (decomposition in Gaussian bands, PCA and SIMPLISMA) point together to the presence of two Co^{2+} species in CoA dehydrated at 400°C . One of the components (component 2, figure 4B) closely matches the experimental spectra both in band position and in intensity course. For proper use of SIMPLISMA the following must be considered: (1) the components must be pure, (2) the different components may not be correlated and (3) the law of Lambert-Beer must be valid, which means that spectra in the non-linear absorption regime can't be used for the analysis.

Klier proposed a single nearly trigonal symmetry of Co^{2+} in CoA, calcined at 350°C , where Co^{2+} is coordinated to three framework oxygens almost in the plane of the six-ring,⁹ Heilbron and Vickerman suggested the existence of a pseudo-tetrahedral $\text{Co}(\text{Ox})_3\text{O}^{2-}$ or $\text{Co}(\text{Ox})_3\text{OH}$ species (Ox=lattice oxygen) after dehydration at 400°C and the development of trigonal CoO_3 at higher temperatures.¹⁰ From our chemometrical methods a co-existence of two coordinations after dehydration at 400°C is most probable. The bonding of cations with non-lattice oxygens is common for polyvalent cations such as Ca^{2+} , La^{3+} and Ce^{3+} in X- and Y-type zeolites.¹¹⁻¹³ These two components are also present in Co^{2+} -exchanged faujasite-type X- and Y-zeolites, as was found in a recent study.⁶

The question is how to assign the coordination types to real sites in zeolite A. There are three six-ring sites in zeolite A: in the cubo-octahedron, in the plane of the six-ring and in the supercage.^{14,15} When located in the plane of the six-ring, the coordination is trigonal. In the two other cases the coordination is pseudo-tetrahedral if a fourth extra-lattice ligand is present. We suggest that the pure spectrum of the first component with two absorptions in the 610-680 region and one at 525 nm (figure 4A) corresponds to pseudo-tetrahedral symmetry and that the pure spectrum of the second component with three bands at 635, 582 and 546 nm and with a small band at 730 nm (figure 4B) corresponds to trigonal symmetry. Pseudo-tetrahedral cobalt is thus assumed to make up part of the coordination when CoA is fully dehydrated, but the component which matches best the experimental spectrum is trigonal. For the exact interpretation of the pure spectra calculations of theoretical spectra of the coordination of Co^{2+} at the six-rings are in progress.

6. CONCLUSIONS

A combination of band decomposition, PCA and SIMPLISMA applied on DRS spectra, has proved to be useful for the determination of Co^{2+} coordinations in zeolite A. After dehydration at 400°C two components have been identified, which were assigned to trigonal and pseudo-tetrahedral symmetry of cobalt at the six-ring sites of zeolite A. Both components are common to two of the three earlier defined components in faujasite-type X- and Y-zeolites. Future work will be directed towards an extension of the chemometric techniques which can aid in the spectroscopic investigation of zeolites and of heterogeneous catalysts in general.

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