

Chemometric analysis of diffuse reflectance spectra of Co^{2+} -exchanged zeolites: spectroscopic fingerprinting of coordination environments

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Received in revised form 30 December 1996; accepted 31 December 1996

Abstract

A new method for spectroscopic fingerprinting of the coordination environments of Co^{2+} in zeolites is proposed and discussed. The method is based on the application of different chemometric techniques (curve fitting, Principal Component Analysis (PCA) and SIMPLEx-to-use Interactive Self-Modeling Analysis (SIMPLISMA)) on a series of diffuse reflectance (DR) spectra of Co^{2+} -exchanged zeolites dehydrated at 400°C and 500°C. Two Co^{2+} species were determined for CoA and assigned to trigonal and pseudo-tetrahedral coordination of Co^{2+} at the hexagonal windows of six oxygens. Three components were determined for CoX and CoY: two of them are similar to those of zeolite A; the third one is ascribed to pseudo-octahedral Co^{2+} in the hexagonal prisms.

Keywords: DRS; Cobalt; SIMPLISMA

1. Introduction

Identifying and quantifying coordination environments of transition metal ions (TMI) in TMI-exchanged catalysts is fundamental for understanding their chemistry and catalytic action. Diffuse reflectance spectroscopy (DRS) is one of the least expensive and, in principle, the most versatile spectroscopic technique for studying metal supported catalysts, as both $d-d$ and charge transfer transitions can be probed [1]. The simultaneous occurrence of several coordina-

tions of TMIs in the activated state of the catalysts makes the analysis difficult and, in most cases, only qualitative information can be obtained. Chemometrics is slowly finding its way in surface spectroscopy [2–4]. To our knowledge, we were the first to apply it to DR spectra of TMI on amorphous oxides and in zeolites. DR spectra of these materials can be noisy, especially in the NIR region (PbS detection instead of a photo-multiplier in VIS–UV region). In addition they are characterized by a baseline which increases non-linearly from the visible region into the UV region. Here, we propose a chemometric analysis of the DR spectra of Co^{2+} -containing zeolites as a

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function of the zeolite type (A, X and Y) and the Co^{2+} -loading. Zeolites are considered as model systems, because they are crystalline materials with well-defined cation sites. Their structure is based on the condensation of TO_4 units (with T a cation in tetrahedral coordination), resulting in the formation of three-dimensional networks with channels and cavities. Zeolites A, X and Y are aluminosilicate zeolites. They are built up with silicate (SiO_4) and aluminate (AlO_4) tetrahedra. The transition metal is Co^{2+} of which the $d-d$ transitions can be probed in the visible and near infrared region. The used chemometric techniques are curve fitting, Principal Component Analysis (PCA) and SIMPLISMA-to-use Interactive Self-Modeling Analysis (SIMPLISMA).

2. Experimental

Zeolite A (HMV 7), X and Y (Ventron) were exchanged with NaCl, then with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to obtain a range of cobalt contents [2,4]. The samples were dried, pelletized (0.25–0.40 mm) and calcined at 400°C for CoA and at 400°C and 500°C for CoX and CoY in a DRS flow cell during 24 h in an oxygen stream. DR 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 BaSO_4 standard (KODAK). The computer processing of the spectra consisted of the following steps: subtraction of the spectrum of the parent zeolite from that of the Co^{2+} -exchanged zeolites measured after the same treatment, subtraction of a linear baseline in the visible region, calculation of the Kubelka–Munk function. The spectra were decomposed in Gaussian bands with the Grams/386 software package of Galactic Industries. The band positions were estimated by eye and were kept almost constant ($\pm 100 \text{ cm}^{-1}$ (3 nm)) when decomposing the series of spectra. Also the bandwidths were kept almost constant ($\pm 150 \text{ cm}^{-1}$ (4 nm)).

PCA [5,6] is a factor analysis method and the model is

$$\mathbf{X} = \mathbf{T} \times \mathbf{P}'$$

\mathbf{X} ($n \times p$) is the original data matrix of n samples (spectra) and p variables (wavelengths). Given a set of p variables, PCA tries to find a set of m variables \mathbf{T}

(with $m < p$), in such a way that by replacement of \mathbf{X} by \mathbf{T} 'no' information is lost. PCA thus results in the transformation of the original x -variables into new t -variables, which are linear combinations of the x -variables. \mathbf{T} ($n \times m$) is called the scores matrix and \mathbf{P} ($p \times m$) the loading matrix. The PCA analysis is performed by using the NIPALS algorithm (pcanip) of the Chemometric toolbox of MATLAB.

SIMPLISMA [7–12] is a method to resolve the spectral data matrix \mathbf{D} ($v \times c$) 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 chemical component only. The matrix notation is

$$\mathbf{D}^T = \mathbf{C} \times \mathbf{S}$$

\mathbf{D}^T ($c \times v$) contains mixture spectra in its rows. The matrix \mathbf{C} ($c \times n$) contains in its columns the fractional contributions of the pure components in the mixture spectra, where n is the number of pure components. \mathbf{S} ($n \times v$) contains the pure spectra. When using in \mathbf{C} the observed intensities of the pure variables in the spectra in \mathbf{D} , \mathbf{S} can be resolved by least-squares. The SIMPLISMA software has been developed by Willem Windig and runs under MATLAB [7,8].

3. Results and discussion

3.1. Evaluation of SIMPLISMA

To evaluate the possibilities of the SIMPLISMA method when applying to DR spectra three aspects are first investigated: band separation, noise and baseline variation.

3.1.1. Band separation

Series of theoretical spectra, built from two normal Gaussian curves with the same absorbance, were constructed and evaluated with SIMPLISMA as a function of the relative distance between the two curves. Gaussian bands are the best representation of the DRS bands, because DRS bands are inhomogeneously broadened due to heterogeneous siting of Co^{2+} in zeolites and instrument factors. Fig. 1 shows the spectrum of two overlapping Gaussian curves with different relative intensities of which the separation of

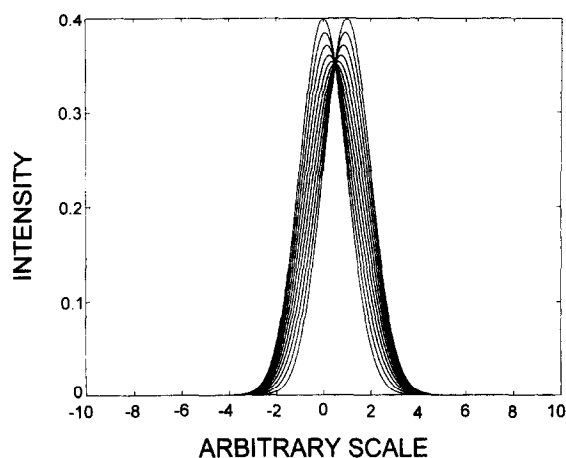


Fig. 1. Theoretical generated spectra of two overlapping normal Gaussian curves at 5% distance of the total scale of the spectrum.

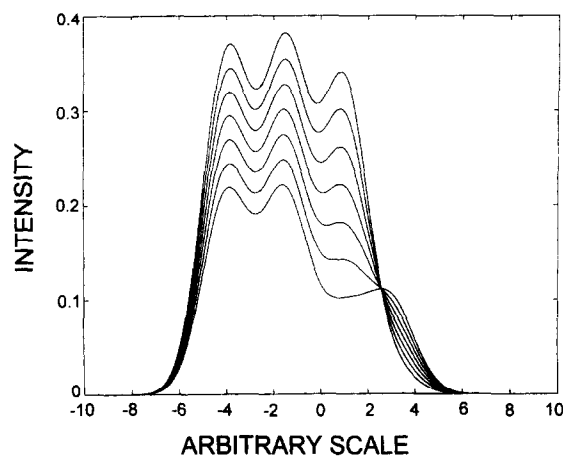


Fig. 2. Theoretical spectrum built from two species, each existing of three Gaussian bands; species 1 has band maxima at -4 , -1.5 and 1 ; species 2 has band maxima at -4 , -1.5 and 3 .

the maxima of the individual curves is 5% of the total scale of the theoretically generated spectra. At this separation a mixture of two pure components can be separated without loss of the characteristics of the original components. It must be mentioned that SIMPLISMA results in a mathematical solution, which is not unique. This means that the shape of the pure spectra resolved with SIMPLISMA corresponds with that of the original spectra, but the intensity of the pure spectra and their intensity contributions only correspond relatively with the original intensities.

Fig. 2 is built from two species, each consisting of different Gaussian bands. The first species is built from three Gaussian bands with band maxima at -4 , -1.5 and 1 , all with the intensity of the normal Gaussian curve. Species two is built from three Gaussian curves with band maxima at -4 , -1.5 and 3 . The intensity of the first two maxima is 0.4 times the intensity of the normal Gaussian curve, the intensity of the maximum at 3 is 0.3 times the intensity of the normal Gaussian curve. The intensity of one species increases, when the intensity of the second decreases. Fig. 3 gives the pure components. They represent the original spectra extremely well. Thus, there is no contamination of closely spaced bands. When two species with closely spaced band positions have the same intensity profile, a successful separation is more difficult and negative contributions to the pure component spectra are observed.

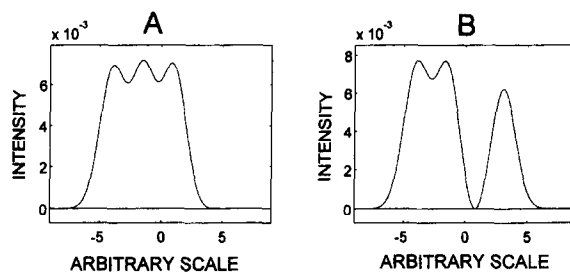


Fig. 3. Pure component spectra of the theoretical spectra in Fig. 2: species 1 (3A) and species 2 (3B).

3.1.2. Noise

Spectra can often be rather noisy. One can smooth the data before SIMPLISMA analysis or increase the offset, a parameter to reduce noise. In Fig. 4 1% noise is added to the spectra of Fig. 2. With an offset of 1 (=the lowest value of offset) the pure component spectra of Fig. 5 were detected. Fig. 5 also gives the pure component spectra with 3% and 5% noise. In the latter cases minimum offsets of respectively 4 and 8 are necessary to be able to detect the pure components above the noise. It is sometimes better first to smooth the noisy spectra before analysis.

3.1.3. Baseline variation

Fig. 6 shows the spectra of Fig. 2 but with different gradients of the baseline. This strongly deforms the

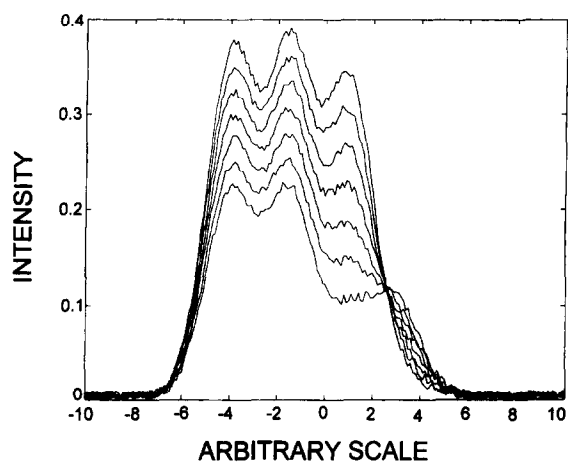


Fig. 4. Theoretical spectra of Fig. 2 with 1% noise.

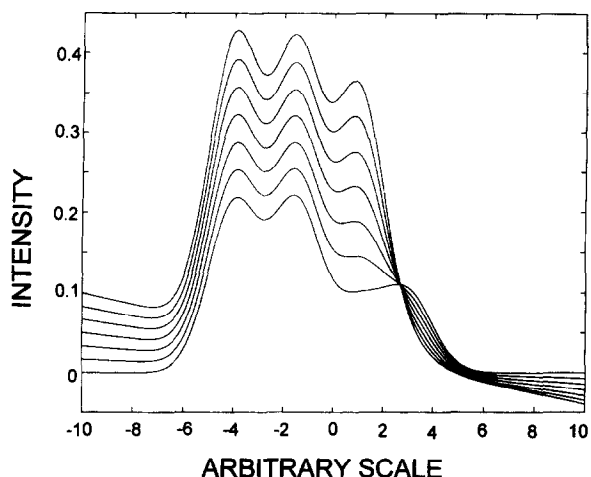


Fig. 6. Theoretical spectra of Fig. 2 with addition of different baselines.

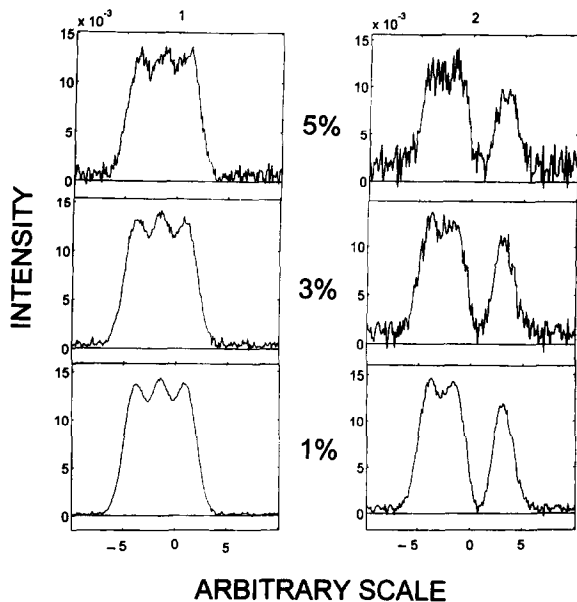


Fig. 5. Pure component spectra of the spectra in Fig. 2 with addition of respectively 1%, 3% and 5% noise.

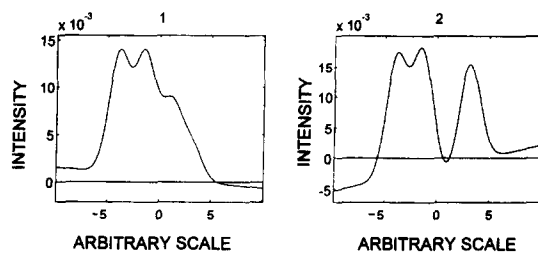


Fig. 7. Pure component spectra of the theoretical generated spectra with different baselines.

pure spectra as can be seen in Fig. 7. The spectra were analysed by using an offset of 1. There is no improvement when inactivating the outer regions during SIMPLISMA analysis. It is therefore advised to subtract the different baselines before analysis so as to obtain an horizontal baseline. In the visible region the baselines can be fitted by straight lines.

3.2. Chemometrics applied to Co^{2+} zeolites

In order to gather information on the spectroscopic fingerprinting of cobalt, different techniques have been applied on the DRS spectra of Co^{2+} -exchanged zeolites. Fig. 8 gives the spectra of CoA zeolites after dehydration at 400°C . With the curve fitting technique the spectra were systematically resolved in Gaussian bands. In addition to the curve fitting of spectra, PCA and SIMPLISMA were introduced. First PCA was used to obtain the number of principal components. This number is called the rank of the data matrix. The rank determination is useful for 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.

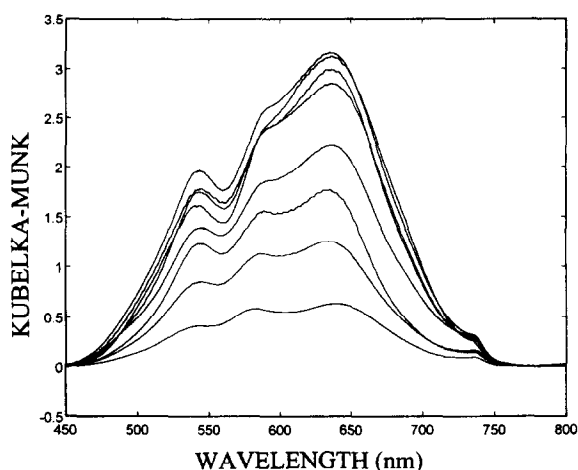


Fig. 8. Series of diffuse reflectance spectra of CoA zeolites dehydrated at 400°C.

In the following paragraph the method will be discussed in detail. For CoA a systematic decomposition in six bands was executed at $13\,650\text{ cm}^{-1}$ (733 nm), $14\,450\text{ cm}^{-1}$ (692 nm), $15\,700\text{ cm}^{-1}$ (637 nm), $17\,250\text{ cm}^{-1}$ (580 nm), $18\,600\text{ cm}^{-1}$ (538 nm) and $19\,800\text{ cm}^{-1}$ (505 nm). The intensity course of the sum of all the bands is not strictly linear, which could indicate that more than one component contributes.

PCA indicates that 97% of the spectral variance can be explained with the first two principal components. The third component contributes less than 1% to the spectral variance and probably only fits experimental noise. Taking into account the PCA determination of two components, SIMPLISMA can generate the pure spectra and their profiles. Fig. 9 shows the two pure spectra of CoA. Component 1 has two band maxima in the $14\,700\text{--}16\,400\text{ cm}^{-1}$ (680–610 nm) region and a band at $19\,500\text{ cm}^{-1}$ (513 nm) and component 2 has three bands at $18\,300\text{ cm}^{-1}$ (546 nm), $17\,200\text{ cm}^{-1}$ (580 nm) $15\,750\text{ cm}^{-1}$ (635 nm) and a weak band at $13\,550\text{ cm}^{-1}$ (738 nm). The intensity profiles of the two components increase with increasing Co^{2+} -content. Component 1 and 2 are suggested to be pseudo-tetrahedral and trigonal Co^{2+} at the hexagonal windows. For the exact interpretation of the pure spectra, angular overlap model (AOM) calculations of theoretical spectra of the coordination of Co^{2+} at the six-ring sites, are in progress [13,14].

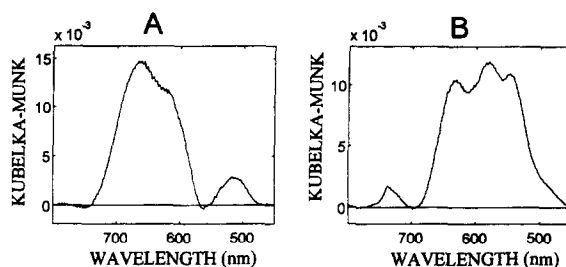


Fig. 9. Experimental pure component spectra of component 1 (9A) and component 2 (9B) of CoA dehydrated at 400°C.

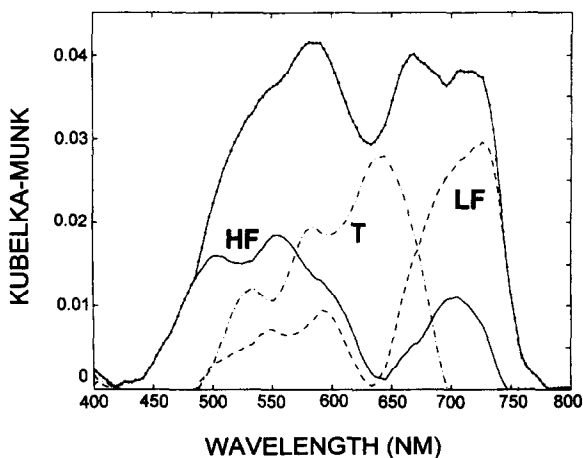


Fig. 10. Experimental pure component spectra determined with SIMPLISMA for CoY dehydrated at 400°C; HF, high-frequency component; T, triplet component; LF, low-frequency component.

For CoX and CoY series of spectra taken after dehydration at 400°C and 500°C and with increasing Co-content were decomposed in five bands being at $13\,700\text{--}13\,800$, $15\,450\pm 200$, $17\,100\pm 100$, $18\,700\pm 100$ and $20\,000\pm 100\text{ cm}^{-1}$. A supplementary sixth band at $14\,600\text{ cm}^{-1}$ was needed in the CoX spectra. PCA gives three pure components in all cases. Fig. 10 gives the pure component spectra for CoY dehydrated at 400°C and Fig. 11 gives the corresponding intensity profiles. The components are called the high-frequency component (HF) with two maxima at $20\,000\text{ cm}^{-1}$ (500 nm) and $17\,850\text{ cm}^{-1}$ (560 nm), a triplet component (T) with three band maxima at $15\,650\text{ cm}^{-1}$ (640 nm), $17\,150\text{ cm}^{-1}$ (583 nm) and $18\,700\text{ cm}^{-1}$ (535 nm) and a low-frequency component (LF) with main purity around $14\,000\text{ cm}^{-1}$ (715 nm). For CoX the HF component has two band

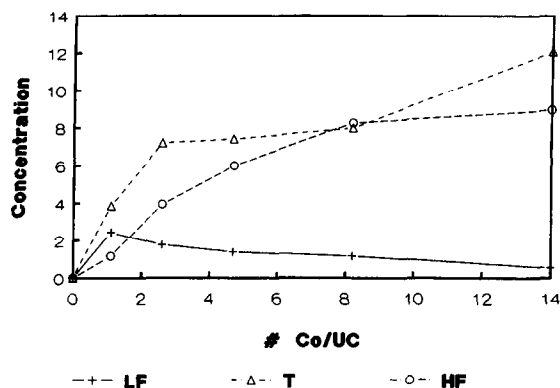


Fig. 11. Intensity course of the pure components in the visible region for CoY dehydrated at 400°C.

maxima at 19 600 and 17 850 cm^{-1} , the T component has three bands at 15 950, 17 000 and 18 750 cm^{-1} and the LF component occurs in the 14 000–14 900 cm^{-1} region. Good agreement was found between the intensity profiles of the decomposed band at 20 000 cm^{-1} and the HF component, between the sum of the three bands at 15 450, 17 100 and 18 700 cm^{-1} and the T component and between the band at 13 800 cm^{-1} and the LF component.

Supplementary decomposition in the near infrared region revealed that similar intensity courses occur for the sum of the triplet bands in the visible and near infrared region. With the aid of La^{3+} - and Cs^+ -exchanged CoX and CoY zeolites the components were assigned as follows: the HF component is Co^{2+} pseudo-octahedral in the hexagonal prisms, the T component is pseudo-tetrahedral Co^{2+} at sites I' and II and the LF component is trigonal coordinated Co^{2+} at the same sites as the T component.

4. Conclusions

A combination of curve fitting, PCA and SIMPLISMA applied on DRS spectra, has proved to be useful for the determination of Co^{2+} coordinations in zeolites A, X and Y. After dehydration at 400°C of CoA two components have been identified, which were assigned to trigonal and pseudo-tetrahedral symmetry of cobalt at the six-ring sites. Both components are common to two of the three components determined in faujasite-type X- and Y-zeolites. The SIM-

PLISMA analysis of DR spectra can be optimized by smoothing in case of noisy spectra and by baseline subtraction.

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 [3].

Acknowledgements

A.A.V. acknowledges a grant of the I.W.T. (Belgium) and B.M.W. a grant as post-doctoral research assistant of the National Fund for Scientific Research of Belgium (N.F.W.O.). This work was financially supported by the Geconcerteerde Onderzoeksactie (GOA) of the Flemish Government and by the Fonds voor Kollektief Fundamenteel Onderzoek (FKFO) under grant no. 2.0050.93.

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