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Diffuse Reflectance Spectroscopy of Supported Chromium Oxide Catalysts: A Self-Modeling Mixture Analysis

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Diffuse reflectance spectra of hydrated, calcined, and reduced chromia/silica-alumina ($Cr/SiO_2 \cdot Al_2O_3$) catalysts with different SiO_2 contents have been investigated by using an interactive self-modeling mixture analysis. Four pure components are revealed in the spectra of Cr-catalysts before and after calcination: these are component A with three characteristic bands at 225, 325, and 495 nm, component B with three bands at 220, 275, and 400 nm, component C absorbing at 565 nm, and component D which absorbs in the region 205–270–350 nm. Components A and B are due to chromate and dichromate, respectively and their relative ratio increases with decreasing SiO_2-content of the support. Component C is assigned to pseudo-octahedral Cr^{3+} and is especially present on SiO_2 after calcination, while component D is a background due to the support. After CO-reduction three (E, F, and G) and four (E, F, G, and H) pure components were extracted from the spectra of Cr/Al_2O_3 and Cr/SiO_2, respectively. Components E and G have absorptions around 225, 355, and 475 nm and are due to Cr^{6+}. They decrease with increasing reduction temperature. Component F absorbs at 635 nm on Al_2O_3 and at 855 nm on SiO_2. These bands are assigned to pseudo-octahedral Cr^{3+} and Cr^{2+}, respectively. Pure component H, only present on Cr/SiO_2, absorbs at 305 and 540 nm and is possibly due to traces of Cr^{3+}. All these findings are discussed in relation with previous results obtained by spectral deconvolution.

INTRODUCTION

Identifying and quantifying oxidation states and coordination environments of transition metal ions (TMIs) in supported catalysts is fundamental for understanding their chemistry and catalytic action. Various spectroscopic techniques are available to perform this task, but the heterogeneous nature of the catalysts and the simultaneous occurrence of several oxidation states of TMIs in the activated state of the catalysts makes the analysis difficult and, in most cases, only qualitative information can be obtained.

For 3d TMIs the most popular techniques for direct probing of the oxidation state and coordination environments are X-ray photoelectron spectroscopy (XPS) (1–7), electron spin resonance (ESR) (8–12), X-ray absorption spectroscopy (EXAFS-XANES) (13, 14), Raman spectroscopy (15–21), and diffuse reflectance spectroscopy (DRS) (22–30). The last one is the least expensive and, in principle, the most versatile technique, as both *d–d* and charge transfer transitions can be probed (31). The technique has been successfully applied by us on supported chromium oxide catalysts (32, 33). Quantitative analysis of activated and reduced catalysts was possible by decomposition of the spectra in a consistent set of Gaussian bands due to chromate, dichromate, pseudo-octahedral Cr^{3+}, pseudo-octahedral Cr^{2+}, and pseudo-tetrahedral Cr^{2+} with a commercial software package entitled SPECTRA CALC (Galactic Industries Inc.). The band maxima are given in Table 1. The consistency of the analysis over a large data set and the agreement of the results with the expected chemistry of Cr were taken as indications for the physical meaningfulness of such a procedure.

To avoid biased analysis a statistical analysis of the dataset is necessary. The data matrix D, consisting of n spectra, each with m datapoints, is decomposed as a linear combination of spectra of independent pure components, each with a specific weight. These weights are proportional to the concentrations of the pure components in the mixtures in accordance with Beer's law.

Different techniques such as factor analysis (FA), principal component analysis (PCA) and partial least squares (PLS) can be used (34). Here, we propose SIMPLISMA[2] (Simple-to-Use-Interactive-Self-Modeling-Analysis) developed by Windig *et al.* (35–38), because it gives not only the number of pure components and their spectra, but the researcher can also intervene and decide by himself whether to accept a pure component or not.

METHODS

1. *Principles of SIMPLISMA*

Consider the data matrix $D = \{d_{ij}\}(i = 1, \ldots, n$ and $j = 1, \ldots, m)$ of n spectra, each with m wavelengths at which

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[2] The SIMPLISMA software can be obtained upon request from Willem Windig at Eastman Kodak Company, Rochester, NY 14652-3712.

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TABLE 1

Band Positions of Surface Cr^{6+}, Cr^{3+} and Cr^{2+} on Dehydrated Surfaces (32, 33)

Cr-species	Band positions (nm)
Chromate	275, 370
Dichromate	275, 322, 445
Pseudo-octahedral Cr^{3+}	295, 465, 625
Pseudo-octahedral Cr^{2+}	800
Pseudo-tetrahedral Cr^{2+}	1000

the absorption d_{ij} is measured. The dimension of D is $n \times m$, with n, the number of spectra and m, the number of wavelengths. If these spectra are linear superpositions of spectra of independent pure components, then

$$D^{\mathrm{T}} = C \times E \qquad [1]$$

with E a matrix containing the spectra of the pure components and C the matrix of the weight factors. (D^{T} is the transpose of D.) E can be resolved with the least squares method:

$$E = (C^{\mathrm{T}} \times C)^{-1} \times C^{\mathrm{T}} \times D^{\mathrm{T}} \qquad [2]$$

It has dimensions $m \times l$, with l the number of pure components. C is an $l \times n$ matrix. If $m > l$ and $n > l$, the rank of D is l, the number of pure components. Then, $P = D \cdot D^{\mathrm{T}}$ with dimensions $m \times m$ and $Q = D^{\mathrm{T}} \cdot D$ with dimensions $n \times n$ have the same number of nonzero eigenvalues l. Diagonalizing Q is easier because its dimensionality is much smaller than that of P. Therefore, the l eigenvalues are easily obtained and their corresponding spectral matrix is E. The selection of pure components is based upon purity values, p_j ($j = 1, \ldots, m$) defined as

$$p_j = w_j \frac{\sigma_j}{\mu_j + \alpha} \qquad [3]$$

with σ_j the standard deviation at a given wavelength j

$$\sigma_j = \sqrt{\frac{\sum_{i=1}^{n} (d_{ij} - \mu_j)^2}{n}} \qquad [4]$$

and μ_j the mean of absorbances at a given wavelength

$$\mu_j = \sum_{i=1}^{n} d_{ij} \frac{1}{n}, \qquad [5]$$

where d_{ij} is the intensity of the ith spectrum at wavelength j. The first pure variable is then taken as that with the highest p_j value. α is a noise reduction parameter. It allows the assignment of lower purity value to variables with a low mean value (i.e., in the noise range) and is defined as

$$\alpha = \frac{\text{offset}}{100} \times \max(\mu), \qquad [6]$$

where an offset between 1 and 3 is used in this work for spectral analysis. The quantity w_j is a weight factor to correct for previously selected pure variables and for the normalization applied to the data matrix. Initially, w_j is equal to one.

2. *Band Separation*

To evaluate the possibilities of the SIMPLISMA method to separate pure components, a theoretical experiment was designed. Series of theoretical spectra, built up with two normal Gaussian curves, were constructed and evaluated with SIMPLISMA as a function of the relative distance between the two curves. The minimal percentage distance between the two overlapping Gaussian curves, necessary for ideal separation, was determined to be equal to 5%. Ideal separation means a separation for which the intensity profiles of the resolved bands correspond to those of the original Gaussian curves. Thus, a mixture of two pure components can be exactly separated in a spectral range of 100 nm if the difference between the band maxima is at least 5 nm.

3. *Spectral Reconstruction*

The diffuse reflectance spectra of supported chromium oxide catalysts are composed of *d–d* and charge transfer transitions of chromate, dichromate, Cr^{3+}, and Cr^{2+}, the band maxima of which are given in Table 1.[3] They originate from a decomposition of the experimental spectra in Gaussian bands with SPECTRA CALC, as given in foregoing papers (32, 33). The corresponding theoretical spectra (no noise and no background) are shown in Fig. 1. The five different theoretical components distinctively marked in Fig. 1 may be labeled as: (1) chromate (main absorptions at 275 and 370 nm), (2) dichromate (main absorptions at 275, 350, and 445 nm), (3) pseudo-octahedral Cr^{3+} (absorption

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[3] The assignment of the 445 nm band in the diffuse reflectance spectra of supported chromium oxide catalysts has been a strong point of discussion in the literature. The assignment has been reviewed by McDaniel (M. P. McDaniel, *Adv. Catal.* **33**, 47 (1985)). The 445 nm band can be assigned in two different ways: (1) to dichromate/polymeric species (with symmetry lower than T_d) because the 445 nm band is present in the UV–VIS absorption spectra of acidic aqueous solutions of Cr(VI) salts and (2) to a highly distorted chromate species (also with symmetry lower than T_d) because this will give rise to low-symmetry components with absorptions near 445 nm as observed for some Cr(VI) salts by Szabó *et al.* (Z. G. Szabó, K. Kamaras, S. Szebini, and I. Ruff, *Spectrochim. Acta* **34**, 607 (1978)). The detailed assignment of the chromate spectrum, however, is not yet clear. Several theoretical calculations show different assignments and our attempts to perform CASSCF/CASPT2 calculations on the chromate ion failed (B. M. Weckhuysen, K. Pierloot, and R. A. Schoonheydt, unpublished results). Detailed experimental studies of our group (see, e.g., Refs. (25, 32, 33)), however, show that the 445 nm band must be indicative for dimeric or polymeric Cr species, diffuse reflectance spectroscopy being unable to distinguish them. The intensity of the 445 nm band gradually increases with increasing SiO_2-content of the support and with increasing Cr-loading. As a consequence, we have assigned in the present investigation the 445 nm absorption band to dichromate as reported in Table 1.

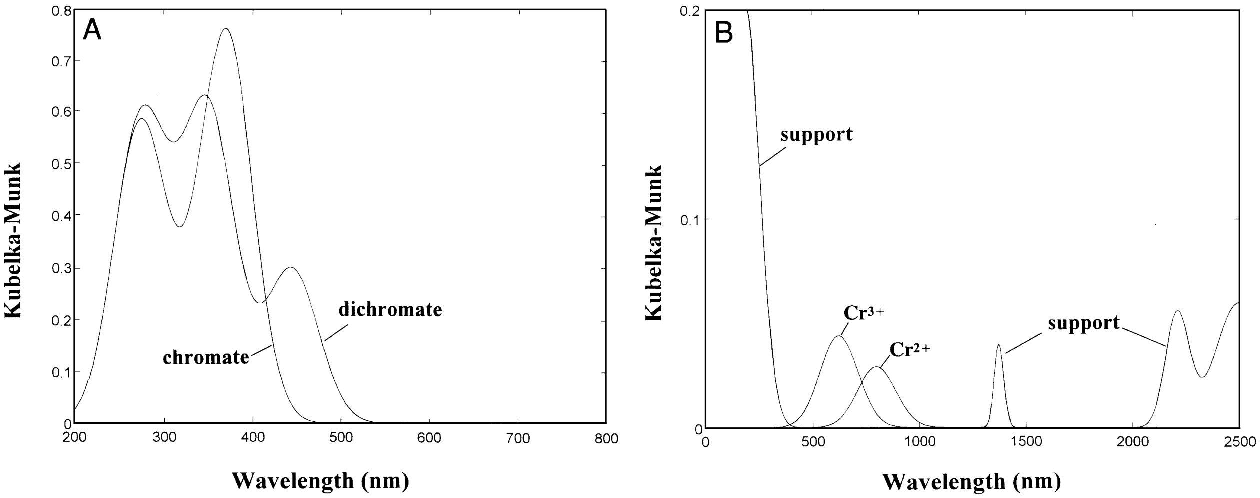

FIG. 1. The five pure components for building up the theoretical spectra: (1) chromate; (2) dichromate; (3) octahedral Cr^{3+}, (4) octahedral Cr^{2+}, and (5) support.

at 625 nm—the two bands at higher energy were excluded because they are negligibly weak when compared with the overlapping chromate and dichromate bands), (4) pseudo-octahedral Cr^{2+} (absorption at 800 nm) and (5) a support background (absorptions at 200, 1375, 2210, and 2500 nm—the three latter bands are overtone and combination bands of the hydroxyls). By linear combination of these pure components series of theoretical spectra can be built up.

Figure 2A is an imitation of diffuse reflectance spectra of calcined chromia/silica-alumina ($Cr/SiO_2 \cdot Al_2O_3$) catalysts with increasing SiO_2 content of the support and is built up with components 1, 2, 3, and 5. This increase in silica-content is seen in an increase of the Cr^{3+} band at 625 nm and of the dichromate band at 445 nm. When a $Cr/SiO_2 \cdot Al_2O_3$ catalyst is reduced, the chromate and dichromate bands disappear gradually and a broad band in the region 625–800 nm (Cr^{3+}, Cr^{2+}) increases in intensity. This is reconstructed in Fig. 2B. When SIMPLISMA is operated on these two idealized data sets, the pure components of Figs. 3 and 4 emerge, corresponding respectively to Figs. 2A and 2B. In the first case (calcined $Cr/SiO_2 \cdot Al_2O_3$) four components are found (Fig. 3), which, with reference to Fig. 1 and Table 1, correspond respectively to dichromate, chromate, Cr^{3+} and a support background. The agreement both in band positions and in intensities is excellent, except for the intensities of the dichromate bands: the 445 nm shoulder is overestimated, whereas the 275 nm band is underestimated. More

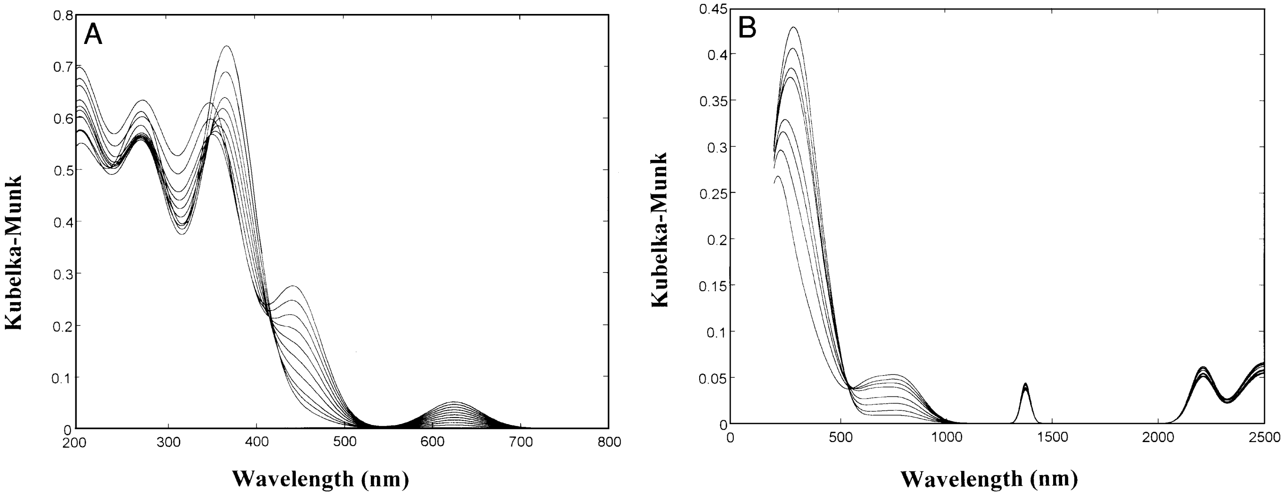

FIG. 2. (A) Theoretical spectra of hydrated and calcined $Cr/SiO_2 \cdot Al_2O_3$ catalysts as a function of the Si : Al ratio of the support. The curves with the lowest and highest values of the *K–M* function at ca. 450 nm are those for the lowest and highest Si : Al ratios, respectively. (B) Theoretical spectra of reduced $Cr/SiO_2 \cdot Al_2O_3$ catalysts as a function of reduction temperature.

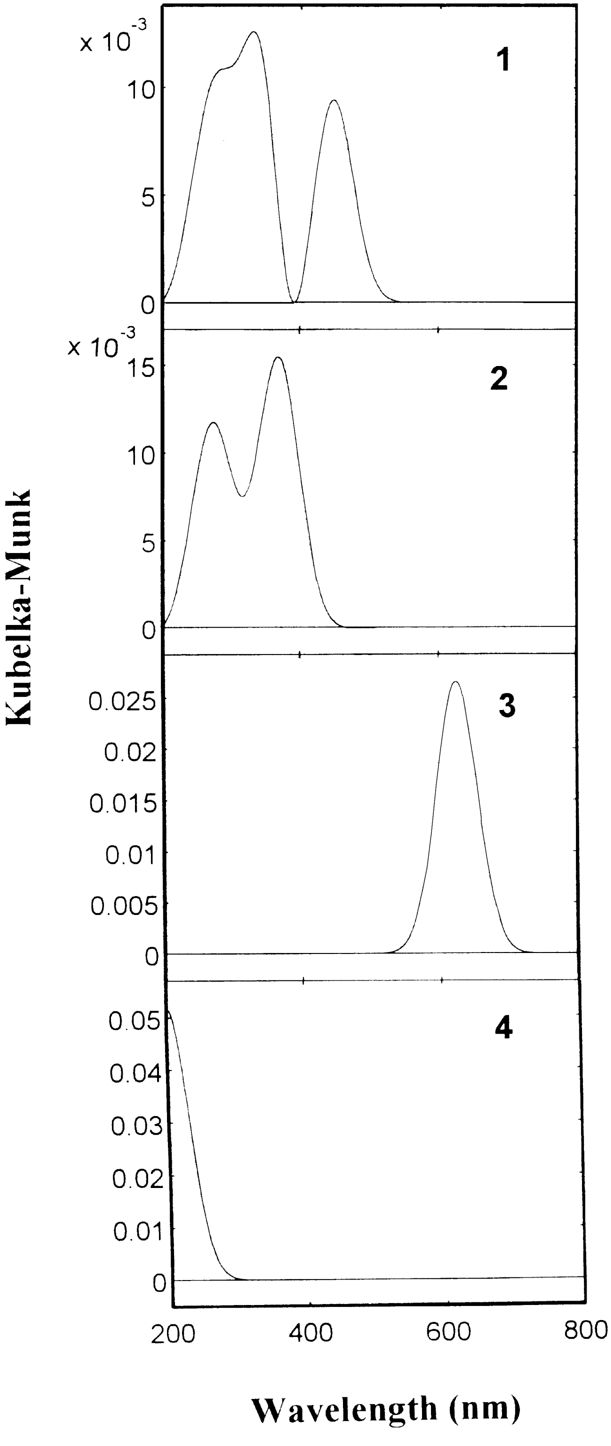

FIG. 3. Absorption profiles of the pure components of the theoretical spectra of hydrated and calcined $Cr/SiO_2 \cdot Al_2O_3$ catalysts: (1) dichromate, (2) chromate, (3) pseudo-octahedral Cr^{3+}, and (4) support.

problems arise with the reconstructed spectra of the reduction of a $Cr/SiO_2 \cdot Al_2O_3$ catalyst (Fig. 4), which are built up with components 1, 3, 4, and 5. Four components were found as expected, but the chromate component was not recovered properly. Another problem is the negative bands, which is important for the Cr^{3+} case (component 4) and Cr^{2+} (component 1), but which also exist in the spectra of the two other pure components. It is clear that real pure variables are not always being recovered by the SIMPLISMA method.

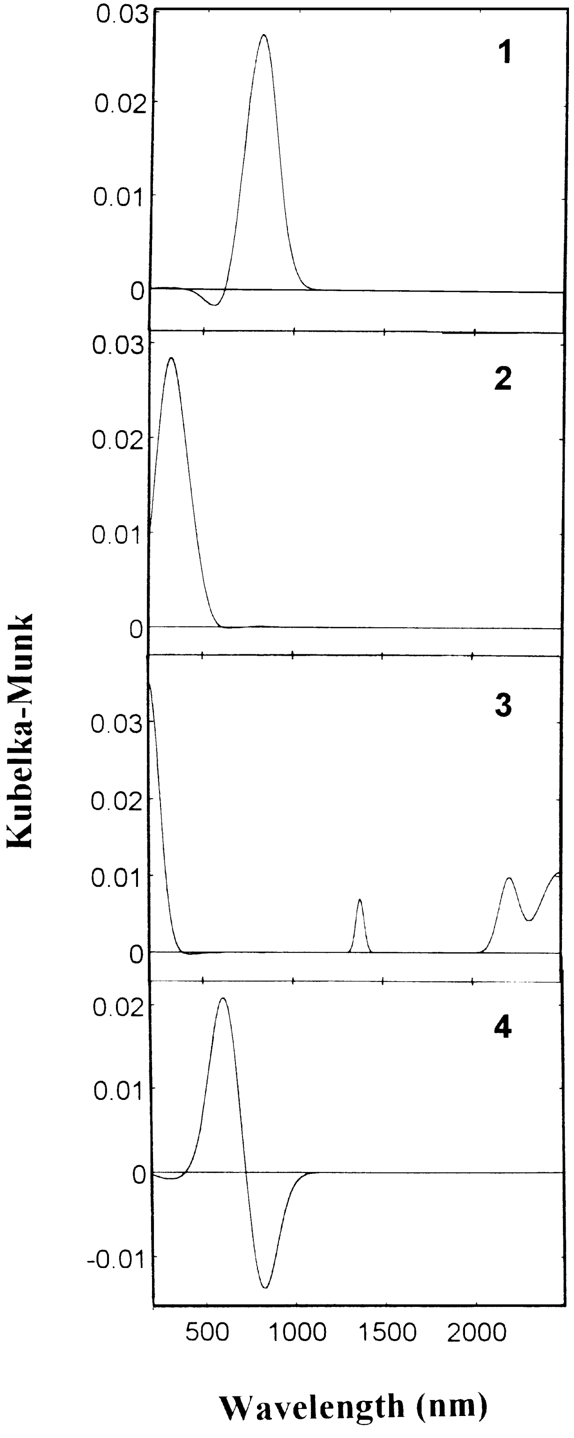

FIG. 4. Absorption profiles of the pure components of the theoretical spectra of reduced $Cr/SiO_2 \cdot Al_2O_3$ catalysts: (1) pseudo-octahedral Cr^{2+}, (2) chromate, (3) support, and (4) pseudo-octaheral Cr^{3+}.

4. *Sample Preparation and Characterization*

Two series of supported chromium oxide catalysts were investigated: (1) a series of $Cr/SiO_2 \cdot Al_2O_3$ catalysts as a function of the Si : Al ratio of the support and (2) a series of 0.2 wt% Cr/SiO_2 and Cr/Al_2O_3 catalysts as a function of the reduction temperature.

4.1. Sample preparation. A series of silica-aluminas was prepared following a modified method of Chen *et al.* (39). They are indicated as SA-*n*, where *n* is the weight percentage of SiO_2. The appropriate amounts of tetraethylorthosilicate (TEOS) and aluminum triisopropoxide $(Al(iP)_3)$ were mixed in 128 ml of ethanol during 30 min at room temperature. After addition of 35 ml of 1 *M* HCl, the acid hydrolysis started and the suspension was mixed for 1 h. The resulting gel was dried at 60°C and 100°C for 8 h and calcined at 550°C for 16 h. The obtained samples were crushed. The prepared $SiO_2 \cdot Al_2O_3$ were SA-5, SA-10, SA-20, SA-30, SA-40, SA-50, SA-60, and SA-80. SiO_2 (SA-100) was prepared by mixing 2 volume parts of water at pH 2 (adding hydrochloric acid) and 1 volume part TEOS during 5 h at room temperature. The mixture was titrated under stirring to pH 6 with a NH_4OH solution of pH 9.5. After 16 h gelation, the gel was dried at 130°C for 72 h and calcined at 250 and 550°C for respectively 3 and 16 h. The obtained cake was crushed. Al_2O_3 (SA-0) was obtained by heating $Al(iP)_3$ in air at 550°C for 16 h. The supported Cr catalysts were prepared by the incipient-wetness method with chromium(VI)oxide (CrO_3) and the chromium loading was 0.2 wt%.

4.2. Pretreatment and spectroscopy. The samples were dried at 50°C for 8 h and granulated. The size fraction 0.25–0.40 mm was loaded in a quartz flow cell with a Suprasil window for diffuse reflectance spectroscopy (DRS). The samples were subsequently dried at 90°C for 16 h followed by calcination at 550°C during 6 h in an oxygen stream. DR spectra were recorded on the hydrated and calcined samples. The samples were then reduced with CO at 200, 250, 300, 350, 400, 450, 500, and 550°C for 30 min. After each reduction step DR spectra were taken. An oxygen flow of 3600 ml/h and a CO flow of 1800 ml/h were used for all the pretreatments. DR spectra were taken on a Varian Cary 5 UV–VIS–NIR spectrophotometer at room temperature. The spectra were recorded against a Halon white reflectance standard in the range 2500–200 nm.

RESULTS

1. *Qualitative Spectroscopy*

Two series of supported chromia catalysts were measured by diffuse reflectance (DR) spectroscopy: (a) hydrated and calcined 0.2 wt% $Cr/SiO_2 \cdot Al_2O_3$ catalysts as a function of the $SiO_2 : Al_2O_3$ ratio and (b) reduced 0.2 wt% Cr/Al_2O_3 and Cr/SiO_2 catalysts as a function of the reduction temperature between 200 and 550°C in steps of 50°C.

1.1. Hydrated and calcined $Cr/SiO_2 \cdot Al_2O_3$ catalysts. The DR spectra of hydrated $Cr/SiO_2 \cdot Al_2O_3$ catalysts are shown in Fig. 5A. These spectra are essentially the same as discussed in previous papers (32, 33), but more intermediate spectra were included because a large database of spectra is required for our statistical approach. All the spectra are dominated by two intense $O \rightarrow Cr^{6+}$ charge transfer bands of chromate around 365 and 270 nm, the latter being relatively broad. The former band shifts to 350 nm

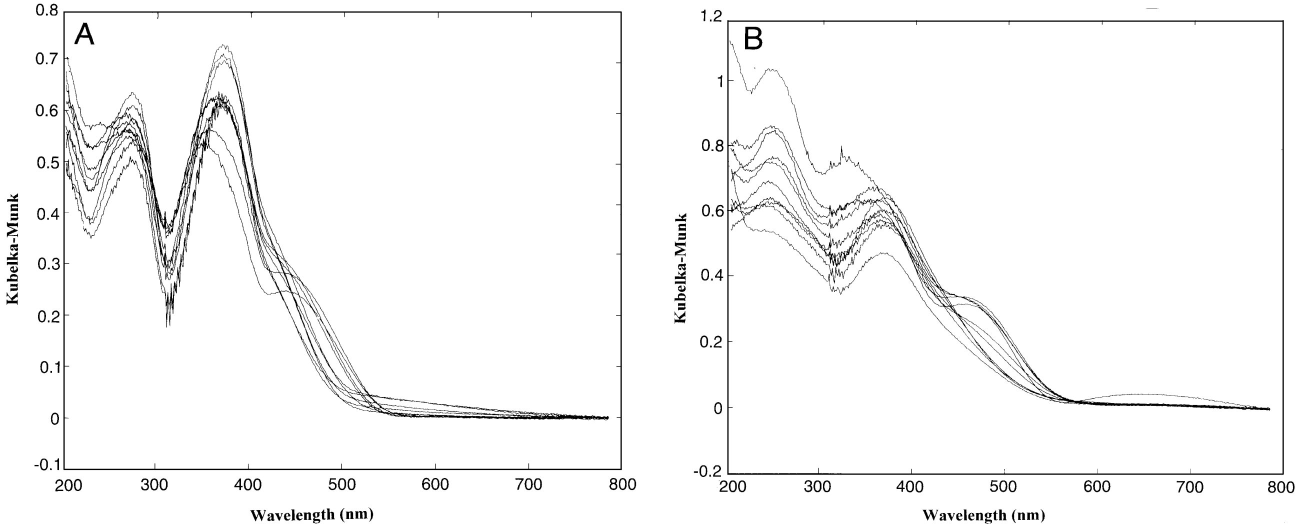

FIG. 5. (A) Diffuse reflectance spectra of hydrated supported Cr catalysts as a function of Si : Al ratio of the support. The curve with the maximum intensity at ca. 365 nm is that for the lowest silica content and that which has lowest intensity at this wavelength is the curve for highest silica content. (B) Diffuse reflectance spectra of calcined supported Cr catalysts as a function of Si : Al ratio of the support.

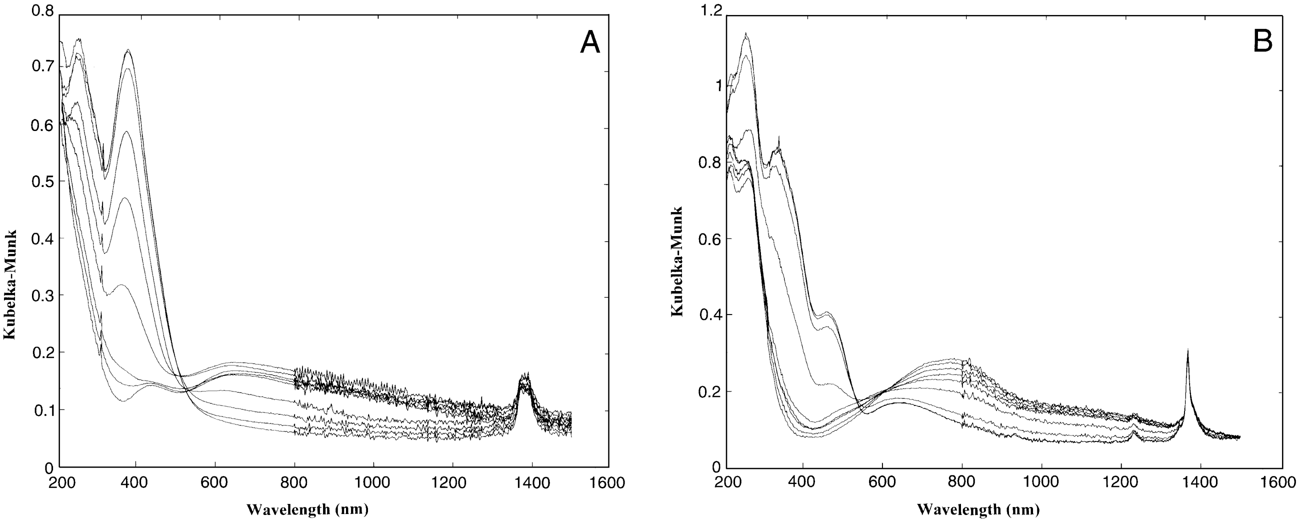

FIG. 6. (A) Diffuse reflectance spectra of reduced Cr/Al_2O_3 catalysts as a function of reduction temperature. (B) Diffuse reflectance spectra of reduced Cr/SiO_2 catalysts as a function of reduction temperature.

with increasing silica-content of the support. A shoulder around 445 nm, typical for dichromate, is also present and its intensity increases with increasing silica-content. The DR spectra of calcined Cr/$SiO_2 \cdot Al_2O_3$ catalysts are very similar to those of the hydrated catalysts, except for the relative intensities of the two major bands. When they are considered as a function of the SiO_2-content of the support (Fig. 5B) the following observations are made: (1) an increase of the intensity of the shoulder around 460 nm with increasing SiO_2-content to a well resolved band for Cr/SiO_2 and (2) a decrease of the intensity of the band around 370 nm with increasing SiO_2-content and a concomitant increase of the 330 nm band, the latter being especially prominent for Cr/SiO_2 and (3) a pronounced intensity increase of the 250 nm band with respect to the 360 or 330 nm band.

1.2. Reduced Cr/Al_2O_3 and Cr/SiO_2 catalysts. Reduction with CO results in the formation of Cr^{2+} and Cr^{3+}, as illustrated in Figs. 6A and 6B for Cr/Al_2O_3 and Cr/SiO_2 catalysts, respectively. The color of the catalysts turns to green (Cr/Al_2O_3) or blue (Cr/SiO_2) after reduction above 300°C and the DR spectra change dramatically. The Cr^{6+}-bands completely disappear at high reduction temperature. Above $\lambda = 500$ nm weak broad bands come up, asymmetric towards higher wavelength, the maximum of which is at 650 and 800 nm for Cr/Al_2O_3 and Cr/SiO_2, respectively. This suggests the predominant presence of respectively Cr^{3+} and Cr^{2+}. These observations are in line with our previously published spectra (32, 33).

2. *SIMPLISMA Analysis*

2.1. Pure spectra and intensity courses of hydrated and calcined Cr/$SiO_2 \cdot Al_2O_3$ catalysts. Four pure components (labeled as A, B, C, and D) are revealed by SIMPLISMA. Their absorption profile and intensity course are shown in Figs. 7 and 8, while the positions of the absorption maxima of the pure components are given in Table 2. The relative contributions (R.C.) of the pure components to the overall spectrum are included in Table 2 and are cited in parentheses in the text below.

Table 2 shows that the pure components of the hydrated and dehydrated catalysts have almost the same absorption profiles. Component A (54%) has three bands and increases in intensity with the silica content of the supports to reach a maximum value above $SiO_2 : Al_2O_3$ equal to 2. This behavior is typical for dichromate. Component B (42%) is also characterized by three bands, the low frequency (long wavelength) one being the most intense. Its intensity decreases slightly with increasing silica content to reach a minimum at $SiO_2 : Al_2O_3$ of 4. This component is typical for chromate. Component C (3%) has a broad asymmetric band in the range 500–665 nm and additional bands which are only resolved in the calcined samples. These bands are typical for pseudo-octahedrally coordinated

TABLE 2

Positions of Absorption Maxima of the Pure Components in Hydrated and Calcined Cr/$SiO_2 \cdot Al_2O_3$ Catalysts

Pure component	Hydrated Cr-catalysts (nm)	Dehydrated Cr-catalysts (nm)	Relative contribution (%)
A	225, 325, 495	250, 320, 485	54
B	220, 275, 400	245, 290, 380	42
C	565	250, 320, 460, 650	3
D	205, 270, 350	200, 282	1

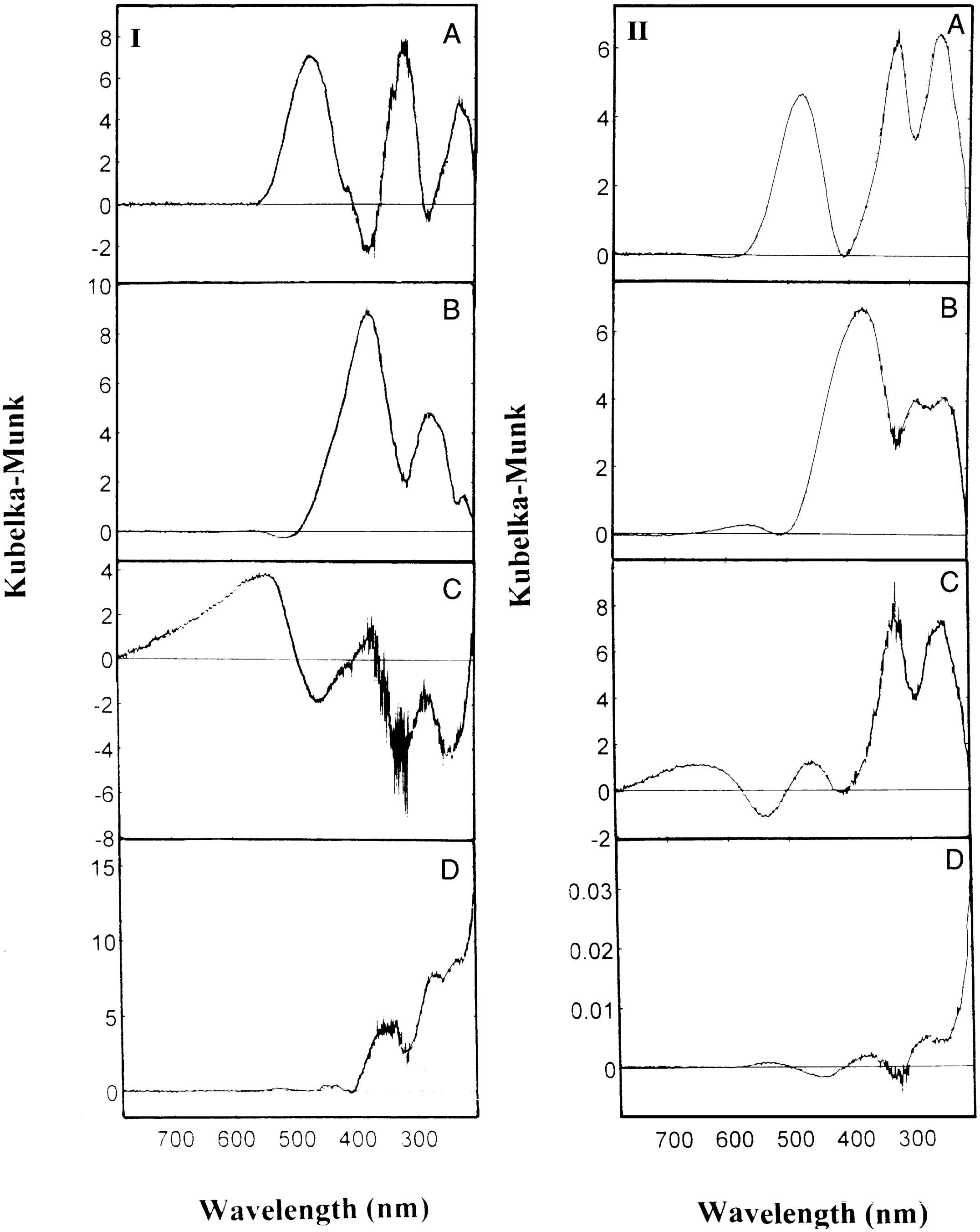

FIG. 7. Absorption profiles of the pure components: I, hydrated samples, and II, calcined samples.

Cr^{3+}. They are especially pronounced for silica after calcination. The residual bands in the ultraviolet region (pure component D, 1%) are ascribed to the background of the supports.

From the intensity profiles of the chromate and dichromate components (I_{chromate} at 380 nm and $I_{\text{dichromate}}$ at 320 nm), the chromate : dichromate ratio on the surface is calculated as a function of the silica : alumina ratio, according to

$$\frac{I_{\text{chromate}}}{I_{\text{dichromate}}} = \frac{\varepsilon_{\text{chromate}} \times C_{\text{chromate}}}{\varepsilon_{\text{dichromate}} \times C_{\text{dichromate}}} = K \times \frac{C_{\text{chromate}}}{C_{\text{dichromate}}} \quad [6]$$

where K, the ratio of the extinction coefficients of chromate and dichromate respectively, is assumed to be equal to 1.1 (32). The calculated chromate : dichromate ratios, as

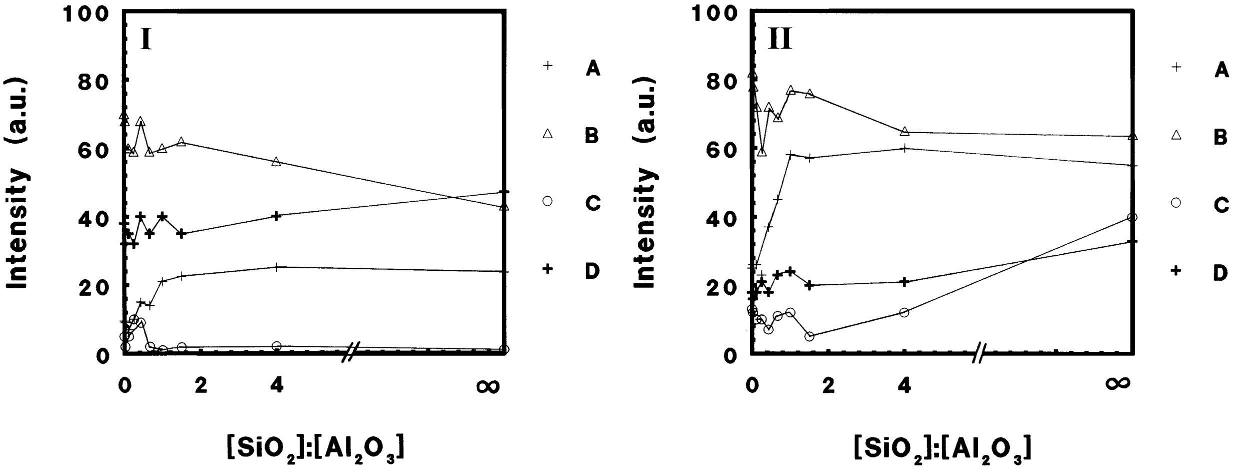

FIG. 8. Intensity courses of the pure components A, B, C, and D: I, hydrated samples, and II, calcined samples.

shown in Fig. 9, decrease with increasing silica-content of the support and is lower after calcination than for hydrated samples. Thus, chromate is the dominant species on alumina, while silica surfaces prefer dichromate.

2.2. Pure spectra and intensity courses of reduced Cr/SiO$_2$ and Cr/Al$_2$O$_3$ catalysts. The processing of the DR spectra of reduced Cr/SiO$_2$ and Cr/Al$_2$O$_3$ catalysts with SIMPLISMA as a function of the reduction temperature gives four and three pure components, respectively. These pure components are labeled as E, F, G, and H and their absorption profiles, relative contributions and intensity courses are shown in Figs. 10 and 11, respectively.

Table 3 summarizes the absorption maxima of the obtained pure components. The absorption bands of pure components E (355 nm) (36%) and G (475–500 nm and 220—230 nm) (33%) are likely to be due to Cr^{6+}-species and decrease in intensity with increasing silica content. The other pure components represent reduced Cr, either Cr^{2+} and Cr^{3+}. On silica component F (29%) is located at 855 nm and is ascribed to pseudo-octahedral Cr^{2+}. Component F (31%) on alumina absorbs at 635 nm, typical for (pseudo-) octahedral Cr^{3+}. Component H (2%) for reduced Cr/SiO$_2$ is probably due to some octahedral Cr^{3+}.

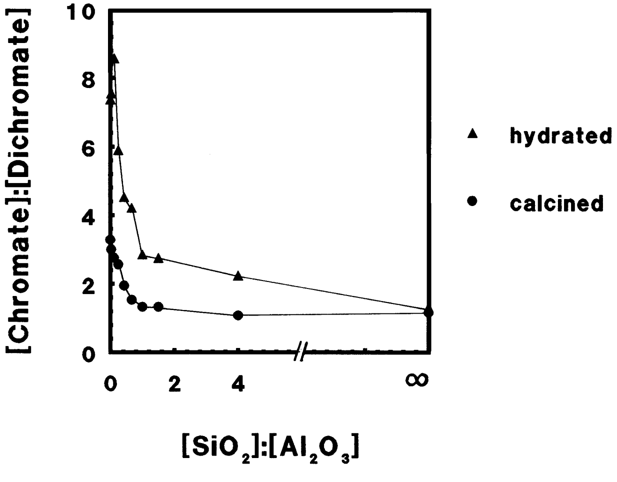

FIG. 9. The chromate : dichromate ratio in hydrated and calcined supported Cr catalysts.

DISCUSSION

Spectroscopic fingerprinting is of key importance in heterogeneous catalysis to develop general structure-reactivity relationships. In this study, a novel mathematical tool was applied, which allows one to extract spectroscopic signatures of chromate, dichromate, Cr^{3+} and Cr^{2+} (and their corresponding concentration profiles) from a series of diffuse reflectance spectra of supported chromium catalysts. The extent to which this spectroscopic fingerprinting is possible depends on various circumstances, such as band intensities, spectral noise and separation of band maxima. The ease of spectroscopic fingerprinting is dataset-dependent and merits a more detailed discussion. This discussion will cover the following subjects: (1) evaluation of the SIMPLISMA method, (2) comparison with the earlier developed

TABLE 3

Position of Absorption Maxima of the Pure Components in Reduced Cr/Al$_2$O$_3$ and Cr/SiO$_2$ Catalysts

Pure component	Reduced Cr/Al$_2$O$_3$ (nm)	Reduced Cr/SiO$_2$ (nm)	Relative contribution (%)
E	355	355	36
F	635	445, 855	29 (SiO$_2$)/31 (Al$_2$O$_3$)
G	475, 225	220, 500	33
H	—	305, 540	2

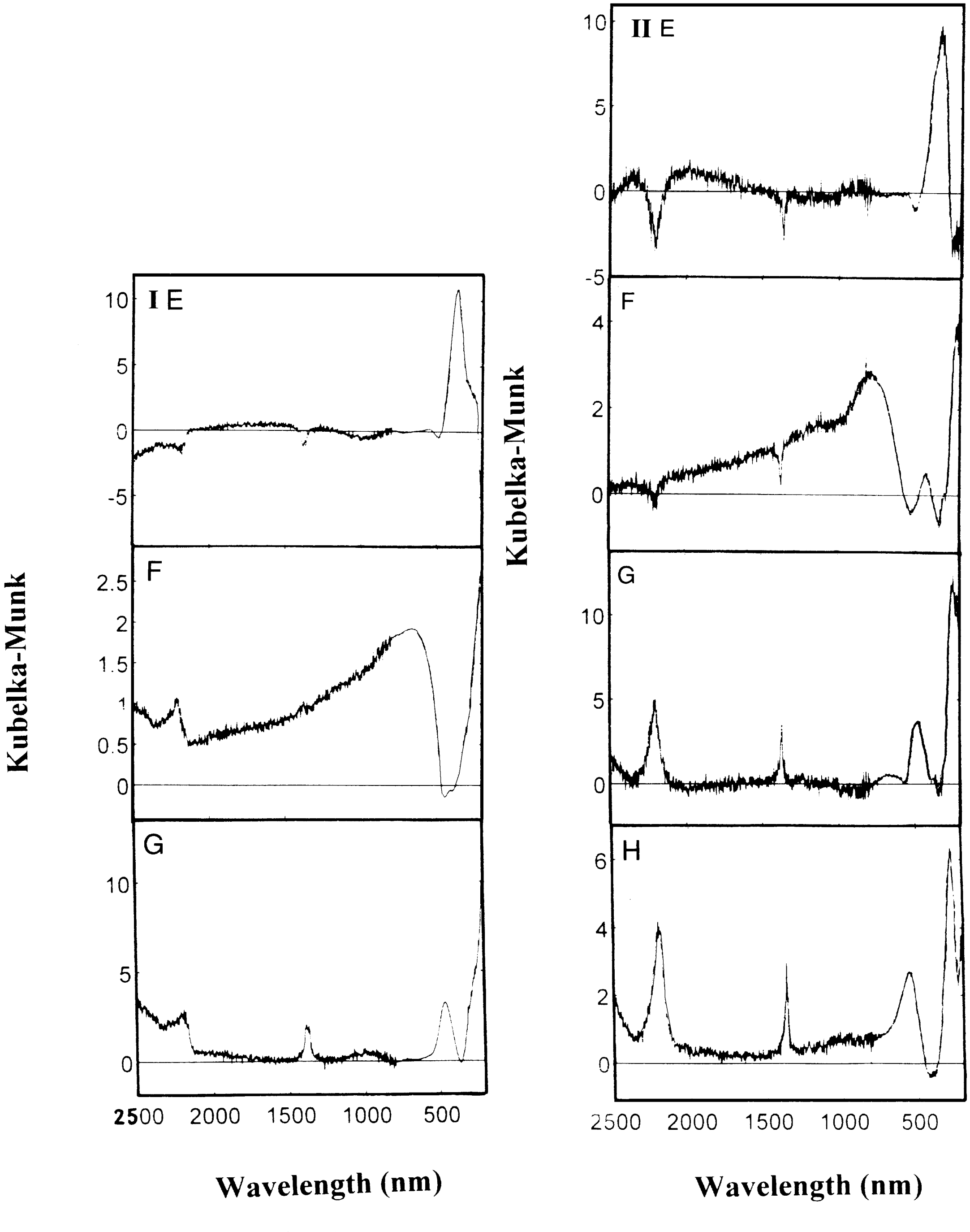

FIG. 10. Absorption profiles of the pure components: I, reduced Cr/Al_2O_3, and II, reduced Cr/SiO_2.

SPECTRA CALC method, and (3) the chemical information obtained.

1. Evaluation of the SIMPLISMA Method

The key task of the SIMPLISMA method in our work was the resolution of series of complex spectra into concentration profiles and spectra of pure components. To give a good interpretation of our results and an evaluation of the proposed method, we need to discuss the possibilities to separate pure variables with correct intensities and band positions. To give a fundamental basis for this issue, we have developed a theoretical proof for band separation based on two overlapping Gaussian curves. The absolute resolution of the SIMPLISMA technique, i.e., the percentage separation between two overlapping Gaussian curves, was determined to be equal to 5%. This means for a spectral range of 600 nm (200–800 nm), the minimum wavelength

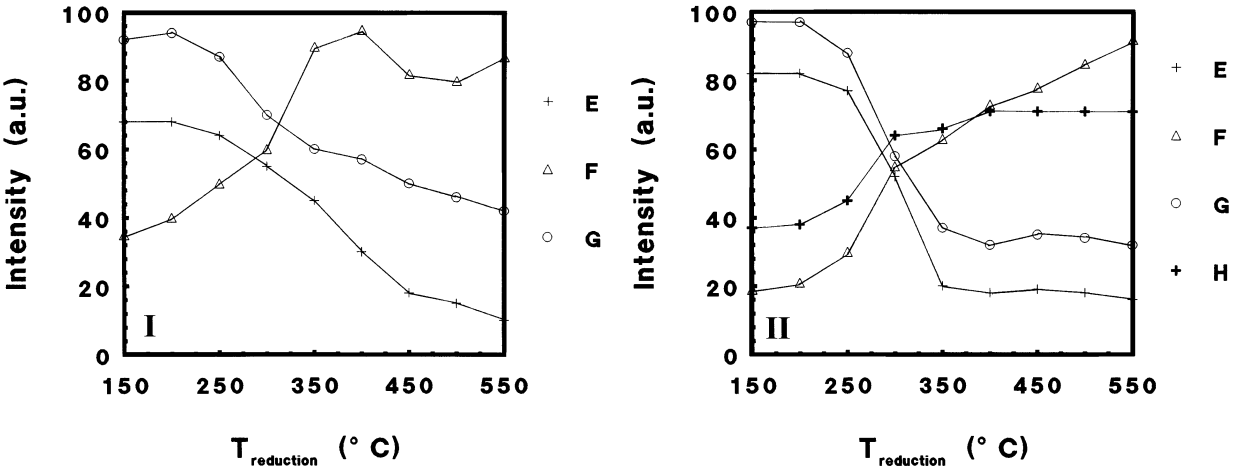

FIG. 11. Intensity courses of the pure components E, F, G, and H: I, reduced Cr/Al_2O_3, and II, reduced Cr/SiO_2.

distance between the band maxima of two pure components must be about 30 nm. For the spectral range of 2300 nm (200–2500 nm) this distance is 115 nm. Thus, chromate and dichromate can be separated in the region from 200 to 800 nm because the spectral distance between chromate and dichromate is about 42 nm (for the 370 and 322 nm band of chromate and dichromate, respectively—see Table 1), although the relative band intensities are not fully correct. However, this separation is no longer possible for the region from 200 to 2500 nm, and consequently, chromate and dichromate cannot be separated in such wide spectra. A second problem arises when two species, with band positions close to each other, have the same intensity profile. In that case, successful separation is difficult because SIMPLISMA analysis uses the intensity profile to determine new pure components. This explains why pseudo-octahedrally coordinated Cr^{2+} and Cr^{3+} are so difficult to distinguish by our method. Thus less pure components are obtained and this is revealed by the presence of negative band contributions. Thus, although SIMPLISMA is an ideal tool to extract pure components and their concentration profile, the obtained pure spectrum is not always fully pure and is contaminated by other pure spectra. Summarizing, although SIMPLISMA is a user-friendly tool, data sets are often not very user-friendly.

2. *Comparison with Previous Analysis*

The earlier developed SPECTRA CALC method for Cr speciation is based, in essence, on the use of a curve fitting routine, which calculates the best fit of bands which make up the complex set of overlapping peaks in *one single spectrum*. The starting variables are a guess of the number of bands, their peak positions, peak widths, and peak types. Thus, the DR spectra of supported Cr catalysts were consistently analyzed with a set of characteristic spectra of the following components: chromate, dichromate, Cr^{3+}, and Cr^{2+}. This analysis was made possible by (1) careful visual inspection of the data; (2) comparison with spectra of model compounds, and (3) setting limits on variations in positions of band maxima and band widths. The major drawback of the SPECTRA CALC method however, is its objectivity and accuracy. Instead, SIMPLISMA is a computational technique, which resolves in *one single mathematical operation* mixture data into pure component spectra and concentrations without using prior information about these mixtures. This analysis is much faster, less subjective and easier to handle, but still the user may decide which pure variables are selected. A disadvantage is that a large dataset is required for a statistical analysis and this requires a lot of experimental work and also a judicious choice of the experiments so as to obtain a reliable database. In addition, because the user may intervene in the data processing, selection criteria for pure components are recommended. The key criteria, based on our current experience, to terminate the selection of new pure components are: (1) the residual spectrum must be different from noise to choose a new pure component and (2) the intensity course of a new pure component must be quasi-linear and (3) the R.C.'s (relative contributions) of each pure component must be at least 1%.

3. *Chemical Information*

Components A and B of the hydrated and dehydrated chromium catalysts, interpreted as dichromate and chromate respectively, have frequencies close to those obtained by SPECTRA CALC (Table 1), although the relative intensities of the bands do not correspond. In component B (chromate) the first band is by far the most intense, while in component A (dichromate) the 485 nm is more intense than expected. Thus, as discussed above, the two revealed components are not fully pure, the chromate being contaminated by dichromate and vice versa.

Nevertheless, the SIMPLISMA analysis confirms the expected trends in that the chromate : dichromate ratio decreases with increasing silica content of the supports. Also, on hydrated catalysts Cr^{3+} is negligibly small, but not after calcination: a well-defined spectrum is resolved, corresponding to that of Cr^{3+} from SPECTRA CALC analysis (Table 1). Thus, quantitative information of three chromium species (chromate, dichromate, and pseudo-octahedral Cr^{3+}) in the hydrated and calcined Cr catalysts is obtained by the SIMPLISMA approach. The observed trends in Cr speciation can be explained in the following way. The higher the Al_2O_3 content of the support, the more basic the support, the stronger the interaction with chromate/dichromate. If a stronger interaction means a better dispersion, then the dispersion decreases with increasing SiO_2 content from pure Al_2O_3 to pure SiO_2. There are two indications that this is the case: (1) after calcination some residual pseudo-octahedral Cr^{3+} is found, especially on SiO_2 and (2) the decrease of the chromate : dichromate with increasing SiO_2 content. Thus, dichromates are always dominant on silica, whereas alumina surfaces prefer chromates.

For the reduced samples, the situation is clear for alumina: components E and G are ascribed to Cr^{6+} and component F is the first *d–d* transition of Cr^{3+}. However, on the basis of the band positions it is impossible to assign E and G to chromate or dichromate. From the intensity decrease of the components E and H of Cr/SiO_2 with reduction temperature it is reasonable to assign them to Cr^{6+}, with (as for alumina) no possibility to distinguish chromate from dichromate because of a too broad spectral range. F should then be pseudo-octahedral Cr^{2+}, assigned on the basis of the position of the first band (855 nm) and G is then Cr^{3+}. From the number of bands and their positions, it looks as if for Cr/SiO_2, all components are contaminated by others and successful separation into pure components was not achieved. In any case, it is comforting to see that the reduction trends as observed by SPECTRA CALC are also evident after SIMPLISMA analysis. Thus, Cr^{6+} is reduced by CO to $Cr^{2+/3+}$ and Cr^{2+} is the dominant species on silica, whereas on alumina mainly Cr^{3+} is present. The reasons for this difference in redox behavior have been discussed in detail elsewhere (32, 33). Our main hypothesis is that deep reduction is easier the "softer" the support. With SiO_2 being chemically softer than Al_2O_3, this means that reduction proceeds further to Cr^{2+} on a silica surface. Theoretical calculations are underway to substantiate this point.

CONCLUSIONS

The main conclusions from this study are:

(1) A novel strategy for spectroscopic fingerprinting of Cr^{n+}-species on surfaces of amorphous supports is proposed based on a self-modeling analysis of diffuse reflectance spectra of a series of $Cr/SiO_2 \cdot Al_2O_3$ catalysts.

(2) In the DR spectra of hydrated and calcined $Cr/SiO_2 \cdot Al_2O_3$ catalysts, pure spectra of chromate, dichromate, Cr^{3+}, and the support are revealed. The chromate : dichromate ratio increases with decreasing Si : Al ratio of the support. The DR spectra of reduced $Cr/SiO_2 \cdot Al_2O_3$ catalysts possess pure spectra of Cr^{6+}, octahedral Cr^{3+} and Cr^{2+} and the support, depending on the support composition.

(3) The SIMPLISMA method is a viable alternative to the earlier developed SPECTRA CALC method and we propose this method as an interesting tool for investigating complex spectra of supported transition metal oxide catalysts.

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