

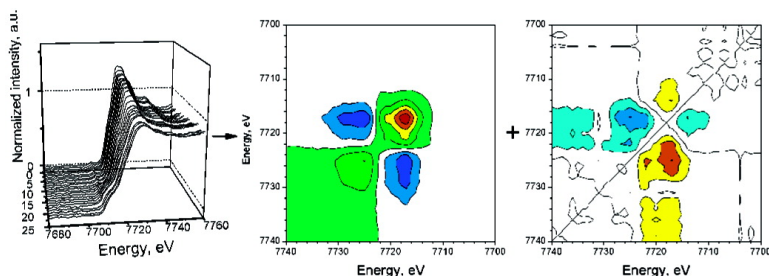
Article

Application of the Generalized 2D Correlation Analysis to Dynamic Near-Edge X-ray Absorption Spectroscopy Data

Peter Haider, Yuan Chen, Sangyun Lim, Gary L. Haller, Lisa Pfefferle, and Dragos Ciuparu

J. Am. Chem. Soc., **2005**, 127 (6), 1906-1912 • DOI: 10.1021/ja045391m • Publication Date (Web): 19 January 2005

Downloaded from <http://pubs.acs.org> on March 24, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Application of the Generalized 2D Correlation Analysis to Dynamic Near-Edge X-ray Absorption Spectroscopy Data

Peter Haider, Yuan Chen, Sangyun Lim, Gary L. Haller, Lisa Pfefferle, and Dragos Ciuparu*

Contribution from the Department of Chemical Engineering, Yale University, New Haven, Connecticut 06520

Received July 30, 2004; E-mail: dragos.ciuparu@yale.edu

Abstract: Application of the generalized 2D correlation analysis to a series of in situ XANES spectra enabled the determination of additional useful information not readily available from the conventional spectra. In addition to the changes in the intensity of the white line and in the pre-edge feature, readily observable in the regular spectra, the generalized 2D correlation analysis clearly evidenced an otherwise imperceptible shift in the main edge energy caused by the gradual reduction of Co^{2+} to metallic cobalt. The 2D correlation spectra also allowed the establishment of a time sequence for the changes occurring in the spectral features during hydrogen reduction, which provides valuable information on the reduction mechanism. While the generalized 2D correlation analysis was found to be very useful in obtaining supplementary information from the series of XANES spectra analyzed, interpretation of the correlation intensities should be checked for consistency with the general trend of each spectral feature, as spectral intensities that do not change monotonically may induce changes in the signs of the correlation intensities leading to inaccurately establishing sequences of changes among the spectral features in the series.

Introduction

X-ray absorption spectroscopy (XAS) is a widely used technique applied to characterize the state of catalytic materials. We have previously used XAS to characterize in situ the changes in the state of a Co–MCM-41 catalyst during the process of synthesizing single-wall carbon nanotubes (SWNT).^{1–5} It was clearly evidenced from our previous experiments that the Co^{2+} ions, initially nearly atomically dispersed by isomorphous substitution of silicon in the amorphous pore wall of the MCM-41 framework, are almost quantitatively reduced to metallic cobalt clusters of the order of few tens of cobalt atoms.

The changes in the oxidation state of the Co species in Co–MCM-41 should produce several changes in the X-ray absorption spectrum. A first spectral feature of interest is the intensity of the white line, which is a direct measure (albeit qualitative) of the density of empty states at the Fermi level of the cobalt species, with oxidized cobalt having strong white line intensity, while the fully reduced Co^0 shows a very weak white line feature. It is therefore expected that reduction of the Co^{2+} ions isomorphously substituted for silicon ions in the MCM-41 matrix will cause a significant decrease in the intensity of the white line. It should also be expected that the reduction of the Co^{2+}

species in the MCM-41 will cause changes in the symmetry of the Co species. Because the dipole-forbidden $1s \rightarrow 3d$ transitions are strong functions of the local symmetry of the Co species,⁶ the intensity of the pre-edge peak, which is generated by these types of transitions, should also show significant changes. Finally, because the position of the K edge varies linearly with the valence, the K edge of the fully reduced Co should shift to lower energy compared to that of the edge of the fully oxidized Co (e.g., Co^{2+}).

In our previous studies, we were able to monitor the changes of the intensities of the white line and of the pre-edge feature in a series of X-ray absorption near-edge structure (XANES) spectra collected in situ during catalyst prereduction in hydrogen and reaction with CO at temperatures as high as 750 °C,^{1–4} and we concluded that in many instances, there are significant changes in the intensity of the white line without any significant modifications of the pre-edge feature of the spectra.³ Also, unlike vanadium, whose reduction from V^{5+} to V^0 produces a relatively large shift in the energy of the K edge,⁷ because Co in MCM-41 exhibits a narrower range of oxidation states (0 to +3) with the concentration of Co^{3+} species <5% of the total cobalt in our samples,⁴ the shift in the K edge energy was very small and could not be systematically observed directly in the X-ray absorption spectra recorded in situ. Since the independent changes in the white line intensity and the pre-edge feature are somewhat intriguing, it is highly desirable that every change in the main features of the X-ray spectra, as well as the order in

(1) Chen, Y.; Ciuparu, D.; Lim, S.; Yang, Y.; Haller, G.; Pfefferle, L. *J. Catal.* **2004**, *226*, 351–362.

(2) Chen, Y.; Ciuparu, D.; Lim, S.; Yang, Y.; Haller, G.; Pfefferle, L. *J. Catal.* **2004**, *225*, 453–465.

(3) Ciuparu, D.; Chen, Y.; Lim, S.; Yang, Y.; Haller, G. L.; Pfefferle, L. *J. Phys. Chem. B* **2004**, *108*, 15565–15571.

(4) Lim, S.; Ciuparu, D.; Chen, Y.; Yang, Y.; Pfefferle, L.; Haller, G. *J. Phys. Chem. B*, published online July 2, 2004 <http://dx.doi.org/10.1021/jp048881+>.

(5) Ciuparu, D.; Chen, Y.; Lim, S.; Haller, G. L.; Pfefferle, L. *J. Phys. Chem. B* **2004**, *108*, 503–507.

(6) Bart, J. C. *J. Adv. Catal.* **1986**, *34*, 203–296.

(7) Wong, J.; Lytle, F. W.; Messmer, R. P.; Maylotte, D. H. *Phys. Rev. B* **1984**, *30*, 5596–5610.

which these changes occur, is carefully monitored in order to better understand the mechanisms of cobalt reduction and cluster nucleation in Co–MCM-41 catalysts.

In the late 1980s, Noda introduced a new analytical concept in vibrational spectroscopy called two-dimensional infrared spectroscopy (2D IR),^{8,9} somewhat analogous to the 2D correlation technique used extensively in NMR,¹⁰ which was shown to accentuate useful information often obscured in the original time-resolved spectra. A few years later, the same author proposed a more generally applicable mathematical formalism to obtain two-dimensional correlation spectra from any transient or time-resolved spectra having an arbitrary waveform.¹¹

The 2D correlation analysis is a quantitative comparison of spectral intensity variations observed at two different spectral variables over some finite observation time interval. The correlation spectrum was expressed in a formal manner elsewhere.¹² In summary, the generic 2D correlation intensity denoted $X(\nu_1, \nu_2)$ represents the measure of a functional comparison of spectral intensity variations, $\tilde{y}(\nu, t)$, measured at different spectral variables, ν_1 and ν_2 , during a fixed interval of the external variable, t . The 2D correlation intensity is treated conventionally as a complex number comprised of two orthogonal components, $X(\nu_1, \nu_2) = \Phi(\nu_1, \nu_2) + i\Psi(\nu_1, \nu_2)$, known, respectively, as the synchronous ($\Phi(\nu_1, \nu_2)$) and asynchronous ($\Psi(\nu_1, \nu_2)$) 2D correlation intensities. It is proposed that the synchronous 2D correlation intensity is regarded as the overall similarity between the two separate spectral intensity variations measured at different spectral variables at different times, while the asynchronous correlation intensity represents sequential or successive changes in the spectral intensities measured at ν_1 and ν_2 .¹² The synchronous spectrum evidences the simultaneous changes of spectral intensity variations measured at ν_1 and ν_2 by showing auto peaks located on the diagonal line corresponding to $\nu_1 = \nu_2$ in the contour plot obtained for $\Phi(\nu_1, \nu_2)$, while the asynchronous spectrum is asymmetric with respect to the diagonal line and develops cross-peaks only if the intensities of two spectral features change out of phase with each other (i.e., delayed or accelerated).¹² The asynchronous spectrum is especially useful in differentiating overlapped bands arising from spectral features of different origins, whose changes occur in a time sequence. In the example to be discussed, the overlapping spectral features are the metallic pre-edge and threshold of the Co K edge absorption. While other ways in which the synchronous and asynchronous correlation intensities can be calculated are discussed in detail elsewhere,^{11,12} for the sake of simplicity, below are given only the equations used to calculate the correlation intensities in this work:¹¹

$$\Phi(\nu_1, \nu_2) = 1/(N - 1) \sum_{j=1}^N \tilde{y}_j(\nu_1) \tilde{y}_j(\nu_2)$$

for the synchronous correlation intensity, and

$$|\Psi(\nu_1, \nu_2)| \approx \sqrt{\Phi(\nu_1, \nu_1)\Phi(\nu_2, \nu_2) - \Phi^2(\nu_1, \nu_2)}$$

for the asynchronous correlation intensity, with the sign of the resulting asynchronous correlation intensity given by a supplementary mathematical condition described in detail in the original publication.¹¹ The individual deviation spectrum is given by

$$\tilde{y}_j(\nu) = y_j(\nu) - 1/N \sum_{j=1}^N y_j(\nu)$$

where N is the number of spectral data in the set.

The generalized 2D correlation analysis, designed as a simple mathematical tool¹³ to reveal useful information often obscured in the original spectra,¹¹ is, therefore, applied here to analyze in detail the changes that occur in the XANES spectra recorded in situ with a Co–MCM-41 catalyst during reduction in hydrogen.

Experimental Section

The X-ray absorption spectra were collected at beam line X23A2 (National Synchrotron Light Source, Brookhaven National Laboratory). Approximately 50 mg of fresh Co–MCM-41 was pressed at ~5 tons into a round self-supporting wafer (1.5 cm in diameter) using a hydraulic pellet press. The thickness of pellets satisfied the condition that the absorption edge steps ($\Delta\mu x$) at Co K absorption edge are smaller or equal to 1. Wafers were placed into a stainless steel reaction chamber described in detail elsewhere.² The reaction chamber, which allows controlled temperature and atmosphere, was placed between two 30 cm long ion chambers filled with pure N₂ located along the beam axis to measure the incident beam intensity, I_0 , and the intensity of the transmissive beam, I_T . A third ion chamber was placed after the one measuring the I_T in order to measure simultaneously a cobalt foil as an internal reference. During the in situ experiments, the Co–MCM-41 sample placed in the reaction cell was heated in flowing hydrogen from room temperature to 700 °C at a rate of 20 °C/min and reduced isothermally for 30 min. XANES spectra were continuously collected from 30 eV below to 50 eV above the Co K edge in 1 eV steps, averaging approximately 4 min/scan in order to monitor the state of the catalyst under these reduction conditions.

The series of normalized spectra collected as described above were analyzed using the 2D Pocha software developed by Daisuke Adachi^{14,15} from Kwansai Gakuin University based on Noda's generalized 2D correlation analysis method.¹¹ The average spectrum was used as the reference spectrum.

Results

The normalized XANES spectra collected during temperature-programmed reduction of Co–MCM-41 in pure hydrogen from room temperature to 700 °C at a heating rate of 20°/min, followed by isothermal reduction at 700 °C for 30 min, are given in Figure 1.

Changes of some spectral features are readily observable in the spectra in Figure 1. As expected, reduction of the Co species in the Co–MCM-41 catalyst produces clear changes in the intensity of the white line and in the pre-edge region of the spectra. However, as previously reported, the shift of the main

(8) Noda, I.; Dowrey, A. E.; Marcott, C. *Mikrochim. Acta* **1988**, *1*, 101–103.

(9) Noda, I. *J. Am. Chem. Soc.* **1989**, *111*, 8116–8118.

(10) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229–2246.

(11) Noda, I. *Appl. Spectrosc.* **1993**, *47*, 1329–1336.

(12) Noda, I.; Dowrey, A. E.; Marcott, C.; Story, G. M.; Ozaki, Y. *Appl. Spectrosc.* **2000**, *54*, 236a–248a.

(13) Noda, I. *Appl. Spectrosc.* **2002**, *56*, 404–405.

(14) Adachi, D.; Katsumoto, Y.; Sato, H.; Ozaki, Y. *Appl. Spectrosc.* **2002**, *56*, 357–361.

(15) Katsumoto, Y.; Adachi, D.; Sato, H.; Ozaki, Y. *J. Near Infrared Spectrosc.* **2002**, *10*, 85–91.

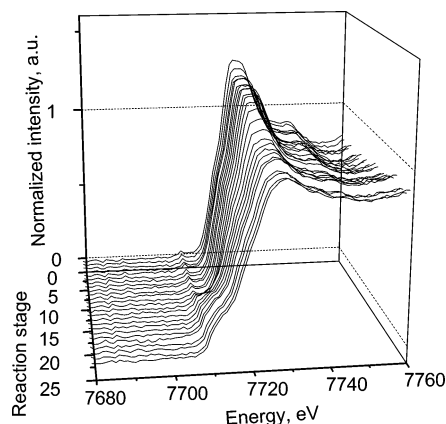


Figure 1. Series of in situ XANES spectra recorded with a Co–MCM-41 catalyst during temperature-programmed reduction between room temperature and 700 °C.

edge energy, defined as the threshold of the absorption edge, is difficult to distinguish within this series of spectra. We have, therefore, applied the generalized 2D correlation analysis in an attempt to accentuate the changes that occur in the near-edge region of the spectra, but are obscured in the original time-resolved XANES.

The synchronous and asynchronous correlation intensities depicted in the contour plots in Figure 2 were obtained from the whole series of spectra recorded under hydrogen flow during the reduction treatment between room temperature and 700 °C. Two diagonal peaks are observed near 7724 and 7714 eV in the synchronous plot. The intensity of these peaks corresponds mathematically to the autocorrelation function of spectral intensity variations observed incrementally between the first and the last of the spectra collected under hydrogen flow. These peaks suggest changes in the intensity of the white line, at 7724 eV, and at energies characteristic for the pre-edge region, as observed in Figure 3. There are also two negative cross-peaks located off-diagonal in the synchronous contour plot in Figure 2, which are indicative of simultaneous changes in the spectral intensities observed at two different energies. While the sign of auto peaks is always positive, the sign of cross-peaks can be either positive or negative, depending on whether the simultaneous changes are in the same direction or in opposite directions. If the intensities at the two different energies increase or decrease simultaneously, the cross-peaks will be positive, otherwise they will be negative. Therefore, the negative cross-peaks in the synchronous plot in Figure 2 show these spectral features change in opposite directions. This is to be expected, that is, as the main edge shifts toward lower energy, accompanied by an increase of the spectral intensity at 7714 eV, the intensity of the white line decreases.

The asynchronous plot obtained with the same series of spectra gives evidence of three pairs of cross-peaks. Unlike the synchronous plot, the asynchronous plot is antisymmetric with respect to the diagonal line. The peaks in the asynchronous plot that develop only when changes in the spectra intensities occur out of phase are further defined by pairs of energy values reflecting their *XY* energy coordinates in the contour plot of asynchronous correlation intensity. There are three clearly defined cross-peaks correlating the spectral intensities at 7724, 7716, at 7716, 7713, and at 7724, 7713 eV. These peaks are clear evidence for the change of a third spectral intensity at

7716 eV, characteristic for the Co K edge, which was not observed in the synchronous plot or in the regular spectra. It becomes apparent, thus, that the very small shift in the Co K energy edge, which is very difficult to observe in the regular XANES spectra in Figure 1, is clearly evidenced by using the 2D correlation analysis. The presence of two distinct peaks at approximately 7716 and 7713 eV in the asynchronous plot suggests that the peak at 7714 eV in the synchronous plot convolutes the correlation intensities resulting from changes both in the pre-edge region and in the K edge energy, and this convolution is most likely due to the wide range of spectra used to calculate the synchronous plot, in which both spectral features undergo comparative changes. As it can be observed in the spectra in Figure 3, the changes in the spectra at 7713 eV correspond to changes in the pre-edge feature of the XANES spectra. These findings are very important since in the previous analysis of our X-ray absorption spectroscopy data, we have had difficulties explaining the significant changes observed in the white line intensity without any apparent change the other two spectral features (pre-edge peak and main edge energy shift).³ It is therefore clear now that there are subtle changes in all of the characteristic spectral features, and the generalized 2D correlation analysis is helpful in identifying these changes.

According to the interpretation rules established by Noda,^{11,12} the sign of an asynchronous cross-peak is positive if the intensity change at energy E_1 occurs before the intensity change at E_2 in the sequence of spectra. However, if the sign of the corresponding synchronous intensity is negative, this rule is reversed. Along these lines, although the peak at 7724, 7716 eV is positive, suggesting the changes in the white line intensity occur before the changes in the main energy, because the corresponding synchronous intensity is negative the main energy is concluded to be the first spectral feature to change in our series of spectra. This result is intriguing as any change in cobalt valence should produce changes in the density of empty states at the Fermi level. However, if this is the case, there should be groups of spectra at the beginning of the series where the main energy shifts before any change is observed in the intensity of the white line. Therefore, we propose a new approach referred to herein as Progressive Correlation Analysis (ProCorA) consisting of sequentially analyzing groups of spectra using the generalized 2D correlation method, starting with the first two spectra, then the first three, then the first four, and so on. The synchronous and asynchronous intensities plotted in Figure 4 were selected to reflect the sequence in which a new peak occurred in either synchronous or asynchronous plots.

In contrast to the sequence of changes suggested by the plots in Figure 2, when the generalized 2D correlation analysis was applied to the first two spectra in the series (far left column in Figure 4), only changes in the intensity of the white line were observed. While this may be caused by a limited sensitivity of the generalized 2D correlation analysis, because the asynchronous plot shows only a “band of noise” at energies between 7720 and 7730 eV, the single auto peak observed in the synchronous plot may actually reflect that changes occur only in the intensity of the white line. When the third spectrum is added to the series analyzed by the 2D correlation method (central column in Figure 4), however, there is a second weak auto peak observed near 7716 eV, which becomes more intense as more spectra are added to the analyzed series. This second

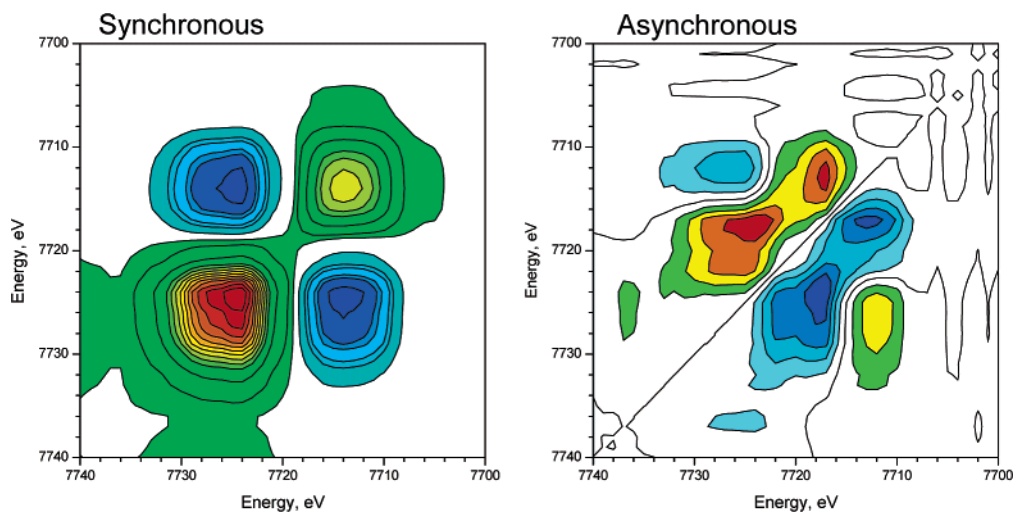


Figure 2. Synchronous and asynchronous 2D spectra obtained using the entire series of XANES spectra collected during reduction. Blue hues show negative peaks.

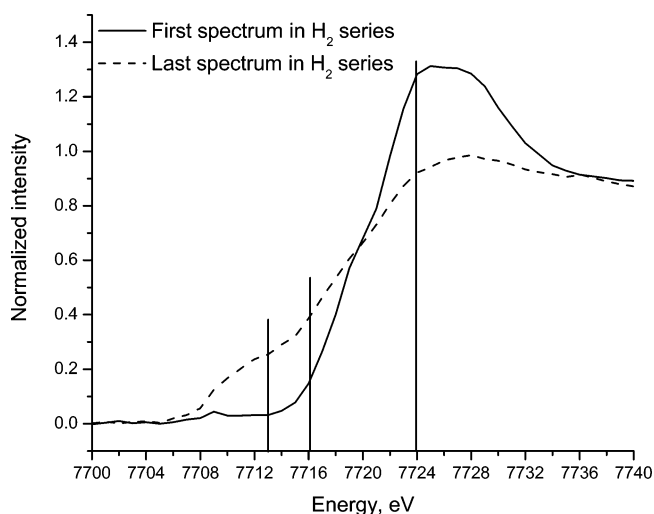


Figure 3. First and last XANES spectra in the series recorded with the Co-MCM-41 catalyst during temperature-programmed reduction.

peak gives rise to negative cross-peaks in the corresponding synchronous plot, consistent with its increased intensity as the intensity of the white line decreases. As expected, the asynchronous correlation intensity plot gives rise to a pair of cross-peaks correlating the spectral intensities at 7724 and 7716 eV. Since the asynchronous cross-peak at 7724, 7716 eV is negative and has a negative corresponding synchronous intensity, we can conclude that the changes in the intensity of the white line occur prior to the shift in the main energy. This sequence is also supported by the fact that only one peak at 7724 eV was observed when only the first two spectra in the series were used for the 2D correlation analysis.

All of the changes in the spectral features observed in the synchronous and asynchronous plots obtained using the first three spectra in the series became better resolved as more spectra were added to the series processed using the ProCorA method, and there were no new features observed until the ninth spectrum was added to the series (far right column in Figure 4). While the synchronous plot shows the same auto peaks at 7724 and 7716 eV, though better resolved, the asynchronous plot gives rise to a second pair of cross-peaks correlating to the spectral intensities at 7716 and 7713 eV. These new peaks suggest

changes started to occur in the pre-edge region of XANES spectra. The positive cross-peak at 7716, 7713 eV, whose corresponding synchronous intensity is also positive, suggests changes in the pre-edge region occur after the main energy started to shift, consistent with the sequence observed by analyzing different groups of spectra in the series.

In the attempt to understand why the sequence derived from the asynchronous plot in Figure 2 obtained with the whole series of spectra is not correct, we continued our step-by-step ProCorA by adding one more spectrum to the series analyzed following systematically the sequence in which the changes in the main spectral features occur, as resulting from the asynchronous plots. The synchronous and asynchronous correlation intensities resulting from spectra 1–12 and 1–14 are given in the contour plots in the left and right columns of Figure 5, respectively. Although the synchronous plots obtained with the two groups of spectra show the same features, the asynchronous cross-peaks correlating the spectral intensities at 7724 and 7716 eV for the two groups have opposite signs, thus suggesting a different sequence of changes to occur in the spectral intensities of the two features. It should also be noted that the sequence of changes resulting from the asynchronous plot obtained with the first 14 spectra is the same with the one derived from the asynchronous plot in Figure 2 obtained with the whole series of spectra.

After a careful observation of the two synchronous spectra in Figure 5, we observed that the changes in the intensity of the white line in the synchronous plot obtained with the first 12 spectra in the series is less intense than that obtained with the first 14 spectra in the series. This observation led us to hypothesize that the change in the sequence in the asynchronous plots may be related with the evolution of the white line intensity. We have, therefore, plotted in Figure 6 the normalized intensity of the white line determined at 7724 eV for each spectrum in the series. Since the white line intensity does not change monotonically, and some strong changes occur after several less intense changes, the statistical data analysis method perceives this behavior as the change in white line intensity is the last to occur in the sequence. It is, therefore, suggested that the interpretation of the asynchronous plots should be carefully approached and checked for consistency within the series of

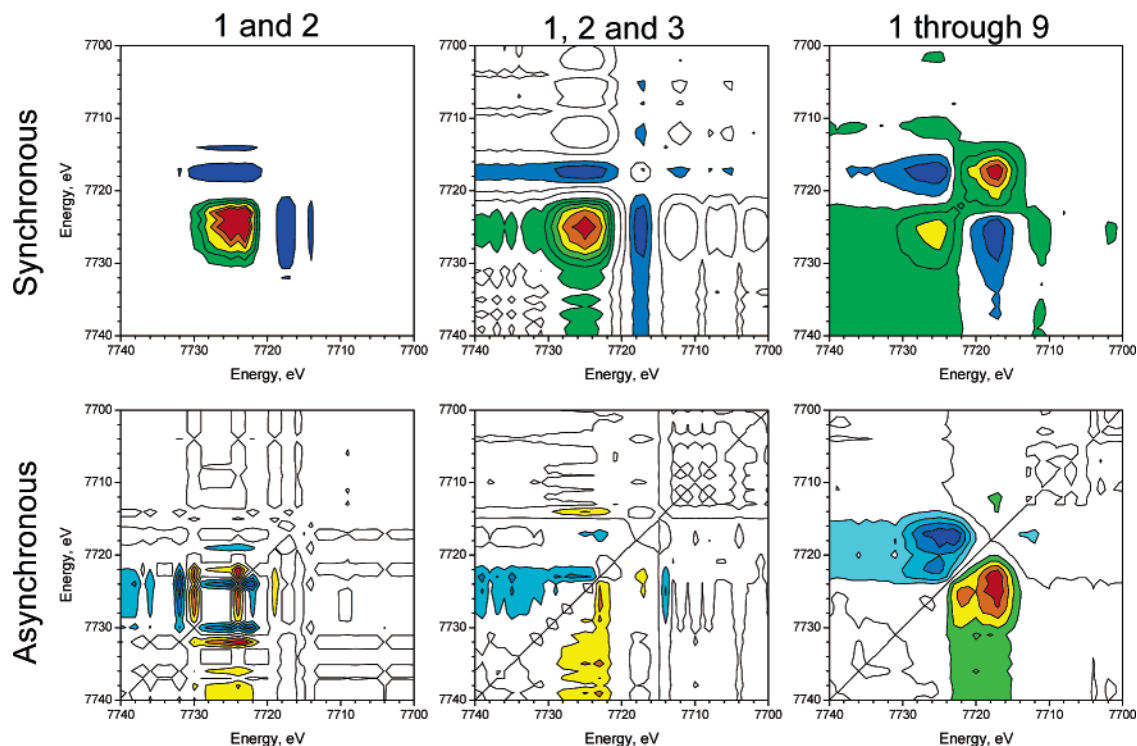


Figure 4. Synchronous (top row) and asynchronous (bottom row) plots obtained using different numbers of spectra recorded during catalyst reduction in hydrogen. Blue hues show negative peaks.

spectra and in conjunction with the synchronous correlation intensities.

Discussion

Compared to the previous interpretations of our in situ XANES results,^{1–4} using the generalized 2D correlation analysis, we were able to confirm that the intensity of the white line changes initially without any change in the pre-edge region of the spectra. However, except for the first two spectra, the decrease in the intensity of the white line was found, using ProCorA, to be associated with changes in the valence of the cobalt species reflected by the shift in the main energy. At the early stages of catalyst exposure to hydrogen, the decrease in the intensity of the white line is most likely caused by exchanging some ligands from the coordination sphere of the Co^{2+} ions in the MCM-41 framework, such as replacing hydroxyl ligands with O^{2-} ligands, following the surface dehydroxylation process described in the cartoon in Figure 7. The stronger negative inductive effect of the O–H group compared to that of the Si^{4+} –O group should cause a decrease in the intensity of the white line on surface dehydroxylation, with no change in either pre-edge feature or edge energy, consistent with the experimental results shown in the far left column in Figure 4. The cartoon in Figure 7 is also consistent with our previous finding that dehydroxylation of the Co–MCM-41 surface leads to a small decrease in the calculated Co–O coordination number, suggesting a change in the electron density on a ligand rather than a full loss of the ligand.⁴ Subsequent further reduction in hydrogen at increasing temperatures (from spectrum 3 to spectrum 12 in Figure 6) likely consists of the removal of surface-isolated terminal hydroxyl groups leading to the formation of oxygen vacancies in the coordination sphere of the cobalt ions embedded in the silica framework. Redistribution of the electrons trapped in the surface

oxygen vacancies to the neighboring Co^{2+} ions in the MCM-41 framework causes an apparent cobalt valence change to an intermediary state between Co^{2+} and Co^0 without a significant change in the density of empty states at the Fermi level and preserves the tetrahedral symmetry, at least until the ninth spectrum in the series, as observed in Figure 4.

As the reduction process further advances, the changes observed in the intensity of the white line are accompanied by significant changes in the pre-edge region, suggesting that completely reduced cobalt atoms migrate on the surface and nucleate into metallic clusters in which Co is in octahedral symmetry. It should also be noted that the main energy shifts throughout the entire series of spectra, except for the first two in the series, suggesting the initially oxidized Co^{2+} species are not quantitatively reduced to Co^0 at the end of this experiment. This is consistent with related work showing some Co–O bonding in the R space EXAFS spectrum recorded with catalysts exposed to identical treatments.^{2–4} The plateau observed in the variation of the intensity of the white line may suggest the presence of some cobalt species in an intermediary oxidation state as discussed above. Whether this is the case or the edge energy shift is produced simply by different fractions of reduced cobalt in the MCM-41 framework at different stages during the reduction process cannot be determined from this analysis and is beyond the purpose of the present contribution.

While the calculation of the synchronous correlation intensity is reliable for all data sets, special caution should be taken in the calculation of the asynchronous correlation intensities, especially for the cases in which spectral features show nonmonotonical or biphasic behavior, that is, the spectral intensity first increases and then decreases, or significant changes appear sequentially with an intermediate insignificant change, as observed with the intensity of the white line in Figure 6.

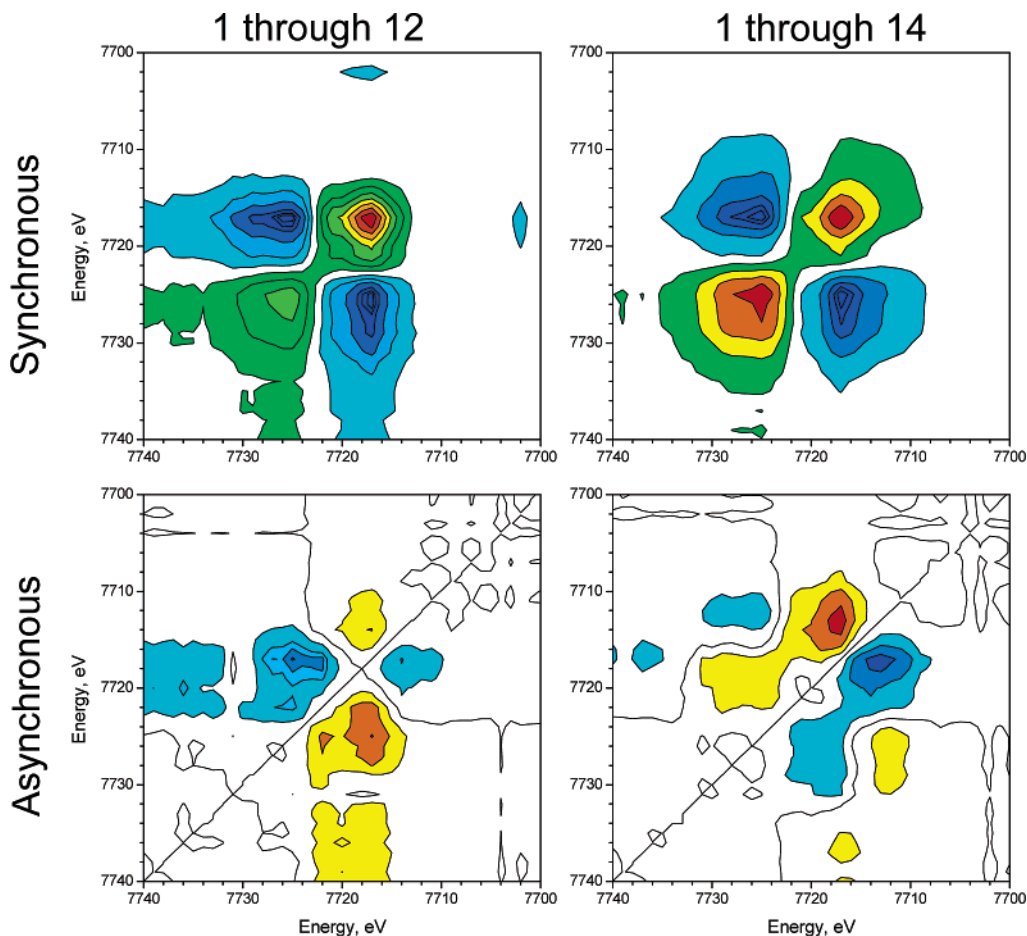


Figure 5. Synchronous (top row) and asynchronous (bottom row) plots obtained using either the first 12 (left column) or the first 14 (right column) spectra in the series. Blue hues show negative peaks.

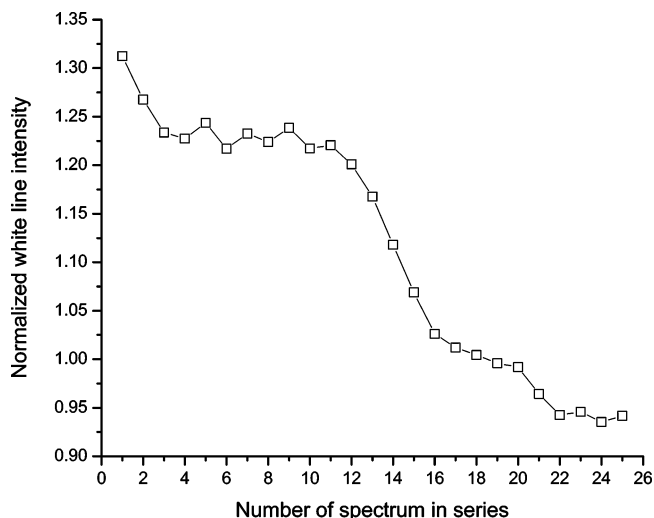


Figure 6. Changes in the intensity of the white line observed within the series of spectra collected during temperature-programmed reduction of the Co–MCM-41 catalyst.

This is of crucial importance when the time sequence in which changes in the spectral features are initiated is key to obtaining mechanistic information relevant for the physical or chemical process investigated. However, the new ProCorA approach proposed in this work minimizes the risks associated with this limitation, and we have successfully used it to obtain useful information otherwise unreachable from regular dynamic XANES

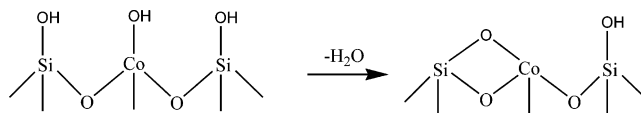


Figure 7. Cartoon showing the surface dehydroxylation.

spectra. This method has been proven to be very reliable through thorough testing using model spectra artificially generated to mimic the behavior observed in a real dynamic series of spectra.¹⁶

Conclusion

The 2D correlation analysis was successfully applied to a series of X-ray absorption spectra recorded in situ with a Co–MCM-41 catalyst during temperature-programmed reduction in hydrogen between room temperature and 700 °C. This data analysis method has been proven useful for the observation of the main energy shift during reduction of the cobalt species embedded in the MCM-41 framework, which is otherwise difficult to observe in the usual spectra because of the small shift caused by the small changes in the valence of the cobalt species (Co²⁺ to Co⁰).

Even more notably, on the basis of the 2D correlation analysis results, we were able to establish a time sequence for the changes occurring in the Co–MCM-41 catalysts. We observed that changes in the white line occur prior to the shift in the main

(16) Haider, P. *Chemometrics in Spectroscopy Applied to Heterogeneous Catalysis*. Master Thesis, Technische Universität München, 2004.

energy, and considerable reduction occurs without major changes in the local symmetry of the cobalt species incorporated in the MCM-41 framework.

While the generalized 2D correlation analysis is very useful for obtaining supplementary information from a series of spectra, interpretation of the asynchronous correlation intensities should be checked for consistency with the synchronous intensities, and with the general trend of each spectral feature as spectral intensities that do not change monotonically may induce changes in the signs of the cross-peaks in the asynchronous plots, leading to inaccurately establishing sequences of changes among the

spectral features in the series. The newly proposed ProCorA approach minimized this risk and enabled us to establish the correct sequence of changes in our dynamic series of X-ray absorption spectra.

Acknowledgment. We thank the Department of Energy, Office for Basic Energy Sciences, for funding, and the National Synchrotron Light Source, Brookhaven National Laboratory, for the X-ray absorption spectroscopy experiments.

JA045391M