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Quantitative Analysis of Mixed Oxidation States in Supported Catalysts

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Heterogeneous catalysts are important for a variety of industrial reactions such as hydrotreating, polymerization, hydrogenation–dehydrogenation, isomerization, reforming, and selective oxidation.[1] These reactions play a key role in the synthesis of fuel, fine chemicals, and a wide range of materials and in the area of pollution control.

Often, industrial catalysts consist of a highly dispersed metal phase deposited on a high-surface-area support. The genesis of a catalyst involves multiple steps as outlined in Figure 1. A high-surface-area support is allowed to react with an aqueous solution containing a metal salt (impregnation) to deposit the metal on the support surface, usually in its air-stable oxidation state (M^{n+}). After impregnation the catalyst precursor is dried at ca. 150 °C to remove excess water. Then this material is heated for an extended period (calcination), typically in air for 24 h at 500 °C. After calcination one has a precursor to a catalyst, often referred to as the "oxidic catalyst". For many reactions this material is *dead*. The oxidic precursor is then activated; for hydrogenation catalysts this, typically, involves reduction in hydrogen, to produce a reduced state (or states) of the metal (M^{p+}), which can be the free metal or an intermediate oxidation state. Now the catalyst can be used to make useful products; as with all things, it eventually deactivates and dies.

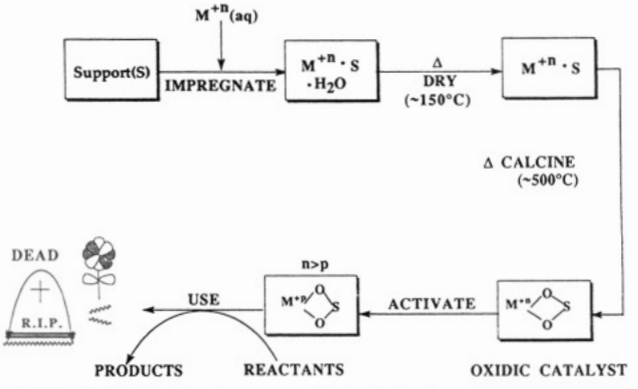

Figure 1. Genesis of a supported catalyst.

In many instances (Mo, W, Re, Cr, V), depending on the activation conditions, the same catalyst may be effective for a variety of reactions. For example, Mo and W catalysts, in their oxidic form, catalyze selective oxidation of hydrocarbons. Reduced catalysts are active for hydrogenation, metathesis, isomerization, and hydrogenolysis reactions. Sulfided, they form the bulk of industrially used hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) catalysts. The versatility of these catalysts has long been recognized to be associated with their capability of forming intermediate oxidation states. It was specu-

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lated but not proven that different oxidation-state requirements may be needed for different catalytic functions. This highlights the need to analyze the *specific oxidation states* present on the surface of the reduced catalysts and to investigate how they relate to the catalytic activity or selectivity. This approach should give insight into the nature of the active site and in turn allow one to tailor the catalyst preparation method to optimize its performance. In practice, it has been difficult to establish a direct correlation between the catalytic activity or selectivity for a given reaction and the nature and abundance of a specific species or oxidation state. This can be ascribed to two main reasons:

(1) The heterogeneity of the surface of conventionally prepared catalysts. The complexity of reduced Mo surfaces was clearly illustrated in our study of the Mo/Al_2O_3 system,[2,3] which shows that catalysts reduced between 350 and 850 °C contain from three to five different oxidation states. Considering that a given oxidation state may also be present in different environments (for example, tetrahedral or octahedral) and may possess different numbers of coordinative unsaturation, one can readily envision the obstacles to finding a clear surface structure/catalytic activity relationship.

(2) The lack of adequate means for measuring the distribution of Mo or W oxidation states. In most previous studies, the extent of reduction was determined, volumetrically or gravimetrically, from hydrogen consumption or oxygen uptake on reoxidation,[4,5] These techniques can only measure the *average* oxidation state, which gives little insight into the *specific* oxidation state that is active for a given probe reaction.

Therefore one can address oxidation state/activity relationships by using one of two approaches: (1) prepare a catalyst having a single species on its surface or (2) sort out multiple species on the surface of a conventionally prepared catalyst. We have used both approaches; the latter will be dealt with here.

This Account will deal with the group VIA transition metals, Cr, Mo, and W, supported on conventional oxide supports: alumina, titania, and silica. The specific problem to be addressed is measurement of the distribution of oxidation states produced on activation and correlation of specific states with catalytic activity.

One approach to the problem that is clearly more informative than measuring the average oxidation state is to use a spectroscopic method that is sensitive to different species and/or oxidation states of the same metal. Several possibilities exist, but most have serious limitations. For example, ESR is sensitive to metal ions having unpaired electron spins, but because of diamagnetic coupling problems has limited value as a quantitative technique.[6] Solid-state NMR yields useful information for nuclei with $^1/_2$ spin states and large cross sections, but is severely limited for more complex nuclei.[7] NMR has particular problems for different oxidation states of the same metal when one is paramagnetic and the other diamagnetic.[8] For example, it has been used to study high-spin $Co,^{3+}$ but is insensitive to Co^{2+}.[7] EXAFS and other forms of X-ray absorption spectroscopy, while applicable to virtually all metals, are still under development with regard to oxidation-state information. The shift seen in the XANES region is a manifestation of oxidation-state changes, but quantification is problematic.[9] Mössbauer spectroscopy is extremely valuable, but can be used effectively for only a few select nuclei.[10] Raman spectroscopy does not provide oxidation-state information per se, but is very valuable for measuring both highly dispersed and "bulk" species on catalyst surfaces.[11] The bottom line is that none of the above is broadly applicable to oxidation-state measurement.

X-ray photoelectron spectroscopy (XPS, ESCA) is a technique which yields spectra for all metals of catalytic importance, provides oxidation-state information, is quantitative, and gives information about the dispersion of species on a surface.[12] Thus it is ideal for examining catalysts and is our technique of choice, along with Raman spectroscopy. This is not to say that XPS is without its limitations; these will be discussed below. It is possible to use XPS to identify single oxidation states and possibly molecular symmetry and to measure mixtures of states and amounts of the individual components therein.

Our research on oxidation state/activity correlation involves a three-prong attack on the problem. First, we acquire XPS spectra as a function of reduction temperature over the range of interest. Second, we determine the number and amounts of oxidation states using data analysis protocols, to be discussed further below. Third, we correlate catalyst activity with the appearance and amounts of specific oxidation states as measured by XPS.

Methodology

General Approach. It is important to stress that complete characterization of a system as complex as the surface of a heterogeneous catalyst requires a multitechnique approach, our traditional way of attacking catalyst problems. For want of space, we will deal here with only one aspect: the use of XPS to determine oxidation-state distributions and the correlation of these data with catalytic activity.

XPS: Pro and Con. The main value of XPS for catalyst research lies in its ability to measure chemical shifts in electron binding energies which correlate with oxidation state. For example, the Mo $3d_{5/2}$ binding energies range from 227.6 to 232.7 eV going from Mo^0

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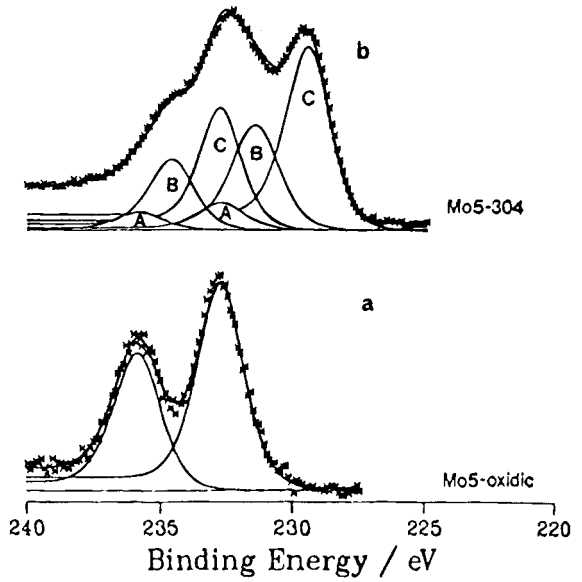

Figure 2. Curve-fitted Mo 3d spectra of a 5 wt % Mo/TiO_2 catalyst in the oxidic form (a) and after reduction at 304 °C (b). Doublets A, B, and C refer to Mo oxidation states +6, +5, and +4, respectively.

to Mo^{6+}.[2,13] Chemical shifts are not necessarily linear and are often complicated by changes in atomic environment which can cause so-called final-state effects and changes due to differences in atomic/molecular potential.[14] The upshot of all of this is that most oxidation states will have a range of binding energies (frequently as large as the difference between states) rather than a single, unique value. In other words, chemical shifts in XPS are not like those in proton NMR.

Another valuable aspect of XPS is its surface sensitivity. The mean photoelectron escape depth for a catalytic material is typically 20 Å. This means that some material in the pores can be seen (although at lower intensity) along with that on the outer surface. Typically, 95% of the signal comes from the top 60 Å. Monolayer coverage of a catalyst having a surface area of 200 m^2/g requires ca. 10 wt % metal. This means that, in most cases, the XPS signal-to-noise ratio is favorable in the concentration range found on typical catalysts.

Also, the technique is quantitative and the signal is linear with concentration, with the intercept at the origin, for highly dispersed phases.[12] The XPS signal from the impregnated metal is usually measured against that from the support as an internal standard. By use of a simple model, one can predict the slope and intercept of a calibration curve. If the behavior deviates significantly from linearity, the deviation can be correlated with changes in dispersion, or loss of support surface area. This provides an additional source of information about phenomena which may occur on a catalyst surface during reaction, such as particle formation.

One problem with XPS spectra is that chemical shifts may be about the same magnitude as peak widths. Also, transition metal spectra occur as doublets. Figure 2a shows a Mo 3d spectrum for the Mo^{6+} oxidation rate. The two components represent the Mo $3d_{3/2}$ and $3d_{5/2}$ components from $l-s$ coupling which occur in a 2:3 intensity ratio. Figure 2b shows the Mo 3d spectrum for the same catalyst reduced at 300 °C along with the individual Mo 3d components.[15] This catalyst has three Mo oxidation states on the surface, +6, +5, and +4. The widths of peaks B and C are 1.9 and 1.8 eV, respectively, and the shift between them is 1.8 eV. Another problem is that, while one can determine the number of doublets under a given envelope and their binding energies, this does not *definitively* assign the peak to a specific oxidation state. Lack of model compounds for intermediate oxidation states frequently exacerbates this problem.

Data Analysis Protocols. A major problem with the use of XPS for catalyst (and other) studies is how to determine that a spectral envelope such as the one shown in Figure 2b actually is composed of three components, as opposed to two or four. This is not a new problem, nor is it unique to catalysts; it has been around since the very early days of XPS. Our group has spent considerable effort developing data analysis protocols for XPS spectra to best accomplish this task. We will deal with three of these here: nonlinear least-squares curve fitting (NLLSCF), factor analysis, and deconvolution.

Nonlinear Least-Squares Curve Fitting (NLLSCF). This method is widely used for XPS data analysis; commercial instruments come with built-in software packages. It should not be confused with deconvolution which, as we will show later, is quite different. The basic idea of NLLSCF is to take an experimental curve, such as that shown by the asterisks (*) in Figure 2b, and to fit it with the minimum number of 3d doublets. To accomplish this task, one must provide considerable information for the computer program. In the case of the above, this would require the correct number of 3d doublets, the spacing between doublets, their relative intensities, their half-widths, and the mathematical peak shape (i.e., Lorentzian, Gaussian, or a combination). Some of these parameters are known (e.g., relative doublet intensities), and one can allow some flexibility in adjusting these parameters, but not too much or the program may relax into an unrealistic local minimum. One must also allow for tailing of peaks toward higher binding energies, even after removal of background.

A major problem with using NLLSCF is to determine the appropriate number of components. How many are there, and what do you gain by adding another? Statistical tests have been proposed to aid in this decision;[16] a look at the residuals is always informative, but most often it is a judgment call. For example, how much poorer would be the fit in Figure 2b if the "A" peaks were eliminated? Would it be better if another set were added? Another problem is that NLLSCF does not deal effectively with noisy data; often filtering to remove noise significantly broadens the spectra, and then getting a good fit becomes problematic. Finally, a given solution is not necessarily unique because of noise: another set of peaks may fit equally well. This is a particular

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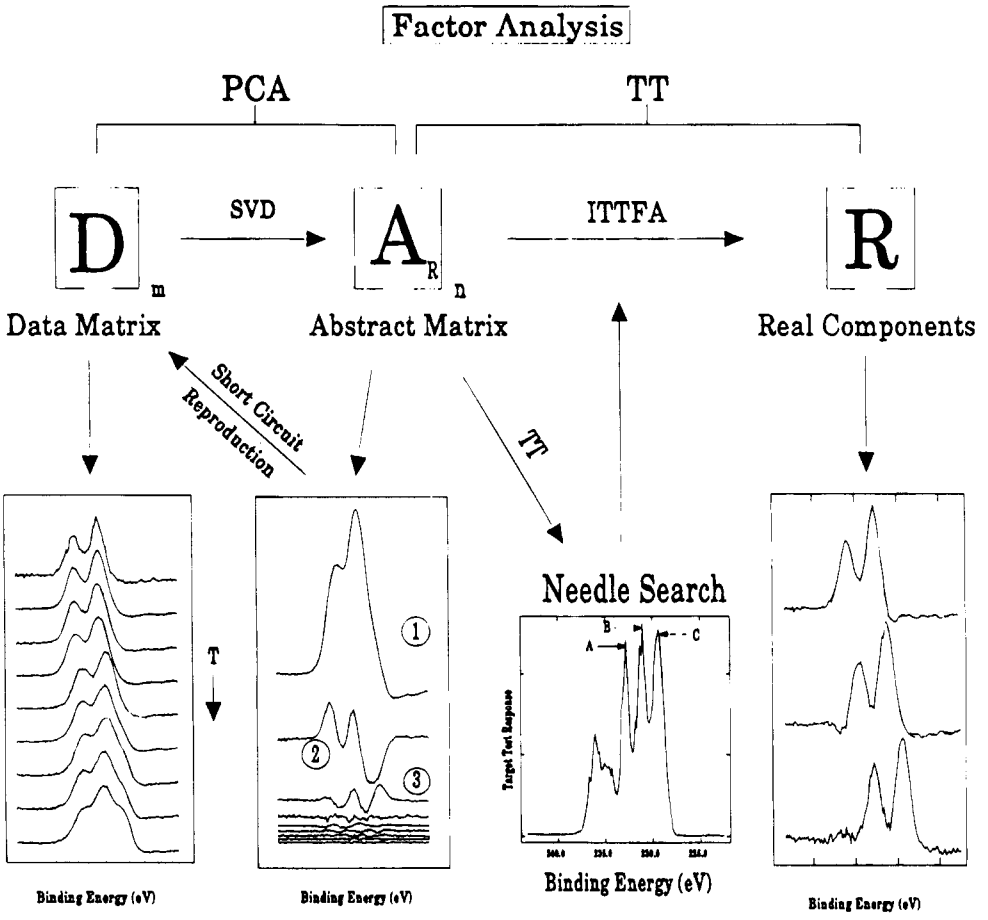

Figure 3. Synposis of factor analysis. The data matrix consists of a series of nine Mo 3d XPS spectra obtained from a Mo/TiO_2 catalyst which has been reduced at successively higher temperatures.

problem with a large number of components (more than three or four).

Factor Analysis (FA). For purposes of this discussion, we will limit our consideration of FA to principal component analysis (PCA) and target testing (TT).[17] The combination of PCA and TT applied to a series of spectra, which are linear sums of several components that vary independently, can provide information about the number, positions, shapes, and fractions of the components in each individual spectrum. In addition, the validity of a spectral component to be a basic component can be tested statistically. Figure 3 shows an overview of this particular FA approach using a series of nine ($m = 9$) Mo 3d XPS spectra. The nine spectra form a data matrix [**D**], obtained from a Mo/TiO_2 catalyst which has been reduced at successively higher temperatures.[15]

Any matrix [**D**] can be decomposed by single value decomposition (SVD) into two abstract (i.e., spectroscopically meaningless) submatrices [$\mathbf{A}_R$] and [$\mathbf{A}_C$], each containing a series of eigenvalues Λ. [$\mathbf{A}_R$] consists of m abstract spectral profiles, and [$\mathbf{A}_C$] consists of weighting factors such that the product $[\mathbf{A}_R]_m \cdot [\mathbf{A}_C]_m$ reproduces [**D**] exactly by short circuit reproduction (SCR). The purpose of PCA is to deduce the minimum number of abstract components n which will reproduce [**D**] by SCR so that only spectral noise has been excluded. Statistical tests and visual inspection of [$\mathbf{A}_R$] are used to help determine n. For example, inspection of [$\mathbf{A}_R$] in Figure 3 reveals three (1, 2, 3) components that are "legitimate" (i.e., show low frequency variation) and six components that contain only noise (high frequency). Given that n abstract components constitute [**D**], we then make a jump in logic and conclude that only n true spectroscopic components are required to reproduce the data set.

Determination of n provides a major piece of information for subsequent curve-fitting analysis, because this tells us that only n components need to be used for NLLSCF. Sometimes it is possible to extend the process and extract real spectroscopic information about components from the data matrix. This is accomplished by a target testing (TT) methodology which does two things: establishes locations of the components and gives estimates of their shapes. TT itself involves taking a test spectrum and selecting a combination of the abstract components so that the variance between the two is minimized. A needle search requires several TT using a δ function at different values of the spectroscopic parameter (binding energy in Figure 3), and plotting the negative residual variance as a function of this parameter. This function maximizes at locations of real components, A, B, and C in Figure 3. So, by combining PCA and the needle search, one knows both the number of components and their locations along the binding energy scale. It is also possible to do iterative target testing (ITTFA) and arrive at an estimate of the shapes of the real components; spectra of the three

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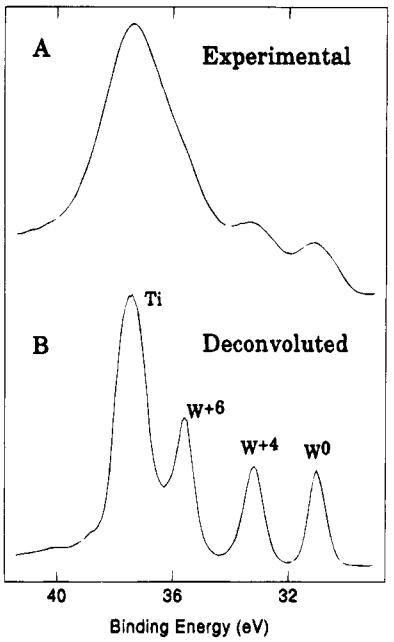

Figure 4. Experimental and deconvoluted spectra of a reduced 5 wt % WO_3/TiO_2 catalyst.

components estimated from the data matrix are shown in Figure 3. The four diagrams along the bottom of Figure 3 are actual results from a study involving Mo catalysts.[15]

Deconvolution. Deconvolution refers to the removal of broadening effects from a spectrum; it is *not* the decomposition of a spectral profile into individual curves, which is NLLSCF. An ideal spectrum is a narrow peak having its height proportional to spectral intensity. This signal is broadened (convoluted) by several broadening functions which for XPS include the natural line width, the exciting X-ray shape and width, the detector response, the spectrometer function, and any charge broadening. Although line broadening is due to real physical processes, mathematically it is simply convolution of the true spectrum by the various broadening functions. In principle, removal of broadening should be relatively straightforward if the broadening functions are known or can be estimated. The problem is that the protocols for doing this are very sensitive to noise, often resulting in nondefinitive solutions.

Iterative methods of deconvolution have proven to be more useful than direct Fourier-based methods; one of the more successful is the iterative point simultaneous method of Jansson.[18,19] This method is described by

$$G_i = G_{i-1} + R(D - G_{i-1}B)$$

G_i is the deconvoluted spectrum for the ith iteration, D is the original spectrum (smoothed) to be deconvoluted, and B is an estimate of the broadening function, that is, an estimate of the total convolution function. R is a relaxation function which controls convergence of the iterative procedure. After each iteration, the difference $G_i - G_{i-1}$ is checked, and when it minimizes, the procedure is terminated. Figure 4 shows an example of the deconvolution of the XPS spectrum of a partially reduced W/TiO_2 catalyst in the region where the Ti 3p and W 4f peaks overlap.

The most important variable in the deconvolution process is the choice of B. The major broadening in XPS is due to the exciting X-ray line width, the spectrometer, and of course the natural photoelectron line width. While the first two functions are essentially constant, the latter contribution will change, depending on the particular electron level being probed. From a practical analytical standpoint we have found that a symmetric 20% Lorentzian Voigt function can be successfully used to deconvolve spectra of the X-ray and spectrometer broadening and to some extent the natural line width. In general, the width of B was chosen to be slightly lower than those used for typical XPS curve fits. Since we cannot predict the outcome of a poor choice of B (it may result in an oscillatory calculation or make the system very noisy), it is a good idea to try several values for B and compare the results.

Examples

Mo/Al_2O_3. As noted in the introduction, supported Mo catalysts are active for a variety of reactions.[1-5,20] The multifunctional ability of these catalysts has been linked to their capability of forming intermediate oxidation states.[4,5] It is evident that this hypothesis, formulated essentially on the basis of average oxidation state measurements, needs to be evaluated in light of current means for measuring the distribution of Mo oxidation states.

We have shown earlier that the distribution of oxidation states in reduced catalysts can be effectively measured by XPS.[2,3,13,15] For the Mo system, this was achieved by monitoring the reduction process over a wide range of temperatures by XPS and analyzing the Mo 3d envelopes by NLLSCF in conjunction with factor analysis. The main advantage of FA methods is that they can determine, *without any assumptions*, the number and positions of the Mo 3d or the W 4f doublets (e.g., oxidation states) present under a given envelope. The study of reduced Mo/Al_2O_3 catalysts indicated that the surface is very heterogeneous, often containing from three to five different oxidation states. Figure 5a shows, for the sake of simplicity, the distribution of the most abundant Mo oxidation states following high-temperature reduction (500-900 °C). The results are compared to the observed catalytic activity for propane hydrogenolysis (Figure 5b). Catalysts reduced at temperatures lower than 500 °C and containing Mo oxidation states higher than +3 were not active. It can be clearly seen from Figure 5 that there is a close correlation between the catalytic activity and the abundance of Mo metal, indicating that metallic sites are the most active centers for this reaction.

Cr/Al_2O_3. Cr-based systems are best known as polymerization and dehydrogenation catalysts. They are as versatile as their Mo counterparts. Reduced Cr species (+6 > Cr > +2) are usually considered to be the active centers for most reactions. The surfaces of the reduced catalysts have been extensively studied by XPS. The results, however, were for most instances inconclusive. One serious impediment to reaching

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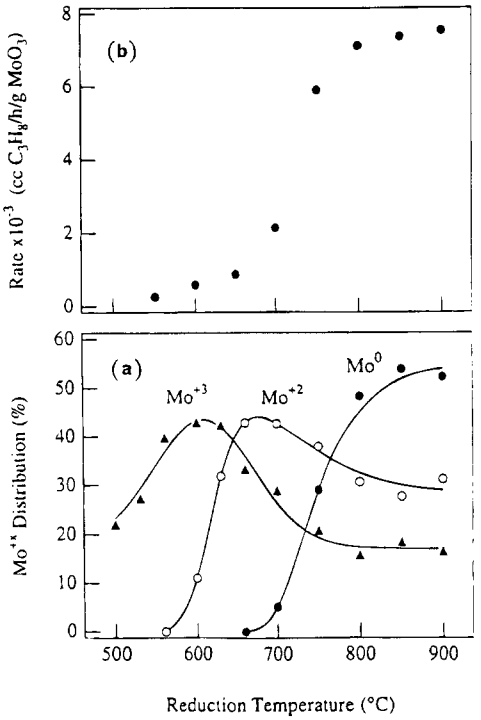

Figure 5. (a) Relative abundance of Mo^{3+}, Mo^{2+}, and Mo metal versus reduction temperature. (b) Propane hydrogenolysis rate versus reduction temperature. Reaction conditions: feed, 10% propane in He; 25 cm^3/min; 1 atm; reaction temperature, 250 °C.

firm conclusions was reduction of the Cr phase in the spectrometer during analysis, presumably by stray electrons. This imposes a limit on the data acquisition time, which in turn leads to a poor signal-to-noise ratio and consequently less reliability of the data.

We have recently used[21] factor analysis (specifically, SCR, Figure 3) to afford a quick means to improve the signal by reconstructing the data matrix using only the basic abstract components. This is illustrated in Figure 6, which compares the initial data matrix (Cr 2p envelopes obtained from the reduction of a 2.5 wt % Cr/Al_2O_3 catalyst at various temperatures) with that reconstructed using the two primary abstract components indicated by PCA. In addition, by the use of target testing, the positions of the real spectroscopic components were obtained. The results of the first step in the TT procedure (needle search) are shown in Figure 7. The positions of the real components (binding energies of the Cr $2p_{3/2}$ peaks) are indicated by the locations of the two largest maxima. These components were attributed to Cr^{6+} and Cr^{3+}. The combined use of factor analysis and NLLSCF showed that reduction of Cr/Al_2O_3 catalysts proceeds primarily from Cr^{6+} to Cr^{3+}.

W/TiO_2. The catalytic properties of W-based systems are similar to those of their Mo analogs. The reduction of W/TiO_2 catalysts has been investigated primarily by temperature-programmed reduction (TPR).[22,23] Conflicting results concerning the reduction mechanism were reported. According to Bond and co-workers,[22] catalysts containing only the W surface interaction species reduce directly to W metal.

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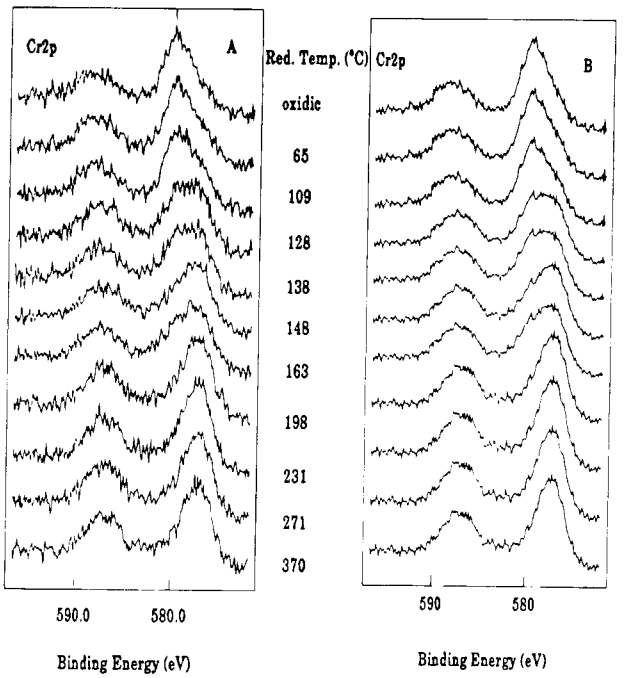

Figure 6. Data matrices of Cr 2p spectra for oxidic and reduced 2.5 wt % Cr/Al_2O_3 catalysts: (A) original data; (B) short circuit reproduced data.

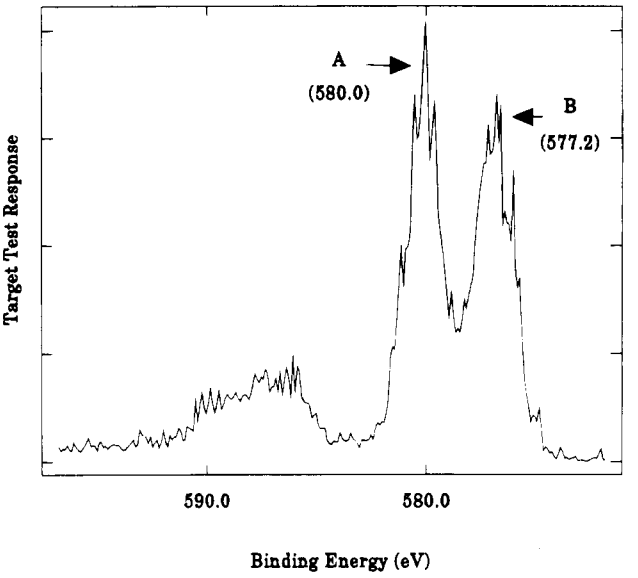

Figure 7. Needle search carried out on data for 2.5% Cr/Al_2O_3 catalysts. The positions of the spectral components are indicated by A and B.

This was at variance with the results of Vermaire and Van Berge,[23] which indicate that reduction to W metal proceeds via formation of an intermediate oxidation state, W^{4+}. Findings based on TPR methods are inherently inconclusive since the technique can only measure average oxidation states. To date, no systematic study of the reduction of W/TiO_2 by XPS has been reported. One can surmise that the scarcity of XPS studies is partly due to the overlap between W 4f and Ti 3p peaks. We have shown (Figure 4) that deconvolution can clearly delineate the position of the Ti 3p peak from those of the W 4f doublets. This procedure was applied to the study of the reduction of a 5 wt % WO_3/TiO_2 catalyst at temperatures up to 700 °C. Deconvolution of the series of Ti 3p–W 4f spectra indicated formation of an intermediate W

oxidation state. Information concerning the W 4f binding energy positions of the oxidation states present in the reduced catalysts can be clearly obtained.

We have also conducted a detailed investigation of the reduction of W/TiO_2 catalysts using factor analysis and NLLSCF. In agreement with the deconvolution data, all evidence from statistical tests (*F* test, indicator function, REV ratios) indicated the formation of an intermediate W oxidation state on reduction of the oxidic phase to metal. This finding is consistent with the results of Vermaire and Van Berge.[23] From the binding energy positions of the W 4f doublet, the intermediate oxidation state was tentatively identified as W^{4+}. It is worth noting that the binding energy positions of the three components (W 4f doublets) which describe the W 4f envelopes of the reduced catalysts determined by NLLSCF and attributed to W^{6+}, W^{4+}, and W metal agree with those obtained by deconvolution.

The simplified reduction process observed for the monolayer-like 5 wt % WO_3/TiO_2 catalyst (e.g., formation of one intermediate oxidation state on reduction from W^{6+} to W metal) should be contrasted with that obtained for the Mo/TiO_2 and Mo/Al_2O_3 systems, where evidence of the formation of several intermediate oxidation states (Mo^{5+}, Mo^{4+}, Mo^{3+}, Mo^{2+}) was found.

Conclusions

We have described methodology for determining the distribution of oxidation states in reduced catalysts. The merit of the above mentioned approach is in its reliance on statistical tests and its avoidance of subjective criteria. It must be noted, however, that the protocol described above is most effective for the analysis of the number of components (oxidation states) required to describe a given envelope. It cannot assign with certainty these components to specific oxidation states. Independent techniques which complement XPS are needed. Furthermore, as stated in the introduction, we have chosen to address in this Account oxidation state/catalytic activity relationships by developing a detailed analysis procedure of the surface of *"conventionally prepared catalysts" containing a mixture of oxidation states.* A more promising avenue which we are also pursuing is to prepare well-defined *"model catalysts" containing a discrete oxidation state.* This approach should give more insight into the type of site that is active for a given reaction. Finally, one must stress that the oxidation state, while important in shaping the properties of the final catalyst, is not the only factor which determines the activity or selectivity of the final catalyst. Other details concerning the structure of the active site such as symmetry, degree of coordinative unsaturation, and degree of association with the neighboring site may be equally important in determining the performance of the final catalyst.

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