New approaches to optimise manufacturing of metal oxides

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Introduction

Functional states on the surface of metal oxide powders are sensitively detected by near infrared (NIR) spectroscopy. The conversion of metal compounds into oxides may be controlled by the temperature of the furnace wall or the atmosphere. However, the same process conditions do not always result in products with the same surface functional state. If functional states are connected to process conditions, NIR qualitative analysis has great potential to evaluate metal oxide surfaces and to provide information for process control. One of the applications of qualitative calibrations is an identification programme which determines whether a new measured spectrum can be associated with a calibrated category. Instead of collecting the NIR spectra of same qualities of the same substances over a long period, it would be more effective for the calibration to use a few samples of different qualities of the same substances. In order to build up the calibration model, pre-treatments are also important for an easy and quick method to evaluate the functional states. Further discussion of physical properties of principal components ascertains the adequacy of the calibration model assuming that physical quantities correlate with each other as long as the differences occurred in the same process changes. Using titanium dioxide (TiO_2) as a common material, this work explored how to connect process conditions with the qualitative results of the near infrared spectra and how to expand the case of TiO_2 to other metal oxides.

Materials and Methods[1–2]

Samples

Eight titanium dioxide powders with three different crystal structures (amorphous, anatase and rutile) were selected on the basis of ingredient brochures. Anatase is a low modification of rutile. The eight TiO_2 samples were numbered: (1) amorphous, (2-4) anatase, (5-7) rutile and (8) nano-rutile. The calibration samples were verified by infrared spectra (IR), a field emission - scanning electron microscope (FE-SEM), a temperature gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS).

NIR spectroscopy

Six vials of each TiO_2 powder were prepared for measurement; the vials had 15 mm outer diameter and 45 mm height with a flat base and PE cap. They were filled with TiO_2 powder to over 1 cm depth from the bottom. NIR spectra were observed using a NIRFlex N-500 (BÜCHI Labortechnik AG, Flawil, Switzerland), with an add-on 6 vials cell holder. Diffuse reflectance spectra were acquired from 12500 to 4000 cm^{-1} at 4 cm^{-1} intervals (2126 points).

Data analysis

Data analyses were performed using the instrument software (NIRCal v.5.2.3000 Std. Ed.). Two spectral pre-treatments were applied: [1] normalisation by closure (ncl) followed by first derivative (db1), and [2] first derivative (db1) followed by normalisation (standard normal variate - SNV). The region for calibration was set between 10000 and 4000 cm^{-1} (1501 points) to exclude noise. Büchi's own identification programme was used for the calibration (Cluster analysis with PCA and Mahalanobis distance) and the calculation. In order to evaluate the performance of a calibration, spectra were divided into two sets: 2/3 spectra as calibration (C-set) and other 1/3 as validation (V-set). The C- and V-Sets of each sample were the same for calibrations. Other sample scores were calculated by the built-up calibration model.

Scores-scores plots adequacy

It is ideal to know the surface state at a glance on the scores-scores plots. The above is adjusted by selecting the sample set and pre-treatments for the calibration. It is important that samples are distributed along the first principal component (PC1) and as parallel as possible. This is because separation would be reliable especially in case that the explained variance is mostly allocated to PC1. Further discussion of physical properties of principal components ascertains the adequacy of the calibration model assuming that physical quantities correlate with scores as long as the differences occurred in the same process changes. Whole

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sample scores can be compared with other physical quantities except for ambiguities. For example, it is appropriate to compare the surface changes with the top thin layer, which are the functional states obtained by NIR chemometrics (scores) to the elemental ratio by XPS ([O]/[Ti]). Ambiguities occur in the case of co-existence of other metal hydroxides (or metal oxides), any impurities like NOx [something influencing the results], and suspecting any replacement of O-H to C=O [reflecting on NIR] etc. These can be discussed by IR, TGA, XPS and NIR itself. The scores of sample - 2, - 6 and - 8 were excluded for the above discussion.

Results and Discussion

Original and pretreated spectra

The original spectra of samples - 1, - 4 and - 7 are shown in Figure 1 (a). The baseline absorption at high (10000 cm^{-1}) and low (4000 cm^{-1}) frequencies between these two points are distinctly different between crystalline and amorphous samples. Referring to the FE-SEM photos, rutile (6 and 7) had bigger particle sizes than anatase and amorphous samples. The aggregation sizes in the amorphous sample (1) were larger than in the anatase (4) and rutile (6 and 7) samples. Diffuse reflectance light intensities are partially dependent on size differences of particles and/or aggregates. Figure 1 (b) is the pretreated spectra [normalisation (ncl)] and Figure 1 (c) shows the pre-treated spectra [normalisation (ncl) followed by 1st derivative (db1)].

Fig.1 (a)

Fig.1 (b)

Fig.1 (c)

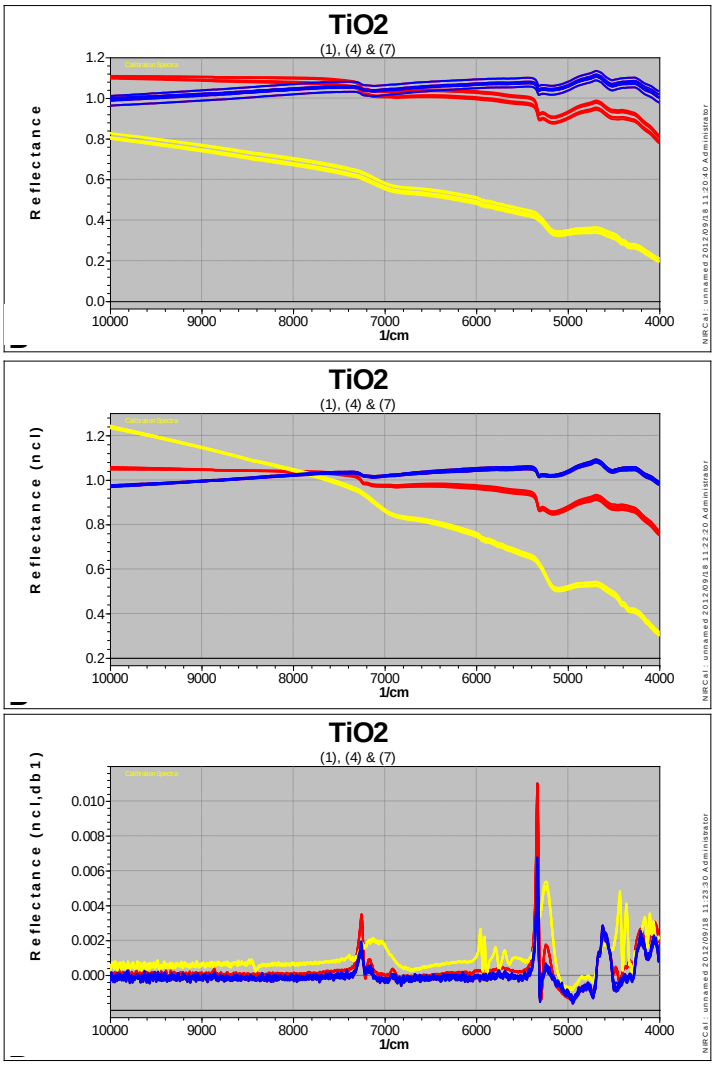

Figure1. Original (a) and pre-treated (b and c) spectra of TiO_2 sample -1 (amorphous / yellow), - 4 (anatase / red) and - 7 (rutile / blue). (b): Pre-treated [normalised (ncl)]. (c): Pre-treated [normalised (ncl), and first derivative (db1)].

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TiO_2 Calibration models built-up by different sample sets and pre-treatments

Figures 2 (a), (b) and (c) show three calibration models built using different sample sets and pre-treatments. Figure 2 (a) was calibrated based on the sample set comprising samples - 1 (amorphous), - 4 (anatase) and - 7 (rutile). Figure 2 (b and c) were calibrated with samples - 4 (anatase), - 7 (rutile) and - 8 (nano-rutile). The pre-treatments of (a) and (b) are normalisation (ncl) followed by 1st derivative (db1). Figure 2 (c) was pre-treated with 1st derivative (db1) followed by normalisation (SNV). The tolerance circles were plotted for the calibration samples. Other samples scores were calculated by the constructed calibration models respectively. The explained variances are shown to the right of principal components.

Figure 2 (a) means hydrogen bonding O-Hs as the biggest difference between amorphous and crystalline TiO_2 when comparing with the spectra of Figure 1(c) that is physically adsorbed water differences on the 1st principal component (PC1). Crystalline TiO_2 was plotted along the second principal component (PC2). Even though PC2 shows surface hydroxyl changes and suggests the process temperature differences, the explained variance is less than 10 %. Therefore the calibration model should be developed in order to place the objective difference on PC1.

The calibration model of sample - 4, - 7 and - 8 distributes other calculated scores along PC1 in the case of pre-treated spectra by ncl and db1 (Figure 2 (b)). The loadings of PC1 show free O-H (bridge O-H: Ti-O(H)-Ti) upward and C=O (5000-4000 cm^{-1})[3] downward (Figure 3 (a)) which means the process temperature is lower at positive PC1 and higher at negative when referring to the information[4] of manufacturing conditions and the investigations[4] of surface hydroxyl natures. Lattice defects (oxygen vacancy) is a well known occurrence by the manufacturing conditions.[4] XPS results ([O]/[Ti]) have a good correlation with PC1 scores for each one of sample -3, - 4, -5 and -7 (the correlation factor r^2=0.9585). It suggests that PC1 may be replaced with the scale of processing heat conditions when scores are calculated for a new measured spectrum by the built-up calibration model.

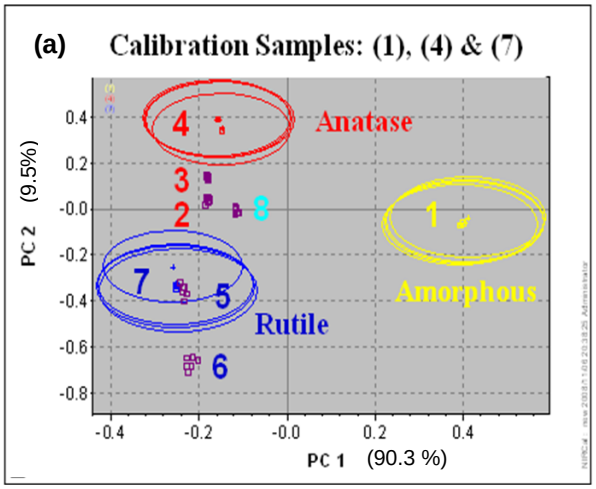
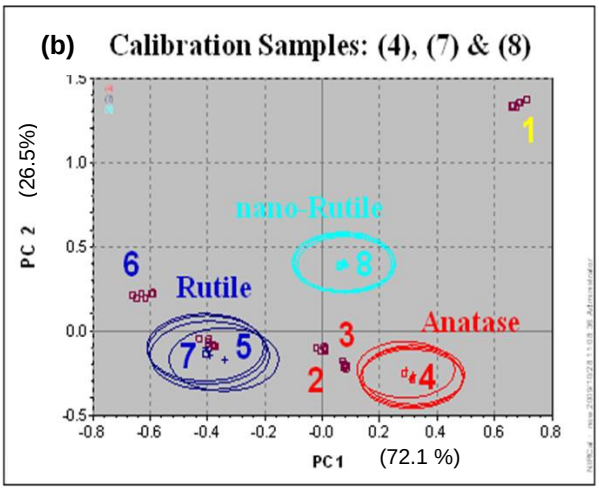
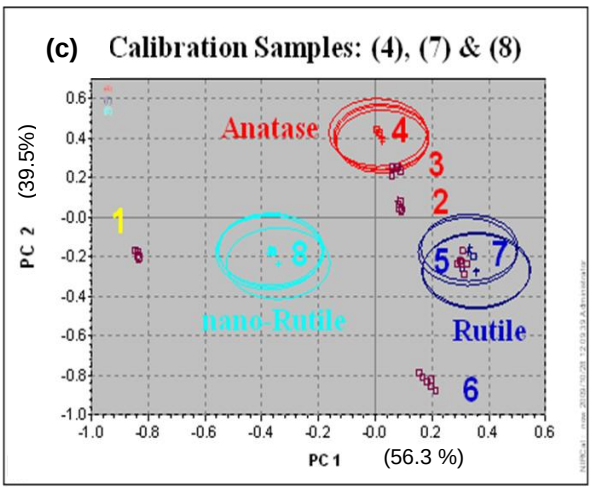


Figure2. Calibration models built-up by different samples sets and pretreatments.

(a) Sample - 1, - 4 and - 7, ncl and db1.
(b):Sample - 4, - 7 and - 8, ncl and db1.
(c) Sample - 4, - 7 and - 8, db1 and SNV.

The tolerance circles were plotted for the calibrated samples. Other sample scores were calculated by the built-up calibration models, respectively.
The explained variances are shown to the right of the principal components.





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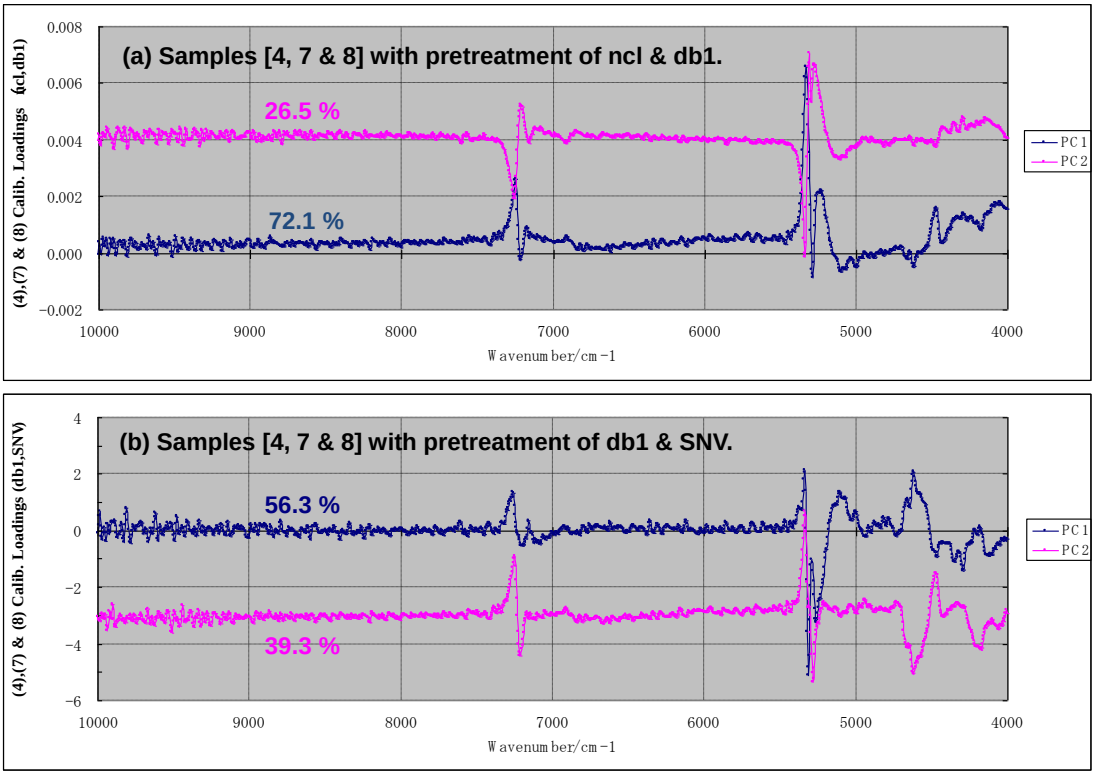

Figure 3. PC1 and PC2 loadings of the calibration models based on samples - 4, - 7 and – 8 with (a) pre-treated spectra (ncl and db1), see Figure2 (b), and (b) pre-treated spectra (db1 and SNV), see Figure 2 (c).

PC2 loadings in Figure 2 (b) show hydrogen bonding O-H upward and free O-H downward (Figure 3 (a)). It suggests the time lapse after manufacture because the adsorbed water increases during storage. It is difficult to confirm this experimentally. Figure 2 (c) was calibrated based on the same sample set as (b) but with differently pre-treated spectra (db1 and SN). Crystalline TiO_2 samples were distributed along PC2 instead of PC1. Additionally it was difficult to connect the loadings of PC1 and PC2 with physical properties and further processing conditions (Figure3 (b)). Therefore Figure 2 (b) is the best one for easily and quickly identifying and providing the information about processes.

How to expand the case of TiO_2 into other metal oxides

The case of TiO_2 provides only processing heat histories on PC1 as long as samples were commercially obtained. In the case of metal oxide manufacture, the calibration samples could be prepared for the objectives. The calibration model should be built-up based on samples selected to have different (as far as possible) qualities of the same substances. In addition to the ideal product, one for PC1 is to be selected in place of heat and for PC2 in place of time. Accidental error products could be used because error suggests the difficult steps to be controlled in the processes. Of course a small amount of lab-scale products could be prepared. Referring to the manufacturing processes, the physical properties of principal components should be discussed with the interpretation of the loadings and other relating physical quantities influenced by the same process changes. Pre-treatments may be better in order of normalisation (ncl) followed by 1st derivative (db1). The interpretation of the loadings could find the physical properties of principal components. The other calculated scores are to be distributed along PC1 as parallel as possible. The physical natures should be confirmed by comparing scores with other physical quantities for which differences may occur by the same process changes. Then PC1 could provide the process information for a newly-manufactured substance by examination of where the calculated scores are plotted.The calibration model could be used to optimise manufacturing conditions on a case-by-case basis; seasonal variances, furnace scale, production site variances and changes of raw materials (or precursors) etc.

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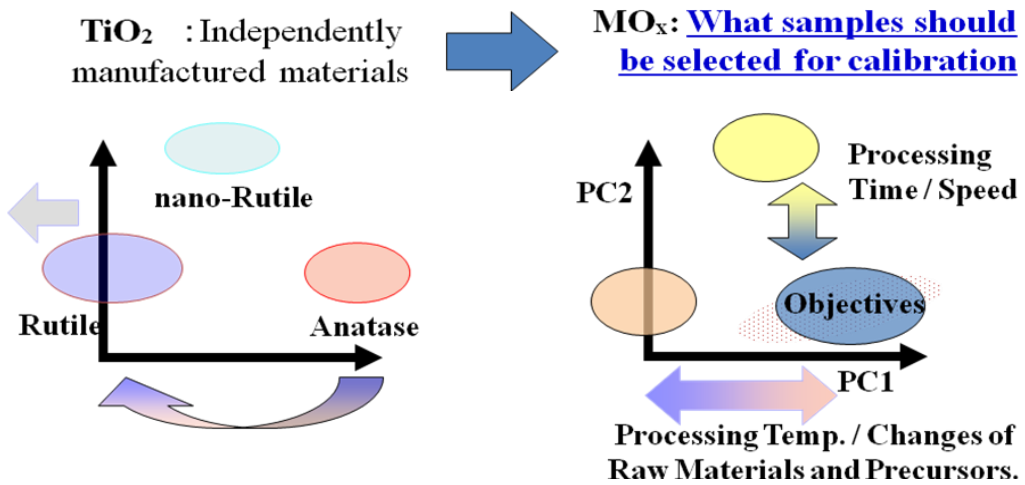

Figure 4. The relationship between the calibration model of TiO_2 and that for other metal oxides. It would be key to connect the interpretation of the loadings to the phenomena that happened in the processes; heat transition, particle/aggregate sizes, sintering level, impurities remaining, etc.

Conclusion

Functional states of metal oxide powders are obviously detected by NIR spectra, specifically for hydroxyl (OH) and carbonyl (C=O) groups. At least three specified types of powders of the same metal oxide can provide an easy and quick tool for the identification of surface status. Based on two dimensional scores-scores plots once calibrated with NIR spectra of specified samples, the product of metal oxide powders can suggest the process condition affected through previous steps. This information could be used to adjust surface status for the sequential steps of surface modification to improve the solubility in organic materials like polymer. This technique has potential to expand applications to other inorganic compounds having X-H functions beyond oxides.

Acknowledgements

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References

1. Y. Kobayashi, *2008ANS (The 1st Asian NIR Symposium) P13B, Tsukuba* (2008).
2. Y. Kobayashi, in *Near Infrared Spectroscopy: Proceedings of the 14th International Conference*, Ed by S. Saranwong, S. Kasemsumran, W. Thanapase and P. Williams, IM Publications, Chichester, UK, p. 1151-1155 (2010).
3. Private communications/experimental experiences that C=O increases by exceeded heat.
4. M. Kiyono, "*Titanium Dioxide – Physical properties and application technology*", Gihodo (2003).

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