Revised model of strain in ceria–zirconia-encapsulated precious-metal particles

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A previously proposed model of strain in ceria–zirconia-encapsulated precious-metal particles is revised to reflect several new observations: encapsulation of unstrained Pt particles, quantitative relation between partial reduction and the change in ceria–zirconia cell parameters, temperature/time dependence of strain relaxation/imposition in encapsulated Pd and Rh particles, and strained PdO. According to the revised model, the main cause of strain is partial oxidation of the precious metal (rather than the change in oxygen content of ceria–zirconia, as originally suggested).

KEY WORDS: catalyst; ceria–zirconia; deactivation; encapsulation; palladium; platinum; rhodium; strain; X-ray diffraction (XRD).

1. Introduction

Deep encapsulation of precious-metal particles by ceria–zirconia support material can occur upon high-temperature aging, when sintering processes cause the ceria–zirconia surface area to drop to just a few m^2/g [1–5]. This phenomenon, which results in catalyst deactivation, may be revealed through a strain in the precious-metal particles, detectable by X-ray diffraction (XRD), induced by a compressive stress applied to the particles within the encapsulating ceramic matrix. According to the initial interpretation of this effect, the applied stress originates from the change in cell parameter of ceria–zirconia, caused mainly by the change in its oxygen content, between a partially-reduced state (having an expanded crystal lattice) at high temperature, where encapsulation presumably takes place, and a fully-oxidized state at room temperature, where XRD measurements are typically made. Though reasonable, this model does not account for the absence of strain in a model Pt catalyst suspected of containing encapsulated particles or the lack of dependence of strain on zirconia content observed in a number of model Pd catalysts [4,5].

Subsequently, new experiments have been performed on the Pt catalyst, showing that it does, indeed, contain encapsulated particles, and *in-situ* XRD measurements have been made to measure the actual change in ceria–zirconia cell parameters under high-temperature aging conditions. These, together with other new observations, described below, which clearly implicate partial oxidation of the encapsulated precious-metal particles in the application of the stress, have been used to construct a revised model of the strain effect that hinges less on the dimensional changes produced in ceria–zirconia by changes in its oxygen content than on the ease of oxygen transport through its lattice. According to this model, the strain is directly proportional to the change in free energy associated with precious-metal-oxide formation and inversely proportional to the precious-metal bulk modulus.

2. Experimental details

The model catalysts used in these experiments are the same Pt, Pd, and Rh catalysts used previously [4]. Briefly, the Pt loading is 8 wt%, and the Pd and Rh loadings are both 4 wt%. The ceria–zirconia support material (DSCI) is a single-phase solid solution, obtained from Degussa, containing about 73 wt% CeO_2 and 27 wt% ZrO_2. The surface areas of the catalysts were about 130 m^2/g initially and about 1.8 m^2/g after aging (12 h at 1150 °C under "redox" conditions). All three aged catalysts were subjected to an oxidation treatment, heating at 700 °C in air for 2 h. Additionally, the Pt catalyst was subjected to an acid etch by placing it in a large excess of boiling aqua regia, periodically replaced with fresh solution by decantation. After 2 days, the sample was placed in a filter, washed thoroughly with distilled water, and dried at 100 °C overnight.

XRD measurements were performed with a Scintag X1 diffractometer, fitted with a Scintag heating stage, using Cu K_α radiation. A gas-handling system allowed the sample to be heated in a flow of oxidizing (0.5 mol% O_2 in N_2), reducing (1 mol% CO/H_2 in N_2), or inert (N_2) gas, which could be switched in about 1 min. The sample, in the form of a thin layer of powder, was

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separated from the Pt–Rh heating strip by a single crystal of $SrTiO_3$ (from Atomergic Chemetals), 1 mm thick, offcut from the (100) orientation by 5°. Temperature calibration was performed using a method based on the difference in coefficients of thermal expansion of alumina and silver [6].

3. Results

In the earlier study, a compressive strain of roughly 3% (by volume) was observed in about 30% of the metal particles present in both the Pd and Rh catalysts, but not the Pt catalyst, after aging at 1150 °C [4]. The absence of strain in the Pt catalyst suggested that it was somehow resistant to the substantial degree of encapsulation exhibited by the other two catalysts. (For example, Pt might be more resistant because of the high volatility of its oxide.) In the present study, as a test of this possibility, the aged Pt catalyst was etched in aqua regia with the expectation that any accessible Pt would be dissolved (taking into account that ceria–zirconia is not soluble in acids). As shown in figure 1, this treatment did reduce the intensity of the Pt peaks in the XRD pattern, by about 65%. When the same treatment was performed on a catalyst that had been aged at only 1050 °C, the intensity of the Pt peaks was reduced by about 95%. The levels of Pt remaining, ~5% and ~35%, after etching the catalysts aged at 1050 and 1150 °C, respectively, are thus comparable with the levels of encapsulated metal found in correspondingly aged Pd and Rh catalysts [4].

The previously proposed model of encapsulation-induced strain considers two possible contributions to the applied stress, one due to the oxygen uptake by ceria–zirconia between high temperature, where it is partially reduced, and room temperature, where it is fully oxidized, and another, relatively minor one, due to differential thermal contraction of precious metal and ceria–zirconia [4]. The first of these contributions was incorporated into the model through the introduction of a parameter, e, which represents the fractional decrease in the linear dimension of ceria–zirconia due to the increase in its oxygen content. A value for e of 3.2% was subsequently inferred from the model. Although this value arose from the analysis of a particular support material, DSCI, the similarity of the strain observed in a number of Pd catalysts with widely varying ZrO_2 content suggested it should be common to a range of ceria–zirconia compositions. In this study, *in-situ* XRD was employed to measure e directly and thus test the validity of the model. The most favorable case was expected to be DSCI. The cell parameter of this material was obtained from the (111) diffraction peak of ceria–zirconia in a Pd catalyst as it was heated (or cooled) under air and is shown by the open circles in figure 2. The same result was found under 0.5 mol% O_2, as shown by the open inverted triangles. The filled circles, on the other hand, correspond to the cell parameter found after switching the gas from 0.5 mol% O_2 to 1 mol% CO/H_2 ($[CO]/[H_2] = 3/1$). The change in cell parameter was found to stabilize well within the time interval needed to acquire the diffraction data (a few minutes), after switching the gas. It then remained constant over tens of minutes and was at least as easily reversed. (In fact, the switch in gas included a 5-min

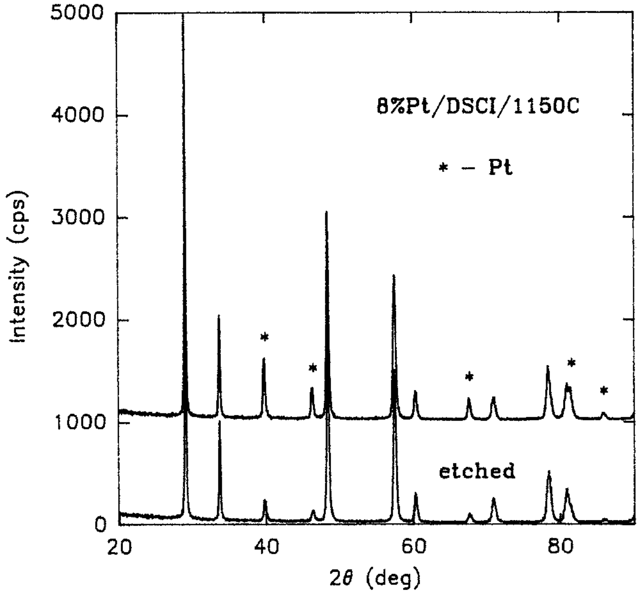

Figure 1. XRD patterns obtained from the aged Pt catalyst (8 wt% Pt on DSCI, "redox" aged at 1150 °C) before and after 2 days in aqua regia (etched). Reduction in the intensity of the Pt diffraction peaks, by about 65%, shows the effect of the aqua regia treatment.

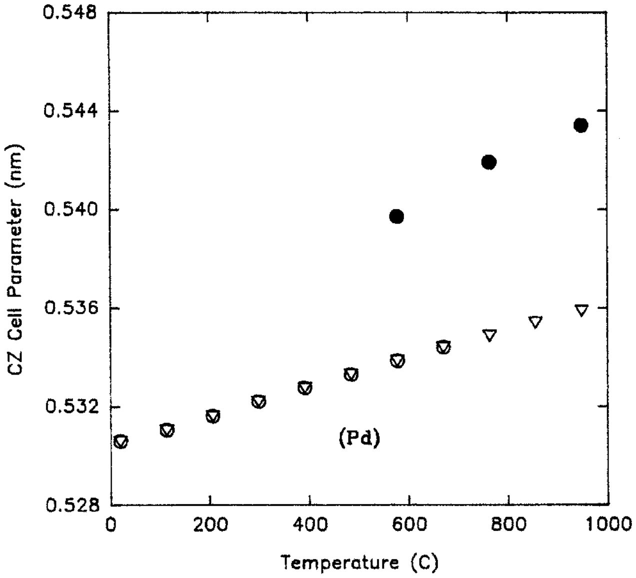

Figure 2. Temperature dependence of the ceria–zirconia (CZ) cell parameter obtained from a catalyst consisting of Pd on DSCI under air (○), 0.5 mol% O_2 (▽), and 1 mol% CO/H_2 (●).

purge with N_2, during which there was little change in cell parameter.) The cell parameter measured under air or 0.5 mol% O_2 would appear to be characteristic of fully-oxidized material, whereas the cell parameter measured under 1 mol% CO/H_2 should reflect that of partially-reduced material. Variation of the cell parameter of the oxidized material with temperature is just the coefficient of thermal expansion, found to be $11.3 \times 10^{-6}\,K^{-1}$, in good agreement with the literature value for ceria [4]. Based on these results, the value of *e* at a temperature of 1150 °C would be about 1.6%, but this is actually an overestimate since the 10 mol% H_2O present during redox aging should shift the reaction equilibrium toward a lower level of ceria–zirconia reduction. The addition of just a few percent H_2O, performed by bubbling the gas through liquid water in the present study, reduced the change in cell parameter to about 1% at 1040 °C. Materials with higher zirconia content were found to yield even smaller changes in cell parameter upon partial reduction. For example, measurements (without H_2O) performed on a Pd catalyst made with ceria–zirconia containing 80 wt% ZrO_2 revealed a change in effective cell parameter (taken as the cube root of cell volume since the structure is tetragonal and reduction mostly affected the degree of tetragonality) of about 0.4%.

In order to further probe the strain effect, the Pd and Rh (111) diffraction peaks were monitored *in situ*. The series of diffraction patterns shown in figure 3, for example, obtained from the (oxidized) Pd catalyst while heating in 0.5 mol% O_2, reveals that the strain starts to decrease at 300 °C and is fully removed before 700 °C, near the temperature at which PdO undergoes thermal decomposition, as indicated by the increase in diffraction peak intensity. This behavior is shown more clearly in figure 4, which also includes results from the Rh catalyst. Here, open circles and inverted triangles correspond to heating (but *not* cooling) under air and 0.5 mol% O_2, respectively, whereas filled circles correspond to cooling under N_2, starting from the highest temperature attained under 0.5 mol% O_2 (where both of the precious-metal oxides had decomposed). The coefficients of thermal expansion were deduced from the filled circles ($10.4 \times 10^{-6}\,K^{-1}$ for Pd and $8.1 \times 10^{-6}\,K^{-1}$ for Rh) and found to be in reasonable agreement with literature values [4]. The temperatures at which decomposition of the precious-metal oxides occurred under 0.5 mol% O_2, found to be slightly higher than where relaxation of strain was complete, also agree with estimates from the literature, 670 °C for Pd and 870 °C for Rh [7,8]. Similarly, extrapolation of the open-circle results (heating under air) to the filled-circle results in figure 4 yield temperatures that are close to the estimated temperatures of stability of the precious-metal oxides in air, 800 °C for Pd and 1070 °C for Rh [7,8].

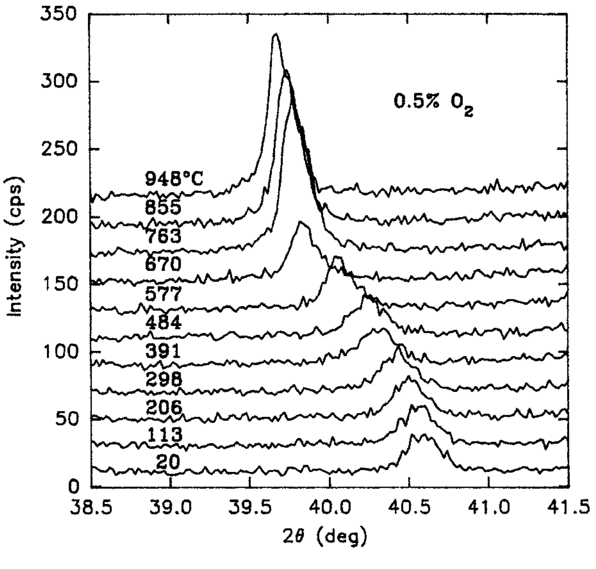

Figure 3. XRD patterns obtained from the aged Pd catalyst (4 wt% Pd on DSCI, "redox" aged at 1150 °C), following oxidation (700 °C in air for 2 h), while heating at the indicated temperatures under 0.5 mol% O_2.

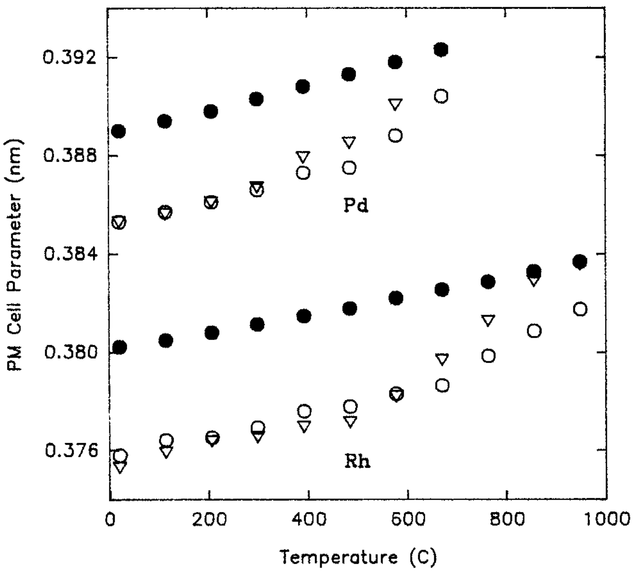

Figure 4. Temperature dependence of the precious-metal (PM) cell parameters obtained from the aged Pd and Rh catalysts (4 wt% PM on DSCI, "redox" aged at 1150 °C), following oxidation (700 °C in air for 2 h), while heating under air (○) or 0.5 mol% O_2 (▽). These data reflect the encapsulated metal particles. (Note that the strain persists to higher temperatures under air than under 0.5 mol% O_2.) The temperature dependence of the PM cell parameters obtained from these catalysts while cooling under N_2 (●), starting from the highest temperature attained under 0.5 mol% O_2, where the PM oxides have decomposed, reflect unstrained metal particles.

Finally, imposition of strain was briefly examined in the case of the Pd catalyst by first heating to at least 700 °C under 0.5 mol% O_2 to remove all strain and decompose any PdO, switching the gas to N_2, cooling to 484 °C, and then switching back to 0.5 mol% O_2. The series of diffraction patterns shown in figure 5 demonstrates how the imposition of strain (causing a shift in the position of part of the diffraction peak) and oxidation of Pd (causing a loss of intensity in the remaining part of the diffraction peak) parallel each other as a

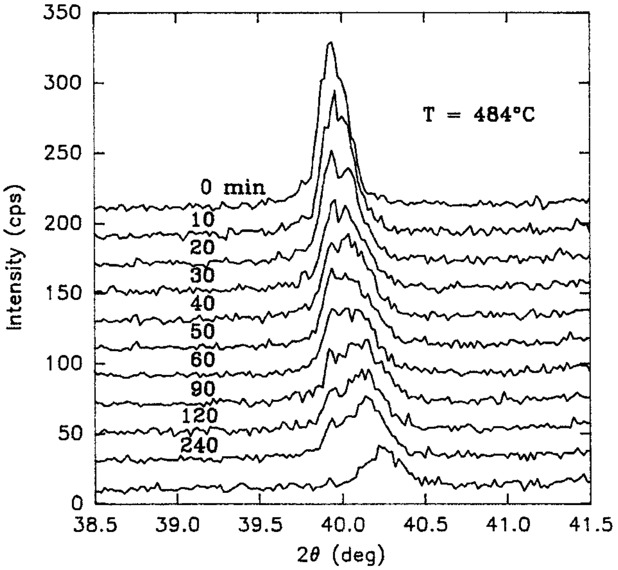

Figure 5. XRD patterns obtained from the aged Pd catalyst (4 wt% Pd on DSCI, "redox" aged at 1150 °C), following relaxation of the strain and decomposition of any PdO (performed by heating to at least 700 °C under 0.5 mol% O_2, switching the gas to N_2, and cooling to 484 °C), as a function of time after switching the gas from N_2 to 0.5 mol% O_2 at 484 °C. (The pattern at the bottom was taken from figure 3.)

function of time. (The pattern at the bottom of figure 5, which should correspond to a very long time at temperature, was taken from figure 3.)

4. Discussion

Clearly, the previously proposed model is incomplete since it does not explain how Pt particles may be encapsulated without exhibiting strain. And although the expected behavior of the ceria–zirconia was observed qualitatively by *in-situ* XRD, the supposed source of the applied stress is too small to account for the observed strain. On the other hand, the correlation between strain relaxation and precious-metal-oxide decomposition, found for both Pd and Rh at two O_2 partial pressures, implies that these two processes are connected. Further, the parallel development of strain and oxidation of Pd, depicted in figure 5, suggests precious-metal oxidation as a possible driving force behind the imposition of strain.

To follow up on this idea, consider an unstrained Pd-metal particle that completely fills a cavity of volume V within a matrix of fully oxidized ceria–zirconia. For simplicity, assume that the bulk modulus of Pd, B, is much less than that of ceria–zirconia. If this system is placed in an oxygen-containing atmosphere, its energy can be lowered through oxidation of Pd, since oxygen can readily be transported through the ceria–zirconia in order to react with the metal [9]. As a result, the particle should become larger, due to the fact that PdO has a lower density than Pd. This is not possible, however, since the particle is constrained by the ceria–zirconia. Instead, the change in volume due to oxidation, ΔV, would be imposed on the particle, creating a strain that raises the energy of the system by approximately $(B/2)(\Delta V)^2/V$. Overall, there is a minimum in the energy when

$$\Delta V/V = \Delta G \rho_m k/B$$

where ΔG is the change in free energy per mole of Pd for the reaction $2Pd + O_2 \rightarrow 2PdO$, ρ_m is the mole density of Pd, and k is a constant that relates the molar volume of Pd to the difference in molar volumes between PdO and Pd. Substituting numerical values ($\Delta G = -5$ kcal/mol-Pd, $\rho_m = 1.13 \times 10^5$ mol-Pd/m^3, $k = 1.46$ and $B = 183$ GPa), the equilibrium value of $\Delta V/V$ is estimated to be -0.019 under 0.5 mol% O_2 at 484 °C. Although this estimate is very crude (*e.g.*, the choice of ΔG assumes constant pressure), it roughly agrees with that observed, about 2% compressive by volume (or about 0.7% by linear dimension, as shown in figure 5). Accordingly, if the original Pd particle were a sphere, the strained particle would consist of a spherical Pd core surrounded by a PdO shell having a thickness equal to about 1.7% of the particle radius, or about 0.4 nm in the case of a 50 nm Pd particle (a typical size). This thickness is comparable with the unit cell dimensions of PdO, and the actual presence of such a PdO shell would be difficult to detect, even with transmission electron microscopy [2].

Suppose, however, that the initially unstrained Pd particle does *not* entirely fill the cavity of volume V within the matrix of fully oxidized ceria–zirconia. Specifically, if its volume is only somewhat greater than 59% of V, it can undergo almost complete conversion to PdO before it, too, becomes constrained by the ceria–zirconia. Since the bulk modulus of PdO is larger than that of Pd (by about 50%), the strain that develops in PdO should be less than in Pd metal. In fact, a compressive strain of about 1% (by volume) was observed in PdO by Raman spectroscopy in a recent study of a similarly aged Pd catalyst made with ZrO_2-rich ceria–zirconia [10].

In applying this approach to the estimation of the full strain observed in the aged catalysts at room temperature, particularly following the post-aging oxidation treatment (700 °C in air for 2 h), it is necessary to choose an average value for ΔG since the precise role of the oxidation kinetics in the development of the strain, as the catalyst cools, is unknown. Taking mean values, -9 kcal/mol-Pd and -16 kcal/mol-Rh [7,8], the compressive strain for the Rh catalyst should be somewhat larger than for the Pd catalyst, 3.5% *versus* 3.3%. For the Pt catalyst, however, since bulk oxidation of Pt is very difficult to effect under normal atmospheric conditions, the strain might well be absent. The very good quantitative agreement between these estimates and the previous observations, 3.6% for Rh, 3% for Pd, and

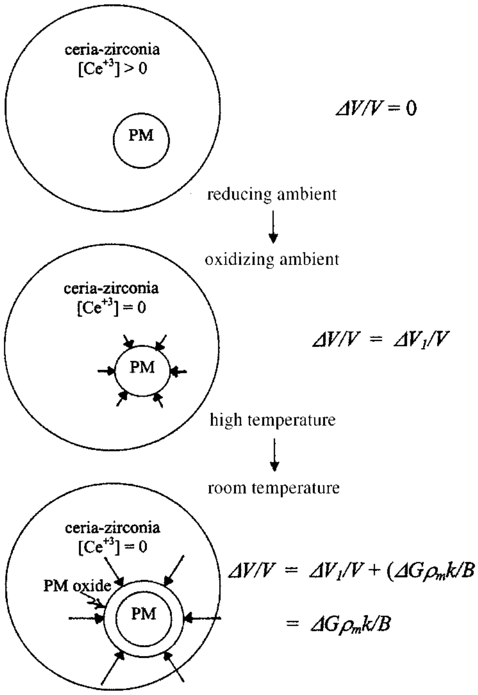

Figure 6. Schematic illustration of the relationship between the originally proposed model and the revised model of the strain effect. In the original model, the strain, $\Delta V_1/V$, arises from the compressive stress applied to the encapsulated precious-metal (PM) particle by the ceria–zirconia matrix when the ambient changes from reducing to oxidizing, causing all Ce^{+3} ions to become Ce^{+4} ions. This process occurs even at high temperature. In the revised model, an additional strain, $(\Delta G\rho_m k/B - \Delta V_1/V)$, arises from the growth of a PM-oxide layer at the interface between the encapsulated particle and the ceramic matrix, which is energetically favorable only when $|\Delta V_1/V < |\Delta G|\rho_m k/B$. (Note that the thickness of the PM-oxide layer, which is of order 1% of the PM-particle diameter, has been greatly exaggerated in this illustration.)

0% for Pt, is undoubtedly fortuitous, since the bulk modulus of ceria–zirconia is not much larger than that of the precious metals, as assumed, and part of the strain should thus be borne by the ceria–zirconia, as in the previous model [4], but the ordering of the metals should be reliable.

In general, the revised model of the strain effect allows for application of stress to the encapsulated precious-metal particle through both contraction of the ceria–zirconia upon its re-oxidation, as originally proposed, and partial oxidation of the precious-metal particle. These two processes are illustrated schematically in figure 6. If the magnitude of the strain due to contraction of the ceria–zirconia, $|\Delta V_1|/V$, is less than $|\Delta G|\rho_m k/B$, then additional strain develops through partial oxidation of the precious-metal particle such that the total strain is equal to $\Delta G\rho_m k/B$. If the contribution due to contraction of the ceria–zirconia exceeds $\Delta G\rho_m k/B$ in magnitude, then partial oxidation of the precious-metal particle would be totally inhibited. Both the observed behavior of the Pt catalyst and the measured effect of reduction on the cell parameter of the ceria–zirconia suggest that the second of these two possibilities does not occur.

5. Conclusions

A revised model for the strain in ceria–zirconia-encapsulated precious-metal particles, involving partial oxidation of the encapsulated precious-metal particle, has been proposed. This model naturally accounts for the absence of strain in encapsulated Pt particles, the lack of strain-dependence on ZrO_2 content, and the more recent observation of strained PdO. Whereas the dimensional change produced by the change in oxygen content of ceria–zirconia was central to the original model, the easy transport of oxygen through the ceria–zirconia lattice is essential to the revised model.

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References

[1] G.W. Graham, H.-W. Jen, W. Chun and R.W. McCabe, Catal. Lett. 44 (1997) 185.
[2] J.C. Jiang, X.Q. Pan, G.W. Graham, R.W. McCabe and J. Schwank, Catal. Lett. 53 (1998) 37.
[3] H.-W. Jen, G.W. Graham, W. Chun, R.W. McCabe, J.-P. Cuif, S. Deutsch and O. Touret, Catal. Today 50 (1999) 309.
[4] G.W. Graham, H.-W. Jen, W. Chun and R.W. McCabe, J. Catal. 182 (1999) 228.
[5] G.W. Graham, H.-W. Jen, R.W. McCabe, A.M. Straccia and L.P. Haack, Catal. Lett. 67 (2000) 99.
[6] A.R. Drews, in: *Advances in X-ray Analysis*, Proceedings of the Denver X-ray Conference, Vol. 44 (CD-ROM produced by the International Centre for Diffraction Data, 2001).
[7] I. Barin, O. Knacke and O. Kubaschewski, *Thermodynamic Properties of Inorganic Substances* (*Supplement*) (Springer, 1977).
[8] T.B. Reed, *Free Energy of Formation of Binary Compounds: An Atlas of Charts for High-Temperature Chemical Calculations* (MIT Press, 1971).
[9] M.Yu. Smirnov and G.W. Graham, Catal. Lett. 72 (2001) 39.
[10] G.W. Graham, A.E. O'Neill, D. Uy, W.H. Weber, H. Sun and X.Q. Pan, Catal. Lett. (in press).