Ultrapure Nanoparticles of Zinc Oxide: Synthesis and Characterization

Mary Margaret Ross

Faculty Advisor: Dr. J.Z. Larese, Department of Chemistry

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Abstract

In recent years, zinc oxide has become a popular object of chemical research. Not only are the electronic properties of this inorganic semiconductor interesting and unique, but it may also be useful as a catalyst. In both realms of investigation, the zinc oxide being used must be pure and have well-known surface properties. This study hopes to show that the zinc oxide made by the Kunnman-Larese method (Patent 6,179,897) admirably adheres to both of these standards, and is ideal for either electronic or catalytic studies. In order to assess the purity of this material, the synthesis method is examined, and the material resulting is analyzed by two separate techniques: Thermogravimetric analysis and Raman spectroscopy. The surface of the material is then characterized, first visually, via Transmission Electron Microscopy (TEM), then via investigation of certain integral thermodynamic properties. These thermodynamic properties, which show the uniformity and character of the zinc oxide surface, are found through methane adsorption isotherms. In the adsorption isotherms, three distinct layers of methane are formed, which shows that the surface of the zinc oxide is indeed very uniform. Both thermogravimetric analysis and Raman spectroscopy confirm the purity of the zinc oxide. TEM images show that the zinc oxide can come in several shapes, depending on the synthesis method: rods, plates, or tetrapods. Overall, this study is successful in showing the unique applicability of Kunnman-Larese zinc oxide to both electronic and catalytic investigations.

Introduction

The recent popularity of zinc oxide as a subject of chemical research is attributable to the several fields that have taken an interest in it. In one field, catalysis, the high affinity of zinc oxide for hydrogen is being exploited.[1,2,3] For example, when the surface of zinc oxide is doped with nanoparticles of gold, the affinity of the gold for carbon dioxide, combined with the affinity of zinc oxide for hydrogen, results in the catalysis of the conversion of carbon dioxide into methane.[4] The other primary field of research utilizing zinc oxide is investigating the optical and electronic properties of the material.[5] Although it has long been known that zinc oxide has unique electronic properties, the difficulty of finding pure ZnO, as well as the difficulty of controlling the electronic characteristics, caused this material to be disregarded for many years. Recently, however, improved doping and synthetic methods have paved the way for more intensive study of the room-temperature lasing and semiconductor characteristics of ZnO.

In both catalysis and optoelectronic research, however, the purity of the material is essential. In catalysis, the studied reaction will take place at the surface of the substrate, so materials with extremely uniform, well-characterized surfaces are required. In optoelectronics, too, certain minimum standards of crystallinity and surface uniformity must be met. The unique Kunnmann-Larese synthesis method creates very high purity metal oxides,[6] and the following study investigates the suitability of the materials produced by this synthetic method for optoelectronic and catalytic studies.

Purity Assessment

The first requirement is that the zinc oxide be extremely pure, and the major source of impurities is the synthesis method. In the Kunnmann-Larese method of metal

oxide synthesis, pieces of 99.999% pure zinc are placed in a graphite crucible under graphite chunks. The whole is then inductively heated by the Lepel instrument seen in

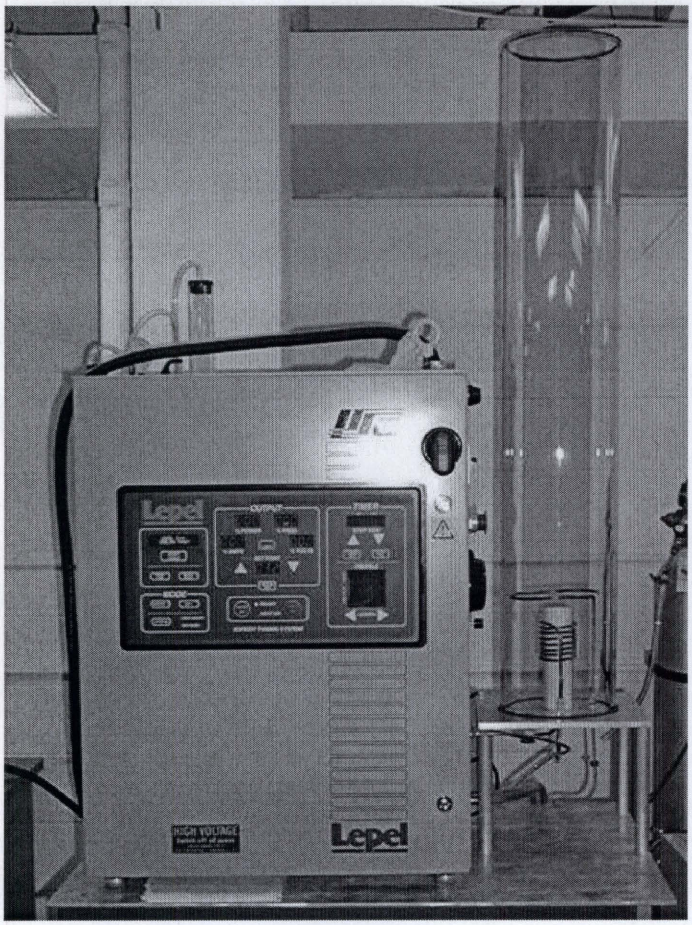
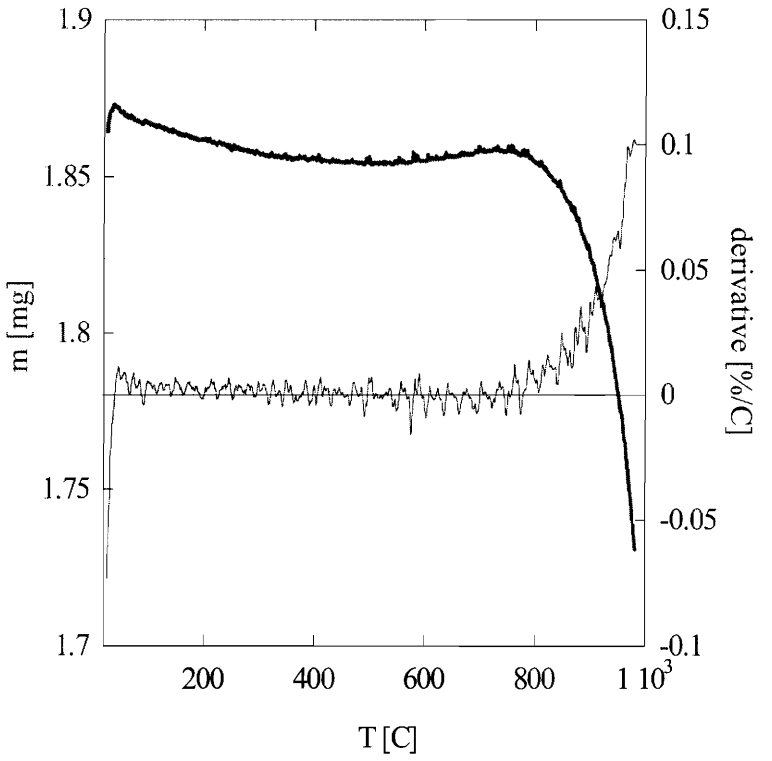


Figure 1. The right side of figure 1 shows the synthesis setup—the copper coils are wrapped around an alumina tube which contains the crucible. Above the alumina is another copper tube, pierced at intervals to allow oxygen to flow through it. The whole is encased in a large quartz chimney to preserve the integrity of the material. As the zinc is heated, it reacts with the oxygen vapor, forming very small, very pure particles of zinc oxide. These particles are carried up and deposited on the chimney by a flow of argon gas. This gas also maintains an inert atmosphere in the reaction vessel, and prevents extraneous atmospheric impurities to enter the reaction.

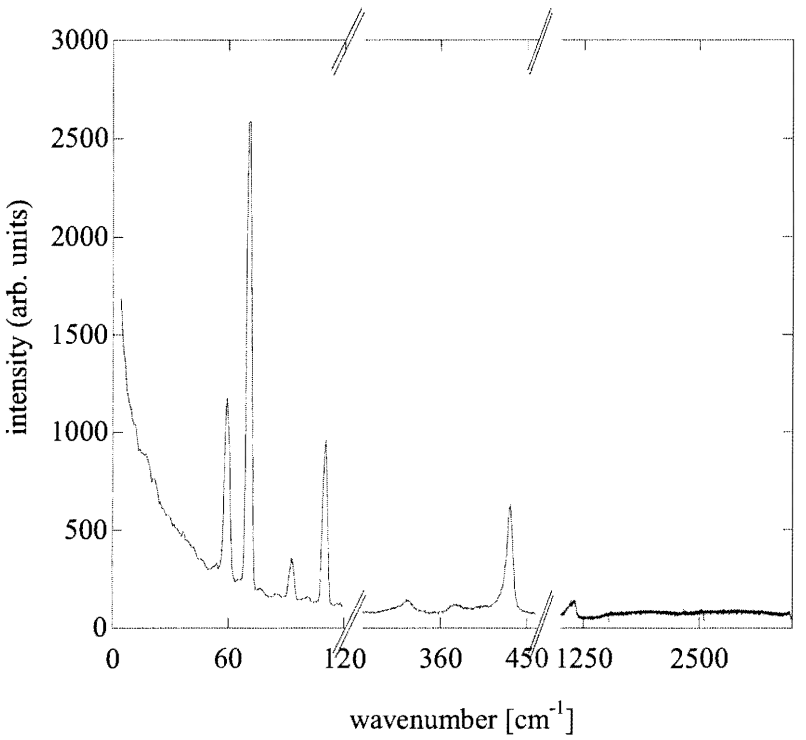
In order to confirm the purity of the synthesized zinc oxide, two separate analytical methods were used. The first of these was Thermogravimetric Analysis, also known as TGA. This method involves heating a sample of material in a mobile inert atmosphere and observing the change in mass. When the mass of the sample changes, some part of the sample has been given off as a gas. In the case of zinc oxide, the pure

material decomposes around 800 degrees Celsius. Any major impurities would cause a significant change in mass as they were eliminated. As can be seen in figure 2, no such major impurities existed. Sample mass did not change significantly before 800 degrees Celsius, and any minor mass changes were attributable to adsorbed species such as water.



The second analytical technique used to determine the purity of the zinc oxide was Raman spectroscopy. In Raman spectroscopy, a laser is used to excite a molecule's electrons, and the resulting photons are collected and studied. Interaction with a molecule changes the energy of the photons in ways characteristic of the molecule, specifically its bonds. Therefore, certain peaks in a Raman spectrum are associated with various bonds; for example, a peak at 3300 cm-1 is associated with an O-H bond. The study of the zinc oxide was conducted on a Dilor Raman Spectrometer using a silicon

diode laser. Figure 3 shows the resulting Raman spectrum.

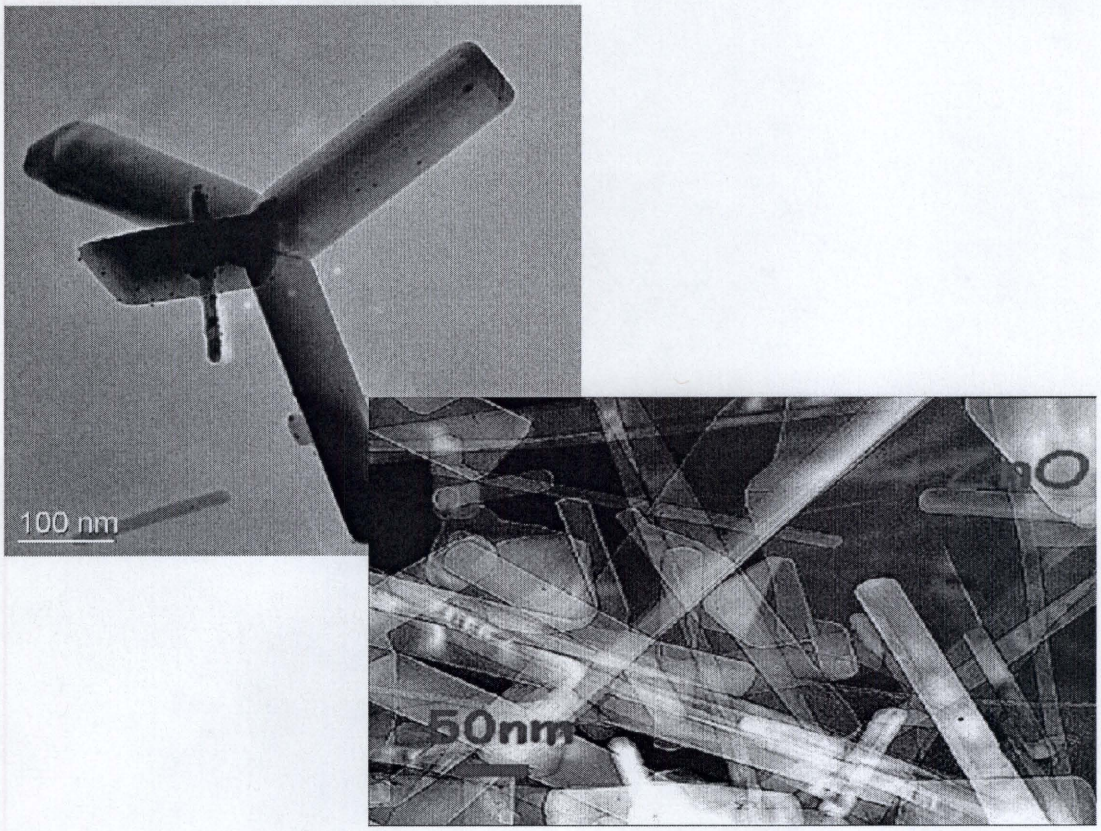


The peaks at 60, 70, and 110 cm-1 are actually caused by the silicon laser, but the smaller peak around 95 cm-1 is caused by the ZnO, as are the peaks around 360 cm-1. What is interesting to note is that at the far right-hand side of the chart, around 3300 cm, there is no evidence of a peak. One of the primary contaminants, both surface and internal, of zinc oxide is hydrogen, and water is another surface contaminant.[7,8] Were there a significant amount of hydrogen or water contamination, the Raman spectrum would have shown the resulting O-H interaction. That it does not further confirms the purity of the zinc oxide synthesized by the Kunnmann-Larese method.

Surface Characterization

The first and most straightforward method by which the zinc oxide was characterized was via Transmission Electron Microscopy (TEM). In this method of analysis, a beam of electrons interacts with the surface of the sample. The manner in

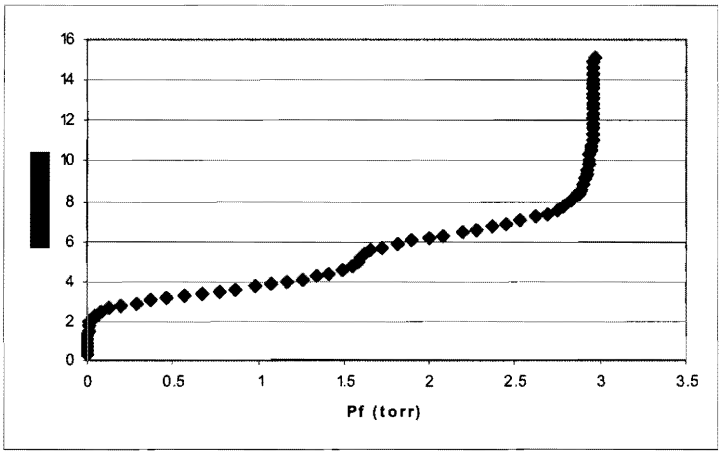
which the electrons are scattered from the surface can be related to the surface's composition and texture, and a two-dimensional image can be formed, as in figure 4 below.



Note that the zinc oxide in question can form tetrapods, as in the upper-left-hand view, or rods and plates, as in the lower-right-hand picture. The different morphologies are due to differing synthesis methods; for example, forming zinc oxide from the decomposition of zinc carbonate gives plates, while the tetrapods are formed by the Kunnmann-Larese synthesis method. Note also that the zinc oxide is crystalline—the edges and faces of the crystal can be seen quite clearly in the tetrapod.

The second, and more important, method by which the zinc oxide was characterized was via adsorption isotherm. This analytical method involves studying the interaction of a gas with a substrate surface.[9,10] Although the ideal model of gases

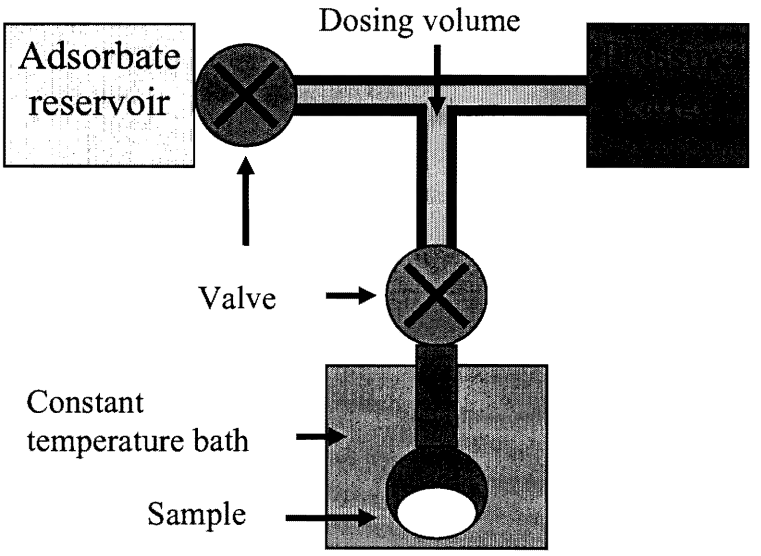
involved gas molecules that do not interact with one another or their surroundings except in perfectly elastic collisions, real gases do have interactions with one another and their surroundings. In particular, gases accumulate on surfaces. When the amount of gas that is interacting with the surface is increased, the gas organizes itself so that as many molecules as possible can fit on the surface. If the surface is particularly uniform, several layers of gas can be formed. This phenomenon, known as adsorption, can be observed by introducing known amounts of gas into a cooled system containing the substance whose surface is being studied, zinc oxide in this case. Methane is a commonly-used gas, for its adsorption properties have been studied by many people. By noting the pressure change, the amount of methane adsorbed on the surface can be calculated. This calculation leads to several others; for example, the surface area of the zinc oxide can be found using the amount of space that each gas molecule takes up.



Sample adsorption isotherms are shown in figures 5 and 6. Figure 5 shows the raw isotherm data, wherein final pressure of the system is plotted against pressure of the adsorbed gas. Figure 8 shows isotherms after data manipulation. The new axes are the moles of gas adsorbed and the reduced pressure, P_f/P_{f0}. An alternative to the use of reduced pressure is the chemical potential, $\mu-\mu_0$. Both units are characteristic of the sample, not the experiment, so several experimental runs can be compared in one figure. In figures 5 and

6, note the places where "steps" occur in the function. These "steps" correspond to the layers of gas adsorbed onto the surface. For example, in figure 5, around 0.01 torr, the isotherm reaches the top of a "step." In physical terms, this is the point at which the first layer of gas is completed. Any additional gas adsorbed goes to form the second layer, which is completed at the "top" of the second "step."

In order to make the measurements associated with an adsorption isotherm, the zinc oxide first had to be pretreated under vacuum at 300 degrees Celsius. This temperature was decided by the TGA. At 300 degrees, the mass in the TGA had reached its lowest point, meaning that all of the atmospheric adsorbed species had dissociated, leaving the surface clean. After pretreating, the sample was transferred under an inert atmosphere to a copper sample cell, which was attached to the isotherm instrument schematically drawn in figure 7. The "constant temperature bath" in this case was actually controlled electronically, as was the dosing of the adsorbate gas. Several methane/ZnO isotherms were taken at various temperatures.



In figure 8, six isotherms taken below the triple point of methane can be observed. The reduced pressure, p/p0, allows these isotherms, which would have differing saturated vapor pressures, to be directly compared. Figure 8 clearly shows the three layer steps for each isotherm., although the formation of second and third layers take place at differing p/p0 depending on the temperature at which the isotherm was taken. Surface area calculations, using the BET equation, found the surface area of the zinc oxide sample to be approximately 4.4 m^2/g.

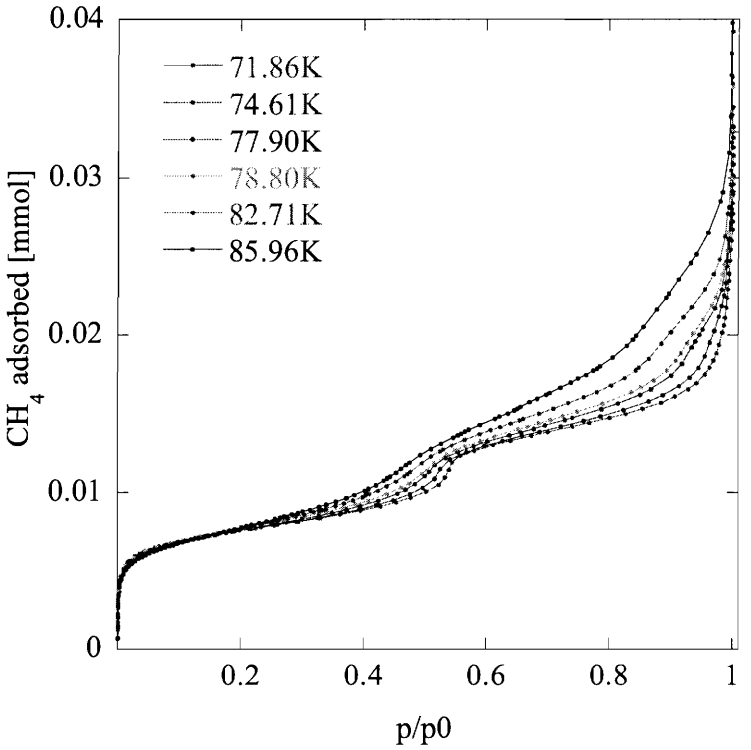


Figure 8: Six CH_4/ZnO Isotherms at Various Temperatures.

Besides surface area, other thermodynamic quantities can be calculated from the isotherm data. From these calculations, one can learn details about the adsorbate-adsorbate and adsorbate-substrate interactions. For each isotherm the derivative of

methane coverage with respect to pressure for example can be used to record the pressure at which each adsorbate layer starts to form. The maxima in the derivative that result from each layering step are used as characteristic points; they give information on the layer formation as function of temperature when a set of isotherms over a temperature range is evaluated. Using the Antoine equation (1), the logarithm to base 10 of the pressure for each adsorption step can be plotted as function of inverse temperature.

$$\log_{10}(p^{(n)}[Torr]) = B^{(n)} + \frac{A^{(n)}}{T} \qquad (1)$$

A linear fit can be made to the resulting plot and the parameters $A^{(n)}$ and $B^{(n)}$ can be determined. These parameters can be used to gain understanding about adsorbate layering as function of temperature.[11] For multilayer adsorption one expects that the layers that are farther from the surface interact less, while closer layers are affected more by the proximity of the surface. This results in the parameter $A^{(n)}$ in equation (1) to become progressively smaller as the number of adsorbed layers increases.

Figure 9 shows the plot from which the Antoine parameters for each adsorbed methane layer were determined.

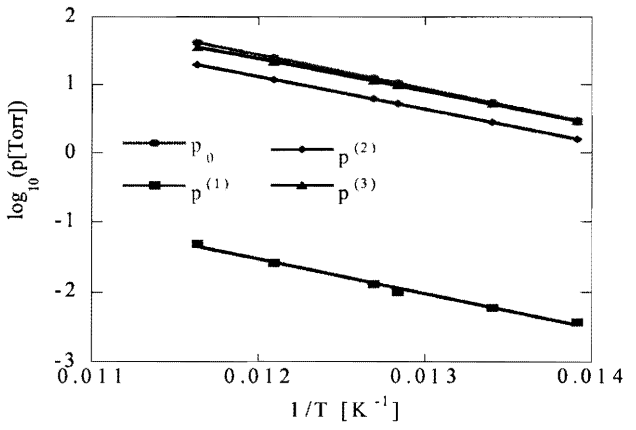


Figure 9: Antoine Plot for the Three Isotherm Layers and the Bulk Gas.

One interesting aspect of figure 9 is that the bulk methane (p_0) and the third isotherm layer (p^3) seem to intersect near the temperature range studied. Using the various fitted lines, the point of intersection was calculated to be about 70 K. Below 70 K, only two distinct layers of methane will form before bulk properties are achieved. Extending these calculations to the first and second layers results in intersections with the bulk at approximately 4.9 and 42.9 K, respectively, but the vapor pressure of methane is too low at these temperatures for experimental verification of these values. This is unfortunate, for the values suggest that methane does not wet zinc oxide at near-absolute-zero temperatures. Table 1, below, lists the Antoine parameters and heats of adsorption found for each layer and the bulk.

Table 1: Values Calculated from Isotherm Data.

	1st layer	2nd layer	3rd layer	∞
$A^{(n)}$	490.53±22.4	477.58±1.9	477.31±2.8	506.21±1
$B^{(n)}$	4.35±0.28	6.85±0.02	7.11±0.04	7.52±0.01
Q_{st} [kJ/mol]	9.4±0.4	9.15±0.04	9.14±0.05	9.7±0.02

Another interesting quantity is the two-dimensional compressibility of the adsorbate film, K_{2D}, which can be calculated using equation (2):

$$K_{2D} = \frac{Ap}{N_A k_B T N^2}\left(\frac{dN}{dp}\right) \qquad (2)$$

Here A is the surface area of the sample, N_A Avogadro's number, k_B the Boltzmann constant, p the pressure, N the number of moles adsorbed and T the temperature. K_{2D} can

give information on the phases of the adsorbate layers and possible phase transitions. Sharp (broad) peaks are in general associated with solid (liquid) layers. The results of the K_{2D} calculations can be seen in figure 10.

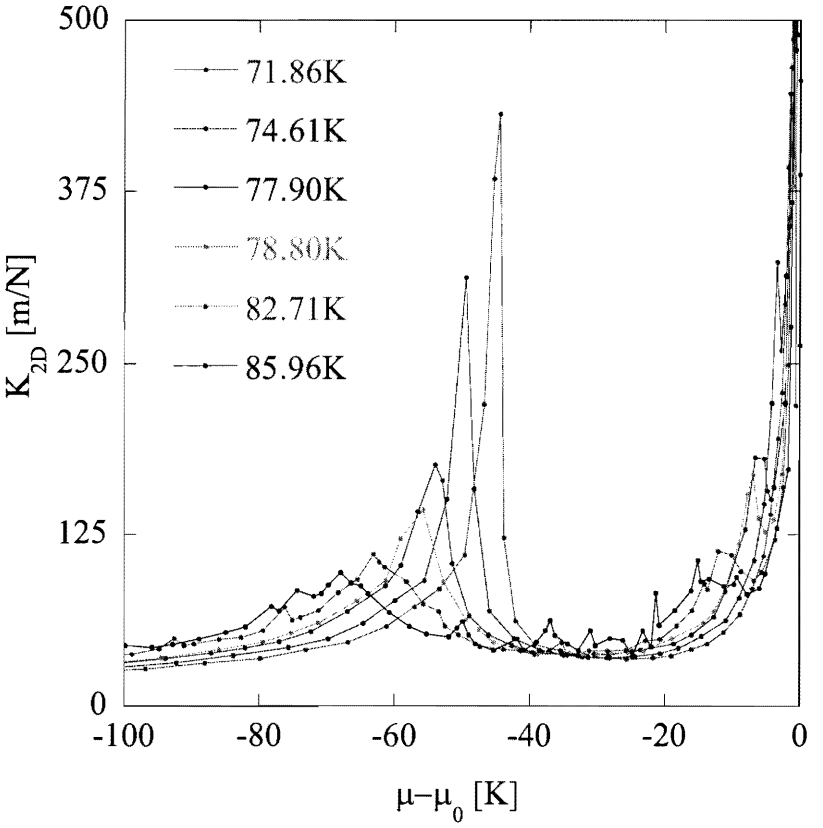


Figure 10: Two-Dimensional Compressibility of the Second Isotherm Layer.

Figure 10 clearly shows that the second isotherm layer undergoes a phase transition within the temperature range studied. The isotherm taken at the lowest temperature has a very sharp peak, associated with the solid phase, while the 86 K isotherm has a very broad peak, associated with the liquid phase. Unfortunately, the number of isotherms in this study was too small to find the exact temperature at which this phase transition occurs. The monolayer K_{2D} plot shows a similar transition.

Finally, the isosteric heat of adsorption, Q_{st}, can be calculated using the following expression:

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T}\right)\Big|_{\theta} \qquad (3)$$

In equation (3) R is the ideal gas constant, and T is the temperature, which is multiplied by the partial derivative of ln p with respect to T at constant coverage, θ. The partial derivative can be approximated with the fraction of the respective differences for sufficiently small temperature interval. Thus, from two isotherms close in temperature one can calculate the isosteric heat of adsorption as function of coverage. Figure 11 below shows the isosteric heat of adsorption, or Q_{st}, calculated from the isotherm data.

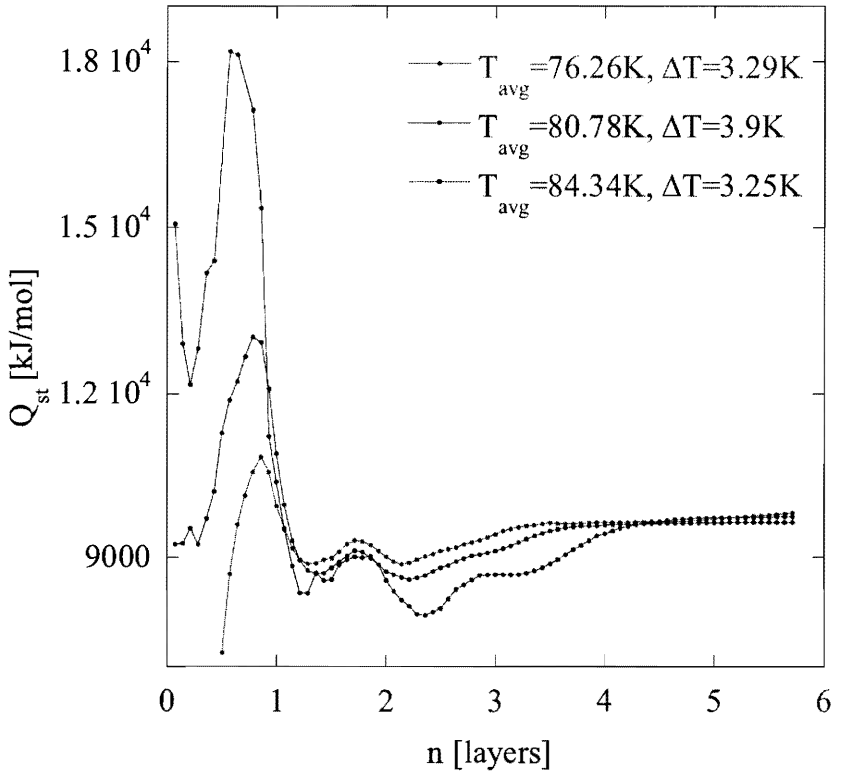


Figure 11: Qst of Methane on ZnO.

In general, it is best to perform Qst calculations on two isotherms taken at close temperatures ($\Delta T<2$), but as that was not possible for this data, ΔT was either 3 or 4 for each set of Qst calculations. It is for this reason that the differences in the Qst between datasets is not easily interpreted—any interpretation might be skewed by the error in value caused by a large ΔT. However, it is clear that the Qst peaks around each layer completion point, and eventually levels out to around 9.6 kJ/mol. This last number is the heat of adsorption at high methane coverage.

Conclusions

From the adsorption isotherms, it is clear that methane forms three distinct layers on the surface of zinc oxide. A phase transition of the adsorbed methane was found within the temperature range studied, as indicated by the K_{2D}, and the isosteric heat of adsorption was found to be 9.6 kJ/mol for large-degree methane coverage. The TEM indicated a high crystallinity of this zinc oxide, while the TGA indicated that there were no major contaminants, only a few surface-adsorbed species. Raman, too, indicated that the zinc oxide was without hydrogen or water contamination. In summary, then, the zinc oxide synthesized by the Kunnmann-Larese method seems to be highly suited to optoelectronic and catalytic research.

Acknowledgments

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References

1. Chang, C.C., L. T. Dixon, and R.J. Kokes. Journal of Physical Chemistry 77 (22): 2634-2640.

2. Conner, W.C. and R.J. Kokes. Journal of Catalysis 36 (2): 199-210.

3. Kokes, R.J. et al. Journal of the American Chemical Society 94 (13): 4429.

4. Liyan Ma, Tam Tran, Mark S. Wainwright, Topics in Catalysis Volume 22, Issue 3 - 4, 287.

5. Özgür, Ö. et. al.; J. Appl. Phys. 98, 041310, 2005.

6. Kunnmann, W.; Larese, J. Z. U.S. Patent 6,179,897, 2001.

7. Meyer, B. et al. Angewandte Chemie-International Edition 43 (48): 6642-6645.

8. Chang, C.C., R.J. Kokes. Journal of the American Chemical Society 93 (25): 7107.

9. Marinelli, F., Y. Grillet, and R.J.M. Pellenq. Molecular Physics 97 (11): 1207-1224.

10. Freitag, A. and J.Z. Larese. Physical Review B 62 (12): 8360-8365.

11. Larher, Y.; Angerand, F.; Europhys. Lett, 1988, 7, 447