Water-Assisted Tetragonal-to-Monoclinic Phase **Transformation of ZrO₂ at Low Temperatures**

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Received March 7, 2000. Revised Manuscript Received June 10, 2000

In-situ Raman spectroscopy has been used to characterize the transformation of amorphous zirconium oxyhydroxide to tetragonal ZrO_2 and then to monoclinic ZrO_2 in both the absence and presence of water vapor. In the absence of H₂O vapor, t-ZrO₂ forms when zirconium oxyhydroxide is treated in air above 673 K and the tetragonal-to-monoclinic transformation occurs at temperatures above 950 K. Treatment at progressively higher temperatures is accompanied by loss of surface area. The tetragonal-to-monoclinic transformation occurs when the size of the zirconia particles is equal to or greater than a critical size determined from an analysis of the thermodynamic stability of small particles of t- and m-ZrO₂. Exposure of t-ZrO₂ to 3 kPa of H₂O or immersion in liquid water at 298 K results in its extensive $(\sim 80\%)$ transformation to m-ZrO₂ without a loss in surface area. This observation is attributed to a decrease in the difference between the surface free energy of m-ZrO₂ and that of t-ZrO₂ caused by the adsorption of H₂O. Treatment in water vapor at 623 K induces the tetragonal-to-monoclinic transformation as well, but it is accompanied by a significant decrease in surface area. Only 80% of the t-ZrO₂ is transformed to m-ZrO₂ at 298 K because of the apparent presence of some crystallites with lattice strain, which increases the temperature for the tetragonal-to-monoclinic phase transformation. The results of this study demonstrate that m- ZrO_2 with high surface areas can be prepared by exposing t- ZrO_2 to water vapor at room temperature.

Introduction

Zirconium oxide has attracted considerable attention recently as both a catalyst and a catalyst support because of its high thermal stability and the amphoteric character of its surface hydroxyl groups. Zirconia catalyzes the hydrogenation of olefins, $^{1-4}$ the isomerization of olefins⁵ and epoxides, 6,7 and the dehydration of alcohols.^{8,9} When zirconia is used as a support, various reactions such as Fischer–Tropsch synthesis,^{10,11} methanol synthesis,^{12–15} and hydrodesulfurization¹⁶ have been

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reported to proceed with higher rates and selectivity than with other supports.

The catalytic applications of zirconia mentioned above have stimulated research aimed at understanding the factors controlling the structural and textural properties of ZrO₂, such as the distribution of ZrO₂ among amorphous, tetragonal, and monoclinic phases, the BET surface area, and the pore size distribution.¹⁷⁻³¹ Aqueous precipitation or sol-gel methods are often used to

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10.1021/cm000212v CCC: \$19.00 © 2000 American Chemical Society Published on Web 08/04/2000

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produce zirconia powders (see ref 31 and references therein). The initial product is an amorphous zirconium oxyhydroxide or a mixture of amorphous and tetragonal ZrO_2 (a- ZrO_2 and t- ZrO_2 , respectively). Calcination of the initial product at progressively higher temperatures leads to the conversion of all of the $a-ZrO_2$ to $t-ZrO_2$, and at higher temperatures to the conversion of t-ZrO₂ to monoclinic ZrO₂ (m-ZrO₂). Since treatments also lead to a decrease in surface area, m-ZrO₂ is usually obtained with much lower surface area than t-ZrO₂. The attainment of high surface area m-ZrO₂ requires methods for inducing the tetragonal to monoclinic transformation at low temperature. The possibility of using water vapor to achieve this goal has been reported in the literature.^{32,33} At temperatures above 673 K, the presence of water vapor was found to promote the tetragonal-tomonoclinic phase transformation of ZrO₂, but with concurrent growth in the crystallite size of both phases. The present work was undertaken in order to determine whether the tetragonal-to-monoclinic transformation can be carried out near room temperatures in order to minimize particle growth.

Experimental Section

Zirconium oxyhydroxide, $ZrO_x(OH)_{4-2x}$ was prepared by the precipitation of an aqueous solution of $ZrOCl_2$ at a constant pH of 10.²⁹ The precipitate was washed with deionized water until the rinse solution was free of chloride ions, and the filter cake was then dried overnight at 393 K. The N₂ BET surface area of the powders was 412 m²/g.

Raman spectra were recorded using a HoloLab 5000 Raman spectrometer (Kaiser Optical) equipped with a Nd:YAG laser that is frequency doubled to 532 nm. The laser was operated at a power level of 45 mW. The resolution of the spectrometer is 5 cm⁻¹. The samples were loaded as powders into a stationary cell that could be heated to 1023 K.³⁴ The sample could then be treated in the Raman cell with 20% O₂/He or with a mixture of 20% O₂/He saturated with H₂O vapor at 298 K.

Powder X-ray diffraction (XRD) patterns were recorded using a Siemens D5000 diffractometer. Cu (K α) radiation was used together with a scanning rate of 0.02 deg s⁻¹. Samples were prepared by spreading a thin layer of powder in Vaseline on a glass plate holder. For a limited number of samples, XRD patterns were also recorded without exposure of the sample to room air. In these cases, the pretreated samples were transferred into a glovebox where they were mixed with a small amount of Vaseline and then spread onto the sample holder. Preparation in this manner ensured that water vapor in the air would not affect the smaples. The volume fraction of m-ZrO₂ was determined via the method described by Toraya et al.³⁵

Thermal analysis was carried out with an SDT 2960 Simultaneous DSC-TGA (TA Instruments). Weight loss and heat flows were measured while samples (~ 0.02 g) were heated from 293 to 1273 K at 10 K/min in flowing O₂. These measurements were used to determine the temperature at which the amorphous-to-tetragonal and the tetragonal-to-monoclinic phase transitions occurred and the amount of heat released during each transformation.

Results

Figure 1 shows Raman spectra taken as a function of time as amorphous zirconium oxyhdroxide was heated



Figure 1. Raman spectra for amorphous $ZrO_x(OH)_{2-2x}$ recorded at 623 K in 20% O₂/He. Spectra were recorded at intervals of 10 min. Temperature was increased from 298 K at 10 K/min.

in flowing 20% O₂/He at 623 K. Spectra acquired for heating times of <50 min exhibited very strong fluorescence and no discernible Raman bands, and hence, they are not shown. The absence of sharp bands in the spectra obtained for heating times between 50 and 200 min indicates that the sample is amorphous. At longer heating times, well-defined bands appear at 146, 259, 307, and 461 cm⁻¹; after 300 min, additional bands become apparent at 595 and 632 cm⁻¹. All these features are indicative of the slow transformation of amorphous zirconium oxyhydroxide into crystalline tetragonal zirconia.³⁶ Spectra similar to those presented in Figure 1 were recorded at 673 K (not shown). In this case, the crystallization of tetragonal zirconia occurred much more rapidly and Raman features for this phase were clearly evident even after heating for only 10 min. Slowly increasing the temperature from 673 to 823 K over several hours produced no new bands, indicating that the tetragonal zirconia formed at 673 K is stable up to 823 K.

When the calcination temperature was raised to 873 K, new Raman features were observed at 174 and 182 cm⁻¹ after 1 h (see Figure 2). These bands became stronger as the temperature was raised to 923 K, and an additional band appeared at 364 cm⁻¹. When the temperature was increased to 973 K after holding at 923 K for 1 h, a new band appeared at 210 cm^{-1} and the band at 256 cm⁻¹ decreased in intensity and shifted to 252 cm⁻¹. A new band also appeared at 325 cm⁻¹, and it became more intense with time. When the temperature was increased to 1023 K, additional bands appeared at 522 and 548 cm⁻¹ and the pair of bands originally at 593 and 627 cm⁻¹ coalesced into a single band at 613 cm^{-1} . The Raman features at 174, 182, 210, 325, 364, 464, 522, 548, and 613 cm⁻¹ in Figure 2 can all be assigned to monoclinic zirconia.33

The differential scanning calorimeter data showed a narrow peak at 714 K associated with the amorphous-to-tetragonal transformation of ZrO_2 and a broad peak occurring between 923 and 1173 K associated with the

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Figure 2. Raman spectra for amorphous $ZrO_x(OH)_{4-2x}$ recorded at 873, 923, and 1023 K. Spectra were recorded at intervals of 10 min. The sample was held at 923, 973, and 1023 K for 1, 0.5, and 1 h, respectively.



Figure 3. BET surface area of ZrO_2 calcined at different temperatures: (a) experimental data; (b) value of SA_c calculated from eq 2.

tetragonal-to-monoclinic transformation.³⁷ The enthalpy for the amorphous-to-tetragonal transformation was estimated to be ~ -13 kJ/mol, whereas the enthalpy for the tetragonal-to-monoclinic transformation was estimated to be ~ -6 kJ/mol.

The progressive transformation of zirconia from its tetragonal to its monoclinic phase shown in Figure 2 is accompanied by a loss in BET surface area and by a corresponding increase in the average crystallite size. These latter trends are illustrated in Figure 3. The surface area decreased from 412 to 15 m²/g over the temperature range 400–1023 K, whereas the particle size, calculated assuming quasispherical crystallites, increased from 2.5 to 68 nm. The temperature ranges over which ZrO_2 was detected by Raman spectroscopy to exist in the amorphous, tetragonal, and monoclinic phases are indicated at the top of Figure 3.

The effects of water vapor on the transformation of tetragonal to monoclinic zirconia at 298 K are illustrated in Figure 4. In this case, amorphous zirconium oxyhy-



Figure 4. Raman spectra recorded at 298 K for amorphous $ZrO_x(OH)_{4-2x}$ after it was exposed to a 3.0 kPa H₂O vapor at 298 K. The sample was calcined at 723 K for 2 h, and Raman spectra were recorded at intervals of 1 min. The first spectrum was recorded before the H₂O vapor was introduced into the gas stream.



Figure 5. Raman spectra H_2O for amorphous $ZrO_x(OH)_{4-2x}$ recorded at 623 K in 20% O_2 /He containing 3.0 kPa of H_2O . The temperature was increased from 298 K at 10 K/min.

droxide was treated at 723 K in 20% O_2 /He for 2 h in order to transform it fully to t-ZrO₂. The sample was then cooled to 298 K and exposed to 3 kPa of H₂O in 20% O₂/He. The spectra shown in Figure 4 indicate that bands characteristic of m-ZrO₂ appeared almost immediately after exposure of crystalline t-ZrO₂ to water vapor at room temperature.

Figure 5 shows Raman spectra taken as the amorphous zirconium oxyhydroxide was treated at 623 K in a stream of 20% O₂/He containing 3 kPa H₂O. Bands at 146, 262, 365, 451, 595, and 632 cm⁻¹, characteristic of t-ZrO₂, appeared almost immediately, followed by a slow transformation from tetragonal to m-ZrO₂ over about 300 min. These results suggest that the presence of water vapor increases the rate of the transformation of amorphous zirconium oxyhydroxide to crystalline t-ZrO₂, as well as that of the transformation of tetragonal to monoclinic ZrO2. Additional evidence of the effect of water vapor on the transformation of tetragonal to monoclinic ZrO₂ is presented in Figure 6. Comparison of spectra a and b in Figure 6 shows that exposure of t-ZrO₂ to ambient air for \sim 10 s is sufficient to start the tetragonal-to-monoclinic phase transition. The bands for

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Table 1. BET Surface Area, Pore Volume, and Phase Composition for ZrO₂ Pretreated at Different Conditions

					particle size (nm)		
pretreatment conditions	SA (m ² /g)	$V_{\mathrm{p}}{}^{a}(\mathrm{cm}{}^{3}\!/\mathrm{g})$	$R_{\mathrm{p}}{}^{b}$ (Å)	monoclinic (vol %)	t-ZrO ₂	m-ZrO ₂	calc
393 K	412						
623 K ^c							
1. 20% O ₂ 16 h	204	0.325	31	0	6.4		5.0
2. 20% O ₂ 16 h, then 3 kPa H ₂ O at 298 K ^{d}	207	0.320	31	69	6.4	5.6	5.0
3. 20% O ₂ 16 h, then liquid H ₂ O at 298 K ^{e}	205	0.315	30	72	6.4	5.6	5.0
4. 20% O ₂ + 3.0 kPa H ₂ O 16 h	128	0.357	53	79	6.6	7.6	8.0
723 K ^c							
1. 20% O ₂ 2 h	167	0.288	31	0	6.3		6.1
2. 20% O ₂ 2 h, then 3 kPa H ₂ O at 298 K ^d	168	0.280	31	74	6.3	6.2	6.1
3. 20% O ₂ 2 h, then liquid H ₂ O at 298 K ^{e}	175	0.297	31	78	6.3	6.2	5.8
4. 20% O_2 + 3.0 kPa \hat{H}_2O 2 h	68	0.302	58	81	8.6	10.8	15.0

^{*a*} Specific pore volume calculated from N₂ adsorption at $P/P_0 = 0.95$. ^{*b*} Pore radius calculated from N₂ BET adsorption data. ^{*c*} Temperature was increased in dry or wet 20% O₂/He containing 3.0 kPa H₂O vapor from 298 K to the desired temperature at 10 K/min. ^{*d*} The sample was exposed to 3.0 kPa of H₂O vapor at 298 K for 100 min. ^{*e*} Liquid deionized H₂O was introduced after the sample was cooled to 298 K, and the sample was kept wet overnight before it was pretreated at 623 K for 1 h with flowing dry 20% O₂/He.



Figure 6. Raman spectra for amorphous $ZrO_x(OH)_{4-2x}$ recorded at 298 K: (a) after it was calcined at 723 K for 1 h; (b) after it was subsequently exposed to room air for 10 s; (c) after the sample was exposed to a 3.0 kPa H₂O vapor for 100 min; (d) after it was heated at 623 K in 20% O₂/He + 3.0 kPa H₂O for 16 h.

m-ZrO₂ are much more intense after the sample is exposed to 3 kPa of H_2O in 20% O_2 /He for 100 min at 298 K (spectrum c). Heating an amorphous zirconium oxyhydroxide at 623 K in 20% O_2 /He containing 3 kPa H_2O for 16 h led to a sample with Raman features (spectrum d in Figure 6) similar to those observed following H_2O exposure at 298 K.

The effects of various pretreatment conditions on the zirconia phase and on its BET surface area and average particle size are shown in Table 1. Treatment of amorphous zirconium oxyhydroxide in 20% O₂ at 623 K for 16 h led to pure t-ZrO₂ with a surface area of 204 m²/g and an average crystallite size of 6.4 nm. Exposure of this sample to 3 kPa of H₂O at 298 K for 100 min does not change the particle size or BET surface area of the crystalline ZrO₂ but changes its structure to 69% m-ZrO₂. Immersion of t-ZrO₂ treated at 623 K in liquid H₂O increases the fraction of m-ZrO₂ slightly (72%),



Figure 7. XRD patterns taken after (a) calcining amorphous $ZrO_x(OH)_{4-2x}$ at 723 K in 20% O₂ for 2 h (sample mixed with Vaseline in a drybox prior to air exposure); (b–d) exposure of the calcined sample to ambient air at 298 K for 10 s, 12 h, and 24 h, respectively; (e) exposure of the calcined sample to 3.0 kPa of H₂O at 298 K for 100 min; (f) immersion of the calcined sample in liquid H₂O overnight and then drying in 20% O₂ at 623 K for 1 h; (g) calcining amorphous $ZrO_x(OH)_{2-2x}$ at 723 K in 20% O₂ and 3.0 kPa H₂O.

without any loss in surface area. In contrast, treating the amorphous zirconium oxyhydroxide sample at 623 K in 20% O₂/He containing 3 kPa of H₂O for 16 h led to a sample containing 79% m-ZrO₂, but with a lower BET surface area (128 m²/g). Similar results were obtained when an amorphous zirconium oxyhydroxide sample was first calcined at 723 K in 20% O₂/He for 2 h. XRD patterns for this series of experiments are shown in Figure 7. Treatment in 20% O₂/He at 723 K converted the sample to 100% t-ZrO2 with a BET surface area of 167 m²/g. Exposure of this sample to H_2O (3 kPa of H_2O for 100 min) at 298 K or immersion of the sample in liquid H₂O for 12 h led to samples containing 74% and 78% m-ZrO₂, respectively; these treatments had no effect on the BET surface area. Treating zirconium oxyhydroxide at 723 K in 20% O₂/He containing 3 kPa H₂O led to a sample that is 81% m-ZrO₂ with a surface area of 68 m²/g. Figure 7 also shows that the tetragonalto-monoclinic transformation occurs readily even at 298 K upon exposure to ambient air. Consistent with the results presented in Figure 6, a significant fraction of t-ZrO₂ is converted to m-ZrO₂ within the first 10 s of exposure to air, after which further conversion occurs slowly.

Discussion

As demonstrated by the Raman spectra presented in Figures 4–6, water vapor increases the rate of crystallization of amorphous zirconium oxyhydroxide into t-ZrO₂ and the subsequent transformation of this phase to m-ZrO₂. While Murase and Kato³⁰ have reported that H₂O vapor facilitates the tetragonal-to-monoclinic transformation of ZrO₂ at temperatures above 673 K, it is remarkable that this transformation can occur even at 298 K. A possible explanation for the effects of water vapor can be found by considering the thermodynamics of the tetragonal-to-monoclinic transformation.

Garvie and co-workers³⁸⁻⁴¹ have proposed that the stabilization of small particles of t-ZrO₂ at temperatures below those required for the tetragonal-to-monoclinic transformation of bulk ZrO2 (1447 K) reflects the higher surface free energy of m-ZrO₂. On the basis of this interpretation, the critical particle size, $d_{\rm c}$, for the tetragonal-to-monoclinic transformation is given by

$$d_{\rm c}^{-1} = \left(\frac{q}{6\Delta\sigma}\right) (T/T_{\rm b} - 1) \tag{1}$$

where q is the heat of the tetragonal-to-monoclinic transformation, $\Delta \sigma$ is the difference in surface free energies between the monoclinic and tetragonal phases of ZrO_2 , T_b is the temperature at which the tetragonalto-monoclinic transformation occurs for an infinite crystal of ZrO_2 (1447 K), and T is the temperature at which particles of a given size $d_{\rm f}$ undergo the tetragonalto-monoclinic transformation. The validity of eq 1 has been confirmed by experimental data for strain-free ZrO₂ particles with average sizes between 9.7 nm and 9 μ m. Garvie and Goss³⁷ have noted that the value of $d_{\rm c}$ can shift to larger or smaller values than those determined for strain-free crystals, depending on the circumstances under which ZrO₂ is prepared. For example, any strain in the ZrO₂ lattice caused by the formation of polycrystals will increase $d_{\rm c}$ above its value for strain-free crystals; a similar effect can arise from the adsorption of sulfate anions. On the other hand, the value of $d_{\rm c}$ will be lower than that for strain-free crystals when crystals are prepared such that the value of $\Delta \sigma$ is lower than that measured in the absence of strain.

Since the total Gibbs free energy for a given mass of crystals is proportional to its specific surface area, it is useful to define a critical surface area, SA_c, required for the tetragonal-to-monoclinic transformation. This quantity is related to $d_{\rm c}$ for quasispherical crystals as follows:

$$SA_{c} = \frac{6}{\rho d_{c}}$$
(2)

where ρ is the particle density. Figure 3 shows a plot of the critical surface area versus calcination temperature. The following parameter values were used to generate

this plot: $q = -5.94 \text{ kJ/mol}; \Delta \sigma = 0.36 \text{ J/m}^2; T_b = 1447$ K; and $\rho = 5.89$ g/cm². ⁴¹ Surface areas that lie above this critical surface area line lead to stable $t-ZrO_2$, whereas surface areas below this line will result in the stabilization of m-ZrO₂. A comparison of the experimentally observed surface area (Figure 3) with that required for the onset of the tetragonal-to-monoclinic transformation shows that t-ZrO₂ is expected to be the stable phase at temperatures below 950 K. This is in good qualitative agreement with the Raman spectroscopy observations presented in Figure 2, which show the substantial absence of m-ZrO₂ below 923 K and the presence of significant quantities of m-ZrO₂ at temperatures of 973 K and above. The temperature range over which the tetragonal-to-monoclinic transformation occurs is also consistent with that observed in the DSC experiments (923–1173 K). The broad temperature range over which this transformation occurs is believed to reflect a broad range of particle sizes, within which large particles transform at a lower temperature than small particles.34-36

The influence of water vapor can also be explained using the thermodynamic arguments above. Upon exposure to water, the surface free energy of ZrO_2 will change. If this effect is larger for $m-ZrO_2$ than for $t-ZrO_2$, then the value of $\Delta \sigma$ in eq 1 will decrease and $d_{\rm c}$ will also decrease in the presence of water. This, in turn, would lead to an increase in SA_c. For the tetragonalto-monoclinic transformation to occur at 298 K for particles with a surface area of 120 m^2/g , the value of $\Delta \sigma$ would need to decrease from 0.36 to 0.23 J/m² upon water adsorption. While comparative measurements of the heat of adsorption of water on t- and m-ZrO₂ have not been reported, such measurements have recently been published for CO₂ adsorption.⁴² They show that the heat of CO₂ adsorption on m-ZrO₂ is larger than that on t-ZrO₂ by about 10 kJ/mol, which corresponds to 0.16 J/m^2 . This suggests that the proposed interpretation of the effects of water is plausible.

Raising the temperature at which ZrO₂ is exposed to water vapor does not increase the proportion of $m-ZrO_2$ (see Table 1), but it does decrease the surface area relative to that obtained by calcination in dry 20% O₂/ He at the same temperature. This result is qualitatively consistent with the findings of Murase and Kato,³¹ who reported faster crystal growth when heating ZrO_2 in O_2 containing water vapor. It appears that water vapor increases the mobility of zirconia at crystal surfaces, thereby facilitating particle sintering.

The time scale over which the tetragonal-to-monoclinic transformation occurs in the presence of water vapor is very short. As shown in Figure 4, evidence for m-ZrO₂ was detected in the Raman spectrum immediately after t-ZrO₂ was exposed to water vapor. Since the tetragonal-to-monoclinic transformation is a martensitic, diffusionless process, there is no activation barrier for the process.⁴³ The only factor that delays the onset of the transformation is the formation of nuclei. Similarly rapid tetragonal-to-monoclinic transformations at room temperature have been reported by

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Mitsuhashi et al.⁴⁴ for t-ZrO₂ following grinding or ultrasonic treatment at 400 kHz. The authors suggested that nucleation sites required for the transformation were created by these treatments. Incomplete transformation was observed for t-ZrO₂ crystallites containing a large degree of strain. It is, therefore, conceivable that the incomplete tetragonal-to-monoclinic transformation observed in the present study upon exposure of t-ZrO₂ to water vapor might reflect the presence of crystallites with a moderate amount of strain.

It is useful to comment on the practical consequences of the present results. While it is not yet possible to achieve a complete transformation of t-ZrO₂ to m-ZrO₂ at 298 K, nearly 80% of the t-ZrO₂ can be transformed to the monoclinic phase without loss in surface area. Recent studies carried out in our laboratory indicate that the surface properties of ZrO₂ powder consisting of a mixture of monoclinic and tetragonal phases with >50% m-ZrO₂ resemble very closely those of pure m-ZrO₂. This conclusion is based on measurements of CO and CO₂ adsorption and on the dynamics of D₂ exchange of Zr–OH groups.⁴⁵ The net result is that high surface area ZrO₂ supports with the properties of pure m-ZrO₂ can be prepared by water treatment of t-ZrO₂ under ambient conditions.

Conclusions

In situ Raman spectroscopy can be used to follow the tetragonal-to-monoclinic transformation of ZrO₂. In the

(45) Jung, K. D.; Bell, A. T. J. Catal., in press.

absence of water vapor, t-ZrO₂ prepared by calcination of amorphous zirconium oxyhydroxide at 623 K has a surface area of 204 m²/g. This material is stable up to calcination temperatures of 823 K; above that it starts to transform into m-ZrO₂. The tetragonal-to-monoclinic transformation occurs when the size of the t-ZrO₂ particles reaches a critical value, which is determined by thermodynamics (see eq 1). Exposure of $t-ZrO_2$ calcined at 623 K to 3 kPa H₂O vapor or immersion in liquid H₂O at 298 K results in the conversion of nearly 80% of the t- ZrO_2 to m- ZrO_2 without a loss in surface area. This transformation is attributed to a preferential lowering of the surface free energy of the m-ZrO₂ relative to t-ZrO₂ upon adsorption of water. Failure to achieve complete transformation to m-ZrO₂ is attributed to strain stabilization in some t-ZrO₂ particles. Treatment of t-ZrO₂ in water vapor at elevated temperature causes the tetragonal-to-monoclinic transformation to occur concurrently with a significant loss in surface area.

Acknowledgment. The authors would like to thank Kyle Fujdala for carrying out the thermal analysis reported here. This work was supported by the Director, Office of Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under contract DE-AC03-76SF00098.

CM000212V

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