

CHARACTERIZATION OF NANOSTRUCTURED ZIRCONIA PREPARED BY HYDROLYSIS AND REVERSE MICELLE SYNTHESIS BY SMALL-ANGLE NEUTRON AND X-RAY SCATTERING

P. Thiyagarajan¹, X. Li^{1,4}, K.C. Littrell¹, S. Seifert², R. Csencsits³, and C.K. Loong¹.
¹Intense Pulsed Neutron Source, ²Chemistry Division, ³Materials Science Division Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439,
⁴Chemical Engineering Department, University of Louisville, Louisville, KY 40292.

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ABSTRACT

Low temperature techniques such as hydrolysis and reverse micelle syntheses provide the opportunity to determine the relationship between the structural properties and preparation conditions of zirconia powders as well as to tailor their physicochemical properties. We have performed small-angle neutron and synchrotron x-ray scattering (SANS and SAXS) experiments to study the nucleation and organization of zirconia nanoparticles via different preparation routes. First, the formation of reverse micelles in individual and mixed solutions of $(\text{ZrOCl}_2 + \text{D}_2\text{O})/\text{AOT}/\text{C}_6\text{D}_6$, and $(\text{NH}_4\text{OH} + \text{H}_2\text{O})/\text{AOT}/\text{C}_6\text{D}_6$ systems at water/AOT molar ratio of 20 was characterized. Second, the aggregation of zirconia gels obtained from the reaction of the reverse micelle solutions after heat treatments was studied. Third, the nanostructure of zirconia powders prepared by the reverse micelle method is compared with the corresponding powders prepared by hydrolysis after different heat treatments.

INTRODUCTION

Zirconia based materials are widely used as catalysts and catalytic supports by the automobile industry for the automobile-exhaust emission control. These materials offer unique combination of properties such as high surface area, good thermal stability and rich site activity. They can be prepared by a variety of novel preparation methods such as hydrolysis, sol-gel and reverse micelle synthesis. We have demonstrated that doping of zirconia with certain rare earth oxides significantly alter its microstructure and enhance its thermal stability¹. Recently, we have also investigated the structural features of a series of AOT/H₂O/toluene reverse micelle solutions in the presence of reactants for the synthesis of zirconia nanoparticles by SANS².

The nanostructure of the zirconia powder and its thermal stability are closely related to the synthetic conditions used in the solution phase. To gain a better understanding of the structure and function relationship of zirconia we have prepared zirconia by an hydrolysis method at pH = 9.8 and a reverse micelle method in AOT/H₂O/toluene at water/AOT ratio $w = 20$. The obtained gels were calcined at 580 °C for 2 hours in order to remove the residual hydrocarbons and water. The SEM and TEM images of the calcined zirconia powders prepared by the hydrolysis and reverse micelle methods are shown in Figs. 1A and 1B, respectively. It can be seen that the particle size in the zirconia powder from hydrolysis method is in the micrometer range, while it is in the nanometer range from the reverse micelle synthesis. Thus controlled environment used in the reverse micelle method significantly affects the nanostructure of the particles in the zirconia powder.

While TEM provides direct images of the particles in the zirconia powder, the small angle scattering techniques with either neutrons (SANS) or x-rays (SAXS) can characterize the organization of the fundamental structural units in gels, powders and solutions. The latter techniques have high sensitivity to structural features in the length scale of 1 to 50 nm. Our objectives in the present study are: 1) to obtain a structure of the particles in the solution phases used in the hydrolysis and reverse micelle methods for the zirconia synthesis by using SANS, 2) to compare the structure of the reverse micelles in deuterated toluene from SANS and that in n-heptane from SAXS at $w = 20$, and 3) to investigate the systematic changes in the nanostructure of zirconia powders prepared by the two techniques as a function of heat treatment.

MATERIALS AND METHODS

In the hydrolysis method a zirconium hydroxide gel was prepared by the addition of an aqueous ammonia solution to an aqueous solution of 0.2 M zirconium oxychloride under continuous vigorous stirring. Solutions were prepared at pH = 9.8 and the pH was adjusted by using 25 wt.% NH₄OH (Alfa) stock solution. The precipitate was washed with water and filtered several times until no Cl⁻ was detected in the filtrate. The gel was dried at 120 °C for 5 hours followed by calcination at 580 °C in the air to obtain the zirconia powder.

Equation 3 has been derived from model for mass-fractal aggregates⁵ of spheres of radius R , given by

$$I(Q; \xi, D_f, R) = I_{0s} \left(1 + \frac{\sin[(D_f - 1)\arctan(Q\xi)]}{(QR)^D \left(\frac{1}{Q^2\xi^2} + 1 \right)^{\frac{D-1}{2}}} \right) P_{\text{Sphere}}(Q; R) + I_{\text{Background}}, \quad (4)$$

where I_{0s} is the intensity scattered by the fundamental spherical particle extrapolated to $Q=0$. I_{0A} is related to I_{0s} by the expression

$$I_{0A} = I_{0s}(D_f - 1) \Gamma(D_f - 1) \left(\frac{\xi}{R} \right)^{D_f}. \quad (5)$$

This model is a valid approximation when the scattering from the form factor for the fundamental sphere is not visible or, alternately, whenever $\xi \gg R$ and $Q_{\text{max}}R \ll 1$, where Q_{max} is the value of Q at which the power-law scattering fades into the background scattering.

RESULTS AND DISCUSSION

SANS data for the reverse micelles of AOT containing D_2O , $ZrOCl_2$, NH_4OH - D_2O and Zirconia in D-toluene on absolute scale are presented in Fig. 2A. For clarity of presentation the data for the above systems were multiplied by 1, 0.1, 10 and 3, respectively. Similarly scaled SAXS data of AOT containing H_2O , $ZrOCl_2$, NH_4OH and zirconia in n-heptane are in Fig. 2B. The important features in the SANS data are the secondary peaks whose maxima occur at different Q values. In the case SAXS data the secondary peaks are not prominent.

SANS data of the reverse micelles were fitted by using equation 1 to obtain the information on the scattering length density of the core and the results are shown in Table 1. The size of the water core of AOT reverse micelles in D-toluene at $w = 20$ is influenced by its constituents. In the presence of D_2O the core radius is 18 Å with a rms spread of 4 Å, while it decreases to 8 Å in the presence of NH_4OH . The shell thickness remains around 12 Å, except for the micelle with NH_4OH . It is interesting to note that α varies from -1.43 to 0.04 consistent with the composition changes in the core. The effect of the small α values for the NH_4OH and zirconia reverse micelles can be seen in the blurred secondary peaks in the SANS data (Fig. 2A). Another important feature seen for the zirconia containing reverse micelle is the power-law scattering of $Q^{-2.16}$ in the low Q region, implying the presence of vesicles⁶.

SAXS data in Fig. 2B were modeled by using equation 1 to obtain the core radius, shell thickness and α and the results are given in Table 2. SAXS data show that the core radius is larger for the micelle with water, but it becomes smaller for the other cases. The solvent effect is significant on the size of the AOT/water reverse micelles at $w = 20$ as the radius is about 42 Å in n-toluene (SAXS) while it is 30 Å in D-toluene (SANS). Comparison of the SANS data of AOT/water reverse micelles at $w = 20$ in D-toluene and the SAXS data of reverse micelles in n-heptane indicate the strong effect of organic solvent on the reverse micelles size. This is consistent with the fact that the solvent-solute interactions in the aromatic solvents with π electrons will be stronger than that in the aliphatic solvents.

SANS data for the heat-treated zirconia powder samples from the hydrolysis and reverse micelle methods are shown in Figs. 3A and 3B. The presence of peaks in Fig. 3A implies that the zirconia particles are organized at specific distances and the movement of peak positions (Q_{max}) indicates that the particles grow with increasing temperature (Table 3). The approximate particle size ($2\pi/Q_{\text{max}}$) at 300 °C is 60 Å and grows to 423 Å at 800 °C. The power-law slope in the high Q region reaches a value of -4 at 800 °C implying that the surface of the particles became smooth.

SANS data for the zirconia powder prepared from the reverse micelle method are shown in Fig. 3B. This data exhibit power-law scattering Q^{-D} behavior in a wide Q region, but have no peaks. In the case of fractal aggregates the power-law exponent values can be used to identify the mass and surface fractals. For example, mass fractal aggregates will have $1 < D < 3$, while the surface fractals will have $3 < D < 4$. The data were fitted by using equation 3 and obtained the mass fractal dimensions that vary in the range of 2.7 to 2.9 and the cut-off lengths vary in the range of 180 to 340 Å (see Table 4). Thus the zirconia from the reverse micelle method would be better for the high temperature applications than that from the hydrolysis method.

The details of the synthesis of zirconia by the reverse micelle method have been presented elsewhere². Briefly, sodium bis(2-ethylhexyl) sulphosuccinate (AOT) was dissolved in toluene to form a 0.1 M solution. Deionized water was then added to form the reverse micelle with [water]/[AOT] molar ratio $w = 20$. To obtain the Zr-containing reverse micelles, appropriate amounts of 0.2 M $ZrOCl_2$ stock solution corresponding to $w = 20$ was added to the AOT/toluene solution. Similarly, ammonium hydroxide was added to AOT/toluene solution to achieve $w = 20$. All solutions were stirred continuously during the formation of reverse micelles. Subsequently, the Zr- and ammonium-containing solutions of the same w value were mixed and stirred for 20 minutes at room temperature to ensure equilibrium.

SANS experiments were carried out at the time-of-flight small-angle neutron diffractometer (SAND) at the Intense Pulsed Neutron Source of Argonne National Laboratory. This instrument provides a useful range of wave vectors ($Q = 4\pi\sin(\theta)/\lambda$, where θ is half the scattering angle and λ is the neutron wavelength) of $0.0035 - 0.6 \text{ \AA}^{-1}$ in a single measurement. In order to obtain the best contrast for SANS, D_2O (Alfa) and $C_6D_5CD_3$ (Alfa, 98% D-atom) were used. The following four systems, $D_2O/AOT/C_6D_5CD_3$, $ZrOCl_2$ in $D_2O/AOT/C_6D_5CD_3$, NH_4OH in $AOT/C_6D_5CD_3$ and $ZrOCl_2$ reacted with NH_4OH in $AOT/C_6D_5CD_3$ were considered for the present study. The data were corrected following routine procedures³.

SAXS experiments on AOT/ H_2O/n -heptane solutions at $w = 20$ were carried out at the ASAXS instrument on the BESSRC ID-12 beam line at the Advanced Photon Source⁴ also at Argonne National Laboratory. Data were collected using a position sensitive 15 cm x 15 cm CCD area detector and exposure times for each measurement were 1 - 2 seconds. A known quantity of a solution was injected into a flow cell using motorized syringes that can position the sample into the 1.5 mm diameter cylindrical capillary tube viewed by the x-ray beam. The sample to detector distance was 0.7 m and the energy of x-ray radiation was set at 13.5 keV.

DATA ANALYSIS

The SAS data from the reverse micelle samples were analyzed by using the core-shell model given in equation 1. In this equation the variables, r , T and α are the core radius, thickness and the ratio of scattering length density difference between the core and shell to that between the shell and the solvent, respectively. The neutron scattering length densities of D_2O , AOT and D-toluene are $6.336 \times 10^{10} \text{ cm}^{-2}$, $0.62 \times 10^{10} \text{ cm}^{-2}$ and $5.644 \times 10^{10} \text{ cm}^{-2}$ respectively. The x-rays are scattered by the electrons and the scattering length densities of H_2O , AOT and n-heptane are $9.36 \times 10^{10} \text{ cm}^{-2}$, $10 \times 10^{10} \text{ cm}^{-2}$ and $6.64 \times 10^{10} \text{ cm}^{-2}$ respectively. The scattered intensity can be expressed as

$$I(Q) = nP(Q)S(Q) \quad (1)$$

where n is the number density of the reverse micelles, $P(Q)$ is the form factor and $S(Q)$ is the inter-particle structure factor which is assumed to be 1 in this case. The form factor $P(Q)$ for a spherical shell with a polydispersity in radius with Shultz distribution is given by

$$P(Q) = \frac{\int_0^{\infty} [\sin(Q(r+T)) - Q(r+T)\cos(Q(r+T)) + \alpha(\sin(Qr) - Qr\cos(Qr))]^2 \left(\frac{r}{r_0}\right)^{x-1} \exp\left(-\frac{zr}{r_0}\right) dr}{\int_0^{\infty} [(r+T)^3 + \alpha^2] \left(\frac{r}{r_0}\right)^{x-1} \exp\left(-\frac{zr}{r_0}\right) dr} \quad (2)$$

where

$$\alpha = \frac{\rho_{\text{core}} - \rho_{\text{shell}}}{\rho_{\text{shell}} - \rho_{\text{solvent}}}, \quad \text{and} \quad z = \frac{r_0}{\sigma}$$

where σ is the rms core radius spread.

The SANS from the zirconia powders are fitted by using equation 3 for fractal aggregates⁵.

$$I(Q, \xi, D_f) = I_{0A} \frac{\sin[(D_f - 1)\arctan(Q\xi)]}{(D_f - 1)Q\xi(Q^2\xi^2 + 1)^{\frac{D_f - 1}{2}}} + I_{\text{background}} \quad (3)$$

where I_{0A} is the overall intensity scattered by the aggregate extrapolated to $Q=0$, D_f is the mass-fractal dimension, ξ is the exponential cutoff length at which the system reaches the macroscopic density, and $I_{\text{background}}$ is the background intensity.

CONCLUSIONS

SAXS and SANS are quite sensitive for the study of the nanostructure of catalytic systems. The high sensitivity of the scattering techniques can be seen from their ability to provide a number of parameters on the structure and organization of the reverse micelles. We obtained unique information on the water core that provides clues to the enhanced properties of zirconia. Coarsening occurs in zirconia powder prepared by hydrolysis method upon heat treatment, while the particles are uniform in size and do not grow upon heat treatment up to 750 °C.

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REFERENCES

1. Loong, C.K.; Thiyagarajan, P.; Richardson Jr., J.W.; Ozawa, M.; Suzuki, S. J. Catalysis 1997, 171, 498-505.
2. Li, X.; Loong, C.-K.; Thiyagarajan, P.; Lager, G.A.; Miranda, R. J. Appl. Cryst. (In Press).
3. Thiyagarajan, P.; Epperson, J.E.; Crawford, R.K.; Carpenter, J.M.; Klippert, T.E.; Wozniak, D.G. J. Appl. Cryst. 1997, 30, 280-293.
4. Seifert, S.; Winans, R.E.; Tiede, D.M.; Thiyagarajan, P. J. Appl. Cryst. (In Press)
5. Freltoft, T.; Kjems, J.; Sinha, S.K. Phys. Rev. 1986, B33, 269.
6. Ravey, J.C.; Buzier, M. J. Colloid. Interface Sci., 1987, 116, 30.

Table 1
Parameters from the Shultz Polydisperse Shell model fits of SANS of Reverse Micelles of AOT/D₂O in D-Toluene, w = 20.

Core in AOT/ D-Toluene Reverse Micelle	Core radius (Å)	RMS Core Radius Spread (Å)	Shell thickness (Å)	$(\rho_{\text{core}} - \rho_{\text{shell}}) /$ $(\rho_{\text{shell}} -$ $\rho_{\text{solvent}})$ (α)	ρ_{core} (10^{10} cm^{-2})
D ₂ O	18.0 ± 0.1	4.0 ± 0.1	12.0 ± 1.0	-1.143	6.36
ZrOCl ₂	10.1 ± 0.7	1.6 ± 0.2	12.0 ± 0.8	-1.019	5.73
NH ₄ OH	8.4 ± 0.4	2.3 ± 0.4	14.1 ± 0.4	-0.051	0.88
ZrO ₂	12.0 ± 2.0	2.6 ± 0.1	11.0 ± 2.0	0.040	0.42

Table 2
Parameters from the Shultz Polydisperse Shell model fits of SAXS of Reverse Micelles of AOT/H₂O in n- heptane, w = 20.

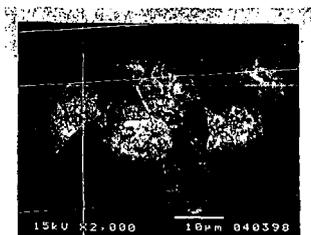
Core in AOT/ n-heptane Reverse Micelle	Core radius (Å)	RMS Core Radius Spread (Å)	Shell thickness (Å)	$(\rho_{\text{core}} - \rho_{\text{shell}}) /$ $(\rho_{\text{shell}} -$ $\rho_{\text{solvent}})$ (α)	ρ_{core} (10^{10} cm^{-2})
H ₂ O	30.7 ± 0.01	8.5 ± 0.01	11.3 ± 0.05	-0.328	8.90
ZrOCl ₂	11.0 ± 0.01	3.9 ± 0.01	10.7 ± 0.06	-0.520	8.25
NH ₄ OH	24.4 ± 0.01	7.8 ± 0.01	12.0 ± 0.1	-0.386	8.70
ZrO ₂	27.2 ± 0.01	8.2 ± 0.01	12.0 ± 0.1	-0.375	8.74

Table 3
Particle size from the SANS data of the zirconia powders prepared by the hydrolysis method upon heat treatment for 2 hours at different temperatures.

Temp. (°C)	Particle Size (Å)
300	60
400	90
500	134
600	203
700	295
800	423

Table 4
Parameters obtained from the Fractal model fit of the SANS data of the zirconia powders prepared using reverse micelle method upon heat treatment for 2 hours at different temperatures.

Temp (°C)	Fractal Dimension	Cutoff Length (Å)
100	2.7	186
200	2.7	197
300	2.7	148
400	2.9	124
550	2.93	223
750	2.9	341



(A)



(B)

Fig. 1. A) STM of calcined Zirconia powder prepared by hydrolysis method B) TEM of calcined zirconia powder prepared by reverse micelle method with H_2O/AOT $w=20$.

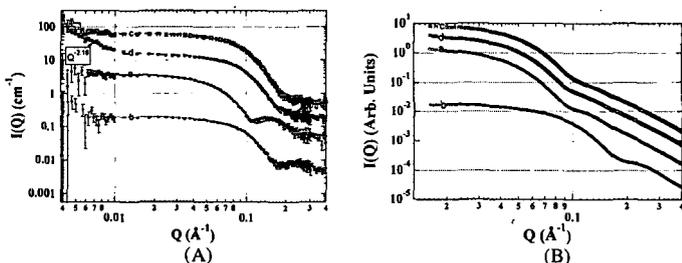


Fig. 2 A) SANS of reverse micelle solutions at $w = 20$: (a) $D_2O/AOT/C_6D_5CD_3$, (b) $(ZrOCl_2+D_2O)/AOT/C_6D_5CD_3$, (c) $(NH_4OH+H_2O)/AOT/C_6D_5CD_3$, and (d) the mixture of (b) and (c). B) SAXS of reverse micelle solutions at water/AOT molar ratio = 20: (a) $H_2O/AOT/C_7H_{16}$, (b) $(ZrOCl_2+H_2O)/AOT/C_7H_{16}$, (c) $(NH_4OH+H_2O)/AOT/C_7H_{16}$ and (d) mixture of (b) and (c). For clarity, the absolute intensities of data a, b, c and d are multiplied by 1, 0.1, 10 and 3, respectively. Lines are the fits using equation 1 and the results from the fits of SANS and SAXS data are given in Tables 1 and 2, respectively.

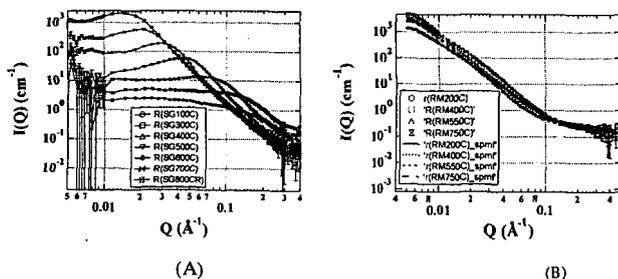


Fig. 3 SANS of ZrO_2 powders prepared by A) hydrolysis and B) reverse micelle synthesis after heat treatment at different temperatures for 2 hours. While the aggregates in ZrO_2 powders prepared by hydrolysis method shows monotonic increase in their size, those in ZrO_2 powders from reverse micelle method seem to be stable up to 750 °C.